CORRELATIONAL ASPECTS OF THE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP OF LUBRICATING OILS

PROEFSCHRIFT

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DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOREN

PROF. DR. IR. J. C. VLUGTER EN PROF. IR. H. BLOK

Aan mijn ouders
Aan Irene

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CHAPTER I

INTRODUCTION

I.1. BACKGROUND

The primary aim of lubrication consists in achieving complete separation of the rubbing surfaces of the lubricated machine element so as to reduce detrimental friction and wear to a minimum. In many cases such a separation can be materialized by interposing some flowing oil between the rubbing surfaces. In the consequent *hydrodynamic* lubrication the load imposed on the rubbing surfaces is completely borne by the oil film created. This oil film - whose thickness frequently amounts to only a few microns - may thus be stated to act, by its very nature, as a real constructional element. Accordingly, the lubricating oil should be regarded and treated as a real *constructional material.*

The latter concept has been introduced and consistently applied by Blok, whilst demonstrating convincingly its great importance to the designer of lubricated machine elements 1-6).

It is *viscosity* that has proved the essential constructional property of oils employed in hydrodynamic lubrication. In general, however, viscosity does not simply assume a uniform level throughout a given, hydrodynamically created, oil film. This accrues from the non-uniformity of the temperature and/or pressure prevailing in the oil film. Indeed, many hydrodynamically lubricated machine elements operate over ranges of temperature and/or pressure so extensive that the consequent variations of the oil's viscosity may become quite considerable and, in turn, may seriously affect its lubrication *performance.*

Consequently, sufficient knowledge of the viscosity-temperature-pressure relationship of lubricating oils is indispensable.

The indicated importance in hydrodynamic lubrication alone would constitute sufficient reason for delving as deeply as possible into the pertinent aspects of the viscosity-temperature-pressure relationship of liquids, notably those currently employed in lubrication practice. In addition, however, the knowledge thus gained may advantageously be applied in many other problems encountered with flowing liquids in general.

Therefore, the importance of the present investigation covers various fields of modern technology, and the applicability area is still expanding as widely varying temperatures and pressures are increasingly encountered nowadays. The temperature variation of viscosity plays a significant part in numerous kinds of more or less familiar problems. However, problems where the pressure variation of viscosity has to be accounted for are not quite so numerous and familiar.

Besides in the lubrication of (heavily-loaded) machine elements (see also Section I. 3), the viscosity-pressure effect may become a significant factor in the lubrication of metal-working tools. Other problems where the pressure variation of viscosity assumes considerable importance can be found in the fields of hydraulic engineering and of geophysics (subterraneous flow of oils and molten silicates). More specifically, the viscosity-pressure effect has to be accounted for in the design of fuel-injection equipment.

It would appear that most of the investigations into the viscosity-temperature-pressure relationship of liquids have been induced primarily by the indicated engineering importance. However, such investigations also offer very interesting possibilities for gaining a more profound insight into the viscosity characteristics of liquids and into the nature of the liquid state in general. This holds especially for high-pressure viscometry, as certain particulars of the molecular structure may be greatly accentuated by the high pressures applied[7-18)]. It stands to reason that such more fundamental studies can be really fruitful only if pure compounds of rather simple structure are considered.

Unfortunately, the results achieved with such relatively simple liquids are of comparatively little practical value in the field of the usually very complex lubricating oils.

I. 2. GENERAL REMARKS ON THE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP OF LUBRICATING OILS

I. 2. 1. *Definitions and Units*

According to Newton's definition, the shearing stress, τ, between two adjacent layers in a flowing liquid is proportional to the applied rate of shear, du/dz, taken perpendicular to the direction of flow. The proportionality constant, which is characteristic of the liquid considered, is termed the viscosity, η. In mathematical terms one may thus write:

$$\tau = \eta \frac{du}{dz} . \qquad (I-1)$$

It follows from this definition that the viscosity of a given liquid represents a measure of its resistance against flow or, more precisely, a measure of the frictional forces between its moving molecules. For a given liquid the viscosity will be governed by the forces between, and the flexibility of, its molecules.

For the commonly used liquids viscosity has proved to be essentially independent of the applied rate of shear, at least up to fairly high rates. Such liquids are denoted as *Newtonian* in that they conform to Newton's Definition (I-1). For such Newtonian liquids viscosity is a true quantity of state and thus a function solely of temperature and pressure.

In lubrication practice the great majority of oils currently in use may be regarded as Newtonian under the operating conditions normally encountered in machine elements. For all the various kinds of mineral oils tested, for example, not any appreciable deviation from Newton's law could be detected up to shear rates of the order of 10^5-10^6 sec^{-1}, whilst it has been conjectured that significant deviations would occur only beyond something like 10^7 sec^{-1}. The only exceptions that may assume practical significance are represented by polymer-blended mineral oils and certain types of synthetic (polymeric) lubricating oils[1;19-22].

As can easily be derived from Newton's Definition (I-1), viscosity has the dimension of (force x time)/(length)^2. In the c.g.s.-system of units it is thus expressed in (dyne x sec)/cm^2, which is equivalent to g.mass/(cm x sec). To honor Poiseuille for his fundamental studies on viscometry the latter unit has been called the Poise, P. In practice, viscosity is normally expressed in terms of centipoises, cP (of course, 1 cP = 0.01 P).

I.2.2. *Dynamic and Kinematic Viscosity*

Besides the above-defined viscosity, η, a second "viscosity" criterion is frequently employed, namely the so-called *kinematic* viscosity, ν. However, the latter criterion is not a true viscosity in that it denotes the ratio of viscosity, η, to density (taken at the same temperature and pressure). Accordingly, kinematic viscosity has the dimension of (length)^2/time. In the c.g.s.-system kinematic viscosity is thus expressed in cm^2/sec; as a rule, 1 cm^2/sec is called a Stoke, S. In practice, kinematic viscosity is normally expressed in terms of centistokes, cS (1 cS = 0.01 S).

In order to avoid confusion with kinematic viscosity, ν, the true viscosity, η, as defined by Newton, is frequently termed the *dynamic* viscosity. But, unless necessary or desirable, the adjective "dynamic" has been omitted throughout this thesis, the single term "viscosity" invariably standing for dynamic viscosity.

It is well known that in lubrication it is usually the performance of an oil in terms of hydrodynamic lubrication that counts most of all in so far as viscosity characteristics are concerned. Since the relevant hydrodynamic effects can be judged only from *dynamic* viscosity, it is the latter viscosity that is really significant in both the theory and practice of lubrication.

It is admitted that as long as only mineral oils and (synthetic) oils with densities in the same range, say, from 0.8 to 1.0 g/cm^3, are considered, kinematic viscosity might still be taken as not too crude a measure of their dynamic viscosity. But nowadays certain types of synthetic oils have entered the market whose density, at any normal temperature, lies far enough above the aforementioned range to make their kinematic viscosity quite untenable as a viscosity criterion. For fluoro oils, for example, the density amounts to about twice that of mineral oils. Thus, taking such a fluoro oil and a mineral oil with the same *kinematic* viscosity at a given temperature, the *dynamic* viscosity of the fluoro oil will be about twice that of the mineral oil. Consequently, the hydrodynamic lubrication performance of the two oils will be markedly different and kinematic viscosity will give a false impression.

All in all, it appears that it is generally incorrect to compare the hydrodynamic lubrication performance of oils on the basis of their kinematic viscosity.

It may be added that the lack of significance, or even the insignificance, of kinematic viscosity as a viscosity criterion becomes particularly evident when such heavy liquids as liquid metals are used for lubrication purposes. For example, mercury displays a dynamic viscosity, in the conventional temperature range, of about 1.5 cP; but the corresponding kinematic viscosity amounts to only about 0.1 cS.

Kinematic viscosity is bound to yield an even more misleading impression of the hydrodynamic lubrication performance when a *gaseous* lubricant is employed. Whilst such lubricants display dynamic viscosities, in the conventional temperature range, of the order of 0.01 cP, their kinematic viscosities may reach - owing to the extremely low densities involved - values in the lubricating-oil range.

I.2.3. *Effects of Temperature and Pressure*

Our knowledge of the properties of liquids - in contradistinction to that of the properties of solids and gases - is not so well founded theoretically. None of the many existing theories of the liquid state has found general acceptance. This situation is not so surprising, since the study of the liquid state is beset not only by difficulties characteristic of the solid and the gaseous state, but also those typical of this peculiar intermediate state.

Viscosity even offers additional complications in being a *transport* property, so that - as distinct from equilibrium properties - it does not lend itself to any rigorous thermodynamic treatment. Indeed, the theory of liquid viscosity may be regarded as still being in its infancy. Nevertheless, particularly in recent years, substantial progress has doubtless been made. But it has simultaneously appeared that much more should be known about the liquid state in general before viscosity can be treated theoretically in a really satisfactory manner.

The indicated lack of fundamental knowledge of liquid viscosity is felt particularly when it is tried to evaluate the effects of temperature and pressure. This applies the more so as these effects assume really gigantic magnitudes as compared with those on other familiar properties. Moreover, the variations of viscosity with temperature and pressure may differ quite spectacularly from one liquid to another. In fact, in the latter respects viscosity has proved a truly *unique* property of liquids.

In order to convey an impression of the magnitude of the effects of temperature and pressure on the viscosity of liquids, notably those used as lubricating oils, Figs.I-1 and I-2 have been prepared. For a great variety of lubricating oils and miscellaneous liquids Fig.I-1 depicts the relative viscosity changes, $\eta_{0,40^\circ C}/\eta_{0,100^\circ C}$ - brought about at atmospheric pressure*) by increasing temperature from 40

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*) Throughout this thesis the subscript "0" relates to atmospheric pressure.

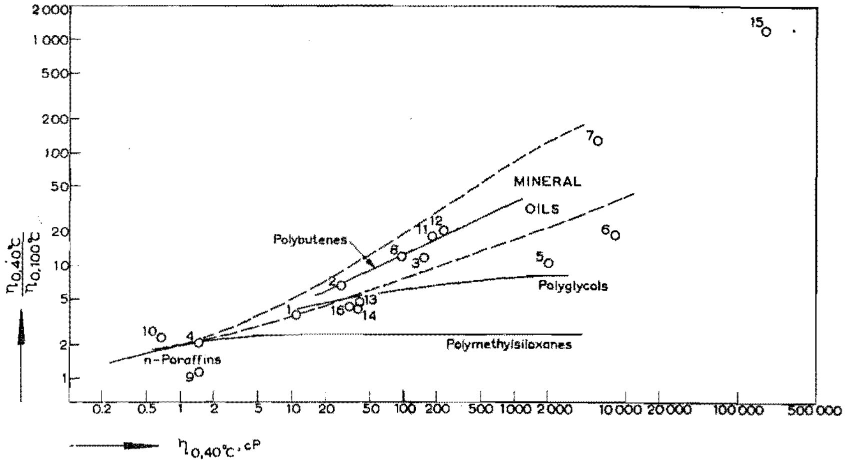

FIG. I-1.

Viscosity-Temperature Dependence of Lubricating Oils and Miscellaneous Liquids.

Designations:

1. Diester
2. ditto
3. Chlorofluorocarbon
4. Silicate Ester
5. Polyalkylstyrene
6. Polymethacrylate
7. Chloroparaffin
8. Triethanol Amine
9. Mercury
10. Water
11. Glycerol
12. Castor Oil
13. Rapeseed Oil
14. Whale Oil
15. Bitumen
16. Water-Glycol Fluid

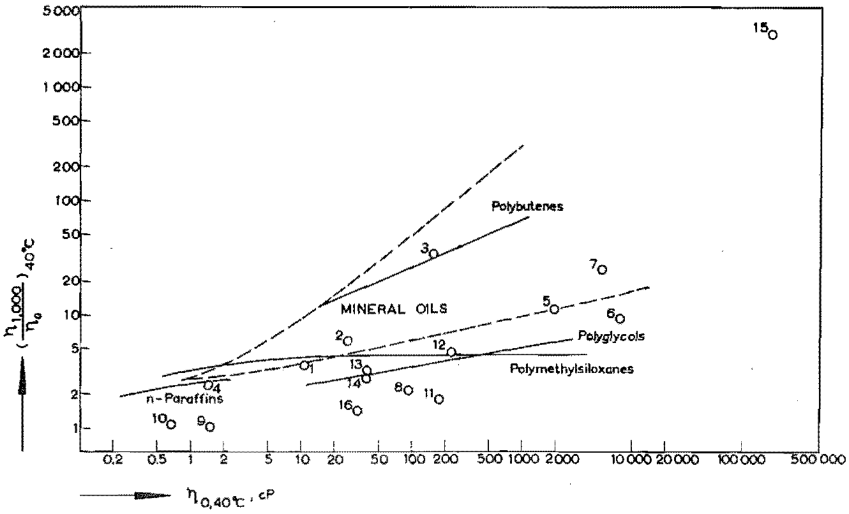

FIG. I-2.

Viscosity-Pressure Dependence of Lubricating Oils and Miscellaneous Liquids.
For designations see Fig. I-1.

to 100°C (104 to 212°F) - as a function of the corresponding atmospheric viscosities at a standard reference temperature of 40°C, denoted by $\eta_{0,40^\circ C}$. For the same liquids[*] Fig. I-2 depicts the relative viscosity changes, $(\eta_{1,000}/\eta_0)_{40^\circ C}$, brought about by increasing gauge pressure, at the aforementioned standard reference temperature of 40°C, from zero to 1,000 kgf/cm^2 (0 to 14,220 psi).

The extensive ranges covered by all the various kinds of mineral oils investigated so far have been approximately traced in Figs. I-1 and I-2 by two converging dashed lines. Further, three important homologous groups of, commercially available, synthetic lubricating oils have also been depicted, namely (linear) polymethylsiloxanes, polyglycols and polybutenes. In addition, the truly homologous group of n-paraffins has been included. Finally, individual points have been indicated in Figs. I-1 and I-2 for 16 miscellaneous liquids, including several important types of synthetic lubricating oils.

These two figures to demonstrate the really enormous effects that temperature and pressure may have on the viscosity of liquids. Moreover, they illustrate the great differentiation as to the magnitude of these effects between the various types of liquids under consideration. Even within the group of mineral oils this differentiation is seen to be quite considerable.

The gigantic magnitude of the effects of temperature and pressure on viscosity, as compared with the corresponding effects on other familiar physical properties of liquids, may be exemplified for their density. For all the various kinds of mineral oils investigated so far - and likewise for many other types of oils - the density change over the temperature range from 40 to 100°C considered in Fig. I-1 proved to amount to only about 5%. Approximately the same, very small, density change is brought about by increasing (gauge) pressure to the reference value of 1,000 kgf/cm^2 considered in Fig. I-2.

The indicated extreme sensitivity of viscosity to both temperature and pressure variations forms a considerable obstacle to the analytical description of the consequent viscosity changes, let alone to their prediction by means of workable correlations. At constant pressure, viscosity has proved to increase more or less exponentially with the reciprocal of absolute temperature (see Chapter III). Similarly, at constant temperature, viscosity increases more or less exponentially with pressure (see Chapter IV). In general, however, the relevant exponential relationships constitute only first approximations and may be resorted to only in moderate temperature and pressure ranges.

I. 3. THE IMPORTANCE OF THE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP OF OILS IN HYDRODYNAMIC LUBRICATION

As indicated in Section I. 1, an oil utilized for achieving hydrodynamic lubrication should be regarded and treated as a real con-

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[*] These liquids have also been depicted in Fig. VII-2, whilst further particulars on them can be found in the pertinent § VII. 2. 2.

structional material. The *constructional value* of such a material is determined essentially by its viscosity characteristics.

Apart from a good stability, non-corrosivity and other functional requirements, the primary requirement for any lubricating oil does consist in that it displays the desired viscosity under the conditions prevailing in the oil film. It is true that the theory of hydrodynamic lubrication, in its most generalized form, also involves the density, specific heat and thermal conductivity of the oil. But, although the latter properties may indeed assume some occasional significance in hydrodynamic lubrication, this has hardly any practical consequence for the selection of oils suitable for a particular application. This accrues from the well-known fact that the oils encountered in lubrication practice show very little differentiation as to the latter three influential properties, particularly in comparison with the really enormous differentiation as to their viscosities (compare § I. 2. 3).

All in all, it thus appears that the hydrodynamic lubrication performance of lubricating oils or, say, their constructional value, may indeed be considered to be essentially determined by their viscosity characteristics. In general, these viscosity characteristics include not only the oil's viscosity *grade*, that is the viscosity at atmospheric pressure and at some standard reference temperature, but also its variations with temperature and pressure as well as with the applied rate of shear. Confining oneself to Newtonian oils (see § I. 2. 1), their viscosity characteristics are thus completely defined by their viscosity-temperature-pressure relationship.

The effect of the atmospheric *temperature* variation of viscosity on the oil's hydrodynamic lubrication performance has long been recognized and accounted for. For proper functioning of a given machine element it is generally necessary that the viscosity of the lubricating oil employed is kept within a more or less restricted range under the varying temperatures the oil is being subjected to. On the one hand, at the lowest temperature encountered - which is normally determined by the climatological thermal conditions at which the machine element has to be started - the viscosity should not exceed a certain upper limit in order to avoid starting difficulties and excessive friction. On the other hand, at the highest temperature encountered - which is determined primarily by the performance characteristics of the machine element considered - the oil should remain sufficiently viscous in order to maintain complete separation of the rubbing surfaces and thus to avoid excessive friction and wear.

Whilst the effect of the (atmospheric) temperature variation of viscosity on the oil's hydrodynamic lubrication performance has long been recognized and accounted for, the effect of its viscosity-*pressure* variation has long been entirely neglected. In fact, data on the viscosity-pressure relationship of lubricating oils are still being generally omitted from specifications.

As indicated in Section I. 1, in hydrodynamic lubrication the load imposed on the rubbing surfaces is, by definition, completely borne by the oil film. This is possible only through the hydrodynamic generation of pressures in this film. The resulting distribution of pressures throughout the oil film determines the load-carrying capacity of the machine element considered.

In principle, therefore, the viscosity-pressure effect would invariably play some part in hydrodynamic lubrication. In practice, however, the latter effect becomes really significant only if the *average* film pressure amounts to at least a few hundred kgf/cm^2 (a few thousand psi). Such high pressures will only seldom occur in journal bearings and thrust bearings. But in oil films between rather rigid counterformal surfaces - which, by definition, do not fit on or into each other -, such as encountered in rolling bearings and particularly in gears, pressures may locally well rise to several thousand and sometimes to more than some ten thousands of kgf/cm^2. In the latter cases the corresponding average film pressures, though markedly smaller than the aforementioned values, are so high that the pressure variation of the oil's viscosity does considerably affect its hydrodynamic lubrication performance.

Particularly during the last decade, lubrication research has made considerable progress. This had led to the establishment of more profound and more generally applicable theories and the development of improved or completely new design directives, even for the rather revolutionary types of machine elements and unusual operating conditions that have recently entered the field of mechanical engineering. At the same time, the aforementioned progress has demonstrated convincingly the ever-increasing importance of basic information on the essential constructional materials of hydrodynamic lubrication, that is on the viscosity-temperature-pressure relationship of lubricating oils.

I. 4. THE PRESENT INVESTIGATION

I. 4. 1. *Introduction*

The effects of temperature and pressure on the viscosity of liquids, in particular those used as lubricating oils, have been studied for many years (see Chapter II). For the great majority, the numerous studies have been confined to the temperature variation of viscosity at atmospheric pressure. Nevertheless, the number of investigations dealing primarily with the effect of pressure on viscosity has gradually become quite considerable.

Although very interesting results have already been achieved, it is only fair to state that the present-day situation with respect to the viscosity-temperature-pressure relationship of lubricating oils still leaves much to be desired. In fact, it appears that the applicability of many previous results obtained in this field is quite restricted. On the other hand, one, should not lose sight of the fact that many previous results date back to quite some years ago, whilst it is only during the last two decades that really reliable and extensive experimental data on the complete viscosity-temperature-pressure relationship of representative oils have become available.

I. 4. 2. *Object and Scope of the Investigation*

The object of the present investigation consists in improving, at least to some extent, the indicated unsatisfactory situation with respect to the viscosity-temperature-pressure relationship of lubricating oils, whilst trying to cast the results into a form that will prove convenient also in the theory and practice of hydrodynamic lubrication.

First, it has been attempted to describe the effects of temperature and pressure on the viscosity of liquids, notably those currently employed as lubricating oils, by means of convenient, yet sufficiently accurate, analytical *equations*.
The resulting equations - involving a *minimum* number of parameters - are shown to combine utmost simplicity with an almost universal applicability. Thus, a minimum amount of experimental information is required for making the desired calculations and estimates. Though designed primarily for mineral oils - not only natural, but also hydrogenated and polymer-blended ones - and various types of synthetic oils encountered in modern lubrication practice, these new equations have proved to apply equally to all the other divergent kinds of liquids investigated so far.

Further, the present equations have appeared particularly suitable as an analytical framework for *correlations* aiming at the prediction of the effects of temperature and pressure either from easily assessable physical constants or from the chemical constitution of the oils.
The relevant correlational attempts have been concentrated upon *mineral oils*, which, notwithstanding their great variety and complexity, are interrelated in being essentially built up from hydrocarbon compounds. After all, even though different types of synthetic oils have increasingly been introduced, mineral oils still constitute the great bulk of oils used in lubrication; and this situation may be expected to continue to exist for at least several decades[23a).
It should be added that the correlations developed for mineral oils become substantially simplified when adapted to any particular homologous group of synthetic lubricating oils or pure compounds because of the well-known regularities observed within each such group. This has been exemplified for various interesting homologous groups of synthetic lubricating oils.

It stands to reason that, owing to the indicated lack of a sound theoretical foundation and the complexity of most types of lubricating oils considered, the present investigation had to be performed on an essentially *empirical* basis.

I. 4. 3. *Concluding Remarks*

Though established empirically, several of the new equations and correlations would appear to have a close bearing on existing theories of liquid viscosity. But whether some theoretical justification can be offered or not, this does not detract from their *practical* significance.

On the other hand, the present findings may well improve our insight into the underlying laws and, finally, contribute to the development of some more satisfactory theory. In fact, these findings are not based on the validity of any - questionable - assumptions but, directly, on accurate experimental data.

In view of the overwhelming amount of work already performed on the subject under discussion, ample attention has been paid throughout this thesis to the results achieved by previous investigators. Thus, it has become possible to indicate - at least to some extent - the merits of the new findings, as contemplated in the light of our present knowledge. After all, no real reason for existence can be claimed for empirical equations and correlations if they cannot bear comparison with available ones.

Such a comparison was deemed the more necessary as technical viscometry is still afflicted with certain rather awkward conventionalities. More particularly, various questions in the field of lubricating-oil viscosities have, in the course of time, become more or less controversial. Notably this applies to the question of classifying lubricating oils according to the temperature dependence of their viscosity; in fact, this has given rise to the notorious "Viscosity-Index problem" (see Chapter VI).

Along the above lines, various important problems associated with the viscosity-temperature-pressure relationship of lubricating oils could be tackled successfully. In general, the equations and correlations finally achieved may be regarded as remarkable by their simplicity. Ultimately, therefore, they may be conceived to substantiate once more the soundness of the guiding principle which has been upheld so successfully - in various fields of research - by the initiator of the present investigation, the late Professor H.I. Waterman[24]:

"Nature itself clearly shows us in many respects that, notwithstanding the abundance and versatility of its forms and phenomena, it proceeds according to very simple general rules."

I. 5. SURVEY OF THE THESIS

The basic experimental data employed in the present investigation are reviewed in Chapter II.

Chapters III and IV are devoted, respectively, to the isobaric viscosity-temperature relationship and the isothermal viscosity-pressure relationship of a given liquid. By combining the resulting isobar and isotherm equations an expression for the complete viscosity-pressure relationship is derived in Chapter V. The latter expression requires a minimum number of parameters for fully characterizing, in very wide ranges, the effects of temperature and pressure on the viscosity of any given liquid.

Chapters VI and VII introduce rational methods for classifying lubricating oils according to their atmospheric viscosity-temperature relationship and their viscosity-pressure relationship, respectively.

These methods are based directly on the newly developed equations for the latter relationships.

The analytical framework developed in Chapters III through V has proved excellently suitable for correlating the viscosity-temperature-pressure relationship of liquids, notably all the various kinds of mineral oils encountered, with their chemical constitution or with readily measurable physical constants. Chapter VIII presents convenient correlations for predicting the atmospheric viscosity-temperature relationship of mineral oils either from their chemical constitution - expressed in terms of the "Waterman analysis" - or from physical constants that are easily assessable at atmospheric pressure. Chapter IX provides similar correlations for predicting their viscosity-pressure relationship. Finally, Chapter X discusses the correlation between the viscosity-pressure relationship of mineral oils and their atmospheric viscosity-temperature relationship.

Chapter XI touches upon certain basic problems concerning oil viscosity in being devoted to the correlation of the viscosity grade - defined as the viscosity at atmospheric pressure and at some standard reference temperature - of mineral oils and pure hydrocarbons both with their chemical constitution and with various easily assessable physical constants.

Chapter XII introduces convenient methods for predicting the viscosity grade and the atmospheric viscosity-temperature relationship of mixtures of mineral oils solely from those of the components.

The concluding Chapter XIII elaborates several applications of the present findings in hydrodynamic lubrication.

CHAPTER II

EXPERIMENTAL DATA

II. 1. REVIEW OF VISCOSITY DATA

As indicated above, the great majority of investigations in the field of the viscosity variation of liquids has been confined to the temperature effect observed at atmospheric pressure. Research at *elevated* pressures has long been hampered by experimental difficulties. Nevertheless, substantial information on the viscosity of liquids, notably those used as lubricating oils, has gradually become available.

The research on *high-pressure viscosity of lubricating oils* may be stated to date back to 1915, when the Special Research Committee on Lubrication of the American Society of Mechanical Engineers (ASME) started to sponsor such research[25,26]). Ultimately, these activities have culminated in an extensive project undertaken by the latter Committee and carried out at Harvard University. Detailed experimental data on over 40 lubricating oils of well-defined composition, including several types of synthetic oils, have been compiled in the famous ASME "Pressure-Viscosity Report"[27,28]). These data are of outstanding interest in that they have been measured over unusually wide ranges of both temperature and pressure.

During the last fifty years, many further investigations have been performed. Hersey and Hopkins have reviewed - on the request of the aforementioned ASME Committee - these various investigations and co-ordinated the data from the more important contributions up to 1950[26]). Besides the work performed in the scope of the indicated ASME pressure-viscosity project, Kuss's very extensive and accurate measurements carried out, since the early fifties, on mineral oils and some synthetic oils should be deemed of paramount importance[13, 15, 17, 29, 30]). Amongst the various other investigations it may suffice here to mention only those performed by Dow and co-workers[31-37]).

The pioneering work on the viscosity-pressure variation of *pure* compounds has been done primarily by Bridgman, in the scope of his classical high-pressure investigations[7-9]). In later years, Kuss systematically studied the effect of chemical constitution on the viscosity-pressure dependence of a great variety of pure compounds[13-18]). Since 1947, viscosity-pressure measurements on pure, high-molecular-weight hydrocarbons of divergent structure have been made at the Pennsylvania State University, in the scope of API Research Project 42[10-12]).

Whereas the experimental data used in the present investigation for studying the atmospheric viscosity-temperature relationship of liquids derive from an extensive number of previous investigations, the data here employed for studying their viscosity-pressure relationship - where possible, in combination with their viscosity-temperature variation - have mainly been taken from the above-indicated investigations. Amongst the really great variety of liquids taken into consideration, attention has been devoted primarily to those used as lubricating oils, not only natural, hydrogenated, and polymer-blended mineral oils but also the various types of synthetic oils that are most important in modern lubrication practice.

As regards the experimental *accuracy* inherent in the various viscosity data employed, it can be stated that usually this would amount to something like 2%, but atmospheric viscosity data will frequently be somewhat more accurate. Accordingly, there is generally not much sense in retaining more than three digits in reporting viscosity values; only when the first digit amounts to one may it be advisable to retain four digits. In accordance with these figures, no more than three decimal places may reasonably be retained in the often employed common logarithm of viscosity.

Since a substantial part of the present investigation has been devoted to correlating the viscosity characteristics of *mineral* oils with other properties, the pertinent data will now be considered more specifically.

II. 2. VISCOSITY DATA ON MINERAL OILS

II. 2. 1. *Review of Viscosity Data Used in the Present Investigation*

Reliable experimental data, taken from various investigations, have been compiled on the viscosity characteristics of numerous well-defined mineral oils displaying a great variety of origin and chemical constitution. For each of the correlational attempts described in this thesis a group of mineral oils have been selected that may be deemed representative of the full range of natural mineral oils known so far. In addition, the completely hydrogenated, or saturated, samples of many natural oils have been taken into consideration.

Most of the mineral oils utilized for correlating their *atmospheric* viscosities with their chemical constitution as well as with various, easily assessable, atmospheric physical constants (see Chapters VIII and XI) constitute part of Waterman's collection and have been the subject of extensive investigations, of various kinds, carried out at the Laboratory for Chemical Technology of the Technological University of Delft 38-44). Moreover, data on no less than 73 oils have been taken from the investigation by Fenske *et al.*45). Further, a smaller number of the oils considered have been tested in the aforementioned ASME pressure-viscosity project 27), in the investigation by van Westen *et al.*46) and in that by André and O'Neal 47).

The data employed for correlating the viscosity-*pressure* variation of mineral oils both with their chemical constitution and with various, easily assessable, atmospheric physical constants (see Chapters IX and X) mainly derive from Kuss's aforementioned investigations[29,30,13]. In addition, high-pressure data on the above-indicated group of oils tested in the ASME pressure-viscosity project have been taken into consideration. Further data derive from various investigations performed by Dow and his co-workers[31-35;37].

Finally, own measurements on a representative group of 20 well-defined mineral oils have been used. The latter measurements have well proved their value in that it was on the basis of these that it appeared possible - presumably for the first time - to establish a really satisfactory correlation between the viscosity-pressure dependence of mineral oils and their chemical constitution. The detailed experimental data and the resulting correlation have already been published[44]. As also indicated in the latter paper, these high-pressure measurements have been performed by means of a falling-needle viscometer*) of the type described by Boelhouwer and Toneman[48].

II. 2. 2. *Characterization of Mineral Oils*

Of course, for correlational purposes "chemical constitution" must be sufficiently characterized in convenient terms.

It was Vlugter, Waterman and van Westen who succeeded, way back in the early thirties, in developing an ingenious - and at the time rather revolutionary - method for characterizing the chemical constitution of mineral oils in both convenient and significant terms[49,50,42]. In later years Waterman and his associates more than once refined and extended the original characterization method[50,42]. The version that has commonly been employed for some fifteen years now is the so-called n-d-M method. In the literature this or some other version of the original "ring analysis" is often referred to as the *"Waterman analysis"*. Certainly, this classical characterization method has rendered excellent services to petroleum technology.

The basis of the Waterman analysis is the concept of the *"average"* oil molecule, which should represent the statistical distribution of paraffinic chains, naphthenic rings and aromatic rings amongst the gigantic variety of (essentially) hydrocarbon molecules present in a given mineral-oil fraction. The consequent *"statistical constitution analysis"* of mineral oils could thus be reduced to a determination of only the number of *rings* per average molecule, of both the naphthenic and the aromatic type, denoted by R_N and R_A, respectively. Their *carbon-type composition* - which has proved of particular significance for correlational purposes - is expressed in terms of the quantities C_A, C_N and C_P, that is the percentages of the total number of carbon atoms that occur in aromatic-ring, naphthenic-

*) The present viscometer has been designed by Mr. J. W. M. Boelhouwer of the Royal Dutch/Shell Laboratory, Amsterdam, Holland.

The author wishes to express his sincere gratitude to Mr. Boelhouwer and to the Management of the latter laboratory for generous support in constructing the viscometer and for lending the timing device employed.

The author is also much indebted to Prof. G. A. M. Diepen, Professor of General and Inorganic Chemistry at the Technological University of Delft, for his permission to use his high-pressure equipment.

ring and paraffinic-chain structures, respectively.

Once the values of R_A and R_N and the (average) molecular weight of a given mineral-oil fraction are known, its carbon-type composition can easily be calculated if only some assumption is made regarding the type and fusion of the rings. It is normally assumed that all rings are six-membered and that they are fused exclusively to kata-condensed types[50,42].

In the n-d-M method, which has invariably been applied to the oils here considered, the above-defined average constitution of a given mineral oil is determined from the following three physical constants: *refractive index*, n (measured for the sodium-D line), taken at atmospheric pressure and at either 20 or 70°C (68 or 158°F); *density*, d, measured under the same conditions as n; and (average) *molecular weight*, M.

It may be added that the n-d-M method also allows for the effect of the sulfur content of the oil on the resulting compositional figures. This boils down to applying a minor correction to the number of naphthenic rings, R_N, and the corresponding percentage C_N. This correction, however, becomes significant only if the sulfur content amounts to at least, say, 1% by weight.

II. 2. 3. *Basic Data on Mineral Oils Considered*

Table II-1 provides basic information on no less than 357 mineral oils which have been utilized in various correlational attempts described in this thesis.

The (atmospheric) physical data*) of the latter table invariably relate to the adopted standard reference temperature of 40°C (104°F).

For all the oils deriving from References 27, 35, 45, 46 and 47, the viscosities at 40°C had to be obtained by interpolating from the experimental values reported for 100°F (37.8°C) and 210°F (98.9°C). This has been done on the basis of the new viscosity-temperature Equation (III-6h) described in Chapter III.

Most of the densities, d_{40^oC}, listed in Table II-1 have been calculated from the experimental values for 20°C (68°F) by means of the accurate method developed by Lipkin and Kurtz[51] (compare § VIII.3.2).

Similarly, the refractive indices, n_{40^oC}, listed in the same table have invariably been calculated from the experimental values for 20°C, using the well-established correlation[52,50a] that, at least over the temperature range involved, the change in the refractive indices of mineral oils amounts to 0.59 times the corresponding density change (density being expressed in g/cm^3).

As already mentioned, the carbon percentages and ring numbers of the present mineral oils have invariably been determined by means of the n-d-M method''**). The carbon-type compositions of the natural minerals oils cover nearly the entire range encountered amongst all the various kinds of oils known so far. As regards the

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*) The viscosity and density data on the representative group of mineral oils coded K-1 through K-29 have been generously provided by Prof. E. Kuss, at the Institut für Erdölforschung in Hannover (see also § IX.1.3).

**) Since their composition appears to fall beyond the scope of the latter method, no figures could be listed for the three oils coded K-13, K-27 and K-28.

extent of this range, reference may be made to Fig. VIII-1. In addition, fully hydrogenated, or *saturated*, samples - having, by definition, a vanishing percentage C_A - of many natural oils have been included. As indicated in Table II-1 (see the pertinent footnote), nearly all these saturated fractions have been obtained by so-called complete, *analytical* (or non-destructive) hydrogenation of the natural samples; this means that the only chemical change brought about would essentially consist in the conversion of the aromatic into the corresponding naphthenic compounds.

Finally, it may be noted that the n-d-M method - and any other such method as well - is bound to yield approximate, and not necessarily exact, composition figures. This should be well realized in criticizing the accuracy of any correlation based on these figures.

TABLE II-1

Characterization of Mineral-Oil Fractions

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al.[38-44)]											
	Venezuela (Tin 1)										
W-1	Fraction 1	1.205	0.8007	1.4462	164	0.1	12	34	54	0.3	0.6
W-1H		1.225	0.7839	1.4322	166	-	-	43	57	-	0.9
W-2	" 2	1.574	0.8087	1.4508	181	0.1	13	31	56	0.3	0.7
W-2H		1.552	0.7933	1.4375	185	-	-	42	58	-	1.0
W-3	" 3	2.09	0.8163	1.4553	203	0.2	13	27	60	0.3	0.7
W-3H		2.08	0.8009	1.4413	201	-	-	42	58	-	1.1
W-4	" 4	2.82	0.8222	1.4590	224	0.3	13	24	63	0.4	0.6
W-4H		2.72	0.8057	1.4442	235	-	-	36	64	-	1.1
W-5	" 5	4.15	0.8292	1.4627	261	0.4	12	23	65	0.4	0.7
W-5H		3.90	0.8122	1.4479	247	-	-	37	63	-	1.2
W-6	" 6	5.85	0.8375	1.4666	277	0.6	13	22	65	0.4	0.8
W-6H		5.27	0.8185	1.4512	275	-	-	36	64	-	1.3
WR-7	" 7	8.79	0.8472	1.4716	303	0.6	13	21	66	0.5	0.8
WR-7H		7.96	0.8290	1.4548	304	-	-	34	66	-	1.4
W-8	" 8	13.24	0.8545	1.4759	339	0.8	13	20	67	0.5	1.0
W-8H		11.12	0.8323	1.4580	344	-	-	33	67	-	1.6
W-9	" 9	23.3	0.8653	1.4814	381	0.9	13	21	66	0.6	1.3
W-9H		19.06	0.8421	1.4626	381	-	-	34	66	-	1.8
	Borneo (Tin 2)										
W-10	Fraction 1	1.242	0.8265	1.4529	176	-	5	56	39	0.1	1.4
W-10H		1.306	0.8176	1.4448	174	-	-	62	38	-	1.5

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Borneo (Tin 2)										
WR-11	Fraction 2	1.493	0.8390	1.4599	177	-	9	55	36	0.2	1.4
W-11H		1.521	0.8258	1.4489	181	-	-	63	37	-	1.6
W-12	" 3	1.706	0.8509	1.4674	180	-	12	55	33	0.3	1.4
W-12H		1.742	0.8335	1.4527	184	-	-	64	36	-	1.7
W-13	" 4	1.964	0.8615	1.4748	184	-	17	50	33	0.4	1.4
W-13H		2.02	0.8407	1.4562	186	-	-	67	33	-	1.8
W-14	" 5	2.30	0.8722	1.4823	190	-	21	47	32	0.5	1.3
W-14H		2.29	0.8459	1.4587	192	-	-	67	33	-	1.8
W-15	" 6	2.73	0.8833	1.4903	198	-	24	43	33	0.6	1.3
W-15H		2.70	0.8528	1.4629	195	-	-	69	31	-	1.9
W-16	" 8	4.02	0.9044	1.5062	214	-	31	35	34	0.8	1.3
W-16H		3.59	0.8612	1.4663	216	-	-	67	33	-	2.1
W-17	" 9	5.68	0.9182	1.5144	227	-	33	35	32	0.9	1.4
W-17H		4.86	0.8730	1.4715	226	-	-	70	30	-	2.4
WR-18	" 10	9.12	0.9316	1.5219	238	-	35	34	31	1.0	1.4
WR-18H		7.10	0.8822	1.4755	238	-	-	69	31	-	2.5
W-19	" 11	20.6	0.9475	1.5315	265	-	36	33	31	1.2	1.6
W-19H		12.85	0.8934	1.4814	266	-	-	70	30	-	2.9
W-20H	" 12	35.6	0.9067	1.4878	310	-	-	70	30	-	3.4
	Mexico (Tin 3)										
W-21	Fraction 1	1.159	0.7909	1.4400	176	0.2	7	30	63	0.2	0.6
W-21H		1.180	0.7796	1.4309	179	-	-	34	66	-	0.8
W-22	" 2	1.496	0.8042	1.4473	194	0.3	8	30	62	0.2	0.7
W-22H		1.500	0.7904	1.4361	198	-	-	36	64	-	0.9

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40°C}$, cP	$d_{40°C}$, g/cm^3	$n_{40°C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Mexico (Tin 3)										
W-23	Fraction 3	2.19	0.8220	1.4572	213	0.4	11	31	58	0.3	0.8
W-23H		2.19	0.8055	1.4433	221	-	-	40	60	-	1.1
W-24	„ 4	3.55	0.8412	1.4677	243	0.7	14	28	58	0.4	0.9
W-24H		3.35	0.8198	1.4503	239	-	-	43	57	-	1.4
W-25	„ 5	6.17	0.8587	1.4770	269	1.0	15	28	57	0.5	1.0
W-25H		5.52	0.8334	1.4568	263	-	-	44	56	-	1.6
WR-26	„ 6	13.46	0.8782	1.4872	308	1.2	16	27	57	0.6	1.2
W-26H		10.33	0.8460	1.4629	301	-	-	44	56	-	1.9
W-27	„ 7	28.6	0.8926	1.4956	355	1.5	17	26	57	0.8	1.3
W-27H		20.4	0.8587	1.4689	342	-	-	45	55	-	2.3
W-28	„ 8	68.4	0.9056	1.5031	396	1.6	19	24	57	0.9	1.6
W-28H		39.0	0.8674	1.4733	395	-	-	44	56	-	2.6
	Borneo (Tin 4)										
W-29	Fraction 1	1.042	0.8209	1.4617	152	-	26	30	44	0.5	0.6
W-29H		1.114	0.7916	1.4339	164	-	-	51	49	-	1.0
W-30	„ 2	1.186	0.8293	1.4669	159	-	27	29	44	0.5	0.6
W-30H		1.262	0.7990	1.4384	168	-	-	54	46	-	1.2
W-31	„ 3	1.343	0.8386	1.4729	166	-	28	29	43	0.6	0.6
W-31H		1.406	0.8061	1.4418	173	-	-	57	43	-	1.2
W-32	„ 4	1.563	0.8484	1.4796	169	-	31	28	41	0.6	0.7
W-32H		1.622	0.8134	1.4453	178	-	-	57	43	-	1.3
W-33	„ 5	1.778	0.8560	1.4847	175	-	32	28	40	0.7	0.6
W-33H		1.770	0.8184	1.4478	186	-	-	56	44	-	1.4
WR-34	„ 7	2.40	0.8672	1.4907	188	-	33	22	45	0.8	0.6
W-34H		2.28	0.8259	1.4516	197	-	-	56	44	-	1.5

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Borneo (Tin 4)										
W-35H	Fraction 9	3.13	0.8286	1.4537	217	-	-	51	49	-	1.5
W-36	" 12	12.47	0.8775	1.4968	313	-	25	16	59	1.0	0.8
W-36H		10.05	0.8481	1.4636	310	-	-	42	58	-	1.9
	Rumania (Tin 5)										
W-37	Fraction 1	1.038	0.7876	1.4393	158	-	11	30	59	0.2	0.6
W-37H		1.064	0.7706	1.4255	164	-	-	34	66	-	0.7
W-38	" 2	1.306	0.7973	1.4451	172	-	12	29	59	0.2	0.7
W-38H		1.343	0.7814	1.4317	175	-	-	37	63	-	0.8
W-39H	" 3	1.718	0.7919	1.4370	199	-	-	36	64	-	0.9
W-40	" 4	2.32	0.8185	1.4578	208	-	15	24	61	0.4	0.6
W-40H		2.27	0.8010	1.4319	219	-	-	37	63	-	1.0
W-41	" 5	3.30	0.8260	1.4612	232	-	15	22	63	0.4	0.7
W-41H		3.14	0.8081	1.4460	240	-	-	36	64	-	1.1
W-42	" 6	4.92	0.8332	1.4652	264	-	14	23	63	0.4	0.8
W-42H		4.50	0.8164	1.4501	277	-	-	35	65	-	1.2
W-43	" 7	7.59	0.8446	1.4716	291	0.2	14	22	64	0.5	0.9
W-43H		6.56	0.8256	1.4545	300	-	-	35	65	-	1.4
W-44H	" 9	18.88	0.8486	1.4655	380	-	-	36	64	-	2.0
	Sumatra (Tin 6)										
W-45	Fraction 1	0.865	0.7937	1.4420	159	-	11	34	55	0.2	0.7
W-45H		0.918	0.7768	1.4281	170	-	-	38	62	-	0.8
W-46	" 2	0.935	0.7971	1.4440	155	-	12	36	52	0.2	0.7
W-46H		0.975	0.7796	1.4295	179	-	-	37	63	-	0.8

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Sumatra (Tin 6)										
W-47	Fraction 3	1.052	0.8027	1.4469	165	-	12	35	53	0.2	0.8
W-47H		1.086	0.7861	1.4326	176	-	-	42	58	-	0.9
W-48	" 4	1.188	0.8088	1.4503	171	-	13	35	52	0.3	0.7
W-48H		1.225	0.7929	1.4360	179	-	-	45	55	-	1.0
W-49	" 5	1.358	0.8153	1.4544	176	-	15	34	51	0.3	0.8
W-49H		1.390	0.7990	1.4388	185	-	-	48	52	-	1.1
W-50	" 6	1.567	0.8225	1.4583	187	-	15	35	50	0.4	0.8
W-50H		1.596	0.8049	1.4418	193	-	-	49	51	-	1.2
W-51	" 7	1.866	0.8298	1.4627	193	-	17	34	49	0.4	0.8
W-51H		1.854	0.8115	1.4449	200	-	-	51	49	-	1.3
W-52	" 8	2.19	0.8374	1.4674	200	0.1	19	34	47	0.5	0.8
W-52H		2.18	0.8174	1.4479	209	-	-	49	51	-	1.4
W-53	" 9	2.66	0.8443	1.4716	209	-	20	30	50	0.5	0.9
W-53H		2.60	0.8232	1.4507	219	-	-	49	51	-	1.5
W-54	" 10	3.41	0.8510	1.4752	222	-	20	29	51	0.5	1.0
W-54H		3.30	0.8298	1.4541	227	-	-	50	50	-	1.6
W-55	" 11	4.70	0.8587	1.4796	243	-	20	27	53	0.6	1.0
W-55H		4.38	0.8369	1.4577	251	-	-	48	52	-	1.7
WR-56	" 12	7.14	0.8728	1.4871	266	-	21	27	52	0.7	1.1
WR-56H		6.50	0.8480	1.4623	269	-	-	48	52	-	1.9
W-57	" 13	15.38	0.8932	1.5000	306	0.3	24	24	52	0.9	1.3
W-57H		11.62	0.8619	1.4694	292	-	-	52	48	-	2.3
	Sumatra (Tin 7)										
W-58	Fraction 2	1.109	0.7987	1.4483	173	-	16	20	64	0.3	0.5
W-58H		1.194	0.7804	1.4311	175	-	-	37	63	-	0.8

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Sumatra (Tin 7)										
W-59	Fraction 3	1.288	0.8065	1.4532	181	-	18	19	63	0.4	0.4
W-59H		1.337	0.7875	1.4346	188	-	-	37	63	-	0.9
W-60	" 4	1.476	0.8137	1.4575	188	-	20	18	62	0.5	0.4
W-60H		1.528	0.7923	1.4370	196	-	-	37	63	-	0.9
W-61	" 5	1.722	0.8206	1.4617	194	-	21	18	61	0.5	0.5
W-61H		1.702	0.7976	1.4394	202	-	-	40	60	-	1.0
W-62	" 6	2.03	0.8258	1.4648	209	-	20	18	62	0.5	0.5
W-62H		2.02	0.8036	1.4425	215	-	-	40	60	-	1.1
W-63	" 7	2.39	0.8266	1.4648	213	-	20	18	62	0.5	0.5
W-63H		2.37	0.8058	1.4439	224	-	-	39	61	-	1.1
W-64	" 8	2.93	0.8252	1.4635	237	-	17	16	67	0.5	0.5
W-64H		2.85	0.8070	1.4451	243	-	-	35	65	-	1.1
W-65H	" 9	3.52	0.8078	1.4622	263	-	-	32	68	-	1.0
W-66	" 10	4.70	0.8261	1.4627	280	-	13	15	72	0.5	0.5
W-66H		4.49	0.8117	1.4484	291	-	-	29	71	-	1.1
WR-67	" 11	6.58	0.8312	1.4650	318	-	12	15	72	0.5	0.6
W-67H		6.15	0.8193	1.4515	321	-	-	30	70	-	1.2
W-68	" 12	9.46	0.8370	1.4677	340	-	12	17	71	0.5	0.7
W-68H		8.87	0.8259	1.4558	353	-	-	30	70	-	1.3
	Venezuela (Tin 8)										
WR-69	Fraction 1	1.556	0.8272	1.4566	175	0.3	12	47	41	0.3	1.0
W-69H		1.563	0.8055	1.4420	176	-	-	55	45	-	1.2
W-70	" 2	1.726	0.8611	1.4767	205	0.8	18	39	43	0.5	1.1
W-70H		2.81	0.8295	1.4538	205	-	-	55	45	-	1.5

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	η_{40^oC}, cP	d_{40^oC}, g/cm^3	n_{40^oC}	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Venezuela (Tin 8)										
W-71	Fraction 3	8.09	0.8898	1.4932	248	1.2	21	35	44	0.6	1.4
W-71H		6.12	0.8498	1.4631	255	-	-	53	47	-	2.0
W-72H	" 4	11.17	0.8617	1.4700	303	-	-	50	50	-	2.3
W-73H	" 5	37.2	0.8750	1.4766	351	-	-	50	50	-	2.7
	Iran (Tin 9)										
W-74	Fraction 1	1.042	0.7830	1.4370	175	0.2	9	26	65	0.2	0.5
W-74H		1.092	0.7723	1.4276	170	-	-	32	68	-	0.7
W-75	" 2	1.294	0.7928	1.4422	174	0.2	10	26	64	0.2	0.6
W-75H		1.291	0.7793	1.4311	186	-	-	31	69	-	0.8
WR-76	" 3	1.683	0.8048	1.4486	186	0.3	12	26	62	0.3	0.6
W-76H		1.377	0.7881	1.4355	193	-	-	35	65	-	0.9
W-77	" 4	2.12	0.8160	1.4554	201	0.5	14	25	61	0.3	0.6
W-77H		2.10	0.7979	1.4403	213	-	-	36	64	-	1.0
W-78	" 5	2.95	0.8277	1.4617	220	0.7	15	26	59	0.4	0.6
W-78H		2.81	0.8071	1.4448	225	-	-	39	61	-	1.1
WR-79	" 6	4.48	0.8408	1.4686	242	1.0	16	23	61	0.5	0.7
WR-80	" 7	6.68	0.8550	1.4767	273	1.2	17	21	62	0.6	0.7
W-80H		5.69	0.8254	1.4539	274	-	-	39	61	-	1.5
WR-81	" 8	11.54	0.8690	1.4845	300	1.4	18	21	61	0.7	0.8
W-81H		8.61	0.8348	1.4585	301	-	-	39	61	-	1.6
W-82	" 9	20.7	0.8793	1.4902	342	1.5	18	19	63	0.8	0.9
W-82H		14.86	0.8446	1.4627	340	-	-	38	62	-	1.9
W-83	" 10	43.2	0.8940	1.4991	387	1.5	20	18	62	1.0	1.1
W-83H		28.2	0.8567	1.4689	377	-	-	40	60	-	2.2

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	η_{40^oC}, cP	d_{40^oC}, g/cm^3	n_{40^oC}	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Iran (Tin 9)										
W-84	Fraction 11	90.4	0.9066	1.5074	434	1.7	22	16	62	1.2	1.1
W-84H		52.8	0.8655	1.4733	426	-	-	41	59	-	2.6
	Texas (Tin 11)										
W-85	Fraction 1	1.084	0.7931	1.4421	164	-	11	30	59	0.2	0.7
W-85H		1.143	0.7812	1.4310	165	-	-	42	58	-	0.9
W-86	" 2	1.321	0.8025	1.4476	176	-	12	29	59	0.3	0.6
W-86H		1.358	0.7893	1.4351	180	-	-	41	59	-	0.9
W-87	" 3	1.686	0.8136	1.4543	187	0.1	15	28	57	0.3	0.7
W-87H		1.710	0.7979	1.4395	192	-	-	43	57	-	1.0
W-88	" 4	2.30	0.8235	1.4603	201	0.1	17	27	56	0.4	0.7
W-88H		2.28	0.8073	1.4442	212	-	-	44	56	-	1.2
W-89	" 5	3.22	0.8323	1.4651	220	0.2	17	27	56	0.5	0.7
W-89H		3.16	0.8155	1.4485	225	-	-	45	55	-	1.3
W-90	" 6	4.86	0.8413	1.4698	246	0.2	16	25	59	0.5	0.8
W-90H		4.49	0.8225	1.4522	260	-	-	40	60	-	1.4
WR-91	" 7	7.87	0.8542	1.4761	276	0.2	16	24	60	0.6	0.9
WR-91H		6.79	0.8333	1.4572	294	-	-	40	60	-	1.6
W-92	" 8	13.46	0.8647	1.4817	304	0.3	17	23	60	0.6	1.1
W-92H		11.14	0.8433	1.4618	330	-	-	39	61	-	1.8
W-93H	" 10	40.5	0.8646	1.4728	415	-	-	41	59	-	2.6
	Rijswijk[43)]										
W-94	Fraction 7	0.897	0.7955	1.4414	158	-	8	41	51	0.2	0.8
W-94H		0.895	0.7793	1.4307	149	-	-	47	53	-	0.9

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Rijswijk[43)]										
W -95	Fraction 8	1.390	0.8056	1.4482	190	-	9	31	60	0.2	0.8
W -95H		1.400	0.7920	1.4374	196	-	-	36	64	-	0.9
W -96	" 9	1.858	0.8102	1.4522	205	-	12	24	64	0.3	0.6
W -96H		1.871	0.7977	1.4398	206	-	-	38	62	-	1.0
WR-97	" 10	2.31	0.8146	1.4546	214	-	12	24	64	0.3	0.7
W -97H		2.25	0.8011	1.4422	219	-	-	36	64	-	1.0
W -98	" 11	2.73	0.8180	1.4564	224	-	11	26	63	0.3	0.7
W -98H		2.68	0.8050	1.4438	222	-	-	38	62	-	1.1
WR-99	" 12	3.33	0.8188	1.4566	240	0.1	11	22	67	0.3	0.7
W -99H		3.05	0.8033	1.4444	240	-	-	31	69	-	0.9
W -100	" 13	3.98	0.8234	1.4590	253	0.1	10	24	66	0.3	0.8
W -100H		3.85	0.8114	1.4475	255	-	-	35	65	-	1.1
W -101	" 14	5.07	0.8320	1.4636	270	0.1	11	25	64	0.4	0.8
W -101H		4.83	0.8190	1.4514	277	-	-	36	64	-	1.3
W -102	" 15	6.50	0.8439	1.4699	280	0.2	13	25	62	0.4	1.0
W -102H		6.15	0.8290	1.4561	285	-	-	38	62	-	1.5
W -103	" 16	8.17	0.8475	1.4725	294	0.2	14	23	63	0.5	1.0
W -103H		7.14	0.8274	1.4562	301	-	-	36	64	-	1.5
W -104	" 17	9.80	0.8476	1.4720	307	0.2	13	24	63	0.5	1.0
W -104H		8.55	0.8318	1.4575	309	-	-	38	62	-	1.5
W -105	" 19	18.49	0.8781	1.4883	336	0.3	16	25	59	0.7	1.3
W -105H		14.55	0.8515	1.4650	322	-	-	43	57	-	2.0
W -106H	" 21	15.74	0.8458	1.4637	400	-	-	33	67	-	1.9
	Oil R[40)]										
W -107	Fraction 6	0.834	0.7744	1.4321	161	0.2	7	24	69	0.1	0.5
W -108	" 15	6.58	0.8615	1.4808	278	1.7	18	20	62	0.6	0.7

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^{o}C}$, cP	$d_{40^{o}C}$, g/cm^3	$n_{40^{o}C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
WATERMAN et al. (Cont.)											
	Oil T[40)]										
W-109	Fraction 9	1.021	0.7861	1.4392	173	0.2	9	22	69	0.2	0.5
W-110	" 18	7.38	0.8614	1.4808	290	1.6	17	20	63	0.6	0.8
FENSKE et al.[45)]											
	Pennsylvania 180 Neutral										
F-1	Original	31.0	0.8593	1.4767	395		10	24	66	0.5	1.5
F-2	Fraction 1	11.62	0.8586	1.4767	338		12	26	62	0.5	1.4
F-3	" 2	13.71	0.8569	1.4759	343		12	25	63	0.5	1.3
F-4	" 3	15.81	0.8543	1.4745	347		12	24	64	0.5	1.3
F-5	" 4	17.50	0.8539	1.4744	353		11	24	65	0.5	1.3
F-6	" 5	19.01	0.8541	1.4744	358		11	24	65	0.5	1.3
F-7	" 6	20.5	0.8545	1.4745	363		11	24	65	0.5	1.3
F-8	" 7	22.0	0.8552	1.4749	368		11	24	65	0.5	1.3
F-9	" 8	22.9	0.8542	1.4743	373		11	22	67	0.5	1.3
F-10	" 9	24.9	0.8543	1.4744	378		10	23	67	0.5	1.3
F-11	" 10	27.0	0.8547	1.4744	383		10	23	67	0.5	1.3
F-12	" 11	29.2	0.8562	1.4755	388		10	23	67	0.5	1.4
F-13	" 12	30.8	0.8572	1.4758	393		10	23	67	0.5	1.4
F-14	" 13	33.5	0.8583	1.4765	398		11	22	67	0.5	1.4
F-15	" 14	35.6	0.8588	1.4769	403		11	22	67	0.5	1.4
F-16	" 15	38.2	0.8590	1.4773	408		11	21	68	0.6	1.3
F-17	" 16	41.0	0.8600	1.4776	414		11	21	68	0.6	1.4
F-18	" 17	44.7	0.8603	1.4778	422		10	22	68	0.6	1.4
F-19	" 18	48.5	0.8610	1.4782	430		10	22	68	0.6	1.4

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
FENSKE et al. (Cont.)											
	Pennsylvania 180 Neutral										
F-20	Fraction 19	53.1	0.8614	1.4785	440		10	21	69	0.6	1.5
F-21	" 20	61.0	0.8626	1.4792	459		10	21	69	0.6	1.5
F-22	" 21	65.8	0.8638	1.4796	482		10	21	69	0.6	1.6
	Rodessa Neutral										
F-23	Original	31.1	0.8656	1.4795	397		11	26	63	0.5	1.7
F-24	Fraction 2	17.95	0.8672	1.4805	356		12	28	60	0.5	1.6
F-25	" 11	35.5	0.8653	1.4791	412		10	26	64	0.5	1.7
F-26	" 13	40.8	0.8662	1.4798	426		10	25	65	0.5	1.8
F-27	" 15	47.2	0.8677	1.4804	442		10	25	65	0.5	1.9
	Midcontinent Neutral 1										
F-28	Original	90.0	0.8997	1.4975	400		15	33	52	0.8	2.2
F-29	Fraction 12	150.3	0.9052	1.5012	422		16	32	52	0.8	2.4
F-30	" 13	196.8	0.9067	1.5026	437		17	30	53	0.9	2.3
F-31	" 15	272	0.9055	1.5018	468		16	29	55	0.9	2.4
F-32	" 17	327	0.9043	1.5017	497		16	27	57	1.0	2.4
	Midcontinent Neutral 2										
F-33	Original	49.8	0.8862	1.4918	377		15	28	57	0.7	1.8
F-34	Fraction 1	12.50	0.8923	1.4964	265		22	34	44	0.7	1.5
F-35	" 2	16.48	0.8902	1.4950	292		20	32	48	0.7	1.6
F-36	" 3	20.3	0.8856	1.4924	311		18	30	52	0.7	1.6
F-37	" 4	23.3	0.8831	1.4906	326		17	29	54	0.7	1.6

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	η_{40^oC}, cP	d_{40^oC}, g/cm^3	n_{40^oC}	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
FENSKE et al.(Cont.)											
	Midcontinent Neutral 2										
F-38	Fraction 5	26.4	0.8826	1.4903	338		17	29	54	0.7	1.7
F-39	" 6	29.5	0.8824	1.4903	348		16	28	56	0.7	1.7
F-40	" 7	33.3	0.8829	1.4898	357		15	29	56	0.7	1.7
F-41	" 8	37.2	0.8834	1.4903	366		15	28	57	0.7	1.8
F-42	" 10	46.7	0.8849	1.4904	381		15	28	57	0.7	1.8
F-43	" 11	51.5	0.8854	1.4905	387		15	28	57	0.7	1.9
F-44	" 12	56.9	0.8854	1.4905	392		14	29	57	0.7	1.9
F-45	" 13	62.2	0.8855	1.4905	398		14	28	58	0.7	1.9
F-46	" 14	69.3	0.8858	1.4907	403		14	28	58	0.7	1.9
F-47	" 15	75.9	0.8854	1.4908	408		14	28	58	0.7	1.9
F-48	" 16	84.9	0.8852	1.4909	412		14	27	59	0.7	1.9
F-49	" 17	94.2	0.8846	1.4908	416		14	27	59	0.7	1.9
F-50	" 18	104.5	0.8853	1.4911	417		14	27	59	0.7	1.9
	California Neutral										
F-51	Original	67.0	0.9193	1.5095	330		22	36	42	0.9	2.1
F-52	Fraction 2	6.90	0.8913	1.4901	239		17	48	35	0.5	1.8
F-53	" 14	163.3	0.9264	1.5142	348		23	36	41	1.0	2.2
F-54	" 16	273	0.9302	1.5156	381		22	36	42	1.1	2.4
F-55	" 18	454	0.9353	1.5170	409		21	38	41	1.1	2.8
	Gulf Coast Neutral										
F-56	Fraction 1	14.09	0.9139	1.5058	268		23	42	35	0.8	1.9
F-57	" 2	18.20	0.9131	1.5051	283		22	41	37	0.8	2.0
F-58	" 3	23.1	0.9110	1.5042	296		21	39	40	0.8	2.0

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
FENSKE et al. (Cont.)											
	Gulf Coast Neutral										
F-59	Fraction 4	29.0	0.9092	1.5040	307		20	39	41	0.8	2.0
F-60	" 5	33.9	0.9076	1.5022	316		20	37	43	0.8	2.0
F-61	" 6	39.4	0.9074	1.5014	325		19	38	43	0.8	2.1
F-62	" 7	45.4	0.9068	1.5010	333		18	38	44	0.8	2.1
F-63	" 8	52.0	0.9066	1.5008	341		18	37	45	0.8	2.1
F-64	" 9	60.3	0.9064	1.5004	348		17	38	45	0.8	2.2
F-65	" 10	70.8	0.9075	1.5012	355		17	37	46	0.8	2.2
F-66	" 11	83.4	0.9090	1.5015	361		17	38	45	0.8	2.3
F-67	" 12	100.0	0.9105	1.5023	366		17	38	45	0.9	2.3
F-68	" 13	122.8	0.9123	1.5032	372		17	38	45	0.8	2.5
F-69	" 14	150.3	0.9145	1.5042	378		17	39	44	0.8	2.5
F-70	" 15	188.4	0.9167	1.5049	383		17	39	44	0.8	2.6
F-71	" 16	231	0.9195	1.5060	387		16	41	43	0.8	2.7
F-72	" 17	275	0.9208	1.5066	392		16	41	43	0.8	2.8
F-73	" 18	316	0.9216	1.5066	396		15	43	42	0.8	2.9
VAN WESTEN et al.[46]											
We-1	Paraffinic Original, Table I	86.9	0.8686	1.4823	525	0.1	10	20	70	0.7	1.7
We-1H		72.3	0.8565	1.4701	513	-	-	30	70	-	2.5
We-2	Naphthenic Original, Table I	87.5	0.8963	1.4945	419	0.1	13	34	53	0.7	2.4
We-2H		55.5	0.8761	1.4767	417	-	-	47	53	-	3.0
We-3	Asphaltic Original, Table I	252	0.9560	1.5343	349	0.2	32	32	36	1.4	2.1
We-3H		80.4	0.9064	1.4890	350	-	-	64	36	-	3.6
We-4	Base Oil A, Table VII	150.0	0.9110	1.5052	425	0.9	18	27	55	1.0	1.9
We-4H		71.1	0.8745	1.4766	430	-	-	45	55	-	2.9

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	η_{40^oC}, cP	d_{40^oC}, g/cm^3	n_{40^oC}	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
VAN WESTEN et al.(Cont.)											
We-5	Hydrolube C, Table VII	69.2	0.8758	1.4806	450	0.1	6	33	61	0.3	2.6
We-5H		54.4	0.8640	1.4724	450	-	-	39	61	-	2.7
We-6	Hydrolube E, Table VII	40.7	0.8632	1.4754	425	-	4	33	63	0.3	2.0
We-6H		39.9	0.8566	1.4688	425	-	-	37	63	-	2.4
We-7	Hydrolube G, Table VII	31.8	0.8463	1.4657	447	-	-	30	70	-	1.8
We-8	Original Oil, Table X	151.0	0.9228	1.5140	414	2.0	23	22	55	1.2	1.6
We-9	Raffinate 1 from We-8	135.2	0.9138	1.5062	426	1.7	18	27	55	1.0	1.9
We-10	" 3 " "	115.1	0.8993	1.4960	442	1.3	13	30	57	0.7	2.1
We-11	" 5 " "	108.5	0.8953	1.4932	453	1.1	12	30	58	0.7	2.2
ANDRÉ and O'NEAL[47)]											
AN-1	East Texas Neutral	43.8	0.8628	1.4740	418	0.1	3	35	62	0.2	2.2
AN-2	Oklahoma City Neutral	43.8	0.8612	1.4755	433	0.1	7	27	66	0.4	1.8
AN-3	West Texas Ellenberger Neutral	41.9	0.8636	1.4773	432	0.1	8	27	65	0.4	1.9
AN-4	California Neutral, Medium VI	69.5	0.8833	1.4822	410	0.3	4	43	53	0.2	2.8
AN-5	" " Low VI	93.5	0.9029	1.4953	358	0.5	12	42	46	0.6	2.4
AN-6	Pennsylvania Neutral	31.0	0.8574	1.4752	332	-	11	28	61	0.5	1.4
AN-7	Gulf Coast Neutral	53.1	0.8944	1.4933	332	0.2	15	38	47	0.6	2.1
ASME[27)]											
A-1	Midcontinent Neutral, coded 24-E	25.1	0.855	1.4695	394		2	35	63	0.1	2.1
A-2	Heavy Gas-Oil Fraction, coded 25-E	7.30	0.864	1.4757	253		12	41	47	0.4	1.5
A-3	Paraffinic Oil, coded 31-G	41.1	0.866	1.4799	450		10	23	67	0.6	1.6
A-4	" " ", 32-G	129.4	0.871	1.4787	576		5	26	69	0.5	2.5
A-5	" Bright Stock, coded 33-G	438	0.890	1.4916	700		10	21	69	1.0	2.5

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
	ASME (Cont.)										
A-6	Paraffinic Oil, coded 34-G	138.7	0.870	1.4787	588		5	26	69	0.4	2.4
A-7	Mixture of A-3 and A-5, coded 35-G	120.5	0.876	1.4845	546		8	25	67	0.6	2.2
A-8	A-4 Dearomatized, coded 41-G	119.7	0.866	1.4751	584		3	24	73	0.2	2.5
A-9	A-3 Undewaxed, coded 49-G	38.9	0.865	1.4788	450		10	21	69	0.6	1.5
	Gulf Coast Crude										
A-10	Distillate Fraction, coded 36-G	44.7	0.903	1.4962	349		14	40	46	0.6	2.3
A-11	„ „ „ 37-G	117.5	0.915	1.5026	383		15	41	44	0.8	2.6
A-12	„ „ „ 38-G	403	0.931	1.5115	400		18	42	40	0.9	2.9
A-13	„ „ „ 39-G	119.4	0.921	1.5066	364		17	41	42	0.8	2.6
A-14	Reduced Crude, coded 40-G	117.5	0.922	1.5067	391		17	39	44	0.9	2.6
A-15	A-11 Dearomatized, coded 42-G	58.2	0.880	1.4764	407		-	49	51	-	3.2
A-16	Aromatic Extract from A-11, coded 52-G	501	0.977	1.5486	340		38	33	29	1.7	2.1
	DOW et al.[35)]										
D-1	Russian Oil "00"	157.8	0.9072	1.5012	435		15	34	51	0.8	2.6
D-2	„ „ "1"	78.5	0.8938	1.4920	393		12	36	52	0.6	2.4
D-3	„ „ "2"	30.1	0.8855	1.4886	364		13	34	53	0.6	2.1
D-4	„ Bright Stock	427	0.8900	1.4910	666		9	27	64	0.7	3.1
D-5	Rumanian Oil "1"	19.19	0.9120	1.5095	285		27	30	43	1.0	1.5
D-6	„ „ "2"	382	0.9347	1.5192	409		24	32	44	1.2	2.5
D-7	„ „ "3"	1,344	0.9461	1.5294	511		28	24	48	1.8	2.5
	KUSS[29,30)]										
K-1	Oil No.1, Table 2[30)]	260	0.8844	1.4900	620	1.0	11	19	70	0.8	2.0

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
KUSS (Cont.)											
K-2	Oil No.2, Table 2$^{30)}$	134.9	0.8857	1.4907	545	0.8	12	22	66	0.8	2.0
K-3	" " 4 " " "	101.0	0.8811	1.4852	550	0.8	8	27	65	0.5	2.4
K-4	" " 5 " " "	159.2	0.8791	1.4868	598	0.8	10	20	70	0.7	2.0
K-5	" " 6 " " "	147.2	0.8873	1.4876	530	0.1	8	32	60	0.5	2.8
K-6	" " 7 " " "	110.9	0.9069	1.5055	429	1.1	20	22	58	1.1	1.6
K-7	" " 8 " " "	58.9	0.8705	1.4772	420	1.1	4	34	62	0.2	2.2
K-8	" " 9 " " "	67.6	0.9213	1.5130	360	1.1	24	28	48	1.1	1.7
K-9	" " 10 " " "; Group W.B.Lub.: Lub.3, Dist.$^{29)}$	328	0.9129	1.5107	370	0.9	24	22	54	1.1	1.4
K-10	Hypoid Gear Oil, No.11, Table 2$^{30)}$	62.4	0.8950	1.4935	421	1.6	13	29	58	0.6	2.0
K-11	" " " " 12 " " "	246	0.9135	1.5055	512	2.4	16	23	61	1.0	1.9
K-12	" " " " 13 " " "	408	0.9131	1.5047	440	2.3	17	26	57	0.9	1.9
K-13	Oil No.14, Table 2$^{30)}$	1.686	0.8229	1.4749	320	-					
K-14	" " 15 " " "; Group High: High G$^{29)}$	7.16	0.8252	1.4558	280	-	3	33	64	0.1	1.2
K-15	Oil No.16, Table 2$^{30)}$; Group Low: Low B$^{29)}$	2.93	0.8613	1.4755	215	-	16	42	42	0.4	1.4
K-16	Oil No.17, Table 2$^{30)}$	12.90	0.8292	1.4579	450	-	-	24	76	-	1.4
K-17	" " 18 " " "	31.8	0.8674	1.4769	385	0.6	6	34	60	0.3	2.0
K-18	" " 19 " " "	36.6	0.8672	1.4786	406	0.4	9	28	63	0.4	1.9
K-19	" " 20 " " "; Group T.J.Lub.: Lub.2, Raff.$^{29)}$	27.3	0.8683	1.4794	325	0.1	12	33	55	0.4	1.7
K-20	Oil No.21, Table 2$^{30)}$	33.5	0.8625	1.4739	395	0.3	4	35	61	0.2	2.0
K-21	" " 22 " " "	173.8	0.8794	1.4830	545	0.9	6	29	65	0.4	2.5
K-22	" " 23 " " "; Group High: High K$^{29)}$	139.5	0.8740	1.4785	510	0.7	2	35	63	0.2	2.7
K-23	Oil No.24, Table 2$^{30)}$; Group High: High O$^{29)}$	355	0.8785	1.4832	690	0.6	5	27	68	0.4	3.0

CONTINUATION OF TABLE II-1

Mineral-Oil Fraction		(Atmospheric) Physical Constants				Wt.%	n-d-M Analysis				
Code*)	Experimenters' Designation	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	$n_{40^\circ C}$	M	Sulfur**)	C_A	C_N	C_P	R_A	R_N
	KUSS (Cont.)										
K-24	Oil No.25, Table 2[30]; Group T.J.Lub.: Lub.3, Raff.[29]	83.7	0.8850	1.4882	430	-	11	31	58	0.6	2.2
K-25	Oil No.26, Table 2[30]; Group W.B.Lub.: Lub.3, Filtr.[29]	192.0	0.8889	1.4853	580	0.8	3	37	60	0.2	3.4
K-26	Oil No.27, Table 2[30]; Group Low: Low D[29]	90.0	0.9151	1.5080	290	-	24	37	39	0.8	1.9
K-27	Oil No.28, Table 2[30]; Group W.B.Lub.: Lub.1, Extr.[29]	19.13	0.9620	1.5450	220	1.8					
K-28	Oil No.29, Table 2[30]; Group T.J.Lub.: Lub.2, Extr.[29]	127.6	1.0042	1.5767	320	3.5					
K-29	Oil No.30, Table 2[30]; Group W.B.Lub.: Lub.2, Extr.[29]	1,290	0.9894	1.5562	350	1.7	41	26	33	1.8	1.8
K-30	" " " " " " Dist.[29] (see also Ref.30, p.196)	88.4	0.9035	1.4959	395	0.1	12	41	47	0.6	2.7
K-31	Group Low: Low C[29] (see also Ref.30, p.196)	19.00	0.9053	1.5017	280	1.2	21	35	44	0.7	1.6

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*) The sulfix "H" refers to a saturated mineral-oil fraction which has been obtained by complete, analytical hydrogenation of the similarly numbered natural fraction.

The prefix "WR" refers to mineral oils whose viscosity-temperature-pressure relationship has been determined by Roelands et al.[44]. The viscosity and density data included in the present table derive from their investigation.

**) In this column dashes denote that the sulfur content is negligible, whilst blank places indicate that this has not been reported.

CHAPTER III

THE ISOBARIC VISCOSITY-TEMPERATURE RELATIONSHIP FOR A GIVEN LIQUID

III. 1. THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP FOR A GIVEN LIQUID

III. 1. 1. *Introduction*

To a first approximation the relationship, at atmospheric pressure, between dynamic viscosity η_0 of liquids and absolute temperature T can be described by the equation*):

$$\log \eta_0 = \frac{C_0}{T} + D_0, \qquad \text{(III-1a)}$$

where C_0 and D_0 denote parameters characteristic of the liquid concerned, the subscript "0" referring to atmospheric pressure**). This simple two-parameter equation was established empirically by de Guzmán as early as 1913[53)].

In later years Equation (III-1a) achieved foundation in several viscosity theories. In fact, irrespective of the particular model assumed for viscous flow, the great majority of viscosity theories prove to lead to expressions essentially identical to the latter equation. In such theories Equation (III-1a) is used rather in the form*):

$$\ln \eta_0 = \frac{E_{vis}}{RT} + D_0' , \qquad \text{(III-1b)}$$

where the parameters E_{vis} and D_0' are characteristic again of a given liquid and R denotes the molar gas constant. Unlike the parameter C_0 in Equation (III-1a), the quantity E_{vis} in Equation (III-1b) is seen to have the dimension of an energy.

An early theoretical interpretation of Equation (III-1b) was provided by Andrade[54,55)]. A few years afterwards, Eyring[56,57)] obtained the latter equation as the result of an elaborate theoretical treatment based on a model for viscous flow of liquids analogous to the model that was employed for a chemical reaction in his well-known reaction-rate theory. Eyring's theory explains viscous flow as resulting from the movement of an "activated" molecule from one equilibrium position to another in the preferred direction of shear, this movement being treated as a jump over a potential-energy barrier. The energy required to pass this barrier is represented by the quantity E_{vis} (relating to one gmole of the liquid), which is appropriately termed the *"activation energy for viscous flow"*.

Eyring's viscosity theory would appear to have found the most

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*) As stated in the Nomenclature, throughout this thesis "log" denotes the common or Briggsian logarithm, $\log_{10}$, whilst "ln" stands for the natural or Napierian logarithm, $\log_e$.

**) In this entire thesis the subscript "0" invariably relates to atmospheric pressure.

wide-spread usage, although several further theories leading to Equation (III-1b) have been proposed.

Unfortunately, Equation (III-1a), or (III-1b), has a very limited applicability. Frequently, it is valid to a reasonable approximation only in a moderate temperature range; only with simple liquids has it generally been found to apply satisfactorily in a wider temperature range.

In fact, whereas according to Equation (III-1a) straight lines should be obtained by plotting log η_0 against T^{-1}, conspicuous deviations from the relevant straight-line relationship are frequently observed, particularly with the rather complex liquids represented by the normally encountered types of lubricating oils. As a rule, such log η_0 - T^{-1} curves are markedly convex towards the reciprocal-temperature axis. Only a few liquids (for example gallium) are known to exhibit a log η_0 - T^{-1} curve that is slightly concave in that direction.

All in all, the (atmospheric) viscosity-temperature curves of liquids may be very different from one another, even in their qualitative aspects. This emphasizes the difficulties encountered in trying to design a generally applicable, yet sufficiently convenient viscosity-temperature expression (let alone any adequate theoretical interpretation). The gigantic number of attempts to provide such an expression may well testify to these difficulties.

III. 1. 2. *Empirical Equations*

An abundance of empirical equations have been proposed for describing, more satisfactorily than by means of Equation (III-1a), the atmospheric viscosity-temperature relationship of liquids, particularly lubricating oils. Unfortunately, most of these equations leave much to be desired with respect to either their correlational accuracy or their simplicity in use.

Nearly all equations that are sufficiently accurate contain *three* or more characteristic parameters. Although some of the available three-parameter expressions do combine sufficient correlational accuracy with reasonable workability, they still remain rather cumbersome in use.

Fortunately, thanks to many painstaking efforts, a few equations have been achieved that are considerably simpler in that they contain only *two* parameters, the number that may be deemed an absolute *minimum* for fully characterizing the viscosity-temperature relationship of an arbitrary liquid. These equations stand out for convenience of analytical and numerical manipulation.

Moreover, each such two-parameter expression permits setting up *"rectifying"* scales for constructing a chart, typical of the expression chosen, in which the viscosity-temperature relationships of liquids are represented by straight lines, at least to a good approximation. The use of such a "rectifying" viscosity-temperature chart entirely obviates any need for calculating the parameters in the basic equation. Last but not least, the slope of the viscosity-temperature lines rectified in the aforementioned chart - or, of course, the corresponding parameter in the basic equation - may constitute a significant viscosity-temperature criterion.

Before introducing a newly developed two-parameter equation, some three- and two-parameter viscosity-temperature equations which, at least from a practical point of view, may be regarded as the most valuable ones available will be briefly discussed.

A. VISCOSITY-TEMPERATURE EQUATIONS CONTAINING THREE PARAMETERS

From an extensive critical review[58)] of the numerous three-parameter viscosity-temperature equations proposed the author has arrived at the conclusion that only a few of these may be deemed really acceptable for practical applications.

Judging from the combination of correlational accuracy and workability achieved, it would seem that the well-known Vogel equation might well be the first choice. In 1921 already, Vogel[59)] introduced the following formula:

$$\log \eta_0 = \frac{A_0}{T+a_0} + B_0, \qquad \text{(III-2)}$$

where A_0, B_0 and a_0 denote parameters characterizing the viscosity-temperature relationship of a particular liquid, the subscript "0" referring again to atmospheric pressure. Many years later Cameron[60,61)] found that for *mineral oils*, and in a wide temperature range, one single value may invariably be employed for the parameter a_0, namely $a_0 = -178°K$ (or $a_0 = 95°C$ if temperature is expressed in deg C).

Another very valuable formula to describe the atmospheric viscosity-temperature relationship of liquids was proposed, in 1955, by Cornelissen and Waterman[62,44)]:

$$\log \eta_0 = \frac{A_0'}{T^{a_0'}} + B_0', \qquad \text{(III-3)}$$

where A_0', B_0' and a_0' are parameters characteristic of a given liquid. For mineral lubricating-oil fractions a common a_0'-value of 3.5 may be used in a wide temperature range.

The author would like to add yet a third equation, which does not seem to have been proposed so far. As regards its correlational accuracy and practical convenience, the latter equation has proved to be practically on a par with the two preceding equations. This Tait-type equation reads:

$$\log \eta_0 = A_0'' \cdot \log\left(1 + \frac{a_0''}{T}\right) + B_0'', \qquad \text{(III-4)}$$

where A_0'', B_0'' and a_0'' represent parameters characteristic of the liquid under investigation.

If sufficient viscosity measurements are available, the three foregoing equations are very suitable for analytically describing the viscosity-temperature relationship of any liquid over a very wide temperature range, usually covering at least 200°C (360°F), and with a good accuracy at that. But, as stated above, even these most prominent three-parameter equations are rather cumbersome for practical purposes.

In practice, therefore, one will normally resort to one of the indicated rectifying charts, based on two-parameter viscosity-temperature expressions, which are now to be discussed in more detail.

B. VISCOSITY-TEMPERATURE EQUATIONS CONTAINING TWO PARAMETERS

Amongst the few rectifying charts available the standardized ASTM *kinematic* viscosity-temperature chart[63] has certainly achieved the most wide-spread usage. It is based on the MacCoull-Walther equation[64,65] relating kinematic viscosity ν_0, in cS, to absolute temperature T as follows:

$$\log\log(\nu_0 + 0.6) = -m_0 \cdot \log T + N_0, \qquad \text{(III-5)}$$

where m_0 and N_0 are two parameters that fully characterize the kinematic viscosity-temperature relationship of a particular oil.

With the fixed constant of 0.6 cS the validity of the ASTM chart has been restricted to kinematic viscosities above 1.5 cS. The chart has been extended down to 0.4 cS by introducing for this constant values that increase as the viscosity level decreases; at $\nu_0 = 0.4$ cS, for instance, this constant has increased from 0.6 to 0.75 cS.

The ASTM chart was originally designed specifically for *petroleum* products of not too low kinematic viscosities. Indeed, for such oils it has proved to yield quite satisfactory results. It is a well-known fact, however, that it applies not quite so well to many synthetic lubricating oils and polymer-blended mineral oils. Moreover, in general it may not be applied to highly fluid oils, such as encountered in modern high-temperature applications.

All in all, the ASTM chart cannot be claimed to be generally applicable to the various kinds of oils that are important in current lubrication practice.

Besides the ASTM chart only very few such rectifying charts are in use, at least to some reasonable extent, in present lubrication practice. Moreover, it would appear that the latter charts are very closely related to the ASTM chart.

Amongst these related charts may be mentioned: the Walther-Ubbelohde chart[66] and the Umstätter chart[67,68], both also based on *kinematic* viscosity. Both these charts - which are frequently employed in Germany and some other European countries - possess a temperature scale proportional to that of the ASTM chart. Although their kinematic-viscosity scales differ slightly from that of the ASTM chart, the differences become more or less significant only in the range of very low viscosities. It should be added, however, that in the latter viscosity range *none* of the available rectifying charts proves to be satisfactory.

III. 1. 3. *The Present Viscosity-Temperature Equation*)*

The following new empirical equation has proved successful, over a very wide temperature range and nearly within the normal viscometric

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*) The greater part of § III.1.3 has already been published in Reference 69.

accuracy, for describing the atmospheric viscosity-temperature relationships of lubricating oils and even of all the other liquids tested so far, including, amongst others, water, liquid metals and molten glasses:

$$\log \eta_0 + 1.200 = \frac{G_0}{\left(1+\frac{t}{135}\right)^{S_0}} \qquad \text{(III-6a)}$$

or, logarithmized:

$$\log(\log \eta_0 + 1.200) = -S_0 \cdot \log \left(1+\frac{t}{135}\right) + \log G_0 . \qquad \text{(III-6b)}$$

The (atmospheric) dynamic viscosity is represented by η_0, in cP, the temperature by t, in deg C, and log stands again for the common or Briggsian logarithm, $\log_{10}$. This equation contains only *two* parameters - the dimensionless quantities G_0 and S_0 -, the number that may be deemed an absolute *minimum* for fully characterizing the viscosity-temperature relationship of an arbitrary liquid.

One parameter, G_0, may be conceived as indicative of the viscosity *grade* of the liquid as expressed in terms of dynamic viscosity at a standard reference temperature. With the above formulas this reference temperature is readily seen to be 0°C (32°F), so that one may write: $G_0 = (\log \eta_{0,0^\circ C} + 1.200)$. The other parameter, S_0, the new viscosity-temperature criterion (see Chapter VI), is a measure of the variation of viscosity with temperature.

Rewriting Equation (III-6a) in the form:

$$\log \frac{\eta_0}{\eta_\infty} = \log \frac{\eta_0}{0.0631} = \frac{G_0}{\left(1+\frac{t}{135}\right)^{S_0}}, \qquad \text{(III-6c)}$$

it is seen that the constant 1.200 may analytically be put equal to the symbolic expression $-\log \eta_\infty$, where η_∞ represents the viscosity, also in cP, that would be reached when extrapolating analytically to infinite temperature, $t = \infty$. Accordingly, this fictitious viscosity, amounting to $\eta_\infty = 0.0631$ cP, would be common to all liquids. The negative value of the constant 135 denotes the fictitious temperature, in deg C, where the analytically extrapolated viscosity becomes infinitely high. Of course, even at temperatures not quite so low as -135°C (-211°F) the present equation will no longer be adequate.

The new equation can be cast into yet another form, which may be convenient for comparing its structure with that of the well-known viscosity-temperature formulas available from the literature, namely:

$$\eta = \eta_\infty \cdot e^{\frac{2.303\,G_0}{\left(1+\frac{t}{135}\right)^{S_0}}} \qquad \text{(III-6d)}$$

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[*] Those preferring to measure temperature in deg F, denoting this by t_F, may rewrite Equation (III-6b) as:

$$\log(\log \eta_0 + 1.200) = -S_0 \cdot \log\left(1 + \frac{t_F}{211}\right) + \log G_0' \,, \qquad \text{(III-6e)}$$

where, for a given oil, S_0 has the same value as in Equation (III-6b), but G_0' differs from G_0 in the latter equation in that it refers to the viscosity grade of the oil at 0°F (-17.8°C), that is $G_0' = (\log \eta_{0,0°F} + 1.200)$.

Likewise, for absolute temperature T, in deg K, one may write:

$$\log(\log \eta_0 + 1.200) = -S_0 \cdot \log\left(\frac{T}{138} - 1\right) + \log G_0'', \qquad \text{(III-6f)}$$

where, for a given oil, S_0 has the same value as in the two preceding equations, but where G_0'' refers to the viscosity grade of the oil at 276°K (3°C, or 37.4°F), that is $G_0'' = (\log \eta_{0,276°K} + 1.200)$.

A most remarkable feature of the new viscosity-temperature equation consists in that, essentially, it utilizes a kind of (dimensionless) *"reduced"* viscosity, namely the ratio of the viscosity, η_0, at an arbitrary reference temperature, t, to the viscosity at $t = \infty$, that is η_∞. It therefore does not make any difference with the new equation - in contradistinction to, for example, the MacCoull-Walther Equation (III-5) - in which particular unit viscosity, η_0, is expressed, provided of course that η_∞ is expressed in the same unit.

For instance, if viscosity is expressed in terms of microreyns, abbreviated as μR (1 μR = 6.895 cP), the viscosity expression ($\log \eta_0 + 1.200$) in Equations (III-6a), (III-6b), (III-6e) and (III-6f) should be replaced by ($\log \eta_0 + 2.039$), where $2.039 = (1.200 + \log 6.895)$.

To give an example, with η_0 in μR and temperature, t_F, in deg F Equation (III-6e) should be rewritten as:

$$\log(\log \eta_0 + 2.039) = -S_0 \cdot \log\left(1 + \frac{t_F}{211}\right) + \log G_0', \qquad \text{(III-6g)}$$

where, for a given oil, the parameter S_0 has again the same value as in the preceding equations.

For the sake of simplicity, Formula (III-6b) is rewritten in the abbreviated form:

$$H_0 = S_0\,\Theta + \log G_0, \qquad \text{(III-6h)}$$

where the (atmospheric) viscosity function H_0*) and the temperature function Θ are seen to be defined as:

$$H_0 = \log(\log \eta_0 + 1.200) \qquad \text{(III-7)}$$

and

$$\Theta = -\log\left(1 + \frac{t}{135}\right). \qquad \text{(III-8)}$$

Thus, by constructing scales proportional to the latter viscosity and temperature functions a "rectifying" chart is obtained, that is a chart in which by definition all viscosity-temperature curves satisfying the basic Equation (III-6b) are represented by straight lines. Of course, essentially the same chart is obtained if one of the aforementioned equivalent versions of the basic Equation (III-6b) is taken as a basis.

The new viscosity-temperature chart reproduced in Fig. III-1 has been provided with a single viscosity scale, in cP, and a double

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*) The symbol H denotes the Greek capital for the viscosity symbol η.

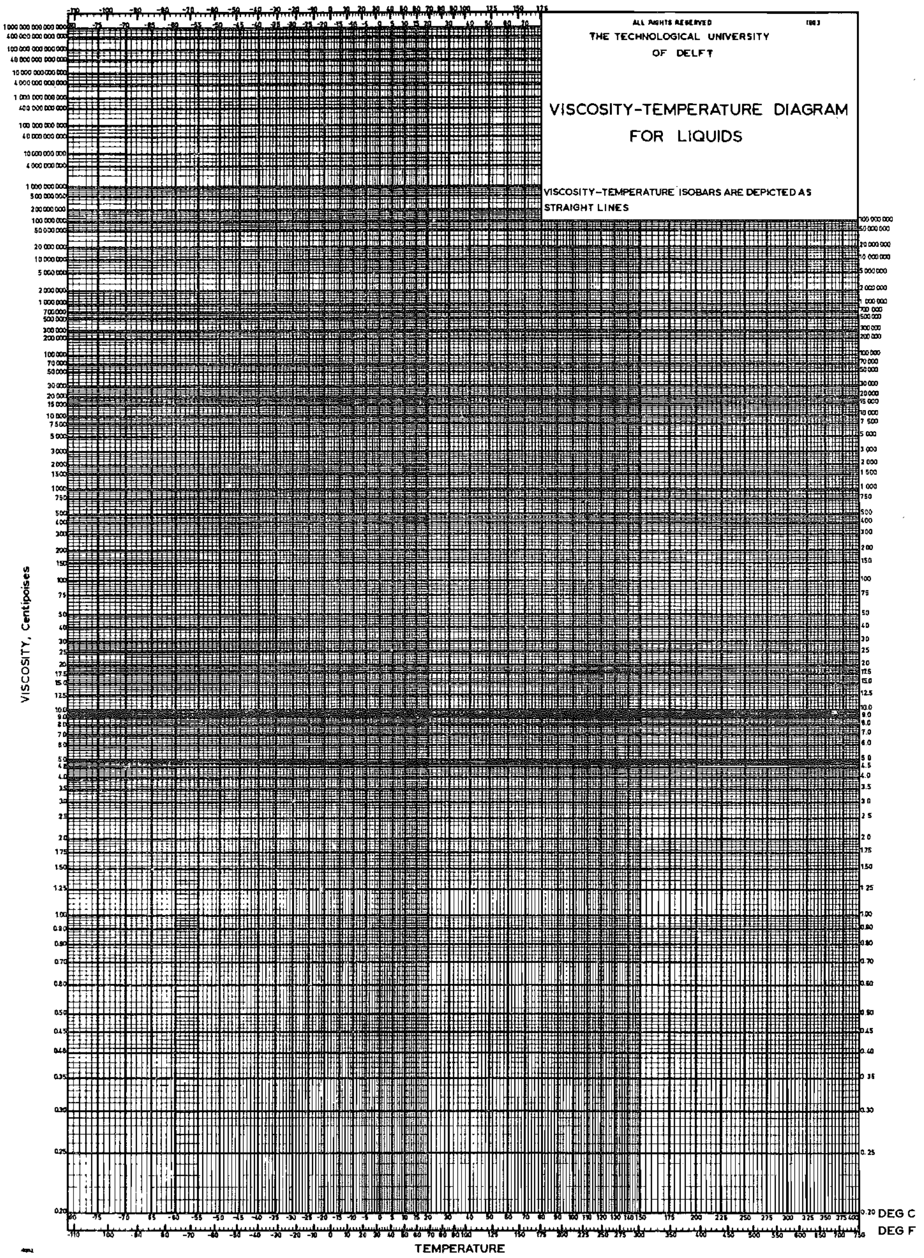

FIG. III -1.
The New Viscosity-Temperature Chart for Liquids.

temperature scale*), temperature being expressed in both deg C and deg F. This chart**) covers much wider viscosity and temperature ranges than the commercially available charts known to the author: viscosities extend from as low as 0.20 up to the exceedingly high value of 10^{15} cP, whilst temperatures comprise the very wide range from -80 up to 400°C (-112 to 752°F).

The scales concerned have been so proportioned that the downward *slope* of viscosity-temperature lines is numerically equal to the parameter S_0 in the basic Equation (III-6h). Therefore, from such charts this dimensionless quantity S_0, the new viscosity-temperature criterion, which will be termed the *"Slope Index"*, can be assessed most readily. The accuracy of such a graphical assessment of this index will usually suffice for any practical purpose***), provided that the chart's format is large enough, like that of the full-size chart reproduced in Fig. III-1.

In addition to the viscosity-temperature chart described, extensive tables have been prepared to facilitate the numerical conversion of viscosities, η_0, expressed in cP, and temperatures, t, expressed in deg C, into the corresponding viscosity and temperature functions of Equation (III-6h), and vice versa. Accordingly, the data compiled in Tables III-1****) and III-2a have been calculated from Equations (III-7) and (III-8), respectively. Further, Table III-2b contains temperatures, t_F, expressed in deg F, and the values of the corresponding temperature function defined by Equation (III-6g), that is the function $\log\left[1+(t_F/211)\right]$.

In Figs. III-2 through III-4 the viscosity-temperature relationships of a great variety of liquids, primarily chosen amongst those used as lubricating oils, have been plotted in a chart according to Equation (III-6h). All the liquids indicated in these figures are specified in Table III-3. Fig. III-2 comprises mineral oils, of several types, both natural and polymer-blended. Fig. III-3 depicts the viscosity-temperature relationships of representative members of those groups of synthetic oils that are currently most important in lubrication practice. In Fig. III-4 miscellaneous liquids have been included.

Since the nature of the liquids represented in Figs. III-2 through III-4 differs widely and quite an extensive temperature range is covered, the validity of the basic Equation (III-6h) has been put to a really severe test. The straight lines in these figures obviously fit the experimental data*****) for all the various liquids remarkably well.

In addition, Equation (III-6h) has been verified for numerous other liquids, not depicted in the present paper, of still other, and very divergent, types. These include many chemically sharply defined pure liquids as well as such complex, high-viscosity, liquids as

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*) For practical reasons the temperature scale has been taken proportional to the negative value of the temperature function in Equation (III-h), that is $-\Theta$.

**) The full-size chart has been printed on a format of 35 by 50 cm (about 14 by 20 in). In addition, similar charts of the same format have been prepared, covering narrower ranges of viscosity (1.00 to 10^7cP) and of temperature (-40 to 200°C, or -40 to 392°F), and thus having more open scales that are more adequate for lubrication practice in particular.

***) It has been found that as a rule there is not much sense in carrying numerical evaluation of the Slope Index, S_0, beyond two decimal places. For instance, a value of 1.354 assessed for a certain Slope Index could reasonably be rounded off to 1.35.

****) For convenience the subscript "0" has been omitted from the viscosity data.

*****) The plotted viscosity data relate to rates of shear low enough to warrant Newtonian behaviour.

TABLE III-1

Viscosity Conversion Table

η, cP	H	η, cP	H	η, cP	H	η, cP	H
0,20	-0,3002	0,88	0,0586	4,3	0,2633	18,5	0,3922
0,21	-0,2822	0,90	0,0623	4,4	0,2656	19,0	0,3942
0,22	-0,2657	0,92	0,0659	4,5	0,2679	19,5	0,3962
0,23	-0,2502	0,94	0,0693	4,6	0,2702	20	0,3981
0,24	-0,2364	0,96	0,0727	4,7	0,2723	21	0,4018
0,25	-0,2234	0,98	0,0760	4,8	0,2744	22	0,4052
0,26	-0,2111	1,00	0,0792	4,9	0,2765	23	0,4085
0,27	-0,1997	1,05	0,0868	5,0	0,2785	24	0,4117
0,28	-0,1890	1,10	0,0939	5,2	0,2824	25	0,4146
0,29	-0,1789	1,15	0,1006	5,4	0,2861	26	0,4175
0,30	-0,1694	1,20	0,1069	5,6	0,2896	27	0,4202
0,31	-0,1603	1,25	0,1129	5,8	0,2930	28	0,4228
0,32	-0,1517	1,30	0,1186	6,0	0,2963	29	0,4253
0,33	-0,1436	1,35	0,1240	6,2	0,2994	30	0,4277
0,34	-0,1358	1,40	0,1291	6,4	0,3024	32	0,4322
0,35	-0,1284	1,45	0,1340	6,6	0,3052	34	0,4364
0,36	-0,1213	1,50	0,1387	6,8	0,3080	36	0,4403
0,37	-0,1145	1,55	0,1431	7,0	0,3107	38	0,4440
0,38	-0,1080	1,60	0,1474	7,2	0,3133	40	0,4475
0,39	-0,1018	1,65	0,1515	7,4	0,3158	42	0,4507
0,40	-0,0958	1,70	0,1555	7,6	0,3182	44	0,4538
0,41	-0,0900	1,75	0,1593	7,8	0,3206	46	0,4568
0,42	-0,0845	1,80	0,1630	8,0	0,3229	48	0,4596
0,43	-0,0791	1,85	0,1665	8,2	0,3251	50	0,4622
0,44	-0,0739	1,90	0,1699	8,4	0,3272	55	0,4684
0,45	-0,0689	1,95	0,1732	8,6	0,3292	60	0,4739
0,46	-0,0641	2,0	0,1764	8,8	0,3313	65	0,4790
0,47	-0,0594	2,1	0,1825	9,0	0,3333	70	0,4836
0,48	-0,0549	2,2	0,1882	9,2	0,3352	75	0,4879
0,49	-0,0505	2,3	0,1936	9,4	0,3371	80	0,4918
0,50	-0,0462	2,4	0,1987	9,6	0,3389	85	0,4955
0,52	-0,0381	2,5	0,2036	9,8	0,3407	90	0,4989
0,54	-0,0304	2,6	0,2082	10,0	0,3424	95	0,5021
0,56	-0,0231	2,7	0,2126	10,5	0,3466	100	0,5052
0,58	-0,0162	2,8	0,2167	11,0	0,3505	110	0,5107
0,60	-0,0096	2,9	0,2207	11,5	0,3542	120	0,5158
0,62	-0,0033	3,0	0,2246	12,0	0,3578	130	0,5203
0,64	0,0027	3,1	0,2282	12,5	0,3611	140	0,5245
0,66	0,0084	3,2	0,2317	13,0	0,3643	150	0,5284
0,68	0,0139	3,3	0,2351	13,5	0,3674	160	0,5320
0,70	0,0192	3,4	0,2384	14,0	0,3704	170	0,5353
0,72	0,0242	3,5	0,2416	14,5	0,3732	180	0,5385
0,74	0,0291	3,6	0,2446	15,0	0,3759	190	0,5414
0,76	0,0337	3,7	0,2475	15,5	0,3785	200	0,5442
0,78	0,0383	3,8	0,2504	16,0	0,3810	220	0,5493
0,80	0,0426	3,9	0,2531	16,5	0,3834	240	0,5539
0,82	0,0468	4,0	0,2558	17,0	0,3857	260	0,5581
0,84	0,0509	4,1	0,2584	17,5	0,3879	280	0,5620
0 86	0,0548	4,2	0,2608	18,0	0,3901	300	0,5655

CONTINUATION OF TABLE III-1

η, cP	H	η, cP	H	η, cP	H	η, cP	H
320	0.5688	8,500	0.7101	6.0×10^{5}	0.8437	3.5×10^{8}	0.9887
340	0.5719	9,000	0.7122	6.5	0.8459	4.0	0.9913
360	0.5748	9,500	0.7141	7.0	0.8479	4.5	0.9936
380	0.5775	1.0×10^{4}	0.7160	8.0	0.8514	5.0	0.9956
400	0.5800	1.1	0.7194	9.0	0.8546	6.0	0.9990
420	0.5824	1.2	0.7226	1.0×10^{6}	0.8573	7.0	1.0020
440	0.5847	1.3	0.7254	1.2	0.8621	8.0	1.0045
460	0.5869	1.4	0.7280	1.4	0.8661	9.0	1.0066
480	0.5890	1.5	0.7305	1.6	0.8695	1.0×10^{9}	1.0086
500	0.5910	1.6	0.7327	1.8	0.8725	2.0	1.0212
550	0.5955	1.7	0.7348	2.0	0.8751	3.0	1.0285
600	0.5997	1.8	0.7368	2.5	0.8807	4.0	1.0335
650	0.6035	1.9	0.7387	3.0	0.8852	6.0	1.0405
700	0.6069	2.0	0.7404	3.5	0.8890	8.0	1.0454
750	0.6101	2.2	0.7437	4.0	0.8922	1.0×10^{10}	1.0492
800	0.6131	2.4	0.7466	4.5	0.8951	2.0	1.0607
850	0.6159	2.6	0.7493	5.0	0.8976	3.0	1.0673
900	0.6185	2.8	0.7518	6.0	0.9019	4.0	1.0720
950	0.6209	3.0	0.7541	7.0	0.9055	6.0	1.0784
1,000	0.6232	3.5	0.7592	8.0	0.9087	8.0	1.0829
1,100	0.6275	4.0	0.7636	9.0	0.9114	1.0×10^{11}	1.0864
1,200	0.6314	4.5	0.7674	1.0×10^{7}	0.9138	2.0	1.0969
1,300	0.6349	5.0	0.7708	1.2	0.9180	3.0	1.1030
1,400	0.6381	5.5	0.7738	1.4	0.9215	4.0	1.1073
1,500	0.6411	6.0	0.7766	1.6	0.9245	6.0	1.1132
1,600	0.6439	6.5	0.7791	1.8	0.9271	8.0	1.1174
1,700	0.6464	7.0	0.7814	2.0	0.9295	1.0×10^{12}	1.1206
1,800	0.6489	8.0	0.7855	2.5	0.9344	2.0	1.1304
1,900	0.6512	9.0	0.7892	3.0	0.9384	3.0	1.1360
2,000	0.6533	1.0×10^{5}	0.7924	3.5	0.9417	4.0	1.1399
2,200	0.6573	1.2	0.7979	4.0	0.9446	6.0	1.1454
2,400	0.6609	1.4	0.8025	4.5	0.9471	8.0	1.1493
2,600	0.6642	1.6	0.8065	5.0	0.9493	1.0×10^{13}	1.1523
2,800	0.6672	1.8	0.8099	6.0	0.9532	2.0	1.1614
3,000	0.6700	2.0	0.8130	7.0	0.9564	3.0	1.1666
3,500	0.6762	2.2	0.8157	8.0	0.9592	4.0	1.1703
4,000	0.6814	2.4	0.8182	9.0	0.9616	6.0	1.1755
4,500	0.6860	2.6	0.8205	1.0×10^{8}	0.9638	8.0	1.1791
5,000	0.6901	2.8	0.8226	1.2	0.9675	1.0×10^{14}	1.1818
5,500	0.6938	3.0	0.8245	1.4	0.9707	2.0	1.1904
6,000	0.6971	3.5	0.8289	1.6	0.9733	3.0	1.1952
6,500	0.7001	4.0	0.8326	1.8	0.9757	4.0	1.1987
7,000	0.7029	4.5	0.8359	2.0	0.9778	6.0	1.2035
7,500	0.7054	5.0	0.8388	2.5	0.9822	8.0	1.2069
8,000	0.7078	5.5	0.8414	3.0	0.9857	1.0×10^{15}	1.2095

TABLE III-2a

Temperature Conversion Table (deg C)

t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$
-80	-0.3899	-33	-0.1217	14	0.0429	102	0.2444
-79	-0.3821	-32	-0.1175	15	0.0458	104	0.2481
-78	-0.3744	-31	-0.1133	16	0.0487	106	0.2517
-77	-0.3669	-30	-0.1091	17	0.0515	108	0.2553
-76	-0.3594	-29	-0.1050	18	0.0544	110	0.2589
-75	-0.3521	-28	-0.1009	19	0.0572	112	0.2624
-74	-0.3450	-27	-0.0969	20	0.0600	114	0.2659
-73	-0.3379	-26	-0.0929	22	0.0656	116	0.2694
-72	-0.3310	-25	-0.0889	24	0.0711	118	0.2728
-71	-0.3241	-24	-0.0850	26	0.0765	120	0.2762
-70	-0.3174	-23	-0.0811	28	0.0819	122	0.2796
-69	-0.3108	-22	-0.0772	30	0.0872	124	0.2830
-68	-0.3042	-21	-0.0734	32	0.0924	126	0.2863
-67	-0.2978	-20	-0.0696	34	0.0976	128	0.2897
-66	-0.2915	-19	-0.0658	36	0.1027	130	0.2929
-65	-0.2852	-18	-0.0621	38	0.1077	132	0.2962
-64	-0.2790	-17	-0.0584	40	0.1127	134	0.2995
-63	-0.2730	-16	-0.0548	42	0.1127	136	0.3027
-62	-0.2670	-15	-0.0511	44	0.1226	138	0.3059
-61	-0.2611	-14	-0.0475	46	0.1274	140	0.3090
-60	-0.2552	-13	-0.0439	48	0.1322	142	0.3122
-59	-0.2495	-12	-0.0404	50	0.1369	144	0.3153
-58	-0.2438	-11	-0.0369	52	0.1415	146	0.3184
-57	-0.2382	-10	-0.0334	54	0.1462	148	0.3215
-56	-0.2327	- 9	-0.0299	56	0.1507	150	0.3245
-55	-0.2272	- 8	-0.0265	58	0.1553	155	0.3321
-54	-0.2218	- 7	-0.0231	60	0.1597	160	0.3395
-53	-0.2165	- 6	-0.0197	62	0.1642	165	0.3468
-52	-0.2112	- 5	-0.0164	64	0.1686	170	0.3540
-51	-0.2060	- 4	-0.0130	66	0.1729	175	0.3611
-50	-0.2009	- 3	-0.0097	68	0.1772	180	0.3680
-49	-0.1958	- 2	-0.0064	70	0.1815	185	0.3748
-48	-0.1908	- 1	-0.0032	72	0.1857	190	0.3816
-47	-0.1858	0	0.0000	74	0.1898	195	0.3882
-46	-0.1809	1	0.0032	76	0.1940	200	0.3947
-45	-0.1761	2	0.0064	78	0.1981	205	0.4012
-44	-0.1713	3	0.0096	80	0.2021	210	0.4075
-43	-0.1665	4	0.0127	82	0.2062	215	0.4138
-42	-0.1618	5	0.0158	84	0.2101	220	0.4199
-41	-0.1572	6	0.0189	86	0.2141	225	0.4260
-40	-0.1526	7	0.0220	88	0.2180	230	0.4320
-39	-0.1480	8	0.0250	90	0.2219	235	0.4379
-38	-0.1435	9	0.0281	92	0.2257	240	0.4437
-37	-0.1391	10	0.0311	94	0.2295	245	0.4495
-36	-0.1347	11	0.0341	96	0.2333	250	0.4552
-35	-0.1303	12	0.0370	98	0.2371	255	0.4608
-34	-0.1260	13	0.0400	100	0.2408	260	0.4663

CONTINUATION OF TABLE III-2a

t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$	t, °C	$\log(1+\frac{t}{135})$
265	0.4718	305	0.5132	345	0.5509	385	0.5857
270	0.4772	310	0.5181	350	0.5554	390	0.5899
275	0.4825	315	0.5229	355	0.5599	395	0.5940
280	0.4877	320	0.5277	360	0.5643	400	0.5981
285	0.4929	325	0.5325	365	0.5687	425	0.6179
290	0.4981	330	0.5372	370	0.5730	450	0.6369
295	0.5032	335	0.5418	375	0.5773	475	0.6550
300	0.5082	340	0.5464	380	0.5815	500	0.6725

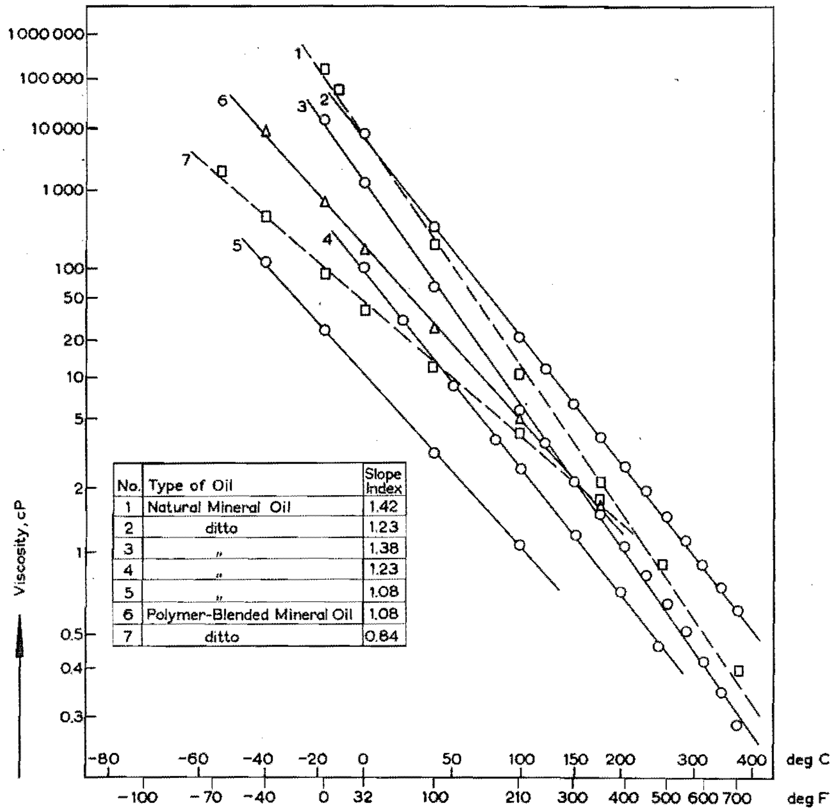
TABLE III-2b

Temperature Conversion Table (deg F)

t_F, °F	$\log(1+\frac{t_F}{211})$	t_F, °F	$\log(1+\frac{t_F}{211})$	t_F, °F	$\log(1+\frac{t_F}{211})$	t_F, °F	$\log(1+\frac{t_F}{211})$
-110	-0.3200	-16	-0.0344	78	0.1367	280	0.3668
-108	-0.3116	-14	-0.0300	80	0.1397	285	0.3713
-106	-0.3033	-12	-0.0252	82	0.1427	290	0.3755
-104	-0.2952	-10	-0.0209	84	0.1456	295	0.3799
-102	-0.2865	- 8	-0.0167	86	0.1485	300	0.3842
-100	-0.2787	- 6	-0.0125	88	0.1514	305	0.3884
- 98	-0.2710	- 4	-0.0083	90	0.1542	310	0.3925
- 96	-0.2635	- 2	-0.0042	92	0.1571	315	0.3967
- 94	-0.2561	0	0.0000	94	0.1599	320	0.4008
- 92	-0.2488	2	0.0040	96	0.1630	325	0.4049
- 90	-0.2416	4	0.0080	98	0.1658	330	0.4090
- 88	-0.2346	6	0.0123	100	0.1685	335	0.4129
- 86	-0.2276	8	0.0163	105	0.1755	340	0.4169
- 84	-0.2202	10	0.0202	110	0.1822	345	0.4208
- 82	-0.2135	12	0.0241	115	0.1889	350	0.4247
- 80	-0.2069	14	0.0279	120	0.1956	355	0.4285
- 78	-0.2004	16	0.0317	125	0.2021	360	0.4323
- 76	-0.1939	18	0.0355	130	0.2084	365	0.4361
- 74	-0.1876	20	0.0392	135	0.2148	370	0.4399
- 72	-0.1814	22	0.0429	140	0.2210	375	0.4437
- 70	-0.1752	24	0.0469	145	0.2272	380	0.4473
- 68	-0.1692	26	0.0506	150	0.2333	385	0.4510
- 66	-0.1627	28	0.0542	155	0.2391	390	0.4546
- 64	-0.1568	30	0.0578	160	0.2451	395	0.4582
- 62	-0.1510	32	0.0613	165	0.2509	400	0.4617
- 60	-0.1452	34	0.0649	170	0.2567	405	0.4653
- 58	-0.1396	36	0.0684	175	0.2622	410	0.4688
- 56	-0.1340	38	0.0718	180	0.2679	415	0.4723
- 54	-0.1285	40	0.0753	185	0.2734	420	0.4758
- 52	-0.1230	42	0.0790	190	0.2789	425	0.4791
- 50	-0.1177	44	0.0824	195	0.2843	430	0.4826
- 48	-0.1119	46	0.0857	200	0.2895	435	0.4860
- 46	-0.1066	48	0.0891	205	0.2948	440	0.4893
- 44	-0.1015	50	0.0924	210	0.3000	445	0.4926
- 42	-0.0963	52	0.0957	215	0.3052	450	0.4959
- 40	-0.0913	54	0.0989	220	0.3101	455	0.4992
- 38	-0.0863	56	0.1021	225	0.3152	460	0.5025
- 36	-0.0813	58	0.1054	230	0.3202	465	0.5057
- 34	-0.0764	60	0.1088	235	0.3251	470	0.5088
- 32	-0.0716	62	0.1120	240	0.3300	475	0.5120
- 30	-0.0664	64	0.1151	245	0.3346	480	0.5152
- 28	-0.0617	66	0.1182	250	0.3394	485	0.5184
- 26	-0.0570	68	0.1213	255	0.3441	490	0.5214
- 24	-0.0524	70	0.1244	260	0.3488	495	0.5245
- 22	-0.0478	72	0.1275	265	0.3533	500	0.5276
- 20	-0.0433	74	0.1305	270	0.3578	505	0.5307
- 18	-0.0388	76	0.1355	275	0.3624	510	0.5337

CONTINUATION OF TABLE III-2b

t_F, °F	$\log(1 + \frac{t_F}{211})$	t_F, °F	$\log(1 + \frac{t_F}{211})$	t_F, °F	$\log(1 + \frac{t_F}{211})$	t_F, °F	$\log(1 + \frac{t_F}{211})$
515	0.5366	580	0.5739	645	0.6082	710	0.6400
520	0.5396	585	0.5766	650	0.6107	715	0.6423
525	0.5426	590	0.5794	655	0.6132	720	0.6447
530	0.5456	595	0.5821	660	0.6158	725	0.6470
535	0.5484	600	0.5848	665	0.6183	730	0.6493
540	0.5513	605	0.5874	670	0.6207	735	0.6517
545	0.5542	610	0.5901	675	0.6231	740	0.6539
550	0.5571	615	0.5927	680	0.6256	745	0.6562
555	0.5600	620	0.5954	685	0.6281	750	0.6585
560	0.5627	625	0.5979	690	0.6305	800	0.6805
565	0.5656	630	0.6005	695	0.6328	850	0.7014
570	0.5684	635	0.6031	700	0.6352	900	0.7214
575	0.5712	640	0.6057	705	0.6376	1,000	0.7588



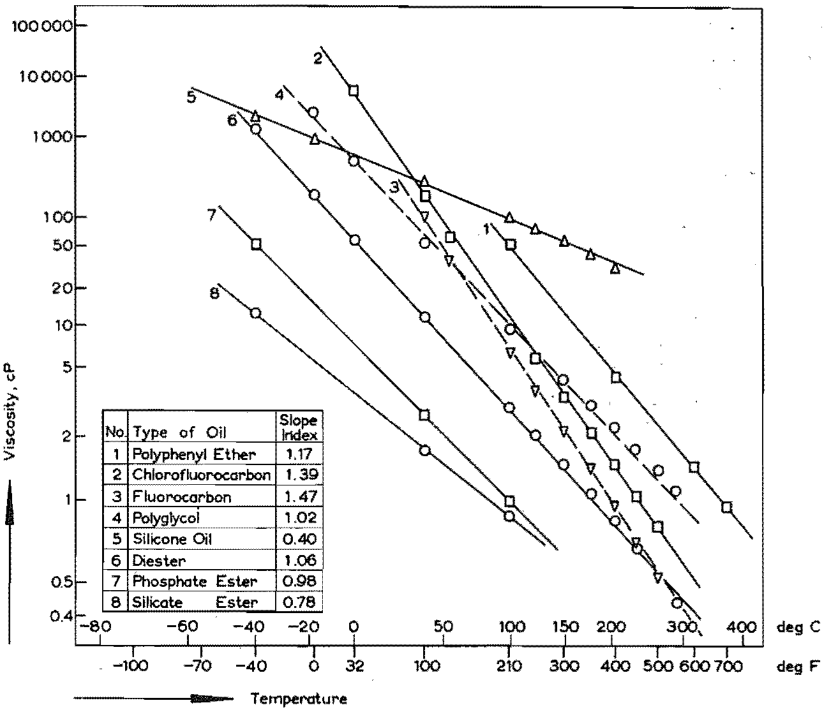
No.	Type of Oil	Slope Index
1	Natural Mineral Oil	1.42
2	ditto	1.23
3	"	1.38
4	"	1.23
5	"	1.08
6	Polymer-Blended Mineral Oil	1.08
7	ditto	0.84

FIG. III-2.
The Applicability of the New Viscosity-Temperature Chart to Natural and Polymer-Blended Mineral Oils.

high-polymers and molten glasses.

Summarizing, the new equation has proved to apply quite satisfactorily to the numerous liquids investigated so far, and in a very wide temperature range at that. The extent of this applicability range depends, of course, on the particular liquid, and in any case is limited by its solidification and boiling point. Usually, however, it may be considered to cover a range of at least 200°C (360°F); only outside this applicability range will the deviations of the experimental points from the straight lines in Figs. III-2 through III-4 result in errors considerably beyond the normal viscometric accuracy. Generally, this range is sufficiently wide for any practical purpose and, to the best of the author's knowledge, is not exceeded by the conventional empirical formulas used hitherto.

Closer examination of the viscosity data plotted in Figs. III-2 through III-4 reveals that, if these are considered over a temperature range



No.	Type of Oil	Slope Index
1	Polyphenyl Ether	1.17
2	Chlorofluorocarbon	1.39
3	Fluorocarbon	1.47
4	Polyglycol	1.02
5	Silicone Oil	0.40
6	Diester	1.06
7	Phosphate Ester	0.98
8	Silicate Ester	0.78

FIG. III-3.
The Applicability of the New Viscosity-Temperature Chart to Synthetic Lubricating Oils.

considerably wider than the aforementioned applicability range of 200°C, they generally tend to follow a sigmoid curve rather than the adjusted straight-line relationship. Although these sigmoid curves are rather similar for the members of a particular class of liquids, notably mineral oils, they may vary conspicuously from one class to another. This means that, through a relatively slight alteration of one or both constants, 1.200 and/or 135, in the basic Equation (III-6b) a significant improvement of its correlational accuracy can be achieved for the various members of a particular class of liquids. However, any adaptation of the present two constants to such a class specifically would interfere with the *universal* applicability of the present Equation (III-6b).

Confining oneself to a still very wide temperature range extending, say, from 0 to 200°C (32-392°F), it is found that the viscosity-temperature relationship of each individual liquid, though coming really close to the relevant straight line depicted in Figs. III-2 through III-4, tends to exhibit a slight curvature, which may be either convex or concave towards the temperature axis. As these curvatures generally prove to be similar for the various members of a particular class of liquids, the applicability of the present chart to all the members of such a class can still be somewhat improved solely by adjusting

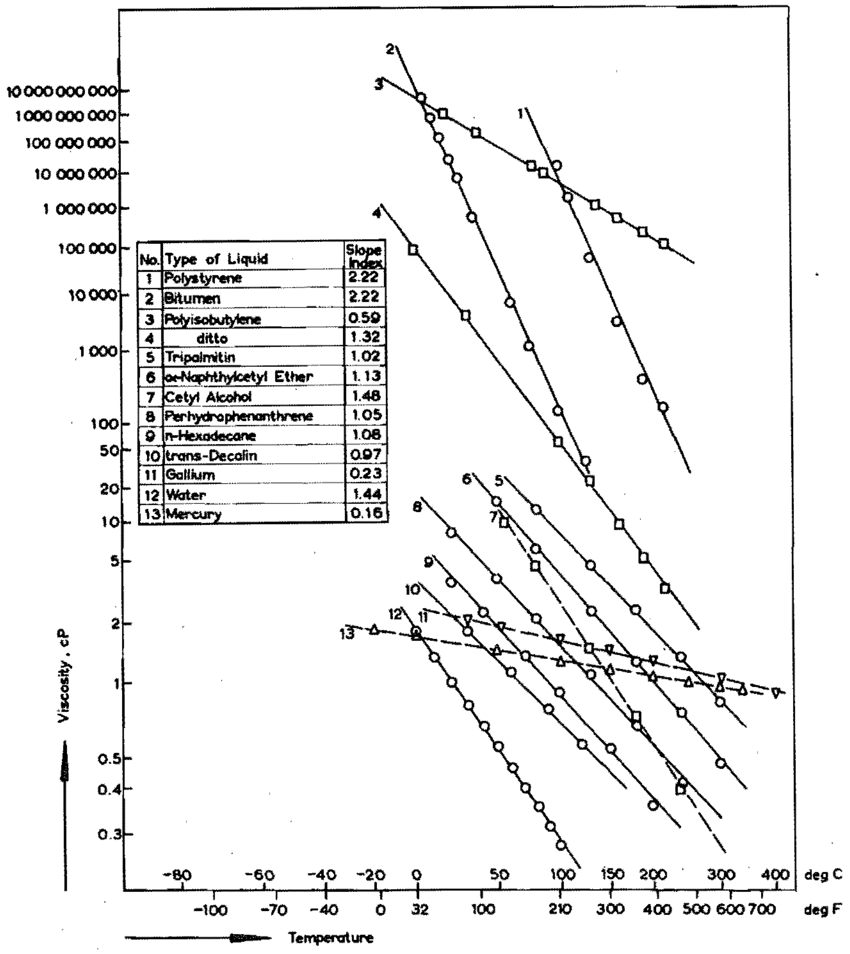


FIG. III-4.
The Applicability of the New Viscosity-Temperature Chart to Miscellaneous Liquids.

one of the two constants, 1.200 or 135, in the basic Equation (III-6b).

For example, for all the various kinds of *mineral* oils investigated so far the viscosity-temperature relationships plotted in the present chart tend to be more or less convex towards the temperature axis, at least throughout the temperature range under consideration (see Fig. II-2). This implies that for all these various kinds of mineral oils the rather systematic deviations from the basic Equation (III-6b) could almost entirely be eliminated solely by substituting a lower value for its temperature constant of 135°C. In fact, it has been found that by replacing this constant by a value of 115°C a significantly improved fit can readily be achieved. However, in view of the good conformance, over the entire temperature range of no less than about

TABLE III-3

Designations to the Oils Depicted in Figs. III-2/III-4

No.	Type of Liquid	Experimenters' Designation	Ref.
	Natural and Polymer-Blended Mineral Oils, Fig. III-2		
1	Natural Mineral Oil	Naphthenic Bright Stock (VI=21)	70,71
2	ditto	Grade 1120 (VI=95)	72
3	"	Navy Symbol 2135 (VI=29)	72
4	"	Öl X	61
5	"	PRL 3000: Base Stock	70,71
6	Polymer-Blended Mineral Oil	PRL 2924: Polybutene Blend (VI=161)	70,71
7	ditto	PRL 2286: Specification MIL-O-5606 Aircraft Hydraulic Fluid: Polymethacrylate Blend (VI=226)	70,71
	Synthetic Lubricating Oils, Fig. III-3		
1	Polyphenyl Ether	Meta-Linked, Unsubstituted Polyphenyl Ether, that is m-Bis [m-(m-phenoxyphenoxy)phenoxy] benzene (Seven-Ring Compound)	23b
2	Chlorofluorocarbon	Commercial Monochlorotrifluoroethylene Polymer, coded "Fluorolube-Standard" (VI=-178)	72
3	Fluorocarbon	Commercial Sample of a Fully Fluorinated Mineral Oil, coded "Fluoro Lubricant FCD-331" (VI=-694)	72
4	Polyglycol	Commercial Polypropylene Glycol Derivative, coded "Ucon LB-250" (VI=148)	72
5	Silicone Oil	Commercial Linear Polymethylsiloxane, coded DC 200 "E"	72
6	Diester	Di(2-ethylhexyl)sebacate (VI=154)	72
7	Phosphate Ester	Tri(n-butyl) Orthophosphate	23c
8	Silicate Ester	Tetra(n-butyl) Orthosilicate	23d
	Miscellaneous Liquids, Fig. III-4		
1	Polystyrene	Polymer Fraction B7 (Molecular Weight: 4,300)	73
2	Bitumen	Non-Plastic Asphaltic Bitumen A (Soft)	74
3	Polyisobutylene	Polymer Fraction PB4F1 (Molecular Weight: 80,000)	75
4	ditto	Polymer Fraction Cut No. 3 (Molecular Weight: 755)	75
5	Tripalmitin	Pure Compound	76
6	α-Naphthylcetyl Ether	ditto	76
7	Cetyl Alcohol	"	76
8	Perhydrophenanthrene	"	76
9	n-Hexadecane	"	77
10	trans-Decalin	"	48
11	Gallium	"	78
12	Water	"	79a
13	Mercury	"	80

200°C, of the viscosity-temperature relationships of mineral oils to the present Equation (III-6b), it is not deemed really necessary to carry out any alteration of the present temperature constant. Moreover, with a less wide temperature range, for instance from 20 up to 150°C (68-302°F) - which still suffices for many cases in lubrication -, the present values of the constants, 1.200 and 135, in Equation (III-6b) will not result in any deviations appreciably beyond the normal viscometric accuracy of 2-3%. Above all, however, it should be emphasized once more that any adaptation of the present two constants to mineral oils - or some other class of liquids - specifically, would make the resulting equation less accurate for many other types of liquids so that it would not be as widely applicable as the present Equation (III-6b) (see also part A of § III.1.4).

III.1.4. *Discussion*

A. THE NEW VISCOSITY-TEMPERATURE CHART IN COMPARISON WITH CONVENTIONAL CHARTS

With the kinds of lubricating oils commonly employed nowadays the new viscosity-temperature equation or chart may, as regards its rectifying accuracy, be claimed to be at least on a par with the ASTM chart[63)] or any other conventional rectifying chart known to the author. With certain types of *synthetic* oils, and in general with *highly fluid* oils, the new equation or chart is even definitely superior. In fact, with such oils the conventional charts are known to leave much to be desired as to their rectifying accuracy, particularly if a wide temperature range is to be covered. Consequently, as to its rectifying accuracy the new chart is to be preferred to the ASTM chart, and in fact to any other conventional chart known to the author.

Indeed, the new viscosity-temperature equation or chart would appear to be the only such equation or chart available that is really sufficiently universal. It may even be claimed that, as a universal two-parameter expression for the viscosity-temperature relationship of liquids over a very wide temperature range, the present equation would be well-nigh unsurpassable with respect to the combination of correlational accuracy and practical convenience achieved.

Moreover, as will be demonstrated in subsequent parts of this thesis, the new viscosity-temperature equation or chart displays several additional - major and minor - advantages over conventional equations and charts. One such major advantage of the present viscosity-temperature equation over the MacCoull-Walther and related two-parameter equations may already be mentioned: it lends itself particularly well as a basis to a simple and convenient method for classifying, according to their temperature dependence of viscosity, all the various kinds of oils encountered in current lubrication practice. The latter point will be elucidated in Chapter VI.

B. ADDITIONAL APPLICATIONS OF THE PRESENT VISCOSITY-TEMPERATURE EQUATION

a. The present viscosity-temperature equation has been designed primarily for *Newtonian* lubricating oils. It should be added, however, that oils exhibiting pronounced non-Newtonian behaviour at high rates of shear comply equally well with the new equation as long as these rates remain sufficiently low. Examples of the applicability of the present equation to the latter kind of oils are represented by the two typical polymer-blended mineral oils and the various high-polymers depicted in Figs. III-2 and III-4, respectively, and designated in Table III-3. As indicated above, the viscosity data plotted in these figures relate to rates of shear low enough to warrant Newtonian behaviour of the oils considered.

Further, it seems quite reasonable to conjecture that the present equation lends itself nearly equally well to describe the temperature dependence of the (apparent) viscosity of non-Newtonian oils subjected to very high rates of shear, provided of course that these assume comparable values at the various temperatures involved. Indeed, in the few cases tested this conjecture could be fully confirmed.

b. In view of the great variety of viscosity-temperature curves comprised (see also point c, below), it may well-nigh certainly be expected that Equation (III-6h) would retain its validity even for those peculiar liquids - sometimes referred to as "clowns" - whose viscosity *increases* more or less with rising temperature. Obviously, the present equation may only apply to such anomalous liquids on the condition that they exhibit a really significant viscosity-temperature behaviour; that is if the occurence of certain physical, or chemical, phenomena that may cause rather abrupt changes in their viscosity-temperature curves is precluded.

For a few such anomalous liquids the viscosity-temperature relationship has been reported in the literature, although over narrow temperature ranges. Unfortunately, the author could not trace reliable data permitting a reasonable test of the applicability of the new equation to such liquids. Nevertheless, it is believed that this potential application may well assume practical importance in future developments of lubricating-oil technology.

c. Finally, a rather peculiar feature of the new viscosity-temperature equation, which has been designed primarily for lubricating oils, will be elaborated: its ability to describe, over a very wide temperature range, the viscosity-temperature relationship of *gases*.

Considering the new viscosity-temperature expression in the form of Equation (III-6c), it has been implied that, as indicated above, the analytically extrapolated viscosity η_∞ should be common to all liquids, namely η_∞ = 0.0631 cP (631 μP). Now, from the validity of the latter equation for gases it follows that the same viscosity value, η_∞ = 0.0631 cP, would likewise be common to all gases.

Consequently, any given *fluid*, either in the liquid or the gaseous state, would reach the same viscosity η_∞ at a temperature amounting to infinity. Whilst the viscosity η_∞ (= 0.0631 cP) would represent the *lower* viscosity limit for the liquid state, it would denote the *upper* viscosity limit for the gaseous state. For an arbitrary liquid and an arbitrary gas the latter finding has been illustrated by the schematic Fig. III-5.

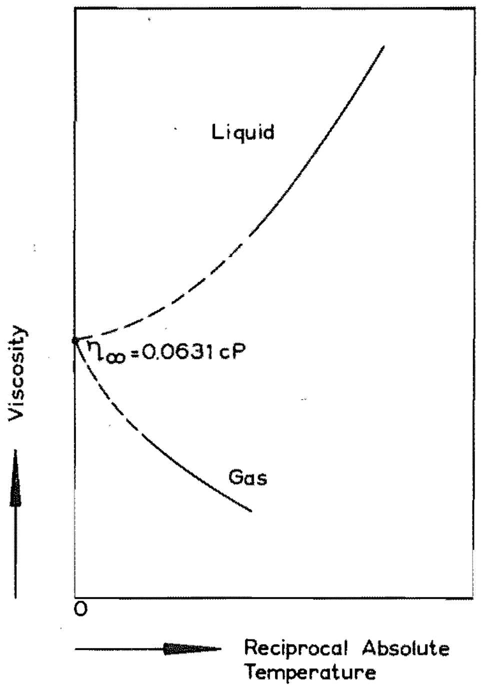


FIG. III-5.
Limiting Viscosity of Liquids and Gases.

In applying Equation (III-6c) to gases it should be noted that the negative value of the constant 135 denotes the fictitious temperature, in deg C, where the analytically extrapolated viscosity becomes zero. Therefore, Equation (III-6c) may be applied to gases only at temperatures markedly above -135°C, the same proviso holding for its applicability to liquids.

Whereas for liquids both the quantities log (η_0/η_∞) and G_0 $[=\log(\eta_{0,0^\circ C}/\eta_\infty)]$ in Equation (III-6c) are always positive, for gases they prove to assume negative values (compare Fig. III-5). Therefore, if applied to gases, Equation (III-6c), or the identical Equation (III-6a), cannot be written in the logarithmized form of Equation (III-6b), so that the basic viscosity-temperature chart developed for liquids cannot directly be applied to gases.

Nevertheless, an analogous viscosity-temperature chart can easily be constructed for rectifying the viscosity-temperature relationships of gases. To this end, Equation (III-6b) is transformed into:

$$\log\left[-(\log \eta_0 + 1.200)\right] = -S_0 \cdot \log\left(1+\frac{t}{135}\right) + \log(-G_0) \qquad \text{(III-6b')}$$

or, in abbreviated form:

$$H'_0 = S_0\,\Theta + \log\,(-G_0), \tag{III-6h'}$$

where the temperature function Θ is identical to that of Equation (III-6h) and where the viscosity function H'_0 is seen to be defined by:

$$H'_0 = \log\,(-\log\,\eta_0 - 1.200). \tag{III-9}$$

According to Equation (III-6h'), the viscosity-temperature relationships of gases satisfying Equation (III-6c) can be depicted as straight lines by employing a chart which has been provided, with essentially the same temperature scale as that used for liquids and a viscosity scale proportional to the viscosity function H'_0. Such a chart is represented by Fig. III-6; for practical reasons in the latter figure the function $-H'_0$ has been plotted against $-\Theta$.

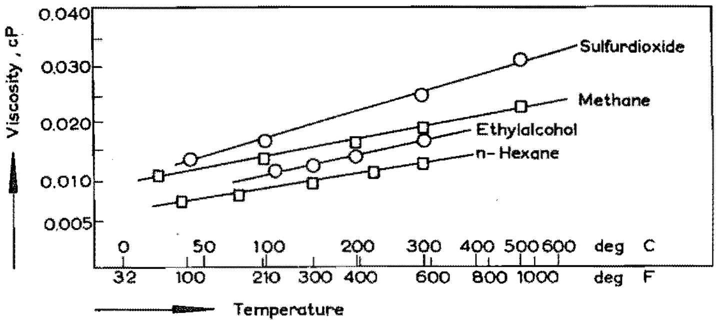


FIG. III-6.
The Applicability of Equation (III-6h') to Gases.

Fig. III-6 depicts the viscosity-temperature relationships of four arbitrarily chosen gases: methane, n-hexane, ethylalcohol and sulfurdioxide[81a)]. Indeed, the plotted viscosity-temperature data prove to conform very well to the depicted straight lines, and over a very wide temperature range at that. In addition, the basic Equation (III-6c) has been verified for many other gases of divergent types.

It has been found that generally the latter equation applies very satisfactorily to gases over a very wide temperature range, extending from at least 50 to 500°C (122-932°F). In this entire temperature range the average deviation from Equation (III-6c) generally amounts to no more than about 2 or 3% and in various cases it even proves to be of the order of only 1%.

C. CONCLUDING REMARKS

In conclusion it is considered worth-while to devote a few - admittedly rather obvious - remarks to the limits set to the adequacy of viscosity-temperature equations in general and of the proposed equation in particular. It should be pointed out that the relevant remarks are made only in order to convey a realistic impression of some practical consequences of the application of viscosity-temperature equations.

a. Viscosity-temperature equations containing a minimum number of only two characteristic parameters should be considered primarily as *interpolating* formulas. Consequently, in order to obtain good conformity with such equations over a wide temperature range, more than two properly spaced points of the viscosity-temperature curve of a given liquid should preferably be known. In addition, safe extrapolations may usually be performed only over quite moderate temperature ranges.

b. Further, it should be emphasized that viscosity-temperature equations may no longer be deemed fully significant at temperatures either so high or so low as to give rise to certain physical, or even chemical, transformations which substantially affect the viscosity of the oils, either in a reversible or irreversible manner.

At relatively high temperatures, even far below the boiling point, considerable volatilization may take place; furthermore, pronounced physical changes in the liquid structure, or chemical transformations, such as oxidation or cracking, may occur. Structure formation and separation of solids are the main phenomena that may seriously interfere with the viscosity-temperature behaviour of an oil at relatively low temperatures, even considerably above its solidification point.

Accordingly, there would be little sense in trying to establish an equation which is intended to apply to a great variety of liquids and over a temperature range so extensive that the aforementioned transformations do seriously interfere with their viscosity-temperature dependence.

In view of these limitations - to be imposed on *any* viscosity-temperature equation - the temperature range covered by the newly developed equation should be considered very wide indeed.

c. Finally, it may be useful to warn against any unrealistic ideas concerning the accuracy to be embodied into viscosity-temperature equations designed primarily for practical applications. In this respect it should be pointed out that in cases where very large viscosity variations are involved it may be highly misleading to report the correlational accuracy of a particular equation in terms of *percentage* deviations between experimental and calculated viscosities. Indeed, whilst at a moderate viscosity level it may be reasonable to insist on relative deviations not exceeding a few per cent, this is no longer fair at a viscosity level so high that a temperature variation of only a few deg C - which, for example, is hardly predictable or controllable in lubrication practice - may cause a viscosity variation of about a hundred per cent.

In the author's opinion a rational criterion for judging the applicability of a given two-parameter equation, such as the proposed equation, simply consists in the "degree of straightness" of the viscosity-temperature lines in the relevant rectifying chart.

III. 2. THE FAMILY OF VISCOSITY-TEMPERATURE ISOBARS CHARACTERIZING A GIVEN LIQUID

III. 2. 1. *Introduction*

As indicated in § III. 1. 2, an overwhelming number of formulas have been proposed to describe the relationship between viscosity and temperature of liquids, particularly lubricating oils, at *atmospheric* pressure. Comparatively little attention has been devoted so far, however, to the temperature dependence of viscosity at *elevated* pressures.

Since the qualitative nature of the atmospheric viscosity-temperature curves of liquids is generally not substantially changed at higher pressures, it may *a priori* be inferred that those viscosity-temperature equations which have proved to hold good at atmospheric pressure will also apply reasonably well at elevated pressures. Indeed, the latter conjecture appears to be substantiated by the relevant investigations described in the literature.

Vogel's Equation (III-2) has been successfully employed by Dow[82] for representing the isobars of *mineral oils* at elevated pressures. Whilst the parameters A_0 and B_0 proved to increase rather strongly with pressure, the "temperature parameter" a_0 was found to be nearly independent of pressure up to pressures of at least a few thousand atmospheres.

The validity of the Cornelissen-Waterman Equation (III-3) at elevated pressures has been established for a great variety of liquids by Roelands *et al.*[44]. It appeared that up to pressures of at least some 3, 000 atm (44, 000 psi) the atmospheric value of the exponent a_0' in Equation (III-3) is generally not substantially changed by pressure, whereas the parameters A_0' and B_0' increase rather rapidly with increasing pressure.

The present author has further found that the third aforementioned three-parameter equation for describing the atmospheric viscosity-temperature relationship of liquids, that is Equation (III-4), may likewise be applied satisfactorily at elevated pressures. Again, the atmospheric value of the "temperature parameter" a_0'' may be maintained at higher pressures, whilst the remaining two parameters, A_0'' and B_0'', increase regularly with rising pressure.

The ASTM chart, based on MacCoull-Walther's two-parameter Equation (III-5) for *kinematic* viscosity, has also been successfully applied by Dow[36,37,83] for depicting the high-pressure isobars of mineral oils (and a few other lubricating oils) as straight lines. During the last war, Blok[84] independently discovered that the same chart holds good if the kinematic viscosity is replaced by the *dynamic* viscosity. Blok's method constitutes an important variant of Dow's method because, as indicated in § I. 2. 2, it is the dynamic viscosity that is really significant in the theory and practice of lubrication.

At present, the use of the ASTM chart would appear to be the most attractive procedure for simply representing the high-pressure isobars of lubricating oils.

It has been found that the foregoing findings may be generalized to the following conclusion:

The same viscosity and temperature scales that are adequate for depicting the atmospheric viscosity-temperature isobar of a given liquid as a straight line may be maintained for rectifying its high-pressure isobars up to pressures of at least a few thousand atmospheres; or, in other words, the family of isobars characterizing a given liquid can be depicted as a family of straight lines in one single viscosity-temperature diagram.

III. 2. 2. *The Present Characterization Method*

A. MATHEMATICAL DESCRIPTION OF THE ISOBARS

In accordance with the conclusion at the end of the preceding § III. 2. 1 it has been found that the applicability of the newly developed viscosity-temperature Equation (III-6h), or any of the equivalent expressions listed in § III. 1. 3, is not at all restricted to atmospheric pressure. In fact, it appears to hold almost equally good at higher pressures, generally up to at least 3,000-5,000 kgf/cm^2 (43,000-71,000 psi). Consequently, the family of isobars characterizing a given liquid is depicted as a family of straight lines in the basic viscosity-temperature chart described in § III. 1. 3.

For *elevated* pressures Equation (III-6h) may be rewritten as:

$$H = S\,\Theta + \log G. \qquad \text{(III-10)}$$

The level parameter G in the latter equation invariably increases with rising pressure. The Slope Index, S, however, may either increase or decrease more or less with rising pressure or may remain substantially constant.

Equation (III-10) has thoroughly been checked for a great variety of liquids primarily chosen amongst those used as lubricating oils. These include numerous mineral oils of very different origin and chemical constitution; a few polymer-blended mineral oils have also been tested. In addition, various types of currently important synthetic lubricating oils have been considered, notably silicones, diesters, polyglycols and fluorocarbons. Finally, Equation (III-10) has been checked for a great number of miscellaneous liquids, comprising many pure hydrocarbons and other pure compounds as well as rather complex polymeric liquids.

Equation (III-10) has proved to hold good for the numerous liquids investigated so far, and in a very wide temperature and pressure range at that. Usually, it may be applied satisfactorily over a temperature range of at least 200°C (360°F) and up to pressures of at least 3,000-5,000 kgf/cm^2 (43,000-71,000 psi). In particular its applicability to all the various kinds of mineral oils tested may be deemed quite satisfactory.

B. THE RELATIONSHIP BETWEEN THE FAMILY OF ISOBARS CHARACTERIZING A GIVEN LIQUID

As stated above, all the isobars of a given liquid are depicted by straight lines in a viscosity-temperature chart according to Equation (III-10). Now, an important feature emerged from this chart in that, to a good approximation, all the isobars proved to converge towards a common point, so that the family of isobars characterizing a given liquid constitutes a *fan*.

This convergence of isobars has been illustrated in the schematic Fig. III-7. The point of convergence, denoted by P_t, is termed the "*viscosity-temperature pole*". It has a viscosity coordinate $H = H_P$ which corresponds to a very low pole viscosity, η_P, roughly of the order of 0.1 cP. The temperature coordinate $\Theta = \Theta_P$ corresponds to an extremely high pole temperature, t_P.

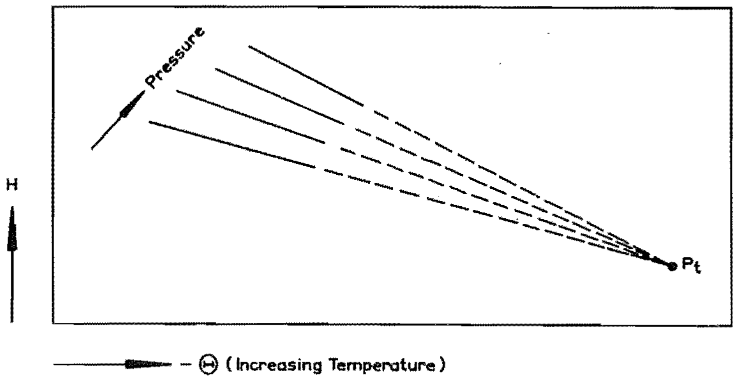


FIG. III-7.
Schematic Representation of Converging Isobars.

For other liquids the viscosity-temperature pole may be located in the opposite region of the H-Θ chart, that is the region of extremely high viscosities and very low temperatures. As a third case, the family of isobars characterizing a given liquid may be represented in the basic viscosity-temperature chart by a family of parallel straight lines, so that they constitute a *sheaf*. Such a sheaf may mathematically be considered to represent a "degenerated" convergence of the isobars, the viscosity-temperature pole being located at infinity, that is at infinite values of the viscosity function H and the temperature function Θ*).

In each of these three distinct cases of converging isobars the viscosity-temperature pole is located far beyond the viscosity and temperature range which assume practical importance. As will be shown below, the value of the delineated pole concept lies primarily in its mathematical convenience, namely for casting the underlying relationships into a really simple analytical form.

Finally, Fig. III-8 provides a concrete example of a family of converging isobars. However, the point of convergence is located at such a high viscosity and such a low temperature that it could not be drawn in the latter figure. The liquid concerned is a paraffinic

*) The corresponding pole viscosity, η_P, and pole temperature, t_P, may be taken to amount either to $\eta_P = \eta_\infty = 0.0631$ cP and $t_P = \infty$, or to $\eta_P = \infty$ and $t_P = -135^\circ C$.

mineral oil whose viscosity data have been determined in the scope of the well-known ASME pressure-viscosity project[27)], namely the oil coded A-4 in Table II-1.

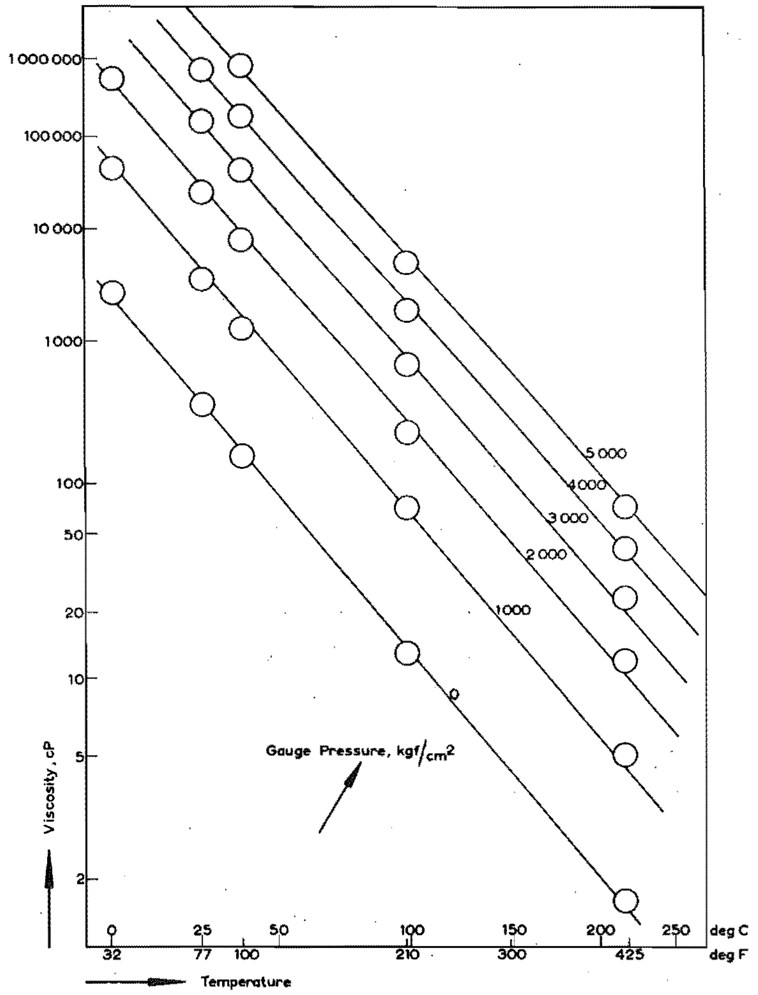


FIG. III-8.
Convergence of Isobars for a Paraffinic Mineral Oil.

C. A COMPLETE VISCOSITY-TEMPERATURE EQUATION

From the outlined convergence of the family of isobars characterizing a given liquid (see Fig. III-7) a simple viscosity-temperature equation can readily be derived that may be deemed *"complete"* in that it implicitly indicates the effect of *pressure* on the temperature variation of viscosity by means of only *one* pressure-dependent parameter, G:

$$\frac{H - \log G}{H_P - \log G} = \frac{\Theta}{\Theta_P} \qquad \text{(III-11a)}$$

In the limiting case where the family of isobars constitutes a *sheaf*, Equation (III-11a) reduces to:

$$H - \log G = S_0 \Theta, \qquad \text{(III-11b)}$$

where the value of the atmospheric Slope Index, S_0, is common to the entire family of isobars characterizing a given liquid.

Equation (III-11a), or (III-11b), in contrast to the basic Equation (III-10), does describe the pressure effect implicitly by only one quantity, that is G (=log $\eta_{0^\circ C}$ + 1.200). Thus, as long as Equation (III-11a) holds good, the viscosity-temperature dependence at any given value of G, and therefore at any given pressure, is completely characterized solely by the two pole coordinates, H_P and Θ_P. In the limiting case where Equation (III-11b) applies satisfactorily the viscosity-temperature dependence at any given pressure is sufficiently defined by one single parameter, namely the atmospheric Slope Index, S_0.

Once a relationship between G and pressure has been established, as will be done later on, Equation (III-11a) can readily be generalized to a complete viscosity-temperature-*pressure* equation.

III. 2. 3. *Discussion*

The existence of a viscosity-temperature pole for a given liquid has first been outlined by Roelands *et al.*[44]. In the "Authors' Closure" to their paper the latter authors have further stated that the feature of converging viscosity-temperature isobars is not at all confined to the particular equation employed in that paper, that is Equation (III-3). Indeed, the occurrence of the indicated convergence does not depend on the particular expressions used for defining the rectifying viscosity and temperature scales, provided only that such expressions are sufficiently accurate.

On the strength of the foregoing *generalized* viscosity-temperature pole concept the conclusion reached in § III. 2. 1 with respect to the applicability of viscosity-temperature equations at elevated pressures can be extended as follows:

Any viscosity-temperature diagram that has proved satisfactory for rectifying the atmospheric viscosity-temperature isobar of a given liquid may be utilized for depicting its family of isobars as a fan.

As a matter of fact, the involved convergence represents another approximation - though a very good one -, so that the validity of the present Equation (III-11a), or (III-11b), should be confined to a somewhat smaller temperature and pressure range if the correlational accuracy inherent in the basic viscosity-temperature Equation (III-10) is to be fully retained.

III. 3. A TENTATIVE STATISTICAL-PHYSICAL BASIS FOR THE NEWLY DEVELOPED VISCOSITY-TEMPERATURE EQUATION

III. 3. 1. *Introduction*

Starting from the concept that the ***mobility*** of the molecules in a liquid is governed by their *"free volume"*, suggestive interpretations can be furnished for molecular transport phenomena such as viscous flow and diffusion.

The paramount role of the free volume in molecular transport in liquids has long been emphasized and accounted for by various investigators, notably by Batschinski[85)], by Frenkel[86)] and by Eyring and his associates[56,87,57)]. Elaborate theoretical treatments of the free-volume concept have first been devised, in the years 1936-1939, by Eyring and his associates[57)], and by Lennard-Jones and Devonshire[88-90)]. In more recent years, Cohen and Turnbull[91-93)] have introduced a free-volume model with certain novel features which proved quite remarkable in describing liquid transport phenomena.

The Cohen-Turnbull free-volume model of the liquid state has also been taken as a starting-point in the present attempts to provide a statistical-physical basis for the newly developed viscosity-temperature equation.

The basic model underlying free-volume theories implies that each molecule in a liquid is confined to a *"cage"* bounded by its immediate neighbours. Owing to the thermal motions of the molecules, both the size and the shape of such cages - which are simultaneously in motion - are continuously changing.

Now, Cohen and Turnbull have introduced the concept that ***statistical redistribution*** of the free volume*) occasionally opens up a ***void*** within such a cage sufficiently large to permit considerable displacement of the molecule contained by it. Further, they assumed - in accordance with Bueche's views[94)] - that, for the molecular displacement to be diffusive, the void created should exceed a characteristic ***minimum volume*** - approaching the molecular volume - just large enough to enable another molecule to jump in after this displacement.

Thus, Cohen and Turnbull interpret molecular transport simply as translation of a molecule across the void created within its cage. According to their view, molecular transport results not from an *activation* in the sense as postulated by, amongst others, Eyring and his associates (see § III. 1. 1), but rather from a statistical redistribution of the free volume which proceeds with a negligibly small energy consumption.

*) Cohen and Turnbull defined the free volume as the volume per cage available for free redistribution (see § III.3.3).

Elaborating their concept of molecular transport for the simplified case of a liquid consisting of hard spheres, Cohen and Turnbull arrived at an exponential relationship between its viscosity - and likewise its self-diffusion coefficient - and its *average* free volume, the minimum required volume of a void entering as a parameter.

To test its applicability to real liquids, an appropriate expression for the average free volume has to be substituted. Confining oneself to the effect of temperature at atmospheric pressure, Cohen and Turnbull supposed that the average free volume increases linearly with temperature. Experimental verification of the resulting viscosity-temperature equation revealed that it would hold good not only for simple liquids - coming close to the hard-sphere model assumed -, but even for liquids of considerably more complex structure[91,93;95-97]. These findings may be taken to indicate that the assumptions on which their final viscosity-temperature expression is based are well fulfilled also for more complex liquids.

All in all, quite some evidence has been gathered to suggest that the Cohen-Turnbull model for liquid flow may well be essentially sound. In this respect, it should also be mentioned that, meanwhile, this model has met with great approval on the part of authorities such as Bondi[98) and Dixon and Webb[99).

In the present study it will be shown that, along the lines set forth by Cohen an Turnbull, a more general expression for the viscosity-temperature relationship of liquids can be deduced, solely by assuming a more general statistical distribution function for the free volumes of the individual molecules of a liquid. Actually, the viscosity-temperature expression thus achieved proves to be essentally identical to the empirically established Equation (III-10).

III. 3. 2. *The Present Approach*

A. STATISTICAL DISTRIBUTION OF FREE VOLUME

The free volume of the individual molecules of a liquid can be treated as a random variable. Accordingly, the distribution of the free volume amongst these numerous molecules can be described by statistical distribution functions.

Whereas Cohen and Turnbull based their aforementioned treatment on a simple exponential distribution function, the present approach is essentially different in that it assumes the distribution of free volume to be approximated very closely by the statistical distribution function introduced by Weibull[100,101). The latter function has proved to possess an unusually wide validity range, being much more generally applicable than, for instance, the well-known normal or exponential distribution functions. The most important features of Weibull's very prominent distribution function have been elaborated in Appendix III-1, at the end of this chapter.

At any fixed conditions of temperature and pressure, the *probability* $P(\omega)$ that an arbitrary molecule has a free volume exceeding the value ω would thus be described by the expression:

$$P(\omega) = e^{-\left(\frac{\omega - \gamma}{\mu}\right)^n}, \qquad \text{(III-12a)}$$

where γ, μ and n denote parameters of location, of scale and of shape, respectively.

It readily follows that the location parameter γ must be zero in order to fulfil the condition: $P(\omega=0) = 1$. Further, in accordance with Equation (III-23b) in the aforementioned appendix, the scale parameter μ can then be written in terms of the *average* free volume $\bar{\omega}$ and the shape parameter n, as follows:

$$\mu = \frac{\bar{\omega}}{\Gamma(1+\frac{1}{n})}, \qquad \text{(III-13)}$$

where the gamma function $\Gamma\,[1+(1/n)]$ comes fairly close to unity for the normally encountered values - varying from about 0.5 to 2.0 - of the shape parameter n.

Equation (III-12a) can now be reduced to the form:

$$P(\omega) = e^{-\left[\frac{\omega}{\bar{\omega}}\Gamma(1+\frac{1}{n})\right]^n} \qquad \text{(III-12b)}$$

In Fig. III-9 the latter probability $P(\omega)$ has been plotted against the involved ratio, $\omega/\bar{\omega}$, of the molecular to the average free volumes for four representative values of the shape parameter n. The resulting distribution curves are rather similar to those depicted in Fig. III-10 of Appendix III-1.

According to Equation (III-12b), the probability of finding a free volume exceeding the minimum value ω^* required for diffusive molecular displacements can be written as:

$$\ln P(\omega^*) = -\left[\frac{\omega^*}{\bar{\omega}}\Gamma(1+\frac{1}{n})\right]^n, \qquad \text{(III-14a)}$$

where ln denotes again the natural or Napierian logarithm, $\log_e$.

Substitution of the corresponding *specific* free volumes - relating to one gram of a particular liquid - leads to the following expression for a given liquid at the temperature and pressure involved:

$$\ln P(v_f^*) = -\left[\frac{v_f^*}{v_f}\Gamma(1+\frac{1}{n})\right]^n. \qquad \text{(III-14b)}$$

It may already be mentioned here that, under ordinary conditions of temperature and pressure, the probability $P(v_f^*)$ usually proves to be very small, being of the order of, say, 1%.

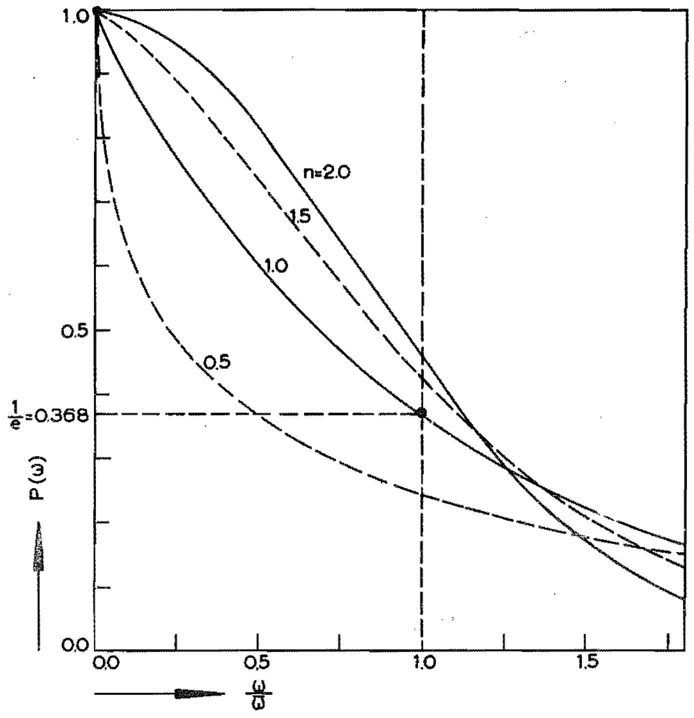


FIG. III-9.
Cumulative Distribution Curves for Free Volume According to Equation (III-12b).

B. MOLECULAR TRANSPORT PROPERTIES

On the basis of the above-described model tne molecular transport properties of a given liquid can be derived by considering that diffusive molecular jumps will occur with a probability directly proportional to the probability of finding molecules with a free volume greater than the minimum required value. As a consequence, both the self-diffusion coefficient and the fluidity - the reciprocal of viscosity - should be directly proportional to the probability $P(v_f^*)$ defined by Equation (III-14b).

Confining oneself to the *viscosity*, η, of a given liquid, this may thus be represented, at any fixed temperature and pressure, by the equation:

$$\ln \frac{\eta}{\eta_e} = \left[\frac{v_f^*}{v_f} \Gamma(1+\frac{1}{n})\right]^n , \qquad \text{(III-15)}$$

where η_e denotes the fictitious viscosity that would be reached for

$v_f = \infty$, that is at infinitely high temperature.

In conclusion, at any fixed temperature and pressure, the "reduced" viscosity η/η_e *of a given liquid would be determined solely by the statistical distribution of its free volume, this distribution being characterized, in harmony with Weibull's function, by three parameters: its specific free volume,* v_f*, its minimum required specific free volume,* v_f^**, and the shape parameter, n, characteristic of the particular liquid.*

C. VISCOSITY-TEMPERATURE EFFECT

Equation (III-15) can be transformed into an explicit viscosity-*temperature* equation by appropriately accounting for the effect of temperature - at constant pressure - on the three parameters occurring on its right-hand side.

Of these parameters the exponent n is essentially independent of temperature. For a given liquid this parameter assumes some characteristic value - usually between 0.5 and 2.0 - which determines the overall form of the statistical distribution of its free volume. In other words, with varying temperature the location of the appropriate distribution curve as represented in Fig. III-9 would remain unchanged. In fact, for a given value of the free volume ω only the ratio $\omega/\bar{\omega}$ - and therefore also the probability $P(\omega)$ - would increase with rising temperature, that is along the path indicated by the particular distribution curve in Fig. III-9.

The second parameter, the minimum required specific free volume, v_f^*, is governed by the configuration and the flexibility of the liquid's molecules. As a rule, this free volume v_f^* amounts to about 80-99% of the specific volume, v, of the liquid considered. For simple liquids the free volume v_f^* may be expected to be almost independent of temperature. However, for more complex liquids, especially those with associated or long-chain molecules*), it may change somewhat with temperature.

At any rate, the effect of temperature on viscosity as comprised by Equation (III-15) will predominantly be determined by its effect on the specific free volume, v_f. To a good approximation, the latter effect can generally be described by a simple linear relationship, although this may be less accurate for more complex liquids[91,93,97].

For assessing the effect of temperature on the ratio v_f^*/v_f in Equation (III-15) the following expression of a very general type can reasonably be resorted to:

$$\frac{v_f^*}{v_f} = \frac{k}{(T - T_0)^r}, \qquad \text{(III-16)}$$

where the exponent r approximates to unity and the parameter T_0

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*) For long-chain molecules the physical significance of the minimum required free volume ω^* - and likewise that of the molecular free volume ω - cannot so easily be visualized. It has been pointed out that in the case of such molecules these quantities should rather be related to their "flow units" (compare § III.3.3).

denotes the absolute temperature where the specific free volume, v_f, of the *liquid* would become zero. Further, the constant k represents the value of the ratio v_f^*/v_f that would be reached when the absolute temperature T is decreased to 1°K above the limiting temperature T_0.

As regards the order of magnitude of the limiting temperature T_0, it can be stated that for all the liquids investigated so far this temperature proved to come close to their so-called *glass-transition* temperature, T_0 being consistently somewhat lower[91,93,97]. Accordingly, for a given liquid the constant k would approximate to the value*) of the ratio v_f^*/v_f in its glass-transition state.

Combination of Equations (III-15) and (III-16) readily yields the following expression for explicitly describing the effect of temperature, at any constant pressure, on the viscosity of a given liquid:

$$\ln \frac{\eta}{\eta_e} = \frac{\left[k\,\Gamma\left(1+\frac{1}{n}\right)\right]^n}{(T - T_0)^m}\,. \qquad \text{(III-17)}$$

Since the numerator and the exponential product rn on the right-hand side of the latter equation are essentially independent of temperature, this equation explicitly defines the effect of temperature, at any constant pressure, on the "reduced" viscosity η/η_e of an arbitrary liquid by means of only *three* parameters.

For comparing the above-derived Equation (III-17) with the empirically developed viscosity-temperature Equation (III-10) the latter is conveniently rewritten in the form:

$$\ln \frac{\eta}{\eta_\infty} = \frac{G^*}{(T - 138)^S}, \qquad \text{(III-10a)}$$

where the constant G* stands for the value of ln (η/η_∞) at the standard reference temperature T=139°K.

It is then readily seen that both equations become identical when the fictitious viscosity η_e and the limiting temperature T_0 are replaced by the fixed constants η_∞ (=0.0631 cP) and 138°K, respectively. As pointed out in the preceding sections of this chapter, experimental verification has proved that the latter constants, η_∞ and 138°K, may invariably be employed as approximative values for all the various kinds of liquids investigated so far.

Conversely, it may be claimed that the new viscosity-temperature Equation (III-10a), which was originally derived along purely empirical lines, can also be obtained on the basis of the foregoing statistical-physical considerations taking the free-volume concept of the liquid state as a starting-point.

Further comparison of Equations (III-17) and (III-10a) leads to the result that the Slope Index, S, may be approximately identified with the exponential product rn. This also implies that, since the para-

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*) According to Williams, Landel and Ferry[102], this value amounts to approximately 40 for many liquids.

meter r is close to unity, the Slope Index would be nearly equal to the shape parameter n in Weibull's function for describing the statistical distribution of free volume amongst the numerous molecules of a given liquid. Conversely, the Slope Index may now be interpreted as the quantity which, in accordance with Fig. III-9, predominantly determines the overall form of the statistical distribution of the free volume of the liquid concerned.

Obviously, Equation (III-17) constitutes a more general expression than Equation (III-10a) in that, in contrast to the latter equation, it also permits the parameters η_e and T_0 to vary from one liquid to another.

It can easily be shown that Equation (III-17) includes, in addition to the newly developed Equation (III-10a), several well-known, previously established viscosity-temperature expressions as special cases. For $T_0 = 0^\circ K$ and rn=1, Equation (III-17) becomes identical to de Guzmán's simple exponential Equation (III-1). Further, Vogel's Equation (III-2)*) is obtained solely by taking rn=1. Finally, substitution solely of $T_0 = 0^\circ K$ yields Equation (III-3) introduced by Cornelissen and Waterman.

Consequently, Equation (III-17) may be deemed significant also in that it clearly indicates the kind and degree of approximations involved in the aforementioned empirically established viscosity-temperature expressions.

III. 3. 3. *Concluding Remarks*

Some concluding remarks may first be devoted to the concept and definition of "free volume". In fact, various definitions have been proposed in the course of time[103-105].

Basically, the free-volume *concept* represents a more or less oversimplified device for (analytically) approximating the very complex, and in many cases presumably inextricable, *molecular distribution function* of liquids and its correlation with their equilibrium and, particularly, their transport properties.

It is no wonder, therefore, that various - more or less loose - *definitions* of free volume have been proposed. Cohen and Turnbull, in their above-described model for the liquid state, defined the free volume of molecules as the volume per cage available for free redistribution[91-93]. Let it suffice here to mention that, under ordinary conditions of temperature and pressure, the thus-defined free volume usually appears to amount to something like 1-20% of the molecular volume. A critical discussion of several earlier definitions of free volume has been presented by Bondi[103].

Whilst for simple liquids free volume can be related to the individual molecules, its physical significance for liquids consisting of long-chain molecules - which display so-called segmental flow (see § VIII. 4. 4, part B) - cannot so easily be visualized. It has been pointed out that in the latter case free volume should be related not to the long-chain molecules as a whole but rather to their *"flow*

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*) Cohen and Turnbull's approximative formulation leads to essentially the same viscosity-temperature equation[91,93,97].

units", that is to their effective segments[94,103,104].

It has become clear that, notwithstanding the indicated deficiencies inherent in any free-volume model of the liquid state, the simplified physical picture represented by some suitable model can be advantageously utilized for deriving basically correct correlations for the equilibrium and transport properties of liquids. As regards the quantitative application of such correlations, one is confronted with the problem that numerical values for one or more of its parameters, although having a plausible physical interpretation, cannot (yet) be assessed *a priori*. The parameters concerned then have to be regarded as adjustable ones, the appropriate numerical values being derived from experimental data.

In the above respect the Cohen-Turnbull free-volume model of the liquid state has proved particularly successful and has meanwhile met with great approval on the part of authorities such as Bondi[98] and Dixon and Webb[99].

Starting from the Cohen-Turnbull model, the present approach has resulted in a very general formulation for the transport properties of liquids. More particularly, the resulting viscosity Expression (III-15), though still *tentative*, may well turn out to be a valuable contribution in further clarifying their viscous properties, the more so as a rigorous solution based on some sophisticated molecular theory would seem hardly conceivable for the very complex liquids encountered in modern engineering practice. After all, the derived Equation (III-17) has proved quite successful, even in the simplified form represented by the empirically developed Equation (III-10a), for describing the viscosity-temperature relationships of all the various kinds of liquids investigated so far.

APPENDIX

Appendix III-1. *Weibull's Statistical Distribution Function*

A *random variable* is characterized by the feature that it can assume a more or less extensive range of values which cannot be assessed more accurately than by means of some appropriate statistical distribution function. Such a statistical distribution function, or rather *cumulative* distribution function, defines the *probability* P(x) of choosing at random an individual having a value of x greater than x. This definition implies that P(x) also denotes the statistical *fraction* of the individuals considered with an x-value exceeding x.

A well-known statistical distribution function, which has proved to possess an unusually wide validity range, has been proposed by Weibull[100,101]. It has been extensively and very successfully applied to a great variety of problems, notably to material-fatigue problems. Since its introduction, in 1939, this versatile distribution function has gained a still increasing prominence[100,101,106].

In its most general form Weibull's *cumulative* distribution function can be written as:

$$P(x) = e^{-\left(\frac{x-\gamma}{\mu}\right)^n}, \qquad \text{(III-18a)}$$

where γ, μ and n denote parameters of location, of scale and of shape, respectively. The location parameter γ represents the lower limit imposed upon the random variable x and may be either positive, or zero or also negative; the scale parameter μ and the shape parameter n, however, can assume only positive values.

By introducing the "reduced" variable:

$$z = \frac{x - \gamma}{\mu} \qquad \text{(III-19)}$$

Equation (III-18a) can be put into the *standardized* form:

$$P(x) = e^{-z^n}. \qquad \text{(III-18b)}$$

Plotting this standardized form of Weibull's cumulative distribution function for different values of the shape parameter n yields distribu-

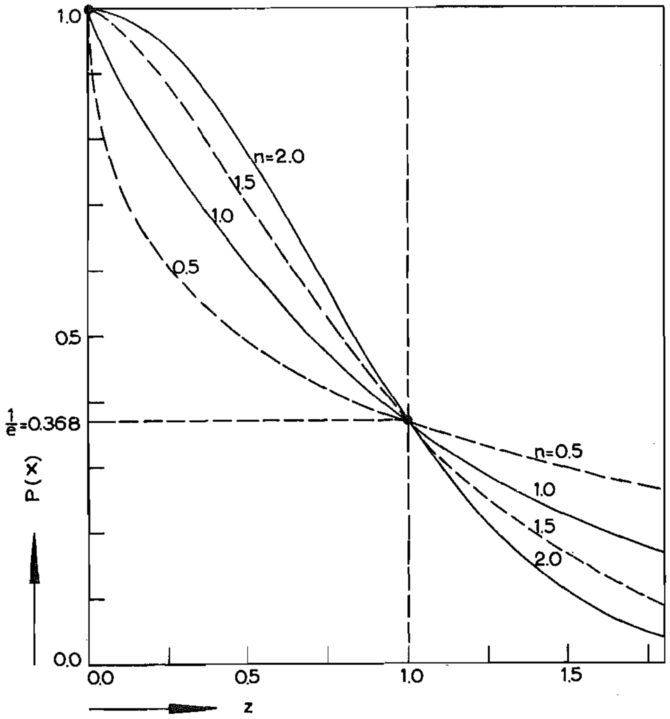

FIG. III-10.
Cumulative Distribution Curves According to Weibull's Function (III-18b).

tion curves of very different shapes. Fig. III-10 depicts four such curves, the shape parameter n having representative values of 0.5, 1.0, 1.5, and 2.0, respectively.

Fig. III-10 clearly demonstrates that the Weibull function comprises a great variety of distribution curves. In fact, it includes various well-known distribution functions as special cases. Thus, the curve characterized by n=1.0 represents an *exponential* distribution of the variable x, whilst the curve resulting for n=2.0 is identical to the statistical distribution described by Rayleigh's function. Further, Weibull has pointed out that for n=3.25 his function constitutes an excellent approximation of the *normal*, or Gaussian, distribution function.

The probability of choosing at random an individual having a value of x located between x and x+dx is defined by the integral:

$$\int_{x}^{x+dx} p(x)\,dx\,,$$

where p(x) represents the so-called *probability-density* function. It is readily seen that this probability-density function p(x) is related to the corresponding *cumulative* distribution function P(x) by the identity:

$$P(x) = \int_{x}^{\infty} p(x)\,dx\,. \qquad \text{(III-20)}$$

In accordance with Equation (III-18a), Weibull's probability-density function can readily be shown to read:

$$p(x) = \frac{n}{\mu}\left(\frac{x-\gamma}{\mu}\right)^{n-1} e^{-\left(\frac{x-\gamma}{\mu}\right)^{n}}. \qquad \text{(III-21a)}$$

By introducing again the reduced variable z and by choosing the scale parameter μ equal to unity the latter equation can be cast into the *standardized* form:

$$p(x) = n\,z^{n-1}e^{-z^{n}}. \qquad \text{(III-21b)}$$

In Fig. III-11 this standardized form of Weibull's probability-density function has been plotted for the same representative values of the shape parameter n as used in constructing the corresponding cumulative distribution curves of Fig. III-10.

It is seen that the probability-density curves according to Weibull's Function (III-21b) may be very different for different values of their shape parameter n. For shape parameters above unity these curves pass through a maximum; the maximum is located closer to the average value of z as the shape parameter approximates closer to the value 3.25, the relevant distribution being practically normal (see above).

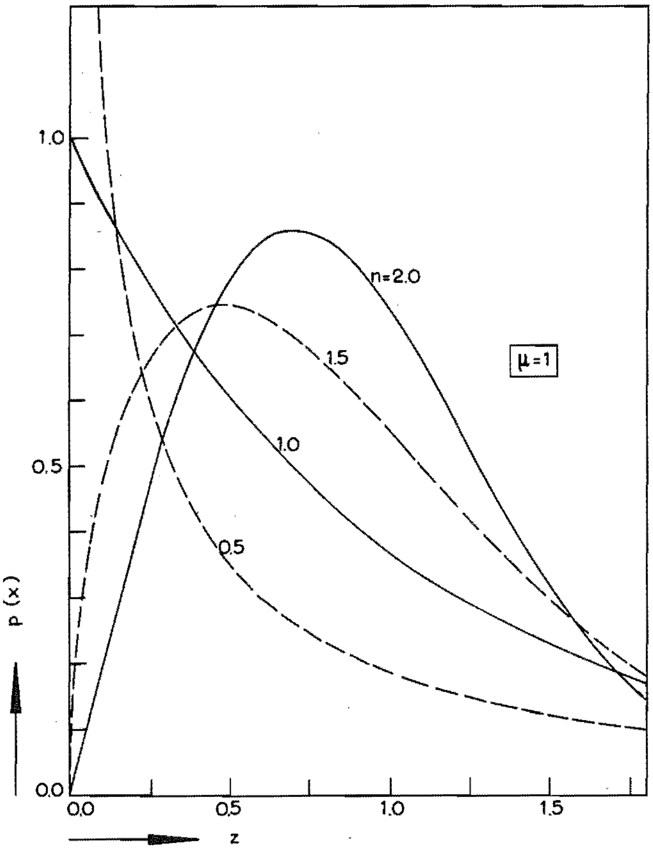

FIG. III-11.
Probability-Density Curves According to Weibull's Function (III-21b).

An important single characteristic of statistical distributions is represented by the particular *average* value $\overline{x}$ over the range of values covered by the random variable x. In accordance with Weibull's probability-density Function (III-21a), this average value $\overline{x}$ is defined by the identity:

$$\overline{x} = \int_{\gamma}^{\infty} x\, f(x)\, dx. \tag{III-22a}$$

Evaluation of the latter integral yields:

$$\overline{x} = \gamma + \mu\, \Gamma(1+\tfrac{1}{n}), \tag{III-22b}$$

where the gamma function $\Gamma[1+(1/n)]$ comes fairly close to unity for the usually encountered values of the shape parameter n.

Besides for computing the average value $\bar{x}$, Identity (III-22b) may sometimes be conveniently employed for replacing the scale parameter μ in Weibull's statistical distribution function by the corresponding expression:

$$\mu = \frac{\bar{x}-\gamma}{\Gamma(1+\frac{1}{n})} \qquad \text{(III-23a)}$$

or, in the frequently encountered case where $\gamma=0$:

$$\mu = \frac{\bar{x}}{\Gamma(1+\frac{1}{n})} \, . \qquad \text{(III-23b)}$$

An example of the advantageous application of the latter expression has been elaborated in § III.3.2.

CHAPTER IV

THE ISOTHERMAL VISCOSITY-PRESSURE RELATIONSHIP FOR A GIVEN LIQUID

IV. 1. INTRODUCTION

To a first approximation the isothermal viscosity-pressure relationship of liquids can be described by the equation:

$$\eta = \eta_0 \cdot e^{\alpha p}, \qquad \text{(IV-1a)}$$

where η denotes the dynamic viscosity at *gauge* pressure p and η_0 the dynamic viscosity at atmospheric pressure and at the same temperature. The only parameter, α, characterizes the liquid considered and would depend solely on temperature, not on pressure. As long ago as 1893 Barus[107] used Equation (IV-1a) as an empirical approximation.

The latter equation can be rewritten in the logarithmized*) forms:

$$\log \eta = \alpha' p + \log \eta_0 \qquad \text{(IV-1b)}$$

or

$$\log \frac{\eta}{\eta_0} = \alpha' p, \qquad \text{(IV-1c)}$$

where $\alpha' = 0.4343\ \alpha$. Formula (IV-1b) for the isothermal viscosity-pressure relationship of liquids proves to be analogous to de Guzmán's Equation (III-1a) for their atmospheric viscosity-temperature relationship.

Though originally established empirically, Equation (IV-1a) - like the analogous viscosity-temperature equation - has later been obtained as a theoretical approximation. In terms of Eyring's theory of viscous flow (see § III. 1. 1), Equation (IV-1a), or rather (IV-1c), may be rewritten as*):

$$\ln \frac{\eta}{\eta_0} = \frac{V_{vis}}{RT}\, p, \qquad \text{(IV-1d)}$$

where the parameter V_{vis} (relating to one gmole) is characteristic of a given liquid, while R denotes again the molar gas constant. Unlike the parameter α' in Equation (IV-1c), the quantity V_{vis} is seen to have the dimension of a volume.

The volume V_{vis} has a suggestive interpretation in Eyring's model for viscous flow (outlined in § III. 1. 1). According to this model, the indicated jumps of activated molecules over a potential-energy barrier are only possible once a suitable "hole" has been created in

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*) Just as in the foregoing, log denotes the common or Briggsian logarithm, $\log_{10}$, whilst ln stands for the natural or Napierian logarithm, $\log_e$. Note further that log e = 0.4343.

their neighbourhood. Now, the size of such holes (per gmole) is represented by the quantity V_{vis}.

Although Formula (IV-1a) is extensively used, it is not generally applicable; usually, it is valid to a reasonable approximation only in a moderate pressure range. In fact, whereas according to this formula log η-p isotherms should be represented by straight lines, they generally prove to be perceptibly curved. As a rule, these isotherms are more or less concave towards the pressure axis. Only in comparatively few cases have they been found to be slightly convex in that direction.

Further, it should be mentioned that at very high pressures log η-p isotherms which initially are either concave downward or straight are often changing gradually into convex ones[27,28,8,9]. Accordingly, in the usual case of initially concave downward curves the indicated "transition" can be characterized by a point of inflection. The occurrence of this transition in log η-p curves has been attributed by Bridgman[8,9] to the "interlocking" of molecules in the strongly compressed liquid. Fortunately, such a transition is generally absent up to pressures of at least some 5,000 kgf/cm^2 (71,000 psi).*)

IV.2. EMPIRICAL EQUATIONS

In trying to describe the isothermal viscosity-pressure relationship of liquids by means of some empirical expression more adequate than Equation (IV-1a), it is highly useful to realize the striking qualitative resemblance between log η-p isotherms and log η-T^{-1} isobars (see § III.1.1). It is no wonder, therefore, that the analytical form of the more prominent viscosity-pressure equations proves to be similar to that of the well-known viscosity-temperature equations. In fact, as will be demonstrated below, these viscosity-pressure equations can formally be obtained from the analogous viscosity-temperature equations simply by substituting pressure for *reciprocal* temperature.

Further, one point - the starting-point - of a given viscosity-pressure isotherm is defined by the corresponding atmospheric viscosity, η_0. Actually, therefore, viscosity-pressure equations aim at describing the effect of pressure on the specified *atmospheric* viscosity of the liquid concerned. Accordingly, the number of characteristic parameters required in viscosity-pressure equations is reduced by one as compared with the number needed in the analogous viscosity-temperature equations. At the same time, however, the occurrence of the atmospheric viscosity as a *fixed* constant in viscosity-pressure equations seriously limits their flexibility. In the latter respect it is rather unfortunate that log η-p isotherms frequently prove to exhibit their strongest curvature in the initial pressure range, that is in the vicinity of this very atmospheric viscosity.

Several empirical viscosity-pressure equations have been proposed

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*) Particularly at low temperatures the log η-p isotherms of certain silicone oils may exhibit a point of inflection already at pressures of about 2,000-4,000 kgf/cm^2 (28,000-57,000 psi).

to replace Barus's simple exponential Equation (IV-1a). Such equations usually contain - apart from the atmospheric viscosity, η_0 - *two*, or more, characteristic parameters instead of Barus's single one.

Before introducing a newly developed equation, a few two-parameter viscosity-pressure equations which, at least from a practical point of view, would appear to be the most valuable ones available will be briefly discussed.

The following two-parameter equation, which is analogous to Vogel's Equation (III-2) for the viscosity-temperature relationship of liquids, has been successfully applied by the present author:

$$\log \frac{\eta}{\eta_0} = \frac{K}{p^{-1}+c}, \qquad \text{(IV-2)}$$

where K and c denote parameters characteristic of a given liquid. Whilst the parameter K decreases rather rapidly with rising temperature, the other parameter, c, may generally be taken constant over a wide temperature range. The new viscosity-pressure Equation (IV-2) would seem to be the most attractive two-parameter equation developed so far.

Another very valuable viscosity-pressure formula, which is analogous to the Cornelissen-Waterman Equation (III-3) for the viscosity-temperature relationship of liquids, has recently been proposed by Roelands *et al.* 44) :

$$\log \frac{\eta}{\eta_0} = K' \, p^{c'}, \qquad \text{(IV-3)}$$

where K' and c' are parameters characteristic of the liquid concerned. In general, the exponent c' proves to be substantially constant over a wide temperature range, whereas the parameter K' decreases rather strongly with rising temperature.

A third viscosity-pressure equation, which is analogous to the Tait-type Equation (III-4), has been proposed by Blok in his discussion on a paper by Hersey and Lowdenslager 108):

$$\log \frac{\eta}{\eta_0} = K'' \cdot \log\left(1 + \frac{p}{c''}\right), \qquad \text{(IV-4)}$$

where K'' and c'' are parameters characteristic of a particular liquid. The latter expression, which has been applied in several lubrication problems, is also known as the generalized Karlson equation 84,26). The present author has found that in a wide temperature range the parameter c'' may generally be taken constant, whereas the parameter K'' decreases fairly strongly with rising temperature.

The foregoing Equations (IV-2), (IV-3) and (IV-4) permit describing not only concave and straight, but also convex log η-p isotherms; of course, they cannot hold at pressures so high as to give rise to the above-indicated transition*). Generally, these three equa-

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*) Actually, this restriction has to be imposed upon any convenient viscosity-pressure equation. Indeed, such an equation can apply only as long as log η-p isotherms show a regular trend; that is if these are either straight or monotonously curved.

tions apply satisfactorily to any given liquid in the same very wide ranges of temperature and pressure where the aforementioned analogous viscosity-temperature equations are applicable, that is in a temperature range covering at least 200°C (360°F) and up to pressures of at least 3,000-5,000 kgf/cm^2 (43,000-72,000 psi).

Moreover, for a given liquid the parameters c, c' and c'' in the three aforementioned equations have proved to remain substantially constant in a wide temperature range. Consequently, each of these equations permits the construction of a diagram, typical of the liquid considered, in which the isotherms characterizing this liquid are depicted, in a wide temperature range and up to very high pressures, as a family of straight lines.

Although the preceding two-parameter equations are very useful for analytically describing viscosity-pressure isotherms, yet they are rather cumbersome to use. In fact, it would be highly desirable to have available some convenient equation for describing the viscosity-pressure isotherms of liquids, particularly those used in present lubrication practice, by means of only *one* characteristic parameter. Such an equation would also permit the construction of a generally applicable "*rectifying*" viscosity-pressure chart, that is a chart - analogous to the viscosity-temperature chart described in § III.1.3 - in which the isotherms of all the various liquids satisfying the basic equation would be represented by straight lines, at least to a good approximation*).

The present attempts described in the subsequent Section IV.3 aim at devising such a viscosity-pressure equation with only one parameter characteristic of the liquid under consideration.

IV.3. THE PRESENT CHARACTERIZATION METHOD

IV.3.1. *Mathematical Description of the Isotherms*

The following new empirical equation has proved successful, over very wide ranges of temperature and pressure, for describing the isothermal viscosity-pressure relationships of lubricating oils and even all the other liquids tested so far:

$$\log \eta + 1.200 = (\log \eta_0 + 1.200)\left(1 + \frac{p}{2,000}\right)^Z \qquad \text{(IV-5a)}$$

or, logarithmized:

$$\log(\log \eta + 1.200) = Z \cdot \log\left(1 + \frac{p}{2,000}\right) + \log(\log \eta_0 + 1.200), \qquad \text{(IV-5b)}$$

where η denotes the dynamic viscosity, in cP, at gauge pressure

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*) Sanderson[109,110] has suggested that such a rectifying chart - though for kinematic viscosity - could be obtained by adjusting a pressure scale, proportional to the square root of pressure, alongside the temperature scale of the ASTM kinematic viscosity-temperature chart (see § III.1.2). However, the indicated viscosity-pressure chart proves to be far from generally applicable; in fact, it generally is bound to fail at lower pressures.

p, in kgf/cm^2, and η_0 the dynamic viscosity at atmospheric pressure and at the same temperature.

According to the latter equations, the viscosity-pressure relationship of a liquid whose atmospheric viscosity, η_0, has been specified is determined *solely* by the dimensionless quantity Z. This quantity Z therefore constitutes a significant and convenient viscosity-pressure criterion (see Chapter VII).

Whilst for a given liquid the parameter Z would be independent of pressure, it usually varies slightly with temperature or - indirectly - with its atmospheric viscosity, η_0, entering into Equations (IV-5a) and (IV-5b). This parameter Z may either increase or decrease somewhat with rising temperature or may remain substantially constant. But the resulting variations of Z generally prove to be so small that it may be taken constant over a fairly wide temperature range.

The present viscosity-pressure Equation (IV-5b) shows a close similarity to the newly developed viscosity-temperature Equation (III-6b). Thus, it is seen that the negative value of the constant 2,000 in Equation (IV-5b) denotes the fictitious negative pressure, in kgf/cm^2, where the analytically extrapolated viscosity becomes equal to η_∞. This fictitious viscosity η_∞ would again amount to 0.0631 cP and would be common to all liquids. Accordingly, this limiting viscosity η_∞ would be reached for any given liquid either by increasing temperature to infinity or by decreasing pressure to -2,000 kgf/cm^2.

Those preferring to measure (gauge) pressure in psi (1 kgf/cm^2 = 14.22 psi), denoting this by p', may rewrite Equation (IV-5b) as:

$$\log(\log \eta + 1.200) = Z \cdot \log\left(1 + \frac{p'}{28,440}\right) + \log(\log \eta_0 + 1.200), \qquad \text{(IV-5c)}$$

where, for a given liquid, Z has the same value as in Equation (IV-5b).

Likewise, for pressure expressed in atm (1 kgf/cm^2 = 0.9678 atm), denoted by p", one may write:

$$\log(\log \eta + 1.200) = Z \cdot \log\left(1 + \frac{p''}{1,936}\right) + \log(\log \eta_0 + 1.200), \qquad \text{(IV-5d)}$$

where, for a given liquid, Z has again the same value as in Equation (IV-5b).

For the sake of simplicity, Formula (IV-5b) is rewritten in the form:

$$H = Z\,\Pi + H_0\ , \qquad \text{(IV-5e)}$$

where H represents the viscosity function already defined in Chapter III, that is H = log (log η + 1.200). Further, the pressure function Π is seen to be defined by:

$$\Pi = \log\left(1 + \frac{p}{2,000}\right), \qquad \text{(IV-6)}$$

so that Π = 0 for atmospheric pressure, p = 0 kgf/cm^2. This pressure function Π appears to be rather analogous to the temperature function Θ, defined by Equation (III-8).

Thus, by constructing scales proportional to the viscosity function H and the pressure function Π a "rectifying" chart is obtained, that is a chart in which by definition all viscosity-pressure curves satisfying the basic Equation (IV-5b) are represented by straight lines. Essentially the same chart is naturally obtained when one of the above equivalent equations is taken as a basis. Obviously, this viscosity-pressure chart will be very similar to the viscosity-*temperature* chart described in § III. 1. 3; in fact, both rectifying charts not only possess a common viscosity scale, but the pressure and temperature scales are also closely related.

The new viscosity-pressure chart reproduced in Fig. IV-1 has been provided with a single viscosity scale, in cP, and a double pressure scale, pressure being expressed in both kgf/cm^2 and psi. This chart*) covers very wide viscosity and pressure ranges, viscosities extending from 1.00 to 10^7 cP and pressures up to 5,000 kgf/cm^2 (71,100 psi).

The scales concerned have been so proportioned that the (upward) *slope* of viscosity-pressure lines is numerically equal to the parameter Z in the basic Equation (IV-5e). Therefore, from such a chart this dimensionless quantity Z, the new viscosity-pressure criterion, which will be termed the *"Viscosity-Pressure Index"*, can be assessed most readily. The accuracy of such a graphical assessment of this index will usually suffice for any practical purpose**), provided that the chart's format is large enough, like that of the full-size chart reproduced in Fig. IV-1.

In addition to the viscosity-pressure chart here described, extensive tables have been prepared to facilitate the numerical conversion of pressures, expressed in either kgf/cm^2 or psi, into the corresponding pressure functions defined by Equations (IV-5b) and (IV-5c), respectively. Accordingly, Tables IV-1a and IV-1b contain pressures, in kgf/cm^2 and psi, and the values of the corresponding pressure functions $\log\left[1+(p/2,000)\right]$ and $\log\left[1+(p'/28,440)\right]$, respectively***).

In Figs. IV-2 through IV-6 the viscosity-pressure isotherms of a great variety of liquids, primarily chosen amongst those used as lubricating oils, have been plotted in a chart according to Equation (V-5e). All the liquids indicated in these figures are specified in Table IV-2.

Fig. IV-2 comprises four divergent types of mineral oils****) tested in the well-known ASME pressure-viscosity project 27). Besides three natural mineral oils representing pronounced paraffinic, naphthenic and aromatic types, one polymer-blended mineral oil (prepared from the latter paraffinic oil) has been included. For each oil two isotherms, relating to 37.8°C (100°F) and 98.9°C (210°F), have been depicted; the involved pressures extend to over 10,000 kgf/cm^2 (142,000 psi).

Besides four important types of synthetic lubricating oils likewise tested in the ASME pressure-viscosity project 27), Fig. IV-3 com-

*) Like the viscosity-temperature chart described in § III.1.3 this full-size viscosity-pressure chart has been printed on a format of 35 by 50 cm (about 14 by 20 in).

**) It has appeared that as a rule there is not much sense in carrying numerical evaluation of the Viscosity-Pressure Index, Z, beyond two decimal places. For instance, a value of 0.754 assessed for a certain index could reasonably be rounded off to 0.75.

***) For the relevant viscosity conversions Table III-1 can be utilized.

****) Further, in the H-Π charts of Figs. IV-8 and IV-9 to be discussed later on in this chapter the entire family of isotherms has been depicted for a natural and a polymer-blended mineral oil, respectively.

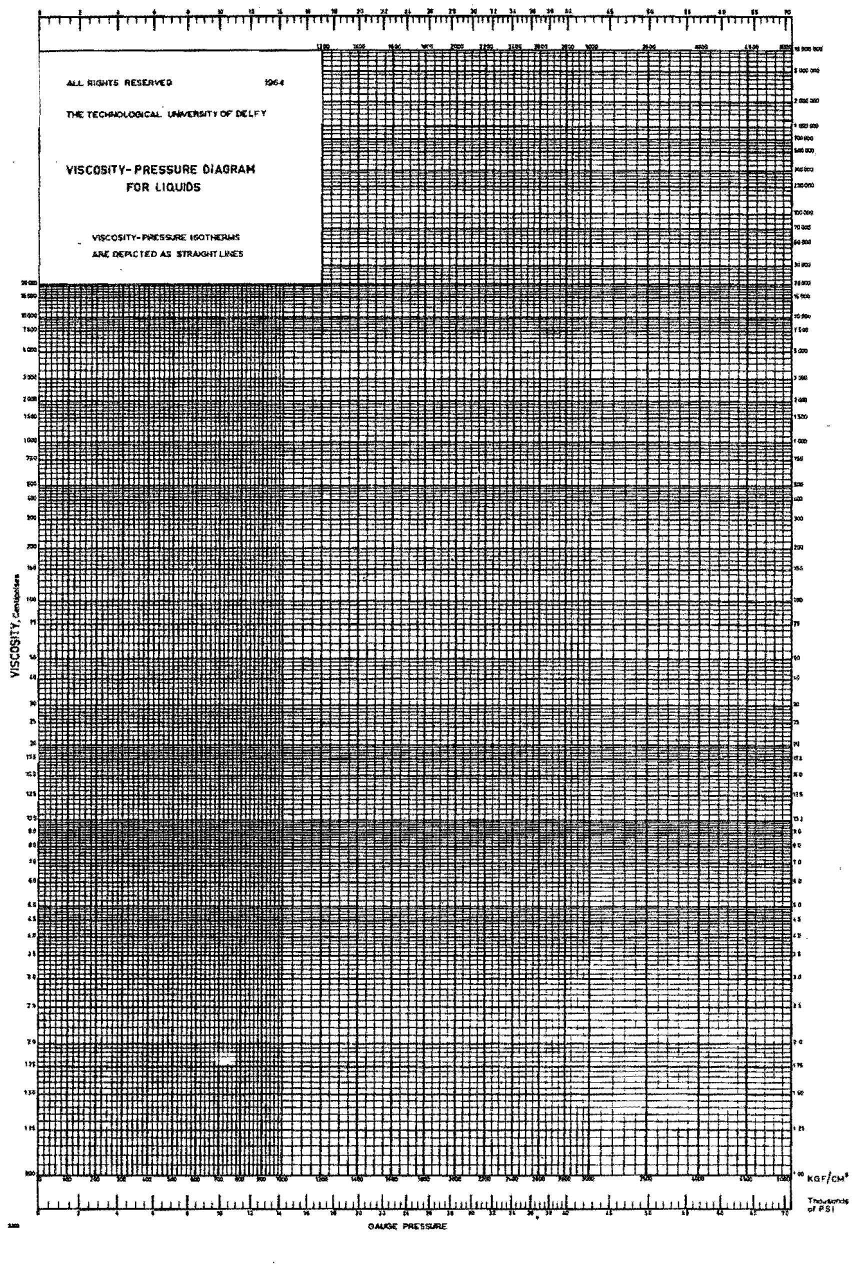

FIG. IV -1.
The New Viscosity-Pressure Chart for Liquids.

TABLE IV-1a

Pressure Conversion Table (kgf/cm^2)

kgf/cm^2	Π	kgf/cm^2	Π	kgf/cm^2	Π	kgf/cm^2	Π
0	0.0000	600	0.1139	1,500	0.2430	3,000	0.3979
20	0.0043	620	0.1173	1,550	0.2492	3,100	0.4065
40	0.0086	640	0.1206	1,600	0.2553	3,200	0.4150
60	0.0128	660	0.1238	1,650	0.2613	3,300	0.4232
80	0.0170	680	0.1271	1,700	0.2672	3,400	0.4314
100	0.0212	700	0.1303	1,750	0.2730	3,500	0.4393
120	0.0253	720	0.1335	1,800	0.2788	3,600	0.4472
140	0.0294	740	0.1367	1,850	0.2844	3,700	0.4548
160	0.0334	760	0.1399	1,900	0.2900	3,800	0.4624
180	0.0374	780	0.1430	1,950	0.2956	3,900	0.4698
200	0.0414	800	0.1461	2,000	0.3010	4,000	0.4771
220	0.0453	820	0.1492	2,050	0.3064	4,100	0.4843
240	0.0492	840	0.1523	2,100	0.3118	4,200	0.4914
260	0.0531	860	0.1553	2,150	0.3170	4,300	0.4983
280	0.0569	880	0.1584	2,200	0.3222	4,400	0.5052
300	0.0607	900	0.1614	2,250	0.3274	4,500	0.5119
320	0.0645	920	0.1644	2,300	0.3324	4,600	0.5185
340	0.0682	940	0.1673	2,350	0.3375	4,700	0.5250
360	0.0719	960	0.1703	2,400	0.3424	4,800	0.5315
380	0.0756	980	0.1732	2,450	0.3473	4,900	0.5378
400	0.0792	1,000	0.1761	2,500	0.3522	5,000	0.5441
420	0.0828	1,050	0.1833	2,550	0.3570	5,500	0.5740
440	0.0864	1,100	0.1903	2,600	0.3617	6,000	0.6021
460	0.0899	1,150	0.1973	2,650	0.3664	6,500	0.6284
480	0.0934	1,200	0.2041	2,700	0.3711	7,000	0.6532
500	0.0969	1,250	0.2108	2,750	0.3757	7,500	0.6767
520	0.1004	1,300	0.2175	2,800	0.3802	8,000	0.6990
540	0.1038	1,350	0.2240	2,850	0.3847	8,500	0.7202
560	0.1072	1,400	0.2304	2,900	0.3892	9,000	0.7404
580	0.1106	1,450	0.2368	2,950	0.3936	10,000	0.7782

TABLE IV-1b

Pressure Conversion Table (psi)

psi x 10^{-3}	Π	psi x 10^{-3}	Π	psi x 10^{-3}	Π	psi x 10^{-3}	Π
0	0.0000	15	0.1339	30	0.3127	50	0.4406
0.5	0.0076	15.5	0.1889	30.5	0.3164	51	0.4461
1	0.0150	16	0.1938	31	0.3201	52	0.4515
1.5	0.0223	16.5	0.1987	31.5	0.3237	53	0.4569
2	0.0295	17	0.2035	32	0.3274	54	0.4622
2.5	0.0366	17.5	0.2082	32.5	0.3309	55	0.4674
3	0.0435	18	0.2129	33	0.3345	56	0.4726
3.5	0.0504	18.5	0.2176	33.5	0.3380	57	0.4777
4	0.0571	19	0.2222	34	0.3415	58	0.4827
4.5	0.0638	19.5	0.2267	34.5	0.3449	59	0.4877
5	0.0703	20	0.2312	35	0.3483	60	0.4927
5.5	0.0768	20.5	0.2357	35.5	0.3518	61	0.4975
6	0.0831	21	0.2401	36	0.3552	62	0.5024
6.5	0.0894	21.5	0.2444	36.5	0.3585	63	0.5071
7	0.0955	22	0.2488	37	0.3619	64	0.5119
7.5	0.1016	22.5	0.2531	37.5	0.3652	65	0.5166
8	0.1076	23	0.2573	38	0.3685	66	0.5212
8.5	0.1135	23.5	0.2615	38.5	0.3717	67	0.5257
9	0.1194	24	0.2657	39	0.3749	68	0.5303
9.5	0.1252	24.5	0.2698	39.5	0.3781	69	0.5348
10	0.1308	25	0.2739	40	0.3813	70	0.5392
10.5	0.1364	25.5	0.2779	41	0.3876	75	0.5607
11	0.1420	26	0.2819	42	0.3938	80	0.5812
11.5	0.1475	26.5	0.2859	43	0.4000	90	0.6195
12	0.1529	27	0.2898	44	0.4060	100	0.6548
12.5	0.1582	27.5	0.2938	45	0.4120	110	0.6873
13	0.1635	28	0.2976	46	0.4178	120	0.7176
13.5	0.1687	28.5	0.3014	47	0.4236	130	0.7459
14	0.1738	29	0.3053	48	0.4293	140	0.7724
14.5	0.1790	29.5	0.3090	49	0.4350	150	0.7975

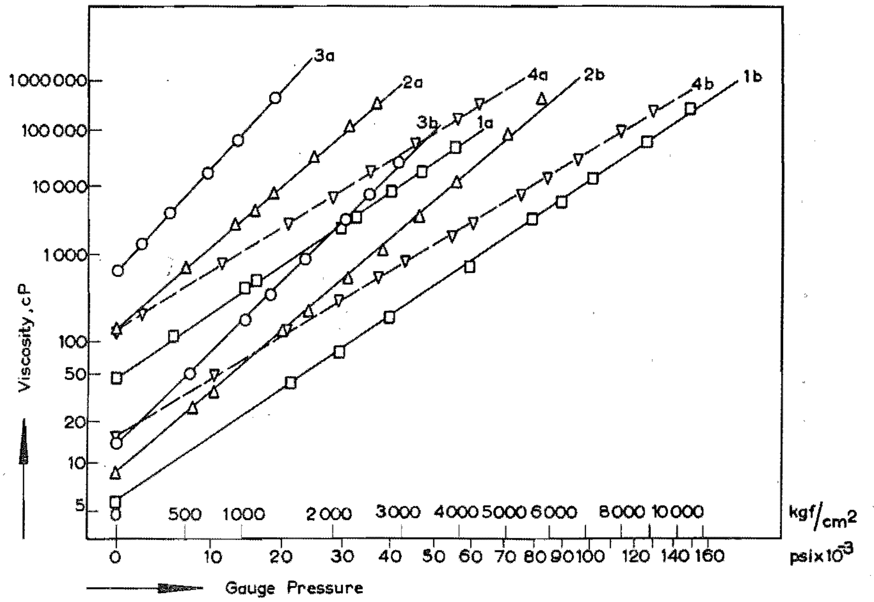

FIG. IV-2.
The Applicability of the New Viscosity-Pressure Chart to Divergent Types of Mineral Oils.
For designations see Table IV-2.

prises six liquids, namely five lower alcohols and liquid mercury, whose viscosity-pressure data have been determined by Bridgman[7,8] in the scope of his classical high-pressure investigations. Various isotherms depicted in Fig. IV-3 extend again up to extremely high pressures.

Fig. IV-4 depicts viscosity-pressure isotherms, up to about 5,000 kgf/cm^2 (71,000 psi), of eight miscellaneous liquids mainly taken again from the aforementioned investigations.

In Fig. IV-5 viscosity-pressure data, up to about 3,500 kgf/cm^2 (50,000 psi), have been plotted for six divergent kinds of pure hydrocarbons. The data on five of these compounds derive from the important investigations carried out by Schiessler *et al.* in the scope of API Research Project 42[11,12].

Finally, Fig. IV-6 comprises a motley of ten liquids, their viscosity data covering pressures up to about 2,000 kgf/cm^2 (28,000 psi).

The 38 liquids included in Figs. IV-2 through IV-6 represent a great variety of chemical constitutions, whilst their 42 isotherms depicted are fully representative of the various possible types of isotherms indicated in Section IV. 1.

Most of these isotherms correspond to log η-p curves that are more or less concave downward, notably in the lower pressure range. Further, several isotherms have been included which are represented in a log η-p chart either by straight lines (for instance, isotherm No. 2a in Fig. IV-2 and isotherm No. 1 in Fig. IV-6) or by convex

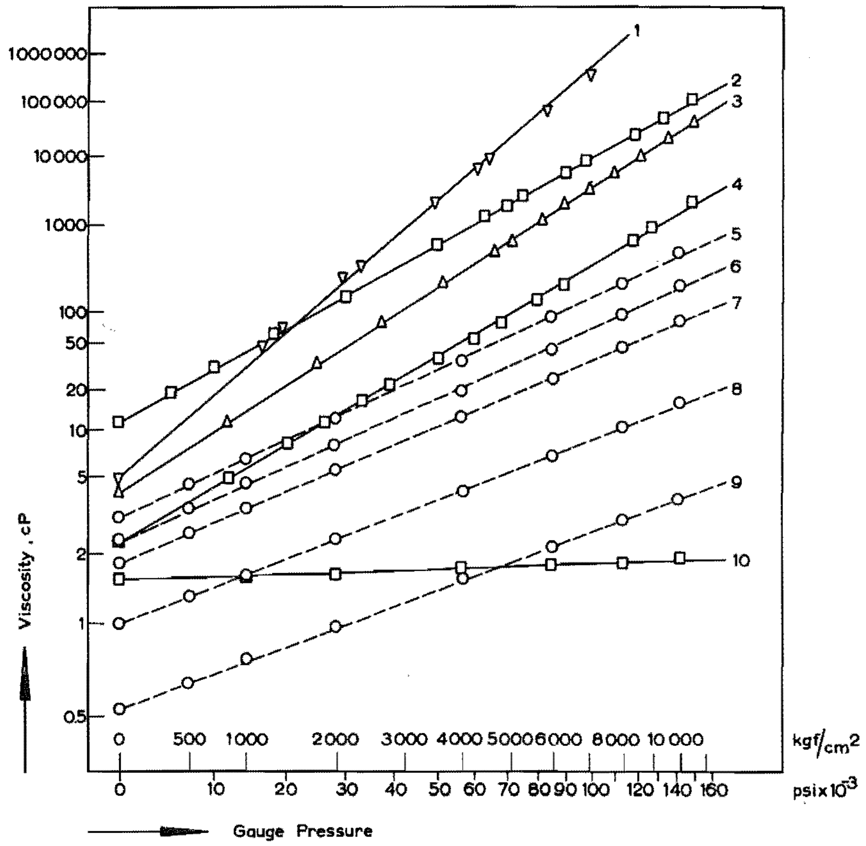

FIG. IV-3.
The Applicability of the New Viscosity-Pressure Chart to Synthetic Lubricating Oils and Miscellaneous Liquids.
For designations see Table IV-2.

downward curves (for instance, isotherm No. 3a in Fig. IV-2 and isotherms Nos. 5 and 7 in Fig. IV-6). Finally, it should be mentioned that even a few isotherms displaying the above-indicated transition in a log η-p chart have been depicted in Figs. IV-2 through IV-6, that is up to pressures markedly above their transition region.

In view of the great variety of viscosity-pressure isotherms comprised by Figs. IV-2 through IV-6 and the quite extensive pressure ranges covered, the validity of the basic Equation (IV-5e) has been put to a really severe test. The straight lines in these figures obviously fit the experimental data*) for all the various kinds of liquids remarkably well.

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*) The plotted viscosity data relate to rates of shear low enough to warrant Newtonian behaviour.

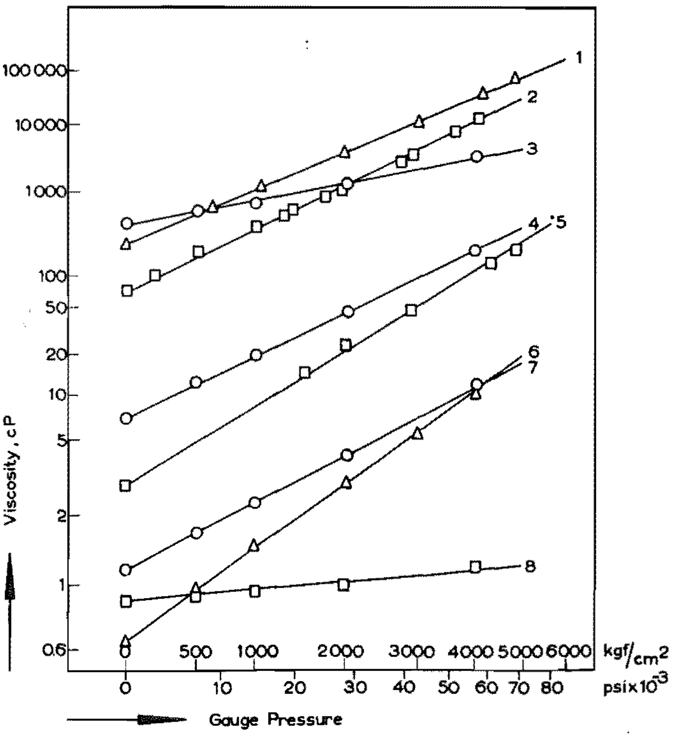

FIG. IV-4.
The Applicability of the New Viscosity-Pressure Chart to Miscellaneous Liquids.
For designations see Table IV-2.

In addition, Equation (IV-5e) has been verified for numerous other liquids, not depicted here, of still other, and very divergent types. These include many pure compounds as well as rather complex mixtures.

The new viscosity-pressure Equation (IV-5e) has proved to apply quite satisfactorily to the numerous liquids investigated so far, and in a very wide pressure range at that. The extent of this applicability range depends, of course, on the particular liquid or, more explicitly, on the type of its isotherms. It stands to reason that a definite limit is set to the applicability range of the present, and any other, viscosity-pressure equation by the pressure where the liquid starts to solidify.

Consequently, the present equation permits satisfactorily describing not only concave downward and straight, but also convex downward log η-p isotherms. Although it obviously cannot hold equally good at pressures so high as to give rise to a transition in the log η-p isotherms considered, yet it has appeared to apply fairly well even at pressures markedly above their transition range.

Usually, the new viscosity-pressure Equation (IV-5e) may be con-

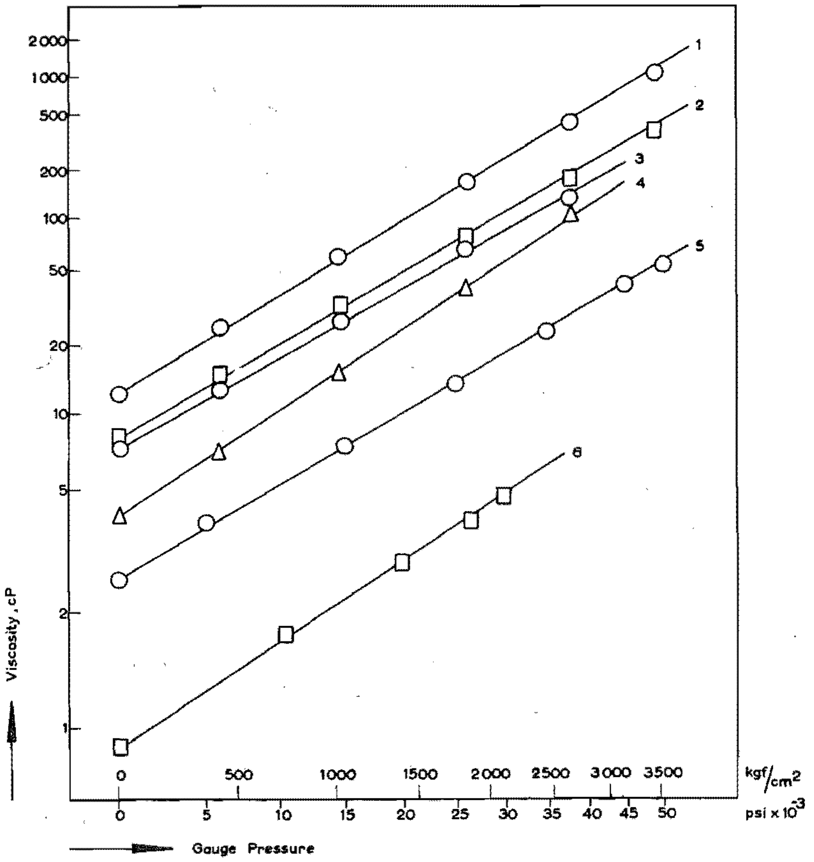

FIG. IV-5.
The Applicability of the New Viscosity-Pressure Chart to Divergent Kinds of Pure Hydrocarbons.
For designations see Table IV-2.

sidered to apply satisfactorily up to pressures of at least 3,000-5,000 kgf/cm^2 (43,000-71,000 psi). Only outside this applicability range will the deviations of the experimental points from the straight lines in Figs. IV-2 through IV-6 result in errors considerably beyond the normal viscometric accuracy. Although as yet the number of reliable viscosity-pressure data measured over a wide *temperature* range is comparatively small, it may be stated that the temperature range where the present Equation (IV-5e) holds good would generally amount to at least about 200°C (360°F).

Summarizing, the present viscosity-pressure Equation (IV-5e) may generally be considered to apply satisfactorily in the same very wide ranges of temperature and pressure where the analogous viscosity-temperature Equation (III-6h) is applicable, that is in a temperature range of at least 200°C (360°F) and up to pressures of at *least 3,000-5,000 kgf/cm² (43,000-71,000 psi).*

In particular, the applicability of the present viscosity-pressure equation to all the various kinds of mineral oils tested may be deemed quite satisfactory.

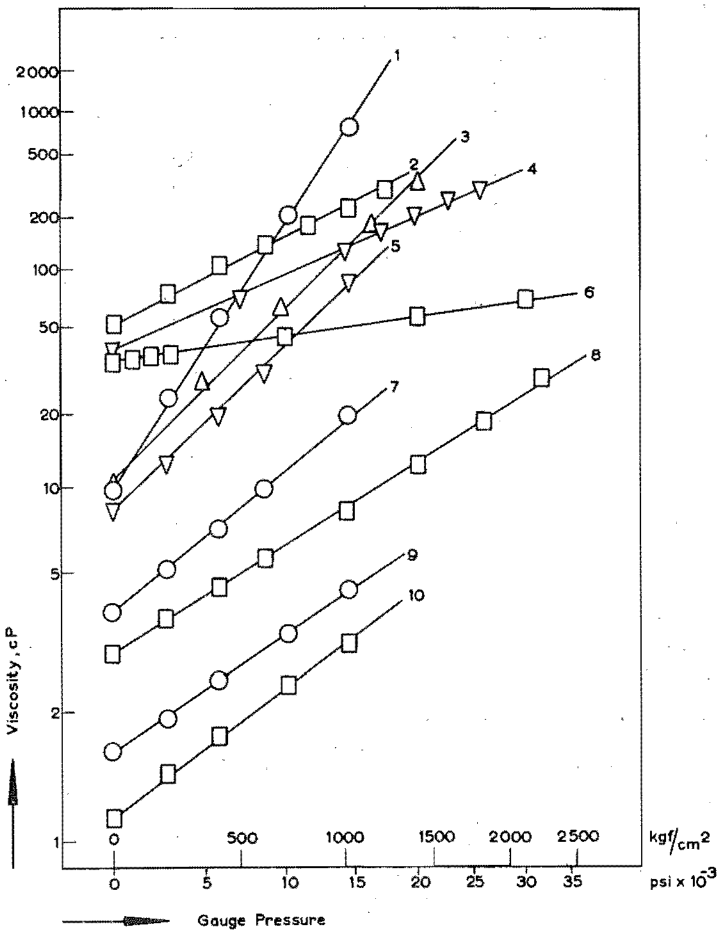

FIG. IV-6.
The Applicability of the New Viscosity-Pressure Chart to Miscellaneous Liquids.
For designations see Table IV-2.

It should be noted that for several liquids included in Figs. IV-2 through IV-6 the deviations from the depicted straight-line relationships are of a rather systematic nature. This implies that most of these deviations could almost entirely be eliminated through a slight alteration of one or both constants, 1.200 and/or 2,000, in the basic Equation (IV-5b).

But in view of the rather unusual width of the pressure range

TABLE IV-2

Designations to the Oils Depicted in Figs.IV-2/IV-6

No.	Type of Liquid	Experimenters' Designation	Temp., deg C	Slope Z	Ref.
	Natural and Polymer-Blended Mineral Oils, Fig.IV-2				
1	Natural Mineral Oil	Paraffinic Oil, coded 31-G; Oil A-3 of Table II-1	1a: 37.8 1b: 98.9	0.67 0.67	27
2	ditto	Naphthenic Oil, coded 37-G; Oil A-11 of Table II-1	2a: 37.8 2b: 98.9	0.85 0.84	27
3	"	Aromatic Extract, coded 52-G; Oil A-16 of Table II-1	3a: 37.8 3b: 98.9	1.05 0.96	27
4	Polymer-Blended Mineral Oil	Oil No.1 Blended With "Paratone"; Blend coded 44-G	4a: 37.8 4b: 98.9	0.61 0.60	27
	Synthetic Lubricating Oils and Other Liquids, Fig.IV-3				
1	Polybutene	Commercial Sample, coded 46-G	98.9	0.86	27
2	Diester	Di(2-ethylhexyl)sebacate, coded 1-A	37.8	0.55	27
3	ditto	o-Di(2-ethylhexyl)phthalate, coded 56-H	98.9	0.65	27
4	Polyglycol	Commercial Polypropylene Glycol Derivative, coded 21-D	98.9	0.58	27
5	n-Amyl Alcohol	Pure Compound	30	0.46	7,8
6	n-Butyl Alcohol	ditto	30	0.45	7,8
7	n-Propyl Alcohol	"	30	0.42	7,8
8	Ethyl Alcohol	"	30	0.38	7,8
9	Methyl Alcohol	"	30	0.37	7,8
10	Mercury	"	30	0.03	8
	Miscellaneous Liquids, Fig.IV-4				
1	Castor Oil	Commercial Sample ("Gilmore")	40	0.43	111,26
2	Silicone Oil	Commercial Linear Polymethyl-siloxane, coded 55-H	37.8	0.50	27
3	Glycerol	Pure Compound	30	0.19	7,8
4	Oleic Acid	ditto	75	0.49	7,8
5	Pure Hydrocarbon	1-Cyclopentyl-4(3-cyclopentyl-propyl)dodecane, coded 10-C	98.9	0.63	27
6	ditto	n-Decane	30	0.73	112,37
7	Aniline	Pure Compound	75	0.53	7,8
8	Water	ditto	30	0.09	7,8

CONTINUATION OF TABLE IV-2

No.	Type of Liquid	Experimenters' Designation	Temp., deg C	Slope Z	Ref.
		Pure Hydrocarbons, Fig.IV-5			
1	Pure Hydrocarbon	9(2-Cyclohexylethyl)heptadecane, coded PSU 88	37.8	0.63	12
2	ditto	9(2-Phenylethyl)heptadecane, coded PSU 87	37.8	0.60	12
3	"	9-n-Octylheptadecane, coded PSU 25	37.8	0.58	12
4	"	1,1-Diphenylheptane, coded PSU 503	60	0.68	12
5	"	1-Phenyl-3(2-phenylethyl)hendecane, coded PSU 18	98.9	0.60	11
6	"	n-Hexadecane, coded 11-C	98.9	0.68	27
		Miscellaneous Liquids, Fig.IV-6			
1	Fluorocarbon	Commercial Sample of a Fully Fluorinated Mineral Oil ("Perfluorolube")	120	1.54	48
2	Silicone Oil	Commercial Linear Polymethylsiloxane, coded DC 200	60	0.51	48
3	Chlorofluorocarbon	Commercial Monochlorotrifluoroethylene Polymer, coded "Fluorolube-Standard", 54-H	98.9	0.99	27
4	Rapeseed Oil	Typical Sample	40	0.43	113
5	Pure Hydrocarbon	1,2,3,4,5,6,7,8,13,14,15,16-Dodecahydrochrysene, coded PSU 574	98.9	0.94	12
6	Water-Glycol Fluid	Commercial Sample of a Water-Glycol Type Hydraulic Fluid, coded "Ucon M-1"	37.8	0.14	114a
7	Pure Hydrocarbon	Perhydrochrysene, coded PSU 575	98.9	0.80	12
8	ditto	1,1-Diphenylethane	37.8	0.62	12
9	"	cis-Decalin	60	0.66	48
10	"	trans-Decalin	60	0.74	48

covered for these liquids - in several cases considerably wider than the aforementioned range of 3,000-5,000 kgf/cm^2 - it is not deemed really necessary to carry out such an alteration. In fact, with a less wide pressure range - for instance up to about 1,000-2,000 kgf/cm^2 (14,000-28,000 psi) - which still suffices for many cases, the present values of the constants, 1.200 and 2,000, in Equation (IV-5b) will not result in any deviations markedly beyond the normal viscometric accuracy of 2-3%.

Above all, however, any adaptation of the present two constants to any liquid or, rather, any class of liquids specifically would make the resulting equation less accurate for many other types of liquids, so that it would not be as widely applicable as the present Equation (IV-5b).

IV.3.2. *The Relationship Between the Family of Isotherms Characterizing a Given Liquid*

Just as the aforementioned *isobars* (see § III.2.2, part B) the isotherms of a given liquid as represented by straight lines in the basic viscosity-pressure chart according to Equation (IV-5e) have proved to converge - again to a good approximation - towards a common point. Accordingly, this family of isotherms characterizing a given liquid also constitutes a *fan*.

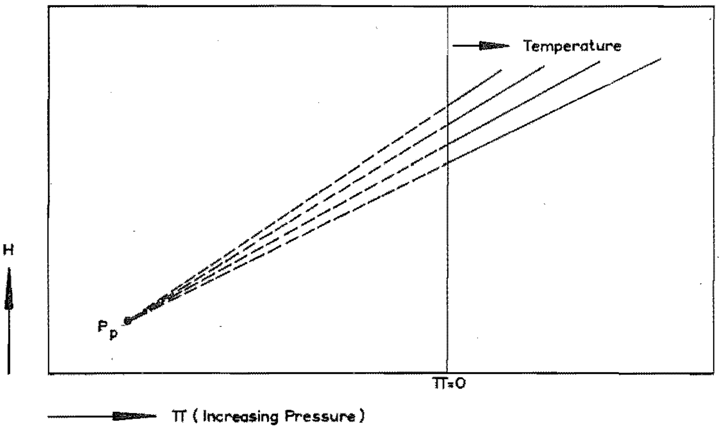

FIG. IV-7.
Schematic Representation of Converging Isotherms.

This convergence of isotherms has been illustrated for an arbitrary liquid in the schematic Fig. IV-7. The point of convergence, denoted by P_p, is termed the *"viscosity-pressure pole"*. It has a pressure coordinate Π_P which is strongly negative, corresponding to a pole pressure p_p of the order of -2,000 kgf/cm^2. The viscosity coordinate H_P corresponds to a very low pole viscosity, η_P, roughly of the order of 0.1 cP. Remarkably enough, for any given liquid this pressure-pole viscosity η_P shows the same value as its *tem-*

perature-pole viscosity, that is the viscosity coordinate of the viscosity-temperature pole (see § III. 2. 2, part B).

For other liquids the viscosity-pressure pole may be located in the opposite region of the H-Π chart, that is the region of extremely high viscosities and pressures. In the third case the family of isotherms characterizing a given liquid may be represented in the basic viscosity-pressure chart by a family of parallel straight lines, so that they constitute a *sheaf*. Such a sheaf may mathematically be considered to represent a "degenerated" convergence of the isotherms, the viscosity-pressure pole being located at infinity, that is at infinite values of the viscosity function H and the pressure function Π*).

In each of these three distinct cases of convergence the viscosity-pressure pole - like the corresponding viscosity-temperature pole - is located far beyond the ranges of viscosity and pressure that are of practical significance. As will be shown hereafter, the value of the delineated pressure-pole concept lies primarily in its mathematical convenience, namely for casting the underlying relationships into a really simple analytical form.

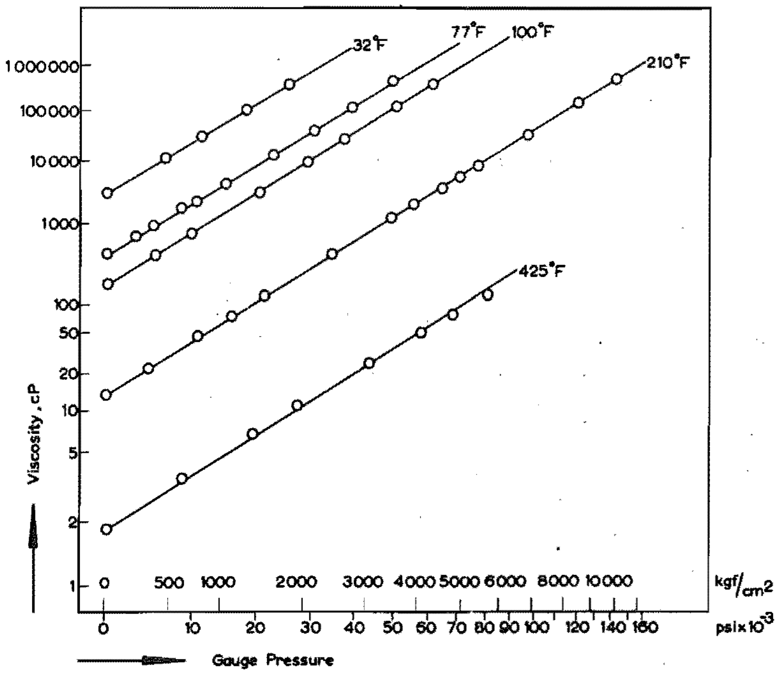

FIG. IV-8.
Convergence of Isotherms for a Paraffinic Mineral Oil.

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*) The corresponding pole viscosity and pressure may be taken to amount either to $\eta_p = \eta_\infty$ and $p_p = -2,000$ kgf/cm^2, or to $\eta_p = \infty$ and $p_p = \infty$.

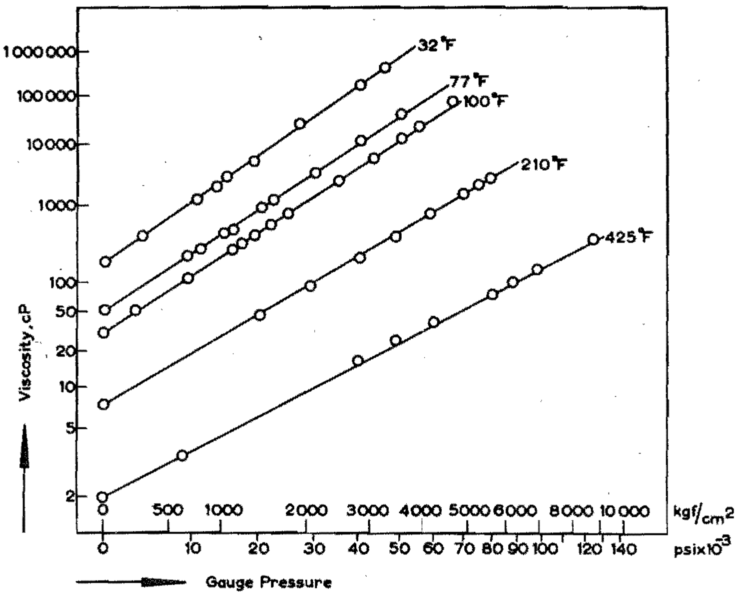

FIG. IV-9.
Convergence of Isotherms for a Polymer-Blended Mineral Oil.

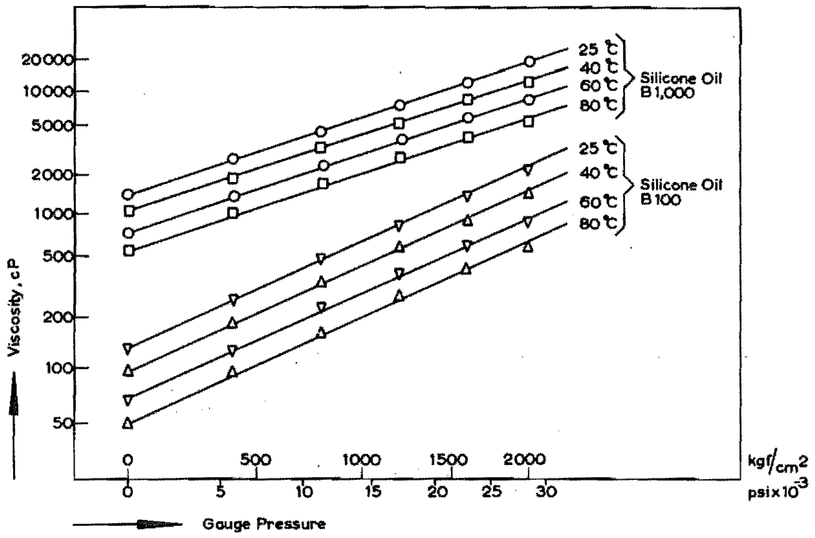

FIG. IV-10.
Convergence of Isotherms for Two Linear Polymethylsiloxanes.

Concrete examples of converging isotherms are provided by Figs. IV-8 through IV-10; for practical reasons the points of convergence could not be indicated in these figures.

Fig. IV-8 depicts the various experimentally determined viscosity-pressure isotherms for the paraffinic mineral oil (coded A-4 in Table II-1) whose family of isobars has been plotted in the preceding Fig. III-8. The family of isotherms depicted in Fig. IV-8 covers the very wide temperature range from 0 to 218.3°C (32-425°F) and extends up to pressures of over 5,000 $\mathrm{kgf/cm^2}$ (71,000 psi). This fan-shaped family of isotherms has a viscosity-pressure pole in the region of extremely high viscosities and pressures. Accordingly, in the pressure range covered by Fig. IV-8 these isotherms are very nearly parallel.

Fig. IV-9 shows a fan of isotherms, covering a similar temperature and pressure range as that in the preceding figure, for a polymer-blended mineral oil[*] coded 27-E in the ASME pressure-viscosity project[27]. The viscosity-pressure pole of this oil is located in the region of very low viscosities and strongly negative pressures, like that indicated in the schematic Fig. IV-7.

Finally, the isotherms of two linear polymethylsiloxanes of widely different viscosity grades have been depicted in Fig. IV-10. The plotted viscosity data[**] on these two silicone oils, coded B 100 and B 1,000, have been determined by Kuss[17]. Over the temperature and pressure ranges covered, that is from 25 to 80°C (77-176°F) and up to 2,000 $\mathrm{kgf/cm^2}$ (28,000 psi), the isotherms of either oil are substantially parallel.

IV.3.3. *A Complete Viscosity-Pressure Equation*

From the outlined convergence of the family of isotherms characterizing a given liquid (see Fig. IV-7) a simple viscosity-pressure equation can readily be derived that may be termed *"complete"* in that it implicitly indicates the effect of *temperature* on the pressure variation of viscosity by means of only *one* temperature-dependent quantity, H_0 (or η_0):

$$\frac{H-H_0}{H_P-H_0} = \frac{\Pi}{\Pi_P} . \qquad \text{(IV-7a)}$$

In the limiting case where the family of isotherms has degenerated into a *sheaf*, Equation (IV-7a) reduces to:

$$H - H_0 = Z_r \Pi , \qquad \text{(IV-7b)}$$

where the Viscosity-Pressure Index Z_r, which can be determined at some arbitrary standard reference temperature, shows one common value for the entire family of isotherms characterizing a given liquid.

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[*] This oil has been specified in Table X-5.

[**] The author is much indebted to Prof. E. Kuss, at the Institut für Erdölforschung in Hannover, for generously placing the complete sets of experimental data at his disposal.

Equation (IV-7a), or (IV-7b), in contrast to the basic Equation (IV-5e), does describe the temperature effect implicitly by only one quantity, that is the atmospheric viscosity function H_0 or simply the atmospheric viscosity η_0. Therefore, as long as Equation (IV-7a) holds good, the viscosity-pressure dependence at any specified value of η_0, and thus at any specified temperature, is completely characterized solely by the two pole coordinates, H_P and Π_P. In the limiting case where Equation (IV-7b) applies satisfactorily, the viscosity-pressure dependence at any given temperature is sufficiently defined by one single parameter, namely the temperature-independent Viscosity-Pressure Index Z_r.

But Equation (IV-7a) is not yet complete as a viscosity-*temperature*-pressure relationship, which will be derived in Chapter V.

IV.4. DISCUSSION

IV.4.1. *The New Viscosity-Pressure Equation in Comparison With Previous Equations*

As compared with previously established equations for satisfactorily describing the isothermal viscosity-pressure relationship of liquids over a wide pressure range (see Section IV.2), the new Equation (IV-5e) has the *unique* feature that it contains only one single parameter, Z, this naturally being the *minimum* number of parameters required for fully characterizing the viscosity-pressure dependence of liquids. Likewise, the rectifying viscosity-pressure chart constructed in accordance with the new equation would seem to constitute the only such chart developed so far.

Notwithstanding the use of one single parameter in the present viscosity-pressure equation, its overall correlational accuracy would appear to be at least on a par with that achieved by the best two-parameter equations available (see Section IV.2). Above all, however, the present equation has the basic advantage over existing equations that it combines an almost unsurpassable simplicity with an almost universal applicability.

Further, the new viscosity-pressure equation has proved to lend itself particularly well as a basis to a simple and convenient method for *classifying*, according to their pressure dependence of viscosity, all the various kinds of oils encountered in current lubrication practice. In fact, the relevant classification is achieved solely by means of the Viscosity-Pressure Index Z. The latter criterion has the additional advantage that it may be taken constant in a fairly wide temperature range. These things will be elucidated in Chapter VII.

Last but not least, as already indicated, the present viscosity-pressure Equation (IV-5e) displays a close similarity to the newly developed viscosity-temperature Equation (III-6h). As will be shown in subsequent parts of this thesis, the latter similarity is very convenient for establishing several attractive interrelationships between the temperature and pressure dependence of the viscosity of a given liquid and for formulating its complete viscosity-temperature-pressure equation. Moreover, this similarity will prove very helpful in devising suitable *correlations* for predicting the viscosity-pressure relationship of interrelated liquids (for example mineral oils) from their atmospheric viscosity-temperature relationship.

IV. 4. 2. *Further Discussion of the Viscosity-Pressure Pole Concept*

Recently, Roelands *et al.* 44) demonstrated that, in a suitable viscosity-pressure diagram, the family of isotherms characterizing any given liquid can be depicted, in a very wide temperature range and up to very high pressures, as a fan (compare § IV. 3. 2). Further, in the "Authors' Closure" to their paper these investigators stated that the described convergence of isotherms is not at all a unique feature of the particular viscosity-pressure equation employed in that paper, that is Equation (IV-3). Indeed, the occurrence of such a convergence does not depend on the particular expressions used for defining the rectifying viscosity and pressure scales, provided only that such expressions are sufficiently accurate.

Accordingly, the involved viscosity-pressure pole concept may be claimed to have general significance, irrespective of the mathematical framework used for representing the viscosity-pressure relationship.

It would appear that Roelands *et al.* 44) were the first to state explicitly the existence of a viscosity-pressure pole for any given liquid. It should be mentioned, however, that previous investigators had suggested more or less related regularities between the isotherms of a given liquid 115,116,84,28,117) . But, without entering into the details of the latter regularities, it can be stated that these represent only special cases of the viscosity-pressure pole concept delineated by Roelands *et al.*. In fact, it is found that these regularities lead up to the existence of a viscosity-pressure pole for a given liquid only in the special case where its isotherms are rectified - in a very wide temperature range and up to very high pressures - by plotting viscosity on a logarithmic 84,28,117) or some closely related 115,116) scale against pressure on a linear scale.

As a matter of fact, the foregoing *generalized* viscosity-pressure pole concept involves another approximation, although, generally, a very good one. Consequently, the applicability of the present viscosity-pressure Equation (IV-7a), accounting for the implied convergence of isotherms, should be confined to a somewhat smaller temperature and pressure range in order to retain fully the correlational accuracy inherent in the basic viscosity-pressure Equation (IV-5e).

IV. 4. 3. *Concluding Remarks*

In conclusion it may be useful to devote a few remarks to the limits set to the validity of viscosity-pressure equations in general and of the proposed equation in particular. As these remarks are similar to those made in part C of § III. 1. 4 on the applicability of viscosity-temperature equations, they will be very concise.

a. Empirical viscosity-pressure equations should be considered and utilized primarily as *interpolating* equations. Consequently, in order to obtain good conformance to the present Equation (IV-5e) over a wide pressure range, more than one high-pressure viscosity value should preferably be known. Further, safe extrapolations may normally be performed only over very moderate pressure ranges.

b. Empirical viscosity-pressure equations may no longer be deemed fully significant at pressures so high as to give rise to certain physical phenomena, such as partial solidification or structure formation, which seriously affect the viscosity of the liquid concerned, either in a reversible or irreversible manner.

c. Referring to the relevant remarks on the accuracy of viscosity-temperature equations, it should finally be emphasized not to exaggerate the accuracy to be embodied into viscosity-pressure equations designed primarily for practical applications.

IV. 5. A TENTATIVE STATISTICAL-PHYSICAL BASIS FOR THE NEWLY DEVELOPED VISCOSITY-PRESSURE EQUATION

Starting from the Cohen-Turnbull free-volume model of the liquid state and applying Weibull's function for describing the statistical distribution of the free volumes of the individual molecules of a given liquid, a tentative viscosity-*temperature* expression essentially identical to the empirically established Equation (III-10a) has been achieved in Section III. 3.

It will be shown in the present section that the same statistical-physical basis may be employed for deriving a viscosity-*pressure* expression which may be regarded as a generalized version of the empirically developed Equation (IV-5a).

As delineated in Section III. 3, the following expression would hold at any fixed temperature and pressure:

$$\ln \frac{\eta}{\eta_e} = \left[\frac{v_f^*}{v_f} \Gamma\left(1+\frac{1}{n}\right)\right]^n . \qquad \text{(III-15)}$$

This expression can be transformed into an explicit viscosity-*pressure* equation by appropriately accounting for the effect of pressure - at constant temperature - on the three parameters occurring on its right-hand side.

Of these parameters the exponent n constitutes a characteristic constant for any given liquid and is essentially independent of pressure (and temperature). The second parameter, the minimum required specific free volume, v_f^*, is governed by the configuration and the flexibility of the liquid's molecules. For simple liquids the free volume v_f^* may be expected to be almost independent of pressure. However, for more complex liquids, especially those with associated or long-chain molecules, it may decrease somewhat with rising pressure[91,92].

At any rate, the effect of pressure on viscosity as comprised by Equation (III-15) will predominantly be determined by its effect on the specific free volume, v_f. To a first approximation, the latter effect can generally be described by a simple linear relationship, although this may be less accurate for more complex liquids.

For assessing the effect of pressure on the ratio v_f^*/v_f in Equation (III-15) the following expression, analogous to the corresponding temperature Expression (III-16), can reasonably be resorted to:

$$\frac{v_f^*}{v_f} = \left(\frac{v_f^*}{v_f}\right)_0 \left(1 + \frac{p}{p_0}\right)^w, \qquad \text{(IV-8)}$$

where the subscript "0" relates again to atmospheric pressure and the exponent w represents a parameter characteristic of the liquid considered, usually assuming values between, say, 0.3 and 1.0. Further, the negative value of the parameter p_0 denotes the pressure where the specific free volume, v_f, of the *liquid* would become infinitely high; to a first approximation, the pressure p_0 might be identified with the *internal* pressure of the liquid concerned.

Combination of Equations (III-15) and (IV-8) readily yields the following expression for explicitly describing the effect of pressure, at any constant temperature, on the viscosity of a given liquid:

$$\ln\frac{\eta}{\eta_e} = \left(\ln\frac{\eta_0}{\eta_e}\right)\left(1 + \frac{p}{p_0}\right)^{wn}. \qquad \text{(IV-9)}$$

Since the exponential product wn is essentially independent of pressure, this equation explicitly defines the effect of pressure, at any constant temperature, on the "reduced" viscosity η/η_e of an arbitrary liquid - with known atmospheric viscosity, η_0 - by means of only *two* parameters.

For comparing the above-derived Equation (IV-9) with the empirically developed Equation (IV-5a) the latter is conveniently rewritten in the form:

$$\ln\frac{\eta}{\eta_\infty} = \left(\ln\frac{\eta_0}{\eta_\infty}\right)\left(1 + \frac{p}{2,000}\right)^Z. \qquad \text{(IV-5a')}$$

It is then readily seen that both equations become identical when the fictitious viscosity η_e and the limiting pressure p_0 are replaced by the fixed constants η_∞ (= 0.0631 cP) and 2,000 kgf/cm^2, respectively. As pointed out in the preceding sections of this chapter, experimental verification has proved that the latter constants, η_∞ and 2,000 kgf/cm^2, may invariably be employed as approximative values for all the various kinds of liquids investigated so far.

Conversely, it may be claimed that the new viscosity-pressure Equation (IV-5a), which was originally derived along purely *empirical lines, can also be obtained on the basis of the foregoing statistical-physical considerations taking the free-volume concept of the liquid state as a starting-point.*

Finally, comparison of Equations (IV-9) and (IV-5a') also yields the result that the Viscosity-Pressure Index, Z, may be approximately identified with the exponential product wn. Further, it has been indicated in § III. 3. 2 that the shape parameter n in Weibull's function for describing the statistical distribution of free volume amongst the numerous molecules of a given liquid would be nearly equal to its Slope Index, S.

These findings lead to the very interesting result that the newly introduced parameter w would approximately represent the ratio of the Viscosity-Pressure Index, Z, to the Slope Index, S, of the liquid under consideration.

CHAPTER V

THE COMPLETE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP FOR A GIVEN LIQUID

V.1. CORRELATION BETWEEN THE CONVERGENCES OF ISOBARS AND ISOTHERMS

A strikingly close connection appears to exist between the convergences of isobars and isotherms as described in the preceding Chapters III (§ III.2.2, part B) and IV (§ IV.3.2), respectively. In fact, it can be shown mathematically that the convergence of the isobars of a given liquid involves the convergence of its isotherms, and *vice versa*. This point has been elaborated in Appendix V-1, at the end of this chapter.

Starting from the convergence of the isotherms of a given liquid and the equation of its atmospheric isobar, that is Equation (III-6h), it has been mathematically deduced in that appendix that all its isobars are represented by straight lines in one and the same H-Θ diagram. Moreover, it has been proved that these isobars converge towards a common point, the viscosity-temperature pole, which has the same viscosity coordinate, η_P, as the viscosity-pressure pole. Thus, the remarkable fact, already indicated in § IV.3.2, that the viscosities of the two viscosity poles possess the same value is found to be also a mathematical consequence of either convergence.

In an analogous way, but by reasoning in an inverse manner, the convergence of isotherms can be deduced from that of the corresponding isobars.

The present discussion of the correlation between the convergences of isobars and isotherms has been based on newly developed empirical formulas for viscosity as a function of temperature and pressure.

It should be emphasized, however, that the relevant statements remain equally valid if other adequate mathematical expressions are employed for the isobaric viscosity-temperature relationship and the isothermal viscosity-pressure relationship, provided only that the same viscosity function is utilized for representing either relationship.

V.2. MATHEMATICAL DESCRIPTION OF THE COMPLETE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP FOR A GIVEN LIQUID

V.2.1. *The Present Viscosity-Temperature-Pressure Equation*

On the basis of the described convergence of both the family of isobars and of isotherms characterizing a given liquid, the following comparatively simple formula for the complete viscosity-temperature-pressure relationship of any of the liquids under consideration can readily be derived:

$$H = S_0\Theta + C\Theta\Pi + D\Pi + \log G_0, \qquad \text{(V-1a)}$$

where the characteristic parameters C and D are defined in terms solely of the two atmospheric quantities, G_0 and S_0, and the coordinates of the viscosity-pressure pole, H_P and Π_P, as follows:

$$C = -\frac{S_0}{\Pi_P} \qquad \text{(V-2)}$$

and

$$D = \frac{H_P - \log G_0}{\Pi_P}. \qquad \text{(V-3)}$$

According to Equation (V-1a), *four* parameters, G_0, S_0, C and D, suffice for describing H as a function of Θ and Π or also, indirectly, for describing dynamic viscosity η, in cP, as a function of temperature t, in deg C, and (gauge) pressure p, in kgf/cm^2. For the latter purpose Equation (V-1a) can be rewritten as:

$$\log(\log\eta + 1.200) = -S_0 \log\left(1 + \frac{t}{135}\right) + \\ + \left[-C\cdot\log\left(1 + \frac{t}{135}\right) + D\right]\log\left(1 + \frac{p}{2,000}\right) + \log G_0 \qquad \text{(V-1b)}$$

or, in delogarithmized form:

$$\log\eta + 1.200 = G_0 \frac{\left(1 + \frac{p}{2,000}\right)^{-C\cdot\log\left(1 + \frac{t}{135}\right) + D}}{\left(1 + \frac{t}{135}\right)^{S_0}} \qquad \text{(V-1c)}$$

It should be emphasized that over a very wide temperature range and up to very high pressures the four parameters characterizing, according to Equation (V-1a), or (V-1b) or (V-1c), the complete viscosity-temperature-pressure relationship of any given liquid, are essentially constant.

For practical purposes it will normally be preferred to introduce the viscosity *grade*, $\eta_{0,r}$ - defined as the viscosity at atmospheric pressure (p=0) and at some arbitrary standard reference temperature (t_r) - into the latter equations for the complete viscosity-temperature-pressure relationship of a given liquid. Substitution of the corresponding viscosity function $H_{0,r}$, relating to Π=0 and $\Theta = \Theta_r$, into Equation (V-1a) yields:

$$H - H_{0,r} = S_0(\Theta - \Theta_r) + C\Theta\Pi + D \qquad \text{(V-4)}$$

According to Equation (V-4), only *three* parameters, namely S_0, C and D, are required for fully characterizing the effect of both temperature and pressure on the viscosity grade of a given liquid.

V.2.2. *Correlation Between the Families of Isobars, Isotherms and Isoviscids Characterizing a Given Liquid*

According to the basic Equation (V-1a), the complete equation for the family of *isobars* characterizing a given liquid may be written as:

$$H = S\Theta + D\Pi + \log G_0, \qquad \text{(V-1d)}$$

where the pressure variation of the non-atmospheric Slope Index S is defined by:

$$S = S_0 + C\Pi \qquad \text{(V-5a)}$$

or, more explicitly, by:

$$S = S_0 + C \cdot \log\left(1 + \frac{p}{2,000}\right). \qquad \text{(V-5b)}$$

Similarly, the complete equation for the family of isotherms characterizing a given liquid may be written as:

$$H = Z\Pi + S_0\Theta + \log G_0, \qquad \text{(V-1e)}$$

where the temperature variation of the viscosity-pressure criterion Z is defined by:

$$Z = D + C\Theta \qquad \text{(V-6a)}$$

or, more explicitly, by:

$$Z = Z_{0^\circ C} - C \cdot \log\left(1 + \frac{t}{135}\right). \qquad \text{(V-6b)}$$

Obviously, the parameter C, defined by Equation (V-2), is a highly significant quantity in that it determines not only the pressure variation of the viscosity-temperature criterion S, but also the temperature variation of the viscosity-pressure criterion Z. The very simple correlation between the involved variations of the criteria S and Z is easily shown to read:

$$\frac{\partial S}{\partial \Pi} = \frac{\partial Z}{\partial \Theta} = C. \qquad \text{(V-7)}$$

For any given liquid the parameter C assumes a characteristic value, which may be positive, zero or negative. Accordingly, three different cases can be distinguished with respect to Equation (V-7).

For C=0 ($\Pi_P = \pm\infty$), both S and Z show a constant value, namely $S=S_0$ and $Z=D(=Z_{0^\circ C})$; thus, both the isobars and the isotherms will constitute a *sheaf*. For positive values of C (Π_P negative), S increases with rising Π (rising pressure), and likewise Z increases with rising Θ (decreasing temperature)*). Finally, for negative values of C (Π_P positive), S decreases with rising Π (rising pressure), and likewise Z decreases with rising Θ (decreasing temperature).

For all the various liquids tested, however, this quantity C proved to be so small that both the pressure variation of the Slope Index, S, and the temperature variation of the Viscosity-Pressure Index, Z, are not very conspicuous. In fact, these variations normally appear to be negligible over fairly wide ranges of temperature and pressure.

"Isoviscids", or constant-viscosity curves, define the way in which temperature and pressure have to be simultaneously increased or decreased so as to keep the viscosity of a given liquid at some specified level.

Rewriting the basic viscosity-temperature-pressure Equation (V-1a) as:

$$\Theta = \frac{-D\Pi + (H - \log G_0)}{C\Pi + S_0}, \qquad \text{(V-1f)}$$

it is readily seen that at any constant value of the viscosity (represented by the function H) of a given liquid a hyperbolic relationship results between the temperature function Θ and the pressure function Π.

Further, for representing the family of isoviscids characterizing a given liquid it may be useful to introduce the three pole coordinates, H_P, Θ_P and Π_P, into Equation (V-1f). The relevant expression readily follows from Equation (V-12a) derived in the subsequent Section V.3:

$$\Theta - \Theta_P = -\frac{\Pi_P}{S_0} \cdot \frac{H-H_P}{\Pi-\Pi_P}. \qquad \text{(V-12b)}$$

Consequently, in a Θ-Π plot the family of isoviscids characterizing a given liquid is depicted by a family of equilateral hyperbolas with a common centre at $\Theta=\Theta_P$ and $\Pi=\Pi_P$; the two asymptotes are defined by the pole temperature and the pole pressure of the liquid considered, that is by $\Theta=\Theta_P$ and $\Pi=\Pi_P$, respectively.

Such a family of isoviscids is depicted, in accordance with Equation (V-12b), in the schematic Fig. V-1. This figure relates to the case where the *isobars* and *isotherms* of the liquid under consideration converge towards some very low viscosity (H_P), as indicated in the preceding Figs. III-7 and IV-7, respectively. It should be noted that there must be two limiting curves in the latter figure, namely one for solidification or solid separation, and the other

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*) This case has been illustrated in the schematic Figs. III-7 and IV-7, respectively.

where the liquid starts to volatilize or to decompose. Further, it may be remarked that the isoviscids extrapolated analytically to $H=H_P$ would degenerate into a pair of straight lines, namely the two asymptotes depicted in Fig. V-1.

The isoviscids plotted in Fig. V-1 for a liquid with a very low pole viscosity (H_p) are more or less concave downward. In the second case, where the isobars and isotherms of the liquid considered converge towards some extremely high viscosity (H_p), its isoviscids are represented in a Θ-Π figure by more or less convex downward curves. In either case, however, the two asymptotes are located so far beyond the physically significant temperature and pressure range that those parts of these isoviscids which assume practical importance generally tend to approximate to straight lines in such a Θ-Π figure. Moreover, these nearly straight lines are practically parallel so that, to a fair approximation, they constitute a *sheaf*. Exactly, such a sheaf of isoviscids would be obtained in the third possible case, namely where the isobars and isotherms of the liquid concerned converge at infinity, so that these isobars and isotherms also constitute a sheaf.

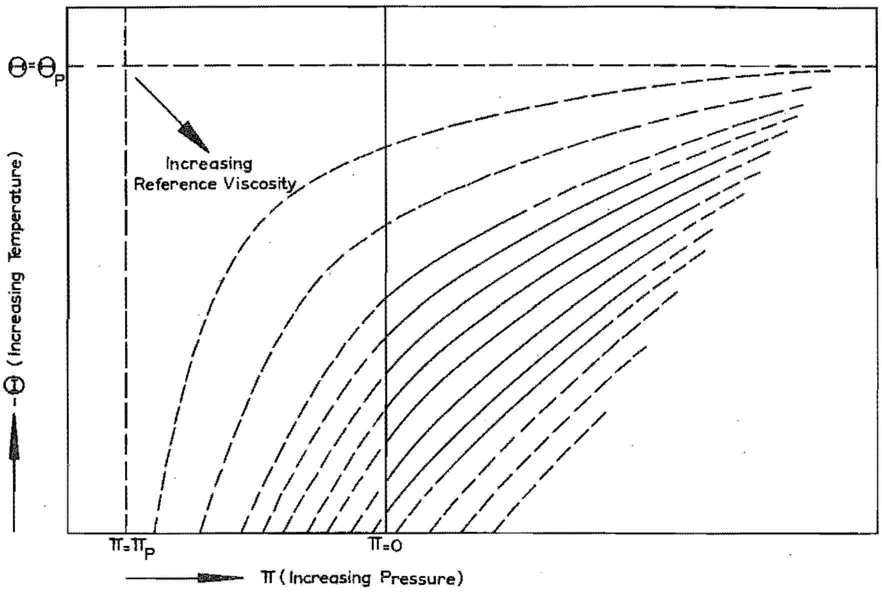

FIG. V-1.

Schematic Representation of Isoviscids According to Equation (V-12b).

Finally, a concrete example for illustrating the foregoing discussion is provided by Fig. V-2. This figure represents the family of isoviscids*), from 0 to 218.3°C (32-425°F) and up to pressures of over 5,000 kgf/cm^2 (71,000 psi), for the paraffinic mineral oil whose families of isobars and isotherms have been depicted in Figs.

*) The plotted data have been interpolated from the experimental isotherms.

III-8 and IV-8, respectively. Since these isobars and isotherms converge towards some extremely high viscosity, the isoviscids in the present Fig. V-2 should be more or less convex downward; but, indeed, the deviations from the depicted straight-line relationships prove to be very small.

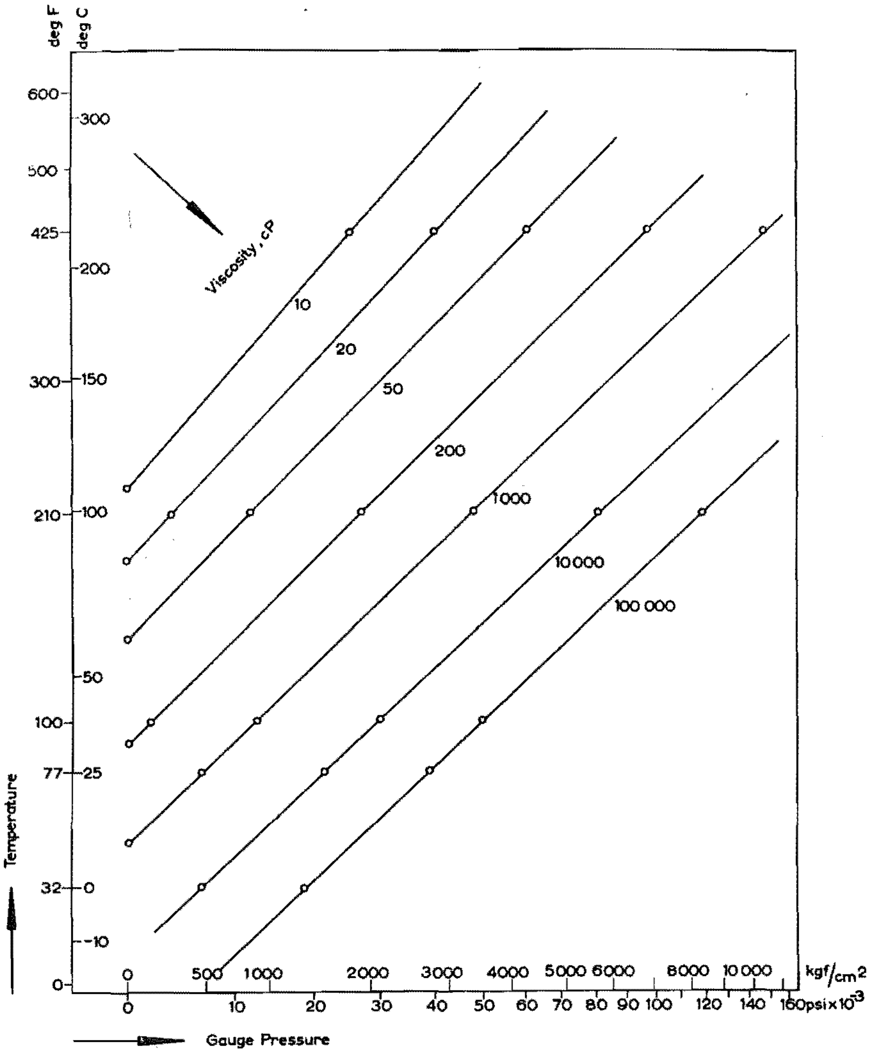

FIG. V-2.
The Family of Isoviscids for a Paraffinic Mineral Oil.

V.2.3. *A Simplified Viscosity-Temperature-Pressure Equation*

As indicated in the preceding § V.2.2, the pressure variation of the Slope Index, S, and likewise the temperature variation of the Viscosity-Pressure Index, Z, of a given liquid normally prove to be relatively small. In fact, over fairly wide ranges of temperature and pressure, extending generally from about 20 to 120°C (68-248°F) and up to pressures of about 2,000 kgf/cm² (28,000 psi), both indices may be taken constant without markedly affecting the correlational accuracy of the basic Equation (V-1a).

In the latter ranges it is practical to maintain for the Slope Index its atmospheric value, S_0, and for the Viscosity-Pressure Index its value, Z_r, determined at some arbitrary standard reference temperature t_r (for instance 40°C), corresponding to $\Theta = \Theta_r$. Thus, the following simplified equation:

$$H = S_0 \Theta + Z_r \Pi + \log G_0 \qquad \text{(V-8a)}$$

will generally apply fairly well in the aforementioned temperature and pressure ranges. In order to bring out the relationship between dynamic viscosity η, in cP, temperature t, in deg C, and pressure p, in kgf/cm², the latter equation may be rewritten as:

$$\log \eta + 1.200 = G_0 \frac{\left(1 + \frac{p}{2,000}\right)^{Z_r}}{\left(1 + \frac{t}{135}\right)^{S_0}} . \qquad \text{(V-8b)}$$

According to Equation (V-8a), or (V-8b), only *three* parameters, G_0, S_0 and Z_r, suffice for defining the complete viscosity-temperature-pressure relationship of a given liquid.

Further, the parameter $G_0 (= \log \eta_{0,0^\circ C} + 1.200)$ may again be ruled out in favour of the viscosity grade, $\eta_{0,r}$, or the corresponding viscosity function $H_{0,r}$. Thus, Equations (V-8a) and (V-8b), respectively, may readily be cast into the forms:

$$H - H_{0,r} = S_0 (\Theta - \Theta_r) + Z_r \Pi \qquad \text{(V-9a)}$$

and

$$\frac{\log \eta + 1.200}{\log \eta_{0,r} + 1.200} = \left(\frac{t_r + 135}{t + 135}\right)^{S_0} \left(1 + \frac{p}{2,000}\right)^{Z_r} . \qquad \text{(V-9b)}$$

Consequently, in the specified ranges of temperature and pressure only *two* parameters - being, of course, the *minimum* number conceivable at all -, namely the atmospheric Slope Index, S_0, and the Viscosity-Pressure Index Z_r, suffice for describing the effect of both temperature and pressure on the viscosity *grade* of a given liquid.

As long as the simplified viscosity-temperature-pressure Equation (V-8a) is valid, both the family of isobars and the family of isotherms characterizing a particular liquid are depicted by a sheaf, in an H-Θ and H-Π chart, respectively. In addition, its family of isoviscids, plotted in a Θ-Π chart, also constitutes a sheaf.

It would appear interesting to devote some further attention to this sheaf of isoviscids, which is represented by the expression:

$$-\Theta = \frac{Z_r}{S_0}\Pi - \frac{H-\log G_0}{S_0}. \qquad \text{(V-10)}$$

Accordingly, the common slope of a family of isoviscids obtained on plotting $-\Theta$ *versus* Π (see Fig. V-1) is equal to the ratio of the viscosity-pressure criterion Z_r to the viscosity-temperature criterion S_0.

In the particular case where it is desired to know the temperatures and pressures that have to be applied in order to retain the atmospheric viscosity $H_{0,r}$ (at some specified temperature Θ_r), these can be calculated from the simple equation:

$$-\Theta = \frac{Z_r}{S_0}\Pi - \Theta_r. \qquad \text{(V-11)}$$

V. 3. THE VISCOSITY-TEMPERATURE-PRESSURE SPACE MODEL FOR A GIVEN LIQUID

Now that the complete viscosity-temperature-pressure Equation (V-1a) has been discussed and the families of isobars, isotherms and isoviscids characterizing a given liquid have been depicted in two-dimensional figures, it has become fairly simple to construct the complete viscosity-temperature-pressure *space model.*

Using H, Θ and Π as rectangular coordinate axes, the complete viscosity-temperature-pressure relationship of a given liquid can be traced by a definite surface which in general is slightly curved. From the basic Equation (V-1a) this curved surface can be shown to constitute a *hyperbolic paraboloid* having two sets of straight generatrices. Fig. V-3 offers a schematic picture of the latter surface*).

It should be emphasized, however, that over fairly wide ranges of temperature and pressure this surface may be considered to have degenerated into a *plane.* In fact, such a plane will prove a good approximation of the actual viscosity-temperature-pressure surface as long as the simplified Equation (V-8a) applies satisfactorily, that is if the parameter C in the basic Equation (V-1a) approaches zero or, in other words, if the isobars and isotherms constitute a sheaf ($H_p = \pm\infty$).

The general case where the viscosity-temperature-pressure surface is slightly *curved* will now be further elucidated with the aid of the schematic Fig. V-3.

For *Π=constant,* H is linear in Θ. This means that the *isobars*

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*) Fig. V-3 depicts this surface for the case where the pole viscosity (H_p) is very low; it should be added that an essentially similar surface is obtained in the opposite case where the pole viscosity is extremely high.

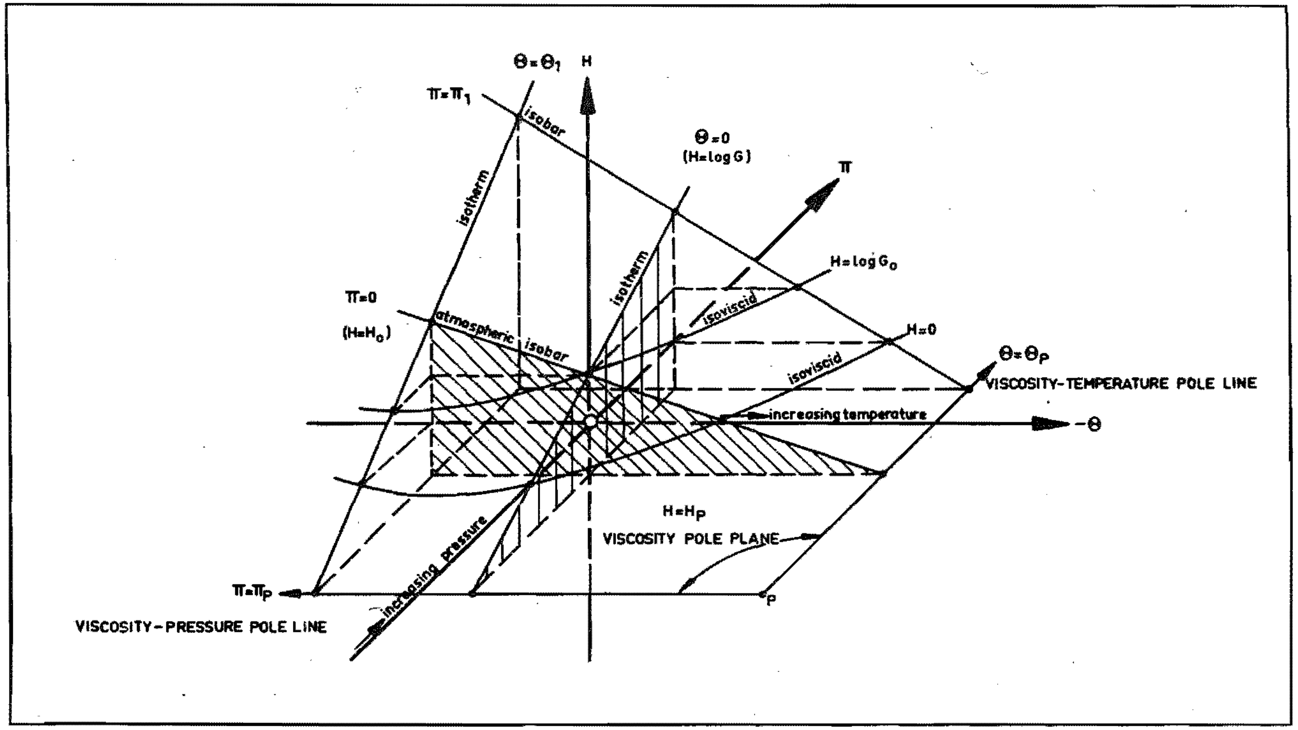

FIG. V-3.
Spatial Representation of the Viscosity-Temperature-Pressure Relationship (V-1a).

are straight, so that these must form one of the two sets of straight generatrices. In fact, in the space model of Fig. V-3 the isobars are represented by the secants of the viscosity-temperature-pressure surface with planes parallel to the H-Θ plane. If projected on the H-Θ plane, as in Fig. III-7, the isobars possess a viscosity-temperature pole having H_p and Θ_p as its coordinates. Therefore, all the isobars intersect a particular straight line which is parallel to the Π-axis. This line ($H=H_p$, $\Theta=\Theta_p$) is termed the *"viscosity-temperature pole line"*.

For Θ=*constant*, H is linear in Π, which means that the *isotherms* are also straight. Spatially the isotherms, which constitute the other set of straight generatrices, are represented by the secants of the viscosity-temperature-pressure surface with planes parallel to the H-Π plane. If projected on the H-Π plane, as in Fig. IV-7, the isotherms possess a viscosity-pressure pole having H_p and Π_p as its coordinates. Therefore, like the isobars, all the isotherms intersect a certain straight line, which is parallel to the Θ-axis. This line ($H=H_p$, $\Pi=\Pi_p$) is termed the *"viscosity-pressure pole line"*.

Since the two pole lines intersect - in the *"viscosity-temperature-pressure pole"* P ($H=H_p$, $\Theta=\Theta_p$, $\Pi=\Pi_p$) -, they are situated in the same plane, the *"viscosity pole plane"* ($H=H_p$), which is parallel to the Θ-Π plane.

Of either set of straight generatrices, that is the isobars and the isotherms, three are shown in Fig. V-3. The isobars correspond to the following Π-values: to $\Pi=\Pi_p$, giving the viscosity-pressure pole line itself; to $\Pi=0$, giving the atmospheric isobar, with the viscosity value $H=H_0$; and to some arbitrary value $\Pi=\Pi_1$. The three isotherms depicted correspond to the following Θ-values: to $\Theta=\Theta_p$, giving the viscosity-temperature pole line itself; to $\Theta=0$ ($t=0^{\circ}C$), where $H=\log G$; and to some arbitrary value $\Theta=\Theta_1$.

For *H=constant*, a hyperbolic relationship between Θ and Π results which implies that the *isoviscids* are projected on the Θ-Π plane, as in Fig. V-1, as a family of equilateral hyperbolas. In the present space model such hyperbolic curves are represented by the secants of the viscosity-temperature-pressure surface with planes parallel to the Θ-Π plane. The three isoviscids depicted in Fig. V-3 correspond to the following H-values: to $H=H_p$, where the isoviscid has actually degenerated into a pair of straight lines, namely the two pole lines; to $H=0$ ($\eta=0.0631$ cP); and to $H=\log G_0$, where the isoviscid intersects the H-axis ($\Theta=0$, $\Pi=0$).

It should be noted that there must be two *limiting curves* on the viscosity-temperature-pressure surface, namely one for solidification or solid separation, and the other where the liquid starts to volatilize or to decompose. Further, it will be evident that these curves comprise only a small portion of the entire surface depicted in Fig. V-3.

Finally, it may be useful to rewrite the basic viscosity-temperature-pressure Equation (V-1a) in terms of the three coordinates of the viscosity-temperature-pressure pole P of Fig. V-3, that is in terms of H_p, Θ_p and Π_p. By simple algebra one finally arrives at the expression:

$$H - H_P = -\frac{S_0}{\Pi_P}\,(\Theta - \Theta_P)\,(\Pi - \Pi_P). \qquad \text{(V-12a)}$$

Accordingly, for a given position of the viscosity-temperature-pressure pole the surface depicting H as a function of Θ and Π will be defined completely if only a second point on this surface is known. Let this second point be given by a reference viscosity, H_r, at for all liquids invariably the same standard reference temperature, Θ_r, and also at invariably the same standard reference pressure, Π_r. Then, the atmospheric Slope Index, S_0, the only parameter in Equation (V-12a) besides the three pole coordinates, can easily be eliminated from that equation. Thus, the following symmetrical expression is achieved:

$$\frac{H - H_P}{H_r - H_P} = \frac{\Theta - \Theta_P}{\Theta_r - \Theta_P} \cdot \frac{\Pi - \Pi_P}{\Pi_r - \Pi_P}. \qquad \text{(V-13)}$$

As long as Equation (V-13) holds good, the viscosity of a given liquid can be calculated at any specified temperature and pressure if only its viscosity-temperature-pressure pole and a reference point (outside this pole) are known.

In practice, this reference point will normally be the viscosity *grade* of the liquid considered, that is its viscosity, $H_{0,r}$, at atmospheric pressure, Π=0, and at some standard reference temperature, Θ_r. In the latter case Equation (V-13) reduces to:

$$\frac{H - H_P}{H_{0,r} - H_P} = \frac{\Theta - \Theta_P}{\Theta_r - \Theta_P} \cdot \frac{\Pi - \Pi_P}{-\Pi_P}. \qquad \text{(V-14)}$$

V.4. DISCUSSION

V.4.1. *Previous Empirical Equations for the Complete Viscosity-Temperature-Pressure Relationship of Liquids*

Several empirical equations have previously been proposed for describing the complete viscosity-temperature-pressure relationship of liquids. Unfortunately, nearly all these equations leave much to be desired as regards their accuracy and/or practical convenience.

The empirical equations developed - primarily for lubricating oils - by Kiesskalt$^{118)}$, Cragoe$^{119)}$, Suge$^{113)}$, Seeder$^{120)}$ and Cameron$^{60)}$ imply that at any given temperature the viscosity-pressure dependence of the liquid considered would be described by Barus's simple exponential Equation (IV-1a). In general, therefore, the applicability of these viscosity-temperature-pressure equations*) is bound to be

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*) In the paper cited$^{119)}$ Cragoe further proposed a second equation which was intended to apply to oils whose isotherms are slightly concave downward in a log η-p diagram. But even if confined to such oils the latter equation has appeared to yield very erroneous results at pressures of only a few thousand kgf/cm^2 (compare Hersey and Hopkins$^{26)}$ and Dow$^{121)}$).

restricted to moderate pressures, say, below 1,000 kgf/cm^2 (14,000 psi).

More accurate equations are that derived by Lederer[112] and, particularly, the one proposed by Bradbury *et al.*[28]. The latter equations, however, are complex in form and contain an unduly high number of characteristic parameters. Accordingly, they are very cumbersome in numerical evaluation and do not lend themselves to convenient graphical representation of the involved viscosity-temperature-pressure characteristics*).

Recently, Roelands *et al.*[44] proposed an equation which has proved really satisfactory over very wide ranges of temperature and pressure. This equation will be discussed in the context of the subsequent § V.4.2.

V.4.2. *The Basic Pole Concept*

The basic feature of the newly developed mathematical framework for characterizing the complete viscosity-temperature-pressure relationship of a given liquid consists in that, in suitable rectifying charts, both its family of isobars and that of isotherms can be depicted as a fan, both fans having the same pole viscosity. This finding has led to the comparatively simple viscosity-temperature-pressure Equation (V-1a), which in the three-dimensional plot of Fig. V-3 is represented by a hyperbolic paraboloid with two sets of straight generatrices.

As suggested in the discussions of Chapters III and IV, respectively, both the family of isobars and that of isotherms characterizing a particular liquid will likewise converge towards a common pole viscosity when plotted in rectifying charts that are based on adequate expressions different from those developed in the present paper, provided only that the same viscosity scale is employed in either chart. In other words, numerous mathematical formulations would be conceivable - at least in principle - for the defining quantities H, Θ and Π of the basic Equation (V-1a).

Consequently, as already indicated by Roelands et al.[44]*, the introduced pole concept may be claimed to have general significance, irrespective of the particular mathematical formulations employed.*

The delineated pole concept has proved very valuable in casting the complete viscosity-temperature-pressure relationship of liquids into a convenient analytical form, whilst minimizing the number of parameters required for characterizing a given liquid.

In fact, this concept also constitutes the basis of an equation, recently proposed by Roelands *et al.*[44], which has proved really satisfactory over very wide ranges of temperature and pressure. The latter equation, which has been obtained by suitably combining Equa-

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*) The equation empirically derived by Bradbury et al.[28] is remarkable in that it would apply even at pressures so high as to give rise to the above-indicated transition (see Section IV.1). Although this complex equation can be considerably simplified if it is confined to pressures where the isotherms display a regular trend, yet it remains unduly cumbersome. It should further be noted that, in contradistinction to the authors' conjecture, the parameter "G" in their simplified Equation [19] would generally vary more or less with temperature.

tions (III-3) and (IV-3), may be rewritten as:

$$\log \eta = \frac{A_0'}{T^{a_0'}} + C' \frac{p^{c'}}{T^{a_0'}} + D' p^{c'} + B_0' . \qquad \text{(V-15)}$$

where the parameters C' and D' have a similar meaning as the corresponding quantities C and D, respectively, in the present Equation (V-1a); the remaining parameters of Equation (V-15) are identical to those in the aforementioned basic equations.

It is seen that Equation (V-15) does represent a particular form of the generalized Equation (V-1a) in that it utilizes only different mathematical formulations for the functions H, Θ and Π occurring in the latter equation.

The temperature function, $T^{a_0'}$, and the pressure function, $p^{c'}$, entering into Equation (V-15) each contain a parameter - the exponents a_0' and c', respectively - which may differ from one liquid to another. As a rule, therefore, Equation (V-15) requires *six* parameters if very wide ranges of temperature and pressure are to be covered. It has appeared, however, that within certain groups of related liquids one or both exponents, a_0' and/or c', may be taken to possess one common value for all the members of such a group. Indeed, for many liquids only the *four* remaining parameters of Equation (V-15) are really needed for satisfactorily describing their viscosity-temperature-pressure relationship over fairly wide ranges of temperature and pressure. Generally, these four parameters suffice for defining the latter relationship if only *moderate* temperature and pressure ranges are involved, both exponents, a_0' and c', being taken equal to unity*).

It is interesting to note that, recently, Appeldoorn[124] has thoroughly checked a viscosity-temperature-pressure equation**) which, as he indicated, may be conceived as another simplified form of the published Equation (V-15). Appeldoorn employed the temperature expression***) $\log t_F$, with t_F in deg F, instead of $T^{-a_0'}$ in Equation (V-15) and simply the pressure p instead of $p^{c'}$ in Equation (V-15), the exponent c' thus being taken equal to unity.

Since the validity of Barus's Equation (IV-1a) for the isothermal viscosity-pressure relationship has again been implied, the viscosity-temperature-pressure equation under discussion may not be applied above about 1,000 kgf/cm^2 (14,000 psi) either; moreover, the temperature range covered is not so wide, that is from about 20 to 120°C (68-248°F). Within these limited ranges of temperature and pressure the latter equation proved very useful for many petroleum-based lubricating oils and pure hydrocarbons, although various other types of oils could not be included.

It should be emphasized that on the strength of the *general* nature of the present pole concept several satisfactory equations for the complete viscosity-temperature-pressure relationship of liquids can

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*) Recently, the author found that the consequent simplified form of Equation (V-15) has previously been used by Sternlicht[123] for describing, over a limited temperature and pressure range, the viscosity-temperature-pressure relationship of the two mineral oils employed in his lubrication experiments.

**) Essentially the same equation had been proposed already by Hersey and Hopkins[26].

***) As elucidated by Appeldoorn, this particular temperature function derives from Slotte's well-known equation for the atmospheric viscosity-temperature relationship of liquids.

easily be written down, simply by substituting adequate expressions for the functions H,Θ and Π in the basic Equation (V-1a). Such adequate expressions can be chosen from the many equations available for the atmospheric viscosity-temperature relationship and the isothermal viscosity-pressure relationship, respectively. Preferably, the temperature and pressure functions to be combined should have an analogous form, such as in Equation (V-15).

For example combination of Equations (III-2) and (IV-2) yields:

$$\log \eta = \frac{A_0}{T+a_0} + \frac{C''}{T+a_0} \cdot \frac{1}{p^{-1}+c} + \frac{D''}{p^{-1}+c} + B_0, \qquad \text{(V-16)}$$

where the four parameters A_0, B_0, a_0 and c are identical to those in the basic equations, whilst C'' and D'' constitute new parameters similar to the corresponding quantities C and D, respectively, in Equation (V-1a). Thus, like the foregoing Equation (V-15), the present Equation (V-16) contains *six* characteristic parameters.

Over very wide ranges of temperature and pressure, Equation (V-16) has proved to hold good for all the divergent kinds of liquids considered, in general even slightly better than Equation (V-15). In addition, the mathematical form of Equation (V-16) is somewhat more attractive than that of Equation (V-15).

All in all, Equation (V-16) is recommended for representing the viscosity-temperature-pressure relationship of liquids in cases where an unusual correlational accuracy is demanded and further in all those cases where it is not a serious drawback to deal with six parameters.

V.4.3. *The Main Features of the Present Viscosity-Temperature-Pressure Equation in Retrospect*

In connection with the preceding discussion of the basic pole concept (§ V.4.2) it should be emphasized that the particular mathematical formulations developed for the quantities H,Θ and Π in the present viscosity-temperature-pressure Equation (V-1a) have the alluring - and apparently unique - feature that they do not contain any additional parameters that would be characteristic of the liquid considered. Indeed, over very wide ranges of temperature and pressure the latter formulations have proved to remain valid for all the divergent kinds of liquids investigated so far, so that they may be claimed to be well-nigh *universally* applicable.

Thus, only *four* parameters are required for satisfactorily describing the complete viscosity-temperature-pressure relationship of all these liquids, generally in a temperature range of some 200°C (360°F) and up to pressures of about 3,000-5,000 kgf/cm^2 (43,000-71,000 psi). In all probability, these four parameters represent the *minimum* number achievable for the very wide temperature and pressure ranges explored.

Consequently, in the aforementioned ranges only *three* parameters suffice for fully characterizing the effect of both temperature and pressure on the viscosity *grade* of a given liquid.

All in all, the complete viscosity-temperature-pressure Equation

(V-1a) has proved to combine an almost unsurpassable simplicity with a well-nigh universal applicability.

Moreover, it has been found that over somewhat more restricted, but still quite considerable, ranges of temperature and pressure the aforementioned number of four characteristic parameters occurring in the complete Equation (V-1a) may be reduced to only *three*. According to the resulting *simplified* Equation (V-8a), both the family of isobars and that of isotherms characterizing a given liquid can then be plotted as a sheaf in an H-Θ and an H-Π chart, respectively.
The validity of the simplified Equation (V-8a) also implies that only *two* parameters - definitely the minimum number conceivable at all - suffice for describing the effect of both temperature and pressure on the viscosity *grade* of a given liquid.

Further, the complete viscosity-temperature-pressure Equation (V-1a), or rather the simplified Equation (V-8a), has proved to lend itself particularly well as a basis to an extremely simple and rational method for *classifying*, according to both their temperature and pressure dependence of viscosity, all the various kinds of oils encountered in current lubrication practice. In fact, the relevant classifications are achieved solely by means of the atmospheric Slope Index, S_0, and the Viscosity-Pressure Index, Z, respectively. These classifications will be elaborated in Chapters VI and VII, respectively.

Last but not least, the complete Equation (V-1a), or the simplified Equation (V-8a), constitutes a very attractive starting-point when it is attempted to establish convenient *correlations* for estimating the viscosity-temperature-pressure characteristics of liquids, notably all the various kinds of mineral oils encountered, from easily assessable physical or chemical properties. This will be elucidated in Chapters VIII through X.

APPENDIX

Appendix V-1. *Deduction of the Convergence of the Isobars of a Given Liquid from That of Its Isotherms*

The convergence of the *isotherms* of a given liquid as described in § IV. 3. 2 is mathematically defined by the expression:

$$\frac{H - H_0}{H_p - H_0} = \frac{\Pi}{\Pi_p} . \qquad \text{(IV-7a)}$$

Besides this convergence of isotherms, the equation of the atmospheric *isobar* is given, that is:

$$H_0 = S_0 \Theta + \log G_0 . \qquad \text{(III-6h)}$$

Substitution of Equation (III-6h) into Equation (IV-7a) leads to:

$$H = S_0\left(1 - \frac{\Pi}{\Pi_P}\right)\Theta + \log G_0\left(1 - \frac{\Pi}{\Pi_P}\right) + H_P\,\frac{\Pi}{\Pi_P}\,. \qquad \text{(V-17)}$$

Accordingly, for a given value of pressure, that is for a given isobar, H is a linear function of Θ, so that the isobars characterizing the liquid considered are represented by straight lines in one and the same H-Θ chart. These isobars form a family of straight lines with pressure as a parameter. The problem to be solved is whether this family is a fan; that is whether it has a viscosity-temperature pole.

For the latter purpose it should be noted that Equation (V-17) constitutes a particular version of the aforementioned isobar expression:

$$H = S\,\Theta + \log G, \qquad \text{(III-10)}$$

where the pressure-dependent parameters S and G have the values specified by Equation (V-17).

Using the relevant expression for G:

$$\log G = \log G_0\left(1 - \frac{\Pi}{\Pi_P}\right) + H_P\,\frac{\Pi}{\Pi_P} \qquad \text{(V-18)}$$

for eliminating the factor Π/Π_P from Equation (V-17), the latter equation can readily be cast into the form:

$$\frac{H - \log G}{H_p - \log G} = \frac{S_0}{H_p - \log G_0}\,.\ \Theta\,. \qquad \text{(V-19)}$$

Denoting the temperature where the atmospheric isobar would reach the viscosity, H_p, of the viscosity-pressure pole by Θ_p, it is seen that Equation (V-19) can be rewritten as:

$$\frac{H - \log G}{H_p - \log G} = \frac{\Theta}{\Theta_p}\,. \qquad \text{(III-11a)}$$

Thus, the latter equation proves to be identical with Equation (III-11a) defining mathematically the convergence of *isobars*. Indeed, like the atmospheric isobar all elevated-pressure isobars appear to reach the viscosity, H_P, of the viscosity-pressure pole at invariably the same temperature Θ_P.

Consequently, it has been demonstrated that the above family of straight isobars does form a *fan;* that is that it has indeed a viscosity-temperature pole. In addition, it has been shown at the same time that the viscosity coordinate, H_p, of this viscosity-*temperature* pole is equal to that of the corresponding viscosity-*pressure* pole.

CHAPTER VI

A RATIONAL METHOD FOR CLASSIFYING LUBRICATING OILS ACCORDING TO THEIR ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP*)

VI. 1. INTRODUCTION

VI. 1. 1 *Background*

There is a long-felt need for a simple, yet sufficiently quantitative, criterion of the atmospheric**) viscosity-temperature dependence of liquids, in particular lubricating oils. Of course, viscosities at various, more or less representative, temperatures may be given or specified. But in many cases, notably for correlational purposes, *one single* quantity for characterizing the viscosity-temperature dependence of lubricating oils would be highly desirable or even indispensable. In addition, for practical - particularly commercial - purposes such a quantity should have a *comparative* nature, in order that its value should be readily appreciated for any given oil irrespective of its particular viscosity grade.

A staggering amount of work has been devoted to the vexing problem of developing such a criterion. Of the many criteria proposed the *Viscosity Index*, originally developed by Dean and Davis (1929) and after some refinement adopted as an ASTM standard, has certainly reached the most wide-spread usage.

VI. 1. 2. *Discussion of the ASTM Viscosity Index (VI)*

In the VI-system[125-128] the viscosity *grade* of a given oil is defined as its *kinematic* viscosity at 210°F (98.9°C). At a second standard reference temperature, fixed at 100°F (37.8°C), the kinematic viscosity of the given oil is compared with the kinematic viscosities of two reference oils of the same viscosity grade. The latter two oils belong to two distinct, arbitrarily selected, standard reference series of natural mineral oils exhibiting strongly different kinematic viscosity-temperature dependence.

Either standard reference series constitutes a *"naturally" homologous* group of oils, which means that the members of such a series have been obtained from one and the same crude by comparable refining methods. The members of the first series, the so-called H-series, derived from a Pennsylvania crude yielding oils with relatively flat kinematic viscosity-temperature curves, whilst the members of the second series, the so-called L-series, derived from a

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*) The greater part of this chapter has already been published in Reference 69.

**) Throughout the present chapter the viscosity-temperature relationship invariably relates to atmospheric pressure; for convenience, however, the term "atmospheric" will generally be omitted.

Gulf Coast crude yielding oils with relatively steep kinematic viscosity-temperature curves. To the oils of the H- and L-series VI-values of 100 and 0, respectively, have been assigned by definition. For an arbitrary oil the VI is obtained from the equation:

$$\mathrm{VI} = 100\,\frac{\nu_L - \nu_U}{\nu_L - \nu_H}\,, \qquad \text{(VI-1)}$$

where ν_U, ν_H and ν_L denote the kinematic viscosities at 100°F of the oil considered and the reference oils of the H- and L-series, respectively.

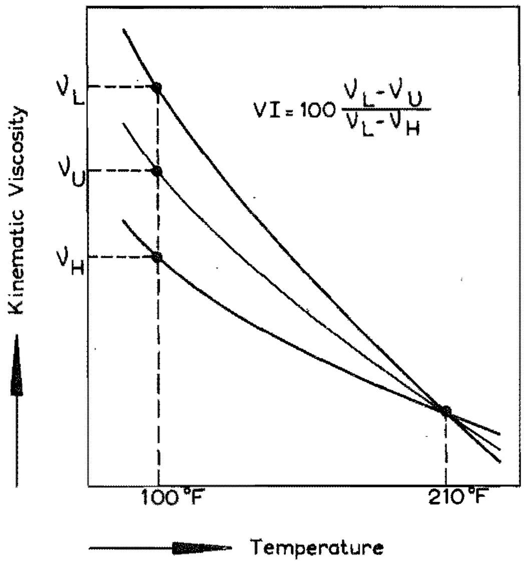

FIG. VI-1.
Schematic Representation of the ASTM Viscosity Index.

As illustrated in the schematic Fig. VI-1, Equation (VI-1) states that the VI of a given oil is calculated simply by linearly interpolating between the kinematic viscosities ν_H and ν_L. For oils whose kinematic viscosity ν_U is not intermediate to the two reference kinematic viscosities the VI is obtained by linearly extrapolating according to Equation (VI-1). In the latter case, of course, the VI either exceeds 100 or assumes some negative value.

Owing to its comparative nature, the VI-scale yields substantially the same indices for oils that, although not belonging to the two standard reference series, are also interrelated by so-called natural homology. Thanks to this attractive feature, the VI soon found almost universal acceptance in the petroleum industry, particularly for commercial purposes.

Indeed, for the *mineral* oils in use at the time of its introduction (1929) the VI proved - at least for technological purposes - a quite satisfactory criterion. The last decades, however, *synthetic* lubricating oils and *polymer-blended* mineral oils have increasingly been introduced. Particularly with such oils the VI-system shows certain well-known ambiguities and irregularities which render it quite inadequate for these fluids[129-134].

In the first place, *ambiguities* have long been recognized to be inherent in VI-values much higher than those originally considered. Whilst theoretically such ambiguities may arise as soon as the VI exceeds 123, they assume practical importance at somewhat higher values, say, above 130. In fact, if, for instance for purchasing purposes an oil should be specified as to its kinematic viscosity-temperature relationship by kinematic viscosity at some standard reference temperature and by so high a VI, *two* oils would meet this specification. One oil would have the very small temperature dependence of kinematic viscosity that is usually intended, but the other would be distinctly worse in this respect.

TABLE VI-1

Kinematic Viscosities of Two Synthetic Oils Having a Common VI

Type of Oil	Kinematic Viscosity, cS			VI
	100°F(37.8°C)	131°F(55°C)	210°F(98.9°C)	
Linear Polymethylsiloxane	247	183	99.5	135
Poly(ethylene-propylene) Glycol Derivative	333	183	58.1	135

This rather awkward ambiguity may be illustrated in Table VI-1 for two oils - encountered in actual lubrication practice - having both a VI of 135. It is seen that either oil would comply with one and the same specification, namely a kinematic viscosity grade of 183 cS at 55°C (131°F) and a VI of 135. But the polymethylsiloxane displays a distinctly smaller kinematic viscosity-temperature dependence than the poly(ethylene-propylene) glycol derivative (compare also § VI.2.4).

It may further be pointed out that the ambiguities inherent in very high VI-values become exceptionally obvious if a series of *"perfect"* oils is considered; that is oils whose (kinematic) viscosity is not affected at all by temperature. Whilst such oils should naturally have a common VI, it appears that the corresponding VI's vary strongly with the kinematic viscosity grade of the member considered[131,135].

In the second place, the VI-system breaks down for relatively fluid oils, that is with kinematic viscosities $\nu_{210^\circ F}$ from about 7 cS downwards. The relevant *irregularities* boil down to an overestimation of differences in kinematic viscosity-temperature dependence by the conventional VI and, moreover, to an underrating of the kinematic viscosity-temperature dependence of such relatively fluid oils as compared with more viscous oils. This will be elucidated in the following Section VI.2.

The fundamental reason for the aforementioned ambiguities and irregularities consists in that the VI cannot generally be upheld as a satisfactory, or even an unambiguous, criterion of the kinematic viscosity-temperature relationship of liquids, since it falls short of being defined on the basis of some adequate expression for the kinematic viscosity-temperature dependence actually exhibited by the liquids in a wide temperature range.

Finally, with synthetic oils of types having density values appreciably greater than that usual amongst mineral oils, say, greater than 1 g/cm^3, the conventional VI is not fair in that it is based on *kinematic* viscosity. In fact, in comparison with mineral oils of the same VI, it has proved to underrate the flatness of the temperature variation of the particular viscosity characteristic that really counts in actual lubrication practice, that is the *dynamic* as against the *kinematic* viscosity (see § I.2.2). Examples of such unfair ratings by means of the conventional VI are provided in § VI.2.4.

VI.1.3. *The Present Status of the Problem*

All in all, there would appear to be a consensus - partly owing to the rapid development of synthetic lubricating oils - that the Viscosity Index can no longer be upheld as a viscosity-temperature criterion that is both reliable and fair [129-134].

In fact, numerous investigators have in the course of time devoted a staggering amount of work to the problem of developing a suitable criterion to replace the VI. This is evidenced by the fact that at least *fifty* criteria may be traced in the literature [129-133;135,136] many of which are more or less interrelated. Since none of these has so far found wide-spread usage or met with fairly general approval, the indications are that a really satisfactory criterion has not yet emerged. In fact, from sheer necessity the conventional VI has remained in wide-spread usage. This rather awkward situation has prompted a resolution at the Fourth World Petroleum Congress, in 1955, and this has been followed up by ASTM who set up a special committee to study this vexing problem [132,133,135,136]. It would appear, however, that no acceptable solution has so far been presented*).

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*) Recently, Wright[137] proposed a revision of the conventional VI-system for calculating VI's above 100; this was accepted as a standard by ASTM, in June, 1964. The modified system retains the standard reference series of oils as well as the standard reference temperatures of the conventional VI-system. In fact, Wright's modification boils down to a repair of the conventional system solely in the range of VI-values above 100, leaving lower values unchanged.

The modified system, which eliminates the indicated ambiguities inherent in the conventional system, may be regarded to meet the principal commercial requirements. However, as recognized by the aforementioned ASTM committee, the modified system does by no means meet the requirements to be imposed on a more fundamental system, fow which a real need continues to exist.

Summarizing, there is still a real need for a significant and fair criterion that is not afflicted with the ambiguities and irregularities inherent in the conventional VI, yet retains its meritorious *comparative* nature in that it is indicative of the viscosity-temperature dependence of the oil concerned, irrespective of its viscosity grade, and that can be appreciated at least equally readily, also by non-experts. Further, in order to prove also significant and fair in lubrication practice such a criterion should be based on *dynamic* viscosity. Moreover, its assessment should preferably be even simpler than that of the VI, for instance by eliminating the need both for standard reference oils and for standard reference temperatures. Such a criterion would thus also be put on a more *absolute* basis. Finally, one might also aim at achieving greater convenience than provided by the VI in predicting the viscosity at any temperature once the oil's viscosity grade, that is its viscosity at some given temperature, is specified in addition. Then it will be serviceable not only as an identifying criterion for commercial and production purposes, but it will also constitute a valuable and convenient tool for design calculations in hydrodynamic lubrication.

It will be shown that the above requirements and aims are indeed fulfilled by the viscosity-temperature criterion to be described in the following parts of this chapter.

VI.1.4. *The New Criterion*

The present criterion is based on the newly developed two-parameter Equation (III-6h) for describing, over a very wide temperature range, the viscosity-temperature relationships of all the various kinds of lubricating oils, including synthetic oils, encountered in present-day lubrication practice. Like any similar previous equation, it has proved to permit the construction of "rectifying" scales for a chart in which the viscosity-temperature relationship of any such oil is represented, to a really good approximation, by a straight line (see Chapter III). But over previous equations it shows the following *basic* advantage.

In the rectifying charts in current usage, such as that issued by ASTM, the viscosity-temperature relationships of oils of different viscosity grades, form more or less as a fan when these are mineral oils belonging to one and the same naturally homologous group in having, for instance, a common Viscosity Index [63,66]. However, in contrast to such conventional rectifying charts, the new chart is of the "parallelizing" type in that, over a wide temperature range, the viscosity-temperature relationships of homologous oils are rectified to straight lines that no longer show different slopes but are *parallel*.

This *"homologous parallelism"* yields the basic advantage that the slope of the parallel lines is a constant parameter characteristic of the entire naturally homologous group to which the oil or oils considered belong, the viscosity grade of the particular member of the group being immaterial in this particular respect. It is considered significant that a similar constancy of the aforementioned slope has also been observed with various groups of pure hydrocarbon liquids, such as the n-paraffins, that are homologous in a truly rigorous chemical sense.

The major advantages of the new viscosity-temperature criterion, denoted as the *"Slope Index"* and defined as the slope in the aforementioned chart, are: the well-nigh unsurpassable simplicity of its assessment, particularly when the relevant chart is used; further, the fact that it dispenses entirely with the need for standard reference temperatures and even standard reference series of oils; last but not least, it is not afflicted with the ambiguities and irregularities inherent in the conventional Viscosity Index.

It should also be emphasized that the new criterion has been based on *dynamic* viscosity, which, in contrast to *kinematic* viscosity, is a really significant property both in the theory and practice of lubrication. Accordingly, there is no longer any masking effect of the irrelevant property of density.

Finally, the Slope Index has been converted empirically into a *"Dynamic Viscosity Index"* (DVI) which comes close to the conventional Viscosity Index throughout the range where the latter is not afflicted with ambiguities or irregularities.

VI.2. THE NEW VISCOSITY-TEMPERATURE CRITERION

VI.2.1. *Slope Indices of Representative Hydrocarbon Oils*)*

In Fig. VI-2 the Slope Indices, S**), of the members of two representative naturally homologous groups of mineral oils, namely

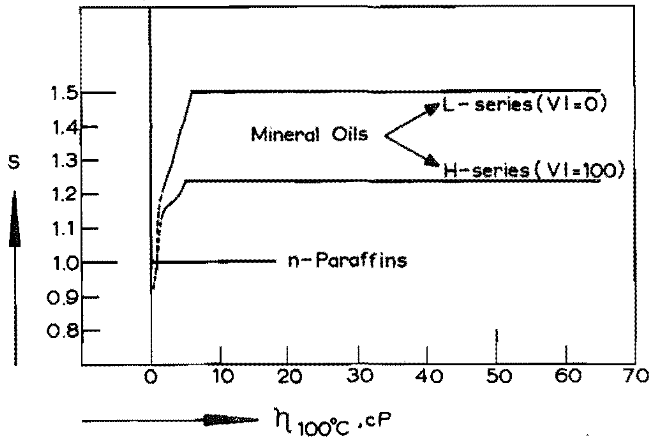

FIG. VI-2.
Slope Indices of Representative Hydrocarbon Oils.

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*) The Slope Indices of hydrocarbon-oil mixtures are extensively discussed in Chapter XII.

**) For convenience, the subscript "0" - referring to atmospheric pressure - has been ommited from the Slope Indices and the viscosities occurring in this chapter (compare the footnote to § VI.1.1).

the H- and L-series standardized by ASTM for the VI-system, having by definition 100 and 0 VI, respectively, have been plotted against the individual viscosity grades as expressed in terms of ***dynamic*** viscosity, in cP, of each member at a standard reference temperature of 100°C (212°F)*). It appears from Fig. VI-2 that for the members of either group the Slope Index is indeed substantially constant over almost the entire range of viscosity grades covered by the ASTM Viscosity Index tables [128]. This range covers, in terms of the originally specified ***kinematic*** viscosity, $\nu_{210^\circ F}$, values from 2.0**) up to 75 cS and this corresponds to a range of ***dynamic*** viscosity at the above standard reference temperature of 100°C, $\eta_{100^\circ C}$, that extends from about 1.6 up to 65 cP.

Further, a similar "***homologous constancy***" of the Slope Index has been found to hold good for other naturally homologous groups of mineral oils having VI's different from those of the H- and L-series.

It should be noted, however, that with the two naturally homologous groups of mineral oils depicted in Fig. VI-2 a sharp breakdown of the constancy of the Slope Index occurs at low viscosity grades, that is $\eta_{100^\circ C}$ from 5 or 6 cP downwards (corresponding to $\nu_{210^\circ F} \approx 7$ cS and lower). Below this rather abrupt transition the two lines concerned do not only fall conspicuously, but they also converge towards each other very rapidly as the viscosity grade decreases. The author has actually found that at the lowest viscosity grades explored, even lower than those of the most fluid oils in the H- and L-series, that is from about $\eta_{100^\circ C} = 1.0$ cP ($\nu_{210^\circ F} \approx$ 1.3 cS) downwards, differences in the origin or the chemical constitution of such oils no longer reflect themselves in their viscosity-temperature dependence (see Chapter VIII). In fact, this dependence is then solely determined by the viscosity grade of such a fluid oil, irrespective of its origin or chemical constitution***). This may be taken to mean that attempting to differentiate amongst oils of viscosity grades approaching the aforementioned level as to their viscosity-temperature dependence amounts to stretching imagination too far.

All in all, Fig. VI-2 clearly demonstrates the inadequacy of the conventional VI-system in the range of low viscosity grades. In fact, the relevant irregularities have frequently been criticized, and thoroughly so by Hardiman and Nissan [138]. As indicated already in § VI.1.2, these irregularities in the VI-system with relatively fluid oils accrue from the fact that the VI falls short of being defined on the basis of some adequate expression for the viscosity-temperature dependence actually exhibited by the oils over a wide temperature range.

The new criterion, the Slope Index, however, is based on the most

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*) This temperature comes quite close to the standard reference temperature of 210°F adopted in the VI-system. It should be pointed out, however, that the following discussion applied irrespective of the particular standard reference temperature selected.

**) In addition, the relevant ASTM standard provides equations for calculating basic data for the H- and L-series if the kinematic viscosity $\nu_{210^\circ F}$ is smaller than 2.0 cS.

***) Accordingly, oils with such low viscosity grades will follow a common line in Fig. VI-2. This line has been drawn as a dashed line, just like the interpolated curves which connect it with the solid lines of the H- and L-series according to the ASTM tables (down to $\eta_{100^\circ C} \approx 1.6$ cP).

universally valid expression found so far for the viscosity-temperature dependence of oils, and thus it removes completely the aforementioned irregularities inherent in the VI-system with relatively fluid oils.

It is recognized that there is some vagueness in the concept of "natural" homology as used above in connection with the H- and L-series of the VI-system and as reflected in the constancy of the Slope Index over the greater part of the range of viscosity grades covered by these natural oils. But also with various groups of pure hydrocarbon liquids, such as the n-paraffins, that are truly homologous in a rigorous chemical sense a constancy that may be regarded as absolute does hold for the Slope Index. For instance, for all the n-paraffins for which the author could find reliable viscosity data[77;139-141] in the temperature range from 0 to 150°C (32-302°F), that is for the members from n-C_5 up to n-C_{64}, the Slope Index showed invariably one and the same value. Accordingly, the line representing in Fig. VI-2 the Slope Indices of the n-paraffins, in contrast to the lines for the H- and L-series, is straight and horizontal through the *entire* range of viscosity grades explored.

It is worthy of note that for other truly homologous groups of pure hydrocarbons, namely the n-α-alkenes, n-alkylcyclopentanes and the n-alkylbenzenes, the Slope Index displays the same value, or very nearly so, as for the n-paraffins. It so happens that this common Slope Index has an easily memorizable value, namely 1.00, which may be considered significant to the last digit.

Before continuing this treatment, it should be pointed out that, owing to the approximative nature of the basic viscosity-temperature Equation (III-6b), the Slope Index of a particular liquid generally tends to vary somewhat with the temperature range considered. In order to avoid the consequent discrepancies it is recommended to indicate, at least approximately, the temperature range covered by a particular Slope Index.

Admittedly, this also imposes the restriction upon the present classification system that, in order to enable a fair evaluation of the viscosity-temperature qualities of different liquids, their Slope Indices should relate to *comparable* temperature ranges. This restriction, however, does not detract from the fact that the present classification system, in contradistinction to the conventional VI-system, does not need the prescription of standard reference temperatures.

VI.2.2. *Conversion of the Slope Index into the "Dynamic Viscosity Index" (DVI)*

It is an alluring feature of the new criterion, the Slope Index, that it correlates fairly strictly with the conventional VI, if only so in the range where the latter criterion may be deemed satisfactory in that it does not show there ambiguities or irregularities. This also opens up the possibility of so converting the Slope Index into still another viscosity-temperature criterion, the *"Dynamic Viscosity Index"*, that within the aforementioned range fits the conventional VI fairly closely. Consequently, the familiar values of the VI can be retained to a good approximation, although this can be achieved only for the range concerned. Moreover, in the remaining range, where the conventional VI is erratic, this can now be replaced by the rational DVI. It should be noted that the soundness of the DVI originates from the fact that it has been based on the essentially sound Slope Index, S. This soundness is not affected by the fact that the DVI has been fitted empirically to the conventional VI.

In principle, the authors consider the conversion into the DVI as an unnecessary extension to the Slope-Index criterion. Indeed, the Slope Index is a straightforward quantity with an analytically well-defined and simple meaning, whereas this is no longer true of the Dynamic Viscosity Index. Nevertheless, from a practical or commercial point of view it is perhaps a wise compromise yet to introduce the DVI, though only temporarily. In fact, for a start it might well prove advantageous that this converted criterion yields numerical values of an order of magnitude that is familiar and, therefore, for the time being more informative than the Slope Index to both manufacturers and users of lubricating oils.

But it is highly discouraged to introduce a "kinematic" Slope Index, such as might be introduced through making the basic Equation (III-6b) suitable for homologous parallelism of the temperature variation of *kinematic* viscosity by readjustment of the constants 1.200 and 135 and, of course, of the present value of the index S. Such an index would, amongst other undesirable features, reintroduce the unfairness towards synthetic oils having densities greater than those of mineral oils.

It is suggested to define the Dynamic Viscosity Index by the conversion formula:

$$\text{DVI} = 220 - 7 \cdot 10^{S}. \qquad \text{(VI-2)}$$

It is fully realized that this conversion is somewhat arbitrary. Therefore, in contrast to the basic criterion, the Slope Index, it is open to modification by others, for instance by some committee.

According to Conversion (VI-2), a small Slope Index, S, which is indicative of a small variation of viscosity with temperature, cor-

TABLE VI-2

Some Corresponding Values of S and DVI According to Conversion (VI-2)

Slope Index		DVI
Rounded off	Exact	
0.00	0.00	213
0.50	0.46	200
1.00	1.00	150
1.25	1.23	100
1.50	1.50	0
1.75	1.78	-200
2.00	2.01	-500

TABLE VI-3

The Relationship Between Slope Index and DVI According to Conversion (VI-2)

S	Values of DVI									
	Second decimal point of S									
	0	1	2	3	4	5	6	7	8	9
0.0	**213.0**	2.8	2.7	2.5	2.3	2.1	2.0	1.8	1.6	1.4
0.1	**211.2**	1.0	0.8	0.6	0.3	0.1	**209.9**	9.6	9.4	9.2
0.2	**208.9**	8.6	8.4	8.1	7.8	7.6	7.3	7.0	6.7	6.4
0.3	**206.0**	5.7	5.4	5.0	4.7	4.3	4.0	3.6	3.2	2.8
0.4	**202.4**	2.0	1.6	1.2	0.7	0.3	**199.8**	9.4	8.9	8.4
0.5	**197.9**	7.3	6.8	6.3	5.7	5.2	4.6	4.0	3.4	2.8
0.6	**192.1**	1.5	0.8	0.1	**189.4**	8.7	8.0	7.3	6.5	5.7
0.7	**184.9**	4.1	3.3	2.4	1.5	0.6	**179.7**	8.8	7.8	6.8
0.8	**175.8**	4.8	3.8	2.7	1.6	0.4	**169.3**	8.1	6.9	5.7
0.9	**164.4**	3.1	1.8	0.4	**159.0**	7.6	6.2	4.7	3.2	1.6
1.0	**150.0**	**148.4**	6.7	5.0	3.2	1.4	**139.6**	7.7	5.8	3.9
1.1	**131.9**	**129.8**	7.7	5.6	3.4	1.1	**118.8**	6.4	4.0	1.5
1.2	**109.0**	6.5	3.9	1.2	98.4	95.5	92.6	89.6	86.6	83.5
1.3	80.3	77.1	73.7	70.3	66.9	63.3	59.6	55.9	52.1	48.2
1.4	44.2	40.1	35.9	31.6	27.2	22.7	18.1	13.4	8.6	3.7
1.5	-1.3	-6.5	-11.8	-17.2	-22.7	-28.4	-34.2	-40.0	-46.1	-52.3
1.6	-58.7	-65.2	-71.8	-78.6	-85.6	-92.7	-100.0	-107.4	-115.0	-122.9
1.7	-130.8	-139.0	-147.4	-155.9	-164.7	-173.6	-182.8	-192.2	-201.8	-211.6
1.8	-221.7	-232.0	-242.5	-253.3	-264.3	-275.6	-287.1	-298.9	-311.0	-323.4
1.9	-336.0	-349.0	-362.2	-375.8	-389.7	-403.9	-418.4	-433.3	-448.5	-464.1
2.0	-480.0	-496.2	-513.0	-530.0	-547.6	-565.4	-583.7	-602.5	-612.5	-641.1
	0	1	2	3	4	5	6	7	8	9

responds with a high DVI. For the extreme case of "perfect" oils displaying no viscosity change with temperature at all, so that S=0, the DVI would attain the value 213. Owing to the analytical nature of Conversion (VI-2), a given change of the Slope Index reflects itself in a relatively great change in the DVI. Thus, particularly at low values of the DVI this is very sensitive, and perhaps even oversensitive, towards a given change in temperature dependence of viscosity as compared with the Slope Index.

TABLE VI-4

Slope Index, DVI and VI of Representative Mineral Oils

Oil Code*)	η_{100^oC}, cP	S	DVI	VI	Oil Code	η_{100^oC}, cP	S	DVI	VI
F-1	4,74	1,22	104	99	A-13	8,07	1,50	-1	-1
F-14	4,94	1,23	101	97	A-11	8,09	1,49	4	5
AN-6	4,95	1,19	112	116	A-14	8,28	1,47	13	13
F-25	5,12	1,24	98	95	F-53	9,06	1,56	-34	-31
We-7	5,15	1,18	114	117	F-69	9,14	1,51	-6	-6
A-9	5,31	1,26	93	91	We-11	9,16	1,37	56	61
F-16	5,42	1,23	101	98	We-1H	9,27	1,17	116	117
A-3	5,48	1,26	93	88	F-50	9,29	1,34	67	71
F-26	5,61	1,24	98	95	We-10	9,38	1,38	52	57
We-6H	5,73	1,22	104	106	We-9	10,02	1,40	44	45
AN-1	5,74	1,26	93	91	We-8	10,28	1,44	27	32
AN-2	5,77	1,26	93	93	We-1	10,33	1,18	114	113
AN-3	5,83	1,22	104	105	F-29	10,42	1,43	32	40
We-6	5,86	1,21	106	107	We-4	10,66	1,41	40	47
F-33	5,86	1,31	77	71	We-3	10,69	1,63	-79	-77
F-18	6,00	1,24	98	98	F-71	11,35	1,55	-28	-13
A-15	6,05	1,37	56	55	A-7	11,70	1,25	96	103
F-27	6,17	1,25	96	96	F-54	11,72	1,60	-59	-47
We-2H	6,55	1,28	87	85	A-4	12,22	1,26	93	98
We-5H	6,67	1,26	93	94	F-30	12,33	1,43	32	42
F-20	6,71	1,24	98	99	A-8	12,47	1,21	106	108
AN-4	6,84	1,36	60	53	F-72	12,47	1,56	-34	-22
We-3H	6,86	1,43	32	25	A-6	12,88	1,25	96	101
We-4H	7,43	1,32	74	78	A-16	13,03	1,77	-192	-213
We-5	7,46	1,30	80	83	F-73	13,74	1,56	-34	-15
F-67	7,52	1,47	13	12	A-12	15,14	1,60	-59	-28
AN-5	7,55	1,43	32	29	F-55	15,28	1,63	-79	-58
F-22	7,78	1,24	98	99	F-31	15,56	1,42	36	52
We-2	8,02	1,36	60	61	F-32	17,95	1,40	44	58
F-28	8,07	1,37	56	58	A-5	27,2	1,28	87	97

*) Refers to similarly coded oils specified in Table II-1.

The concise Table VI-2 may serve as a useful guide for easily memorizing, and for getting acquainted with, the corresponding values of Slope Index and DVI according to Conversion (VI-2). In addition, the extensive conversion Table VI-3 has been prepared. Since there is normally not much sense in carrying numerical evaluation of the Slope Index beyond two decimal places (see § III.1.3), it follows from Table VI-3 that usually the corresponding DVI's could reasonably be rounded off to the nearest integral value; only at very high DVI's, that is above about 180, may it be significant to retain their first decimal place.

At least for ***mineral oils*** a fairly strict correlation has indeed been found between the DVI and the conventional VI but, of course, only in the aforementioned range where no ambiguities or irregularities are inherent in the latter criterion. This may be verified from Table VI-4 where the relevant data on 60 widely divergent mineral oils have been arranged in order of increasing viscosity grade as defined by dynamic viscosity at 100°C. All Slope Indices, S, have been calculated from Formula (III-6e), that is from the known dynamic viscosities at 100 and 210°F.

On the whole, the correlation between the DVI's calculated according to Definition (VI-2) and the conventional VI's is surprisingly good. In fact, it may be seen from Table VI-4 that for most mineral oils the discrepancies between corresponding values of these two criteria are so small as to be hardly significant in view of the accuracy attainable for either DVI or VI. This is indeed surprising, since discrepancies might be expected on the basis of the differences in density amongst the various mineral oils. After all, kinematic viscosity in the VI-system is compared with dynamic viscosity in the DVI-system, so that density is influential. Remarkably enough, even for mineral oils with VI's considerably beyond the usual range from 0 to 100 VI the agreement between DVI's and VI's still remains, in general, quite reasonable.

VI.2.3. *The New Criterion for Non-Hydrocarbon Types of Lubricating Oils*

It has been elucidated above how various values of the new viscosity-temperature criterion - expressed in terms of either, directly, the Slope Index or, indirectly, the Dynamic Viscosity Index - could be tied to the well-known viscosity-temperature characteristics of representative mineral (essentially hydrocarbon) oils and also of various groups of pure hydrocarbon liquids. Accordingly, all these composite or pure hydrocarbon liquids may be taken to instill the ***comparative*** nature of the conventional VI, through Conversion (VI-2), into the new DVI-scale. Therefore, the DVI may indeed be deemed to retain this meritorious comparative nature for ***any*** type of lubricating oil encountered.

Fig. VI-3 conveys an illuminating picture of the actual viscosity-temperature qualities, expressed in terms of both rational criteria, S[*] and DVI, of various important ***non-hydrocarbon*** types of synthetic lubricating oils, namely fluorocarbons [72,142,143] and chlorotrifluoroethylene ***polymers*** [144,72,27,142] ; further, polypropylene and poly(ethylene-propylene) glycol derivatives as represented by the well-

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[*] All Slope Indices, S, have been calculated for the conventional temperature range from about 20 to 120°C (68-248°F) in order to permit a fair comparison of these with the corresponding VI-values.

known "Ucon LB- and HB-series", respectively[114b,72]; and, finally, (linear) polymethylsiloxanes[145,146,17,27,48,72]. Furthermore, individual points have been indicated for two typical mineral-oil extracts[46] and a few individual liquids not so often used for lubrication purposes,

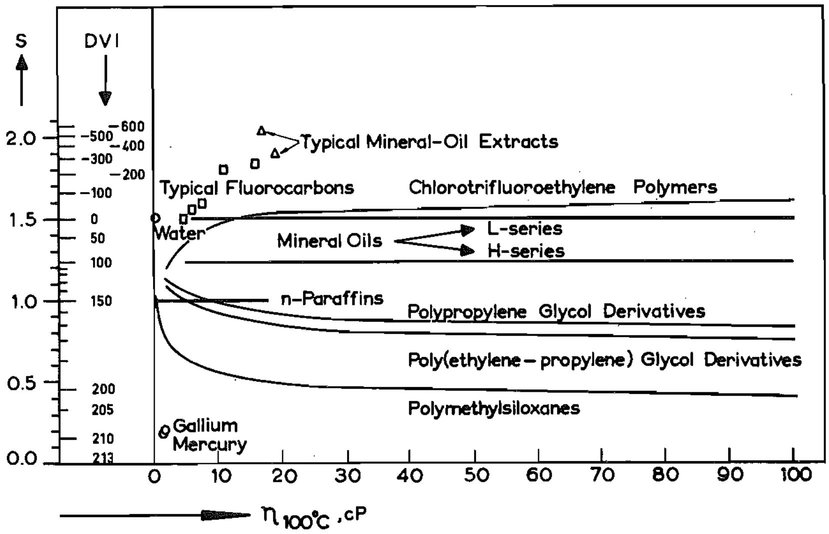

FIG. VI-3.

The New Viscosity-Temperature Criterion for Various Types of Oils.

namely water[79a] and the liquid metals gallium[78] and mercury[80].

For comparison, the horizontal parts of the lines referring to the H- and L-series of mineral oils*) and also the entire line for the n-paraffins have been replotted from Fig. VI-2. It appears that these three kinds of composite or pure hydrocarbon liquids occupy an intermediate position with respect to the Slope Indices or, what in essence amounts to the same thing, the Dynamic Viscosity Indices of the aforementioned non-hydrocarbon liquids.

Fig. VI-3 shows that in the range of higher viscosity grades each of the homologous groups of synthetic non-hydrocarbon oils under consideration has an approximately constant value that is characteristic of the entire homologous group concerned and does not depend on the particular member in the range under consideration. In the range of rather low viscosity grades, however, the differentiation as to Slope Indices, or DVI's, between the various types of liquids under consideration, including the hydrocarbon oils, becomes much

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*) Since several synthetic lubricating oils with relatively small viscosity-temperature dependence display considerably higher viscosity grades than the mineral oils normally encountered in lubrication practice, the lines for the H- and L-series as depicted in Fig. VI-3 have here been extrapolated somewhat beyond $\eta_{100°C}=65$ cP, the highest viscosity grade included in the ASTM standard table, that is up to $\eta_{100°C}=100$ cP.

less and even tends to vanish*) (compare also Fig. I-1).

Moreover, for several homologous groups of liquids the relevant curves prove to *intersect* somewhere in the range of low viscosity grades. This finding clearly demonstrates that a classification of a low-viscosity lubricating oil, belonging to some homologous group, according to its viscosity-temperature dependence need not invariably be quite so indicative of that group as the more viscous oils homologous to the fluid oil. In other words, it now appears that, unless the least viscous members are excluded, for arbitrary homologous groups of lubricating oils it is in general not possible to establish a viscosity-temperature criterion that would show one single value characteristic of the entire group considered. But for the sufficiently viscous members the Slope Index, or the Dynamic Viscosity Index derived from it, would appear to have a unique value that is typical of the homologous group concerned and certainly more so than the ASTM Viscosity Index.

VI.2.4. *Comparison Between DVI's and VI's of Various Types of Lubricating Oils*

Also from the commercial and the productional point of view it is worth-while to verify to what extent the DVI-values of the most important types of synthetic non-hydrocarbon lubricating oils and also those of polymer-blended mineral oils compare with their usually more or less erratic VI-values. For this purpose it is informative to distinguish between two ranges of viscosity grade, namely (see Fig. VI-2):

a. the range where the kinematic viscosity ν_{210^oF} exceeds about 7 cS (corresponding to a dynamic viscosity η_{100^oC} of 5 or 6 cP); and
b. the "transitional" range from about 7 cS down to 2 cS (the latter value corresponding to a dynamic viscosity η_{100^oC} of about 1.6 cP).

a. For the former viscosity range, that is the range where the aforementioned irregularities with relatively fluid oils are not yet inherent in the VI-system, the following conclusion can be upheld:

The real viscosity-temperature qualities of many synthetic oils as assessed from the magnitude of their temperature variation of dynamic viscosity are underrated, as compared with mineral oils, by the conventional VI-system. The underrating is more pronounced according as their DVI's and their viscosity grades are higher.

To support this conclusion two homologous groups of synthetic lubricating oils of which the temperature variation of both dynamic and kinematic viscosity is reputedly small, the commercially available (linear) polymethylsiloxanes and poly(ethylene-propylene) glycol derivatives, are put forward. Fig. VI-4 depicts the trends of their DVI's (see also Fig. VI-3) and VI's with varying viscosity grades. Obviously, except for the least viscous oils, the members of

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*) For the various groups of mineral oils this has already been shown in the preceding Fig. VI-2.

both groups of oils are strongly underrated by the conventional VI-system. Moreover, at higher viscosity grades their VI's continuously decrease, whereas, judging from the trend of their DVI's, their viscosity-temperature qualities actually increase, until they approximate a constant level.

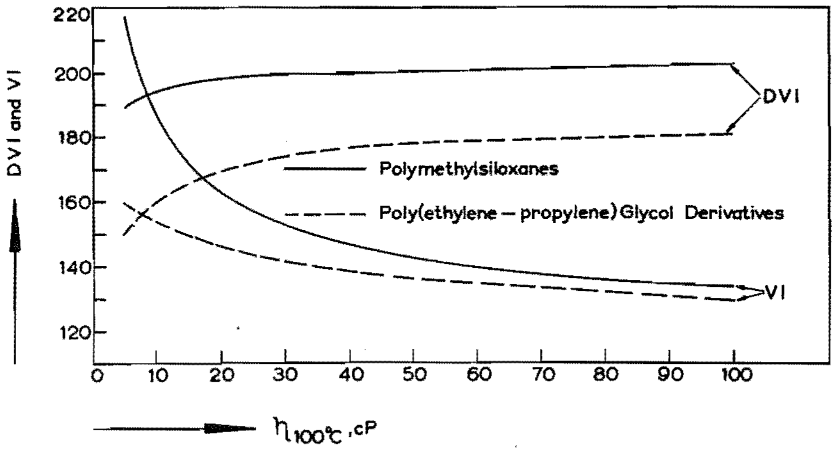

FIG. VI-4.

DVI and VI of Two Homologous Groups of Synthetic Lubricating Oils.

Such an underrating of the real viscosity-temperature qualities of oils by their conventional VI-values, as exemplified by Fig. VI-4, may even lead to the *ambiguities* known to be inherent in the VI-system. These ambiguities have already been discussed in § VI. 1. 2. In the relevant Table VI-1 such awkward ambiguities have been illustrated for two oils - one from either group depicted in Fig. VI-4, that is a (linear) polymethylsiloxane and a poly(ethylene-propylene) glycol derivative - that possess a common VI-value of 135, although their kinematic viscosity-temperature dependence differs considerably.

TABLE VI-5

Slope Index and DVI of Two Synthetic Oils Having a Common VI

Type of Oil	Kinematic and Dynamic Viscosities						S	DVI	VI
	100°F(37.8°C)		131°F(55°C)		210°F(98.9°C)				
	cS	cP	cS	cP	cS	cP			
Linear Polymethylsiloxane	247	236	183	172	99.5	90.4	0.41	202.0	135
Poly (ethylene-propylene) Glycol Derivative	333	347	183	189	58.1	57.9	0.77	179	135

Now, for the latter two oils the Slope Index and the Dynamic

Viscosity Index have been calculated and listed in Table VI-5. It is seen that the new criterion, either in terms of S or DVI, does differentiate between the two oils and, being related to *dynamic* viscosity, in a way that is really significant in lubrication practice.

A similar underrating by the VI-system, though not so pronounced as with the present two homologous groups of synthetic lubricating oils, is found amongst *polymer-blended* mineral oils with sufficiently high viscosities, that is with $\nu_{210^\circ F}$ exceeding about 7 cS. This may be exemplified by the data listed in Table VI-6 on six blends with varying "Paratone" (a mineral-oil solution of polyisobutylene) concentration derived from the same base stock[147].

Further, this table shows that, whilst the viscosity-temperature qualities expressed in terms of S or DVI increase regularly with increasing polymer concentration, the corresponding VI-values are misleasing in that they pass through a maximum.

TABLE VI-6

Slope Index, DVI and VI of Typical "Paratone"-Blended Mineral Oils

Polymer Concentration, Wt.%	$\eta_{100^\circ C}$, cP	S	DVI	VI
0	5.1	1.26	93	87
5	7.6	1.18	114	116
10	10.5	1.13	126	126
20	18.6	1.05	141	129
30	31.4	1.00	150	130
40	49.0	0.98	153	129
44	60.4	0.97	155	126

b. As regards the oils with viscosity grades $\nu_{210^\circ F}$ in the relatively low "transitional" range from about 7 cS down to 2 cS, the following conclusion can generally be upheld:

Conventional VI-values yield an exaggerated impression about the differentiation as to the real viscosity-temperature qualities of such oils, both mineral and synthetic.

This accrues from the aforementioned fact that, whilst the real viscosity-temperature qualities of the members of the basic H- and L-series of the VI-system approach each other closer and closer at viscosity grades $\nu_{210^\circ F}$ from about 7 cS downwards, these two qualities are nevertheless, rather arbitrarily, kept 100 points apart in the conventional VI-scale (compare Fig. VI-2).

It may be added that, as illustrated by Fig. VI-3, at viscosity grades $\nu_{210^\circ F}$ *below* 2 cS - which are not comprised by the ASTM tables - the differentiation as to Slope Indices, or DVI's, between the various types of liquids considered even tends to vanish.

Further, it may be recalled that the viscosity-temperature qualities of *mineral* oils with a kinematic viscosity $\nu_{210^\circ F}$ below about 7 cS are *underrated,* as compared with the more viscous members of the same naturally homologous group, in the conventional VI-system (see Fig. VI-2). This underrating is more pronounced according as the viscosity grade of the mineral oil considered is lower.

Finally, as has already been stated in § VI.1.2, the conventional VI is a clearly unfair viscosity-temperature criterion also for oils with densities differing considerably from those common for mineral oils, that is those lying above the range from 0.8 to 1.0 g/cm^3. The reason is that it is based on ***kinematic*** viscosity which contains density, a property that is irrelevant in normal lubrication practice. Misleading VI's are actually found with various types of synthetic lubricating oils. The examples in Table VI-7 are so illustrative because the densities are comparatively high, fluoro oils being involved.

If the aforementioned "density effect" is to be brought out separately, however, the DVI's and VI's may be directly compared only for the first two oils of this table. This accrues from the above conclusion that for the remaining two oils, having kinematic viscosities $\nu_{210^\circ F}$ below about 7 cS, an additional overrating of the differentiation according to viscosity-temperature qualities is inevitable with the VI-system. Therefore, the picture given by the VI becomes even more distorted with these last two oils.

TABLE VI-7

Slope Index, DVI and VI of Typical Fluoro Oils

Type of Oil	Ref.	$d_{210^\circ F}$, g/cm^3	$\nu_{210^\circ F}$, cS	$\eta_{100^\circ C}$, cP	S	DVI	VI
Fluorocarbon	143	1.85	9.05	15.96	1.84	-264	-674
Chlorofluorocarbon	144	1.831	15.0	26.2	1.54	- 23	-113
Fluorocarbon	72	1.903	3.28	6.03	1.56	- 34	-694
Chlorofluorocarbon	72	1.832	5.61	9.93	1.44	+ 27	-178

VI.2.5. *The New Viscosity-Temperature Criterion in Retrospect*

The simple and convenient Slope Index has proved significant for classifying, according to their temperature dependence of viscosity, all the various kinds of oils encountered in present lubrication practice.

The following features of the Slope Index may finally be emphasized:

1. *It dispenses with the ambiguities and irregularities inherent in the conventional VI-system and several other previous criteria.*
2. *The simplicity of its assessment would appear to be well-nigh unsurpassable, particularly if the relevant viscosity-temperaature chart is used.*
3. *It can be assessed from the viscosities at any two arbitrary temperatures, provided only that these are sufficiently widely*

spaced. This means that there is no need at all for prescribing standard reference temperatures and that international agreement as regards their levels and units, either deg C or deg F, is eliminated as a possible stumbling-block.

4. *Standard reference series of oils can be dispensed with altogether and thus another item of arbitrariness has been eliminated.*
5. *It is based on dynamic viscosity, which, in contrast to kinematic viscosity, is a really significant property both in the theory and practice of lubrication. Accordingly, there is no longer any masking effect of the irrelevant property of density.*
6. *The Slope Index may, if so desired, be converted into the Dynamic Viscosity Index. As regards dispensing with the ambiguities, the irregularities and the lack of significance inherent in the conventional VI-system, there are no essential differences between the Slope Index and the Dynamic Viscosity Index. However, if only for the time being, the DVI might perhaps be preferred to the Slope Index. In fact, in frequently coming close to the conventional VI the use of the DVI might well make for a smoother transition towards the ultimately proposed Slope-Index system for rating the temperature dependence of viscosity.*

VI.3. CONCLUDING REMARKS

VI.3.1. *The Relationship Between the Viscosity-Temperature Coefficient and the New Viscosity-Temperature Criterion*

The effect exerted by the variation of the viscosity of oils with temperature - the "temperature-viscosity effect" - on their hydrodynamic lubrication performance is usually treated in terms of the (atmospheric) *viscosity-temperature coefficient* β. This quantity is defined by:

$$\beta = -\frac{1}{\eta}\frac{\partial \eta}{\partial t} = -\frac{\partial \ln \eta}{\partial t}, \qquad \text{(VI-3)}$$

where ln stands again for the natural logarithm, $\log_e$. Accordingly, the viscosity-temperature coefficient β has a clear physical significance: it represents the relative change of viscosity per temperature unit. It has the dimension of a reciprocal temperature.

By differentiating the basic viscosity-temperature Equation (III-6b) with respect to temperature the following comparatively simple expression for β is readily obtained:

$$\beta = 2.303\ S\left(\frac{\log \eta + 1.200}{t + 135}\right), \qquad \text{(VI-4)}$$

where log denotes again the common logarithm, $\log_{10}$. From the latter equation it is seen that the viscosity-temperature coefficient generally varies rather rapidly with temperature. Therefore, for comparing the viscosity-temperature coefficients of oils some standard reference temperature has to be adopted. For example, at a standard reference temperature of 40°C (104°F), Equation (VI-4) reduces to:

$$\beta_{40^\circ C} = 1.316 \cdot 10^{-2} S \,(\log \eta_{40^\circ C} + 1.200) \qquad \text{(VI-5)}$$

As shown by Equation (VI-4), the new viscosity-temperature criterion, the ***Slope Index***, S, is related very simply to the viscosity-temperature coefficient, β (both quantities taken at atmospheric pressure). The relevant relationship is particularly convenient when oils of the same viscosity grade are considered. Denoting two *isoviscous* oils by the subscripts A and B, it is readily seen that:

$$\frac{S_A}{S_B} = \frac{\beta_A}{\beta_B} \; . \qquad \text{(VI-6)}$$

To put it into words: the ratio of the viscosity-temperature coefficients of oils having the same (specified) viscosity grade is given simply by their Slope-Index ratio. Accordingly, Equation (VI-6) would be very useful in the *selection* of oils, notably in the many cases where a certain viscosity grade has been prescribed and temperature varies considerably (see Section XIII. 2).

It may be added that an interesting simplification of Identity (VI-6) results if the n-paraffins - whose Slope Indices all happen to be unity - are taken as reference liquids. In that case Identity (VI-6) may be rewritten for an arbitrary oil with a viscosity-temperature coefficient β and a Slope Index S as:

$$S = \frac{\beta}{\beta_{Par}} \; , \qquad \text{(VI-7)}$$

where β_{Par} denotes the viscosity-temperature coefficient of the n-paraffin (either real or hypothetical) displaying the same viscosity grade as the oil considered.

Besides in the theory of hydrodynamic lubrication, the viscosity-temperature coefficient is widely employed in theoretical studies on the viscosity-temperature characteristics of liquids. Actually, in the latter studies the use of the closely related quantity E_{vis}, denoted by Eyring as the "activation energy for viscous flow", is frequently preferred (see § III. 1. 1). From the definitions of β and E_{vis} it follows that at any value of the absolute temperature T they are interrelated by the expression:

$$E_{vis} = RT^2\beta \; , \qquad \text{(VI-8)}$$

where R denotes again the molar gas constant.

In addition to its theoretical meaning in several models for viscous flow, the quantity E_{vis} has the practical advantage over the straightforward viscosity-temperature coefficient β that, at least in a moderate temperature range, it is relatively independent of temperature (compare § III. 1. 1).

According to Equation (VI-8), Identity (VI-6) may be rewritten in terms of E_{vis} as indicated by the following Equation (VI-9) which states that the ratio of the Slope Indices of oils displaying the same viscosity grade also equals the ratio of their activation energies for viscous flow:

$$\frac{S_A}{S_B} = \frac{(E_{vis})_A}{(E_{vis})_B} . \qquad \text{(VI-9)}$$

VI.3.2. *Further Information on the Slope Indices of Miscellaneous Liquids*

It may be emphasized that, whilst the Viscosity Index and most other previous criteria have been designed more or less specifically for petroleum-based lubricating oils, the present viscosity-temperature criterion has proved to apply to *any* type of liquid considered so far.

Moreover, the applicability of the new criterion holds irrespective of the particular temperature range where the substance under consideration occurs in the liquid state. On the other hand, quite apart from the other serious shortcomings of the conventional VI-system, this system obviously cannot be applied to substances that have solidified already at its lower standard reference temperature, that is 100°F (37.8°C). The latter point has become of increasing importance with the introduction of liquids developed specifically for modern high-temperature applications[23]. An example of such a liquid is provided by the polyphenyl ether depicted in Fig. III-3.

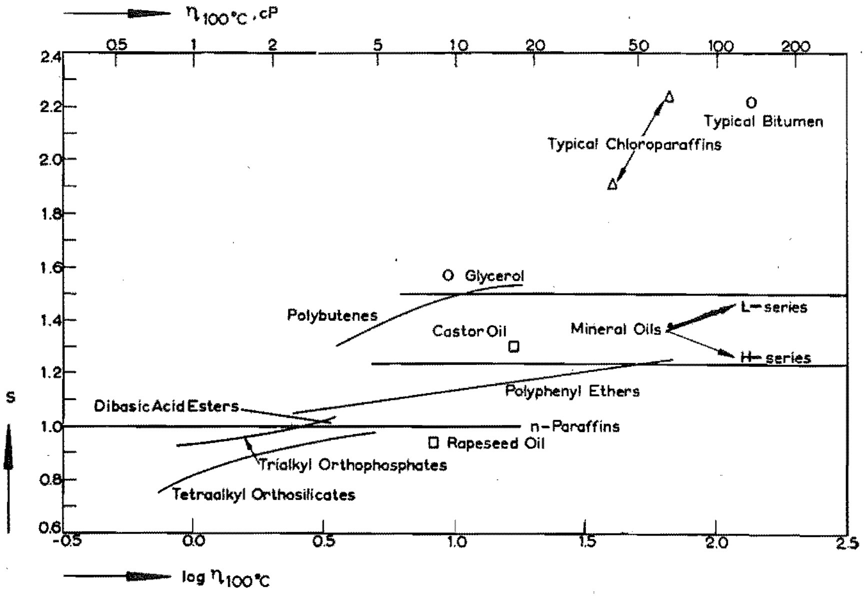

FIG. VI-5.
Slope Indices of Miscellaneous Liquids.

The latter figure and the related Fig. III-4 contain Slope Indices for various types of liquids not yet considered in the present chapter. In conclusion it is thought useful to present some further information on the Slope Indices of a number of miscellaneous liquids*), notably a few series of synthetic oils that have achieved considerable importance in current lubrication practice.

Therefore, in Fig. VI-5 the Slope Indices**) of a variety of liquids have been depicted as a function of their viscosity grades; for practical reasons the viscosity grade $\eta_{100^\circ C}$ has been plotted on a logarithmic scale. For comparison the horizontal parts of the lines referring to the H- and L-series of mineral oils and also the entire line for the n-paraffins have again been included (compare Figs. VI-2 and VI-3).

The depicted dibasic acid esters represent in order of increasing viscosity grade di(2-ethylhexyl)glutarate, -adipate, -azelate and -sebacate, respectively 148). The alkyl groups incorporated into the depicted trialkyl orthophosphates and tetra-alkyl orthosilicates range from n-butyl up to n-decyl and up to n-dodecyl, respectively 23c, 23d). Further, the (meta-linked, unsubstituted) polyphenyl ethers reproduced in Fig. VI-5 contain from 3 to 7 phenyl groups per molecule 23b). The fifth series of synthetic liquids is represented by polybutenes of comparatively low polymerization grade 27, 149).

Finally, individual points have been indicated for several interesting liquids, namely two typical chloroparaffins having a chlorine content of 60 and 70 wt.%, respectively 17); furthermore, a typical bitumen 74), glycerol 7) and two fatty oils, that is castor oil 111, 26) and rapeseed oil 113).

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*) In addition, the Slope Indices of a great variety of pure hydrocarbons are compiled in Table VIII-10 of § VIII.4.3.

**) Practically all these Slope Indices have been calculated from viscosities determined in the temperature range from about 20 to 120°C (68-248°F).

CHAPTER VII

A RATIONAL METHOD FOR CLASSIFYING LUBRICATING OILS ACCORDING TO THEIR VISCOSITY-PRESSURE RELATIONSHIP

VII. 1. INTRODUCTION

For several purposes it would appear highly desirable, or even necessary, to have available some simple, yet sufficiently quantitative, criterion of the viscosity-pressure dependence of liquids, in particular lubricating oils. Such a criterion, all by itself, should satisfactorily characterize the pressure effect on the viscosity grade of a given oil. In addition, for practical purposes it would be very alluring if this criterion had a *comparative* nature, in order that its value should be readily appreciated for any given oil irrespective of the viscosity grade involved.

In fact, such a viscosity-pressure criterion would be rather analogous to the viscosity-*temperature* criterion, the Slope Index, introduced in the preceding Chapter VI.

Now, it has been demonstrated in Chapter IV that, according to the new viscosity-pressure Equation (IV-5e), the pressure effect on the viscosity grade of a particular oil is sufficiently characterized by *one single* quantity, Z. Therefore, the quantity Z does constitute an accurate and convenient viscosity-pressure criterion.

Moreover, as will be shown below, the viscosity-pressure criterion Z may indeed be taken to possess the desired comparative nature. Consequently, the criterion Z should be very useful not only as a characterizing quantity but also for *classifying*, according to their pressure dependence of viscosity, all the various kinds of mineral oils considered - both natural and polymer-blended -, all the divergent types of synthetic lubricating oils tested and even all the other miscellaneous liquids investigated so far.

All in all, the new viscosity-pressure criterion Z, which has appropriately been termed the *"Viscosity-Pressure Index"*, may indeed be deemed to represent the viscosity-pressure *quality* of any given oil irrespective of its viscosity grade.

Just like the analogous Slope Index the Viscosity-Pressure Index can be assessed with a well-nigh unsurpassable simplicity, particularly if the relevant viscosity-pressure chart is employed (see § IV. 3. 1). Thus, the assessment of the unambiguous and straightforward Viscosity-Pressure Index involves neither standard reference pressures nor standard reference series of oils. Another important feature of the latter criterion consists in that it may be taken constant in a fairly wide temperature range without seriously interfering with the correlational accuracy of the basic Equation (IV-5e).

Finally, it may be remarked that the present field of viscosity-pressure criteria, in sharp contrast to the field of viscosity-temperature criteria (compare Chapter VI), has so far remained nearly untrodden. Accordingly, the introduction of the Viscosity-Pressure Index, in contradistinction to that of the Slope Index, will not be hampered by the wide familiarity with previous (unsatisfactory) criteria.

VII. 2. THE NEW VISCOSITY-PRESSURE CRITERION

VII. 2. 1. *The Classification of Oils by Means of the Viscosity-Pressure Index*

Owing to its very nature, the aforementioned classification of oils by means of the new viscosity-pressure criterion or any other criterion conceivable is bound to be a rather arbitrary matter. But the arbitrariness inherent in such a classification does not detract from its *practical* value. In this connection, reference may be made to the method developed in the preceding Chapter VI for classifying oils, according to their temperature dependence of viscosity, by means of the Slope Index.

The *classifying* ability of the Viscosity-Pressure Index, Z, has been derived from an empirical correlation between the viscosity-pressure dependence of *mineral* oils and their chemical constitution. Thus, it has been found that representative mineral oils with familiar viscosity-pressure characteristics may be taken to instill the desired comparative nature into the present Z-scale.

Since the latter correlation will be extensively discussed later on in § IX. 3. 2, the following notes may suffice here.

Adopting 40°C (104°F) as an arbitrary standard reference temperature, the Viscosity-Pressure Indices $Z_{40^\circ C}$ of a great variety of mineral oils have been plotted against their atmospheric viscosity functions $H_{0,40^\circ C}$. Using their total percentage of carbon atoms in ring structure, C_R, as a measure of the chemical constitution of mineral oils, a simple correlation has emerged which permits satisfactory predictions of their Viscosity-Pressure Index $Z_{40^\circ C}$ solely from this percentage C_R and their viscosity grade represented by $H_{0,40^\circ C}$. In fact, it has been found that, to a good approximation, for any series of mineral oils characterized by a common percentage C_R a linear relationship exists between the $Z_{40^\circ C}$-values and the $H_{0,40^\circ C}$-values of the members of such a series. In addition, it has appeared that for all the various series of mineral oils considered the relevant straight lines pass through one and the same point, so that they constitute a *fan*. As indicated in Fig. VII-1, the coordinates of this common point amount to $H_{0,40^\circ C} = 0.1400$, that is $\eta_{0,40^\circ C} = 1.51$ cP and to $Z_{40^\circ C} = 0.74$.

It is seen from the latter figure that within any given series of mineral oils having a common percentage C_R the Viscosity-Pressure Index $Z_{40^\circ C}$ will, in general, either increase or decrease with increasing viscosity grade. But there appears to be one particular *"transitional"* series, depicted by the horizontal line in Fig. VII-1, for which the Viscosity-Pressure Index is substantially constant. Accordingly, this transitional series, which proves to be characterized by a percentage C_R of 48, is also characterized by one single index, namely $Z_{40°C}$ = 0.74

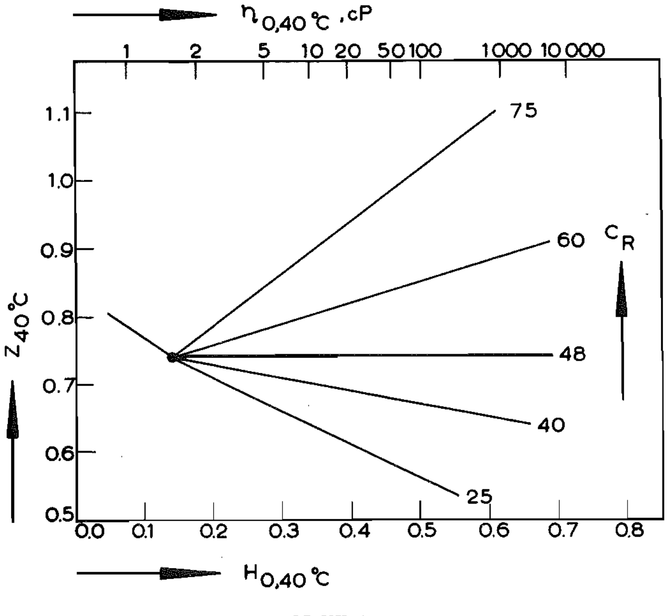

FIG. VII-1.
Correlation Between the Viscosity-Pressure Dependence of Mineral Oils and Their Chemical Constitution.

The indicated constancy of $Z_{40°C}$ for the series of mineral oils showing a common percentage C_R = 48 holds good over the entire viscosity range explored, that is down to $\eta_{0,40°C}$ = 1.51 cP, the aforementioned viscosity coordinate of the point of convergence in Fig. VII-1. For still lower viscosity grades there exists no longer any significant effect of the chemical constitution of mineral oils on their viscosity-pressure dependence, this being then solely determined by the viscosity grade of the very fluid oil considered. It may be added, however, that the latter viscosity grades are so very low that only occasionally they may become of practical importance.

On the basis of the correlation outlined the series of mineral oils characterized by a common percentage C_R of 48 may be considered to serve as a series of *standard reference oils* in the present classification system. It should be emphasized, however, that these reference oils are not needed at all in the assessment of the Viscosity-Pressure Index for a given oil.

It is deemed very desirable that these standard reference oils are represented by a series of mineral oils of a *"mixed"* type in that, with respect to their chemical constitution, they occupy an intermediate position as compared with paraffinic and pronounced naphthenic/aromatic oils. Conversely, therefore, the Viscosity-Pressure Index

$Z_{40^\circ C}$ of not too fluid oils provides, all by itself, some indication of their chemical constitution.

A further remarkable feature of the present standard reference oils consists in that the characteristic value, $Z_{40^\circ C} = 0.74$, established for their Viscosity-Pressure Indices at the adopted standard reference temperature of 40°C is not appreciably affected by temperature in the entire temperature range explored, that is from about 0 to 200°C (32-392°F). This finding leads up to the important conclusion that the present classification system remains equally valid at temperatures different from 40°C.

Summarizing, the present classification system has a sound and well-defined basis), which is closely connected with the chemical constitution of conventional mineral oils as expressed in terms of their carbon-type composition.*

VII. 2. 2. *The Viscosity-Pressure Indices of Various Types of Lubricating Oils and Miscellaneous Liquids*

In Fig. VII-2 the Viscosity-Pressure Indices**) $Z_{40^\circ C}$ of a great variety of lubricating oils and further liquids have been plotted against their viscosity grades as expressed in terms of the viscosity functions $H_{0,40^\circ C}$ (compare also Fig. 1-2).

First of all, three homologous groups of, commercially available, synthetic lubricating oils have been depicted. These groups - being the only ones for which the author could gather sufficient data - are represented by the technically important (linear) polymethylsiloxanes[9,17,27,48], polyglycols[150] and polybutenes[27,149]. Besides, the truly homologous group of pure n-paraffins[7,8,27,37,48,112] has been included. Remarkably enough, within each of the aforementioned homologous groups the Viscosity-Pressure Indices $Z_{40^\circ C}$ of the individual members proved to be linearly related - at least to a good approximation - to their viscosity grades $H_{0,40^\circ C}$. Accordingly, in Fig. VII-2 these four groups have been indicated by straight lines (see also § VII. 3. 3).

Furthermore, individual points have been depicted in Fig. VII-2 for a great variety of liquids, including several important types of synthetic lubricating oils. All these liquids are specified in Table VII-1.

For comparison, the range of Viscosity-Pressure Indices represented by all the various kinds of mineral oils investigated so far has been indicated by broken lines. In addition, the horizontal line for the standard reference oils, that is the group of mineral oils characterized by a common percentage C_R of 48, has been depicted

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*) It stands to reason that a classification based on a similar "homologous parallelism" as described for the Slope Index (see Chapter VI) would be conceivable only if for any mineral oil the Viscosity-Pressure Index would show invariably the same quantitative correlation with its Slope Index, irrespective of its viscosity grade. However, as will be extensively discussed in Chapter X, the viscosity-temperature-pressure characteristics of mineral oils cannot be reduced to such an idealized pattern.

**) Practically all these Viscosity-Pressure Indices have been assessed from experimental data for the pressure range up to 1,000-2,000 kgf/cm² (14,000-28,000 psi).

in the latter figure.

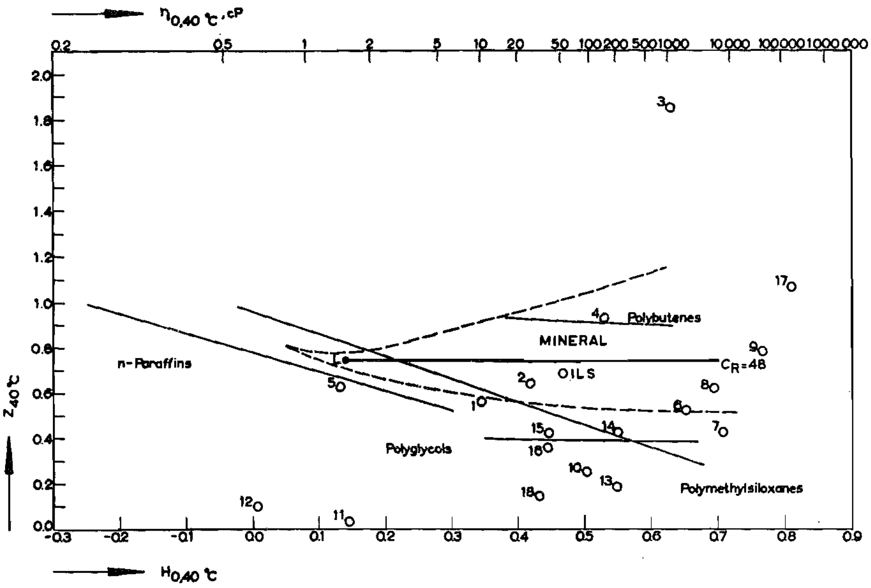

FIG. VII-2.
Viscosity-Pressure Indices of Various Types of Lubricating Oils and Miscellaneous Liquids.
For designations see Table VII-1.

It is seen from Fig. VII-2 that the Viscosity-Pressure Index may differ very widely from one liquid to another, particularly amongst the more viscous liquids. In the range of rather low viscosity grades, however, the differentiation as to Viscosity-Pressure Indices between the divergent types of liquids under consideration, including mineral oils, becomes much less and would even tend to vanish*).

VII. 3. THE TEMPERATURE VARIATION OF THE PRESENT VISCOSITY-PRESSURE CRITERION

VII. 3. 1. *Introduction*

As indicated before, the Viscosity-Pressure Index of a given liquid generally varies only comparatively slowly with temperature. In fact, as stated in Section V. 3, it may normally be taken constant in fairly wide ranges of temperature and pressure, say, from 20 to

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*) Obviously, water and mercury are outstanding in the latter respect. In fact, a similar exceptional behaviour of these liquids has previously been observed with regard to their Slope Indices (see Fig. VI-3).

120°C (68-248°F) and up to pressures of 2,000 kgf/cm^2 (28,000 psi), without markedly affecting the correlational accuracy of the basic Equation (IV-5e). This applies not only to mineral oils but also to all the various kinds of synthetic lubricating oils and additional liquids investigated so far.

TABLE VII-1

Designations to the Individual Liquids Depicted in Fig. VII-2

No.	Type of Liquid	Experimenters' Designation	Ref.
1	Diester	Di(2-ethylhexyl)sebacate, coded 1-A	27
2	ditto	o-Di(2-ethylhexyl)phthalate, coded 56-H	27
3	Fluorocarbon	Commercial Sample of a Fully Fluorinated Mineral Oil ("Perfluorolube")	48
4	Chlorofluorocarbon	Commercial Monochlorotrifluoroethylene Polymer, coded "Fluorolube Standard", 54-H	27
5	Silicate Ester	n-Butyl Orthosilicate	17
6	Polyalkylstyrene	Typical Sample	17
7	Polymethacrylate	ditto (Molecular Weight: abt. 30,000)	17
8	Chloroparaffin	Chlorinated Mixture of Paraffinic Hydrocarbons; Average Number of 14 Carbon Atoms per Molecule; Chlorine Content: 60 Wt.%	17
9	ditto	ditto; Chlorine Content: 70 Wt.%	17
10	Triethanol Amine	Pure Compound	13
11	Mercury	ditto	8
12	Water	"	7,8
13	Glycerol	"	7,8
14	Castor Oil	Commercial Sample ("Gilmore")	111,26
15	Rapeseed Oil	Typical Sample	113
16	Whale Oil	ditto	113
17	Bitumen	Non-Plastic Asphaltic Bitumen A (Soft)	74
18	Water-Glycol Fluid	Commercial Sample of a Water-Glycol Type Hydraulic Fluid, coded "Ucon M-1"	114a

But when a considerably wider temperature range is to be covered, it will usually be inevitable to account for the temperature variation of the Viscosity-Pressure Index. The determination or prediction of the latter variation is greatly facilitated by the validity of Equation (V-6a), which states that for any given liquid the Viscosity-Pressure Index, Z, varies linearly with the temperature function Θ or, what essentially amounts to the same thing, that Z varies linearly with the atmospheric viscosity function H_0. It may be recalled that the linearity between Z and H_0 implies that when the family of isotherms characterizing a given liquid is plotted in an H-Π chart, it is depicted as a fan, the viscosity-pressure pole being located either at very low or extremely high viscosities or, in the limiting case, at infinity.

For the present purpose of estimating the temperature variation of the Viscosity-Pressure Index it has proved convenient to distinguish between the group of mineral oils and other types of liquids.

VII. 3. 2. *Mineral Oils*

Plotting the Viscosity-Pressure Index, Z, against the atmospheric viscosity function H_0 yields, to a good approximation, a straight line for any individual mineral oil. Considering the straight Z-H_0 lines obtained for the great variety of mineral oils investigated, it is found that, again to a good approximation, all these lines converge towards one single point. The relevant point of convergence happens to coincide with the one indicated in Fig. VII-1, so that its coordinates amount to H_0=0.1400 (η_0=1.51 cP) and Z=0.74. The latter finding has been illustrated in Fig. VII-3, where every individual line would relate to a distinct mineral-oil.

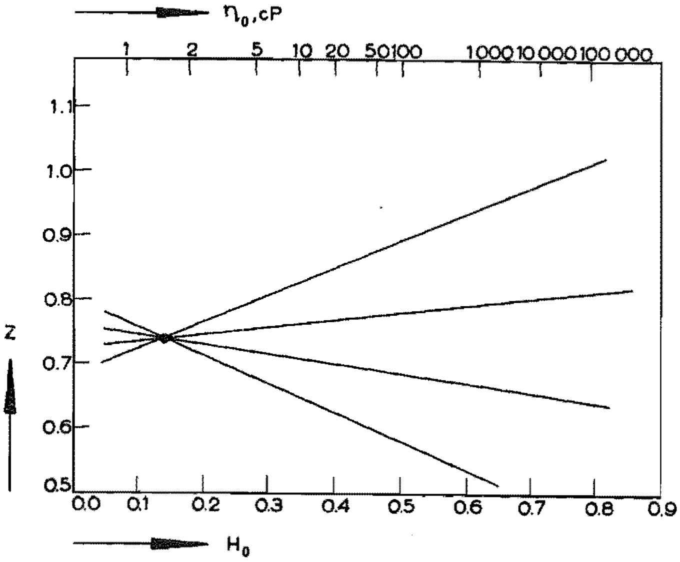

FIG. VII-3.
Correlation Between the Viscosity-Pressure Indices and Atmospheric Viscosities of Mineral Oils.

For the sake of clearness, the following remarks may be made.

a. In the first place it should be emphasized that, although both figures possess one and the same point of convergence, the validity of the convergence illustrated in Fig. VII-3 is essentially independent of the applicability of the particular correlation depicted in Fig. VII-1. But it is true that, according to the latter correlation, a given straight line in Fig. VII-3 is fully characterized solely by the percentage C_R of the mineral oil considered*). Accordingly, mineral oils will show the smaller temperature variation of their Viscosity-Pressure Index, the closer their percentage C_R approximates to the aforementioned value of 48.

b. In the second place it should be pointed out that the temperature variations of Z indicated in Fig. VII-3 are by no means in conflict with the foregoing statement that the Viscosity-Pressure Index of a given liquid may normally be taken constant in a fairly wide temperature range. Indeed, the latter variations of Z would be achieved only through very wide temperature variations, covering a range of at least some 200-300°C (360-540°F).

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*) It should be added that in accordance with Fig. VII-1 very fluid mineral oils with a viscosity grade $\eta_{0,40^\circ C}$ not exceeding 1.51 cP are depicted in Fig. VII-3 by one single straight line, irrespective of their percentage C_R.

Since for all the various kinds of mineral oils investigated so far the temperature variation of their Viscosity-Pressure Index has proved to follow the same simple pattern depicted in Fig. VII-3, the latter variation can readily be estimated solely from their atmospheric viscosity-temperature relationship.

Such estimates can be made either by means of Fig. VII-3 or by means of the following analytical expression for the fan-shaped family of straight lines indicated in this figure:

$$Z = Z_r - (Z_r - 0.74)\left(\frac{H_{0,r} - H_0}{H_{0,r} - 0.1400}\right), \qquad \text{(VII-1a)}$$

where Z_r and $H_{0,r}$ relate to the same standard reference temperature, for example 40°C. If it is preferred to introduce the standard reference temperature Θ_r into Equation (VII-1a), this may be rewritten as:

$$Z = Z_r + S_0\left(\frac{Z_r - 0.74}{H_{0,r} - 0.1400}\right)(\Theta - \Theta_r)\ . \qquad \text{(VII-1b)}$$

The Viscosity-Pressure Indices thus predicted will generally prove reliable over a temperature range extending from about 0 to 150°C (32-302°F) and up to pressures of at least 3,000 kgf/cm^2 (43,000 psi).

Finally, it may be remarked that the validity of Equation (VII-1a) or (VII-1b) permits a substantial simplification of the complete viscosity-temperature-pressure Equation (V-1a) if this is confined to mineral oils. This point will be elaborated in Section IX.2.

VII.3.3. *Synthetic Lubricating Oils and Miscellaneous Liquids*

In general, the temperature variation of the Viscosity-Pressure Index is characteristic of a particular liquid. Confining oneself to the members of a given *homologous group* of liquids, however, a simple interrelationship may be observed between the temperature variations of the Viscosity-Pressure Indices of these various members.

This interrelationship consists in that, to a good approximation, the various straight lines obtained in a Z-H_0 diagram, such as Fig. VII-3, for the individual members of a particular homologous group prove to overlap, so that they conform to *one* continuous straight line. The latter finding implies that in the basic H-Π chart the various families of isotherms - one family for every member of the homologous group - are depicted as one single fan. Consequently, for all the members of a homologous group displaying the aforementioned feature there is only *one* variable, namely the atmospheric viscosity.

Although the present feature need not invariably apply to any homologous group of liquids, it has proved to hold good at least for those homologous groups of synthetic lubricating oils for which the author could find sufficient experimental data. These are the homologous groups of (linear) polymethylsiloxanes, polyglycols and polybutenes. In addition, the latter feature has been found to apply well to the truly homologous series of pure n-paraffins.

The individual members included in each of these four homologous groups are identical to those employed for constructing the relevant $Z_{40^\circ C}$-$H_{0,40^\circ C}$ lines in Fig. VII-2*). The present finding implies that at temperatures different from 40°C the Viscosity-Pressure Indices of the individual members of the groups considered would likewise conform to the relevant straight-line relationships depicted in the latter figure.

VII. 4. THE RELATIONSHIP BETWEEN THE VISCOSITY-PRESSURE COEFFICIENT AND THE NEW VISCOSITY-PRESSURE CRITERION

The effect exerted by the variation of the viscosity of oils with pressure - the "pressure-viscosity effect" - on their hydrodynamic lubrication performance is usually treated in terms of the *viscosity-pressure coefficient* α occurring in the simple exponential Equation (IV-1a). In accordance with the latter equation this viscosity-pressure coefficient α can be defined by:

$$\alpha = \frac{1}{\eta}\frac{\partial\eta}{\partial p} = \frac{\partial \ln\eta}{\partial p}, \qquad \text{(VII-2)}$$

where ln stands again for the natural logarithm, $\log_e$. Thus, the viscosity-pressure coefficient α represents the relative change of viscosity per pressure unit (at some arbitrary reference temperature). It has the dimension of a reciprocal pressure.

However, this viscosity-pressure coefficient is not generally a unique measure of the (isothermal) viscosity-pressure dependence of a given oil, since it may still depend markedly on pressure (see Section IV. 1). In practice, the *atmospheric* viscosity-pressure coefficient, denoted by α_0, is frequently employed; that is the α-value determined for pressure p approaching zero. In accordance with Equation (VII-2) the quantity α_0 is defined by:

$$\alpha_0 = \left(\frac{1}{\eta}\frac{\partial\eta}{\partial p}\right)_0 = \left(\frac{\partial \ln\eta}{\partial p}\right)_0 . \qquad \text{(VII-3)}$$

It will be clear that, whilst for any given oil the atmospheric viscosity-pressure coefficient, α_0, does show a unique value, this can apply only as long as temperature is kept constant.

As regards the numerical evaluation of the atmospheric viscosity-pressure coefficient, α_0, the difficulty arises that the value assessed from an experimentally determined log η-p isotherm is highly sensitive, or even oversensitive, to inaccuracies in the experimental

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*) Likewise, the experimental data on these members derive from the investigations already cited in the discussion of Fig. VII-2 (§ VII. 2. 2).

viscosities. A similar difficulty is naturally encountered when the atmospheric viscosity-pressure coefficient is assessed by means of some analytical expression for the isotherm.

The relationship between the viscosity-pressure coefficient, α, and the new *Viscosity-Pressure Index*, Z, can be obtained by differentiating the basic viscosity-pressure Equation (IV-5b) with respect to pressure. By so doing one readily arrives at the expression:

$$\alpha = 1.151 \cdot 10^{-3} Z \, (\log \eta_0 + 1.200) \left(1 + \frac{p}{2,000}\right)^{Z-1}, \qquad \text{(VII-4)}$$

where log denotes again the common logarithm, $\log_{10}$. As stated above, the Viscosity-Pressure Index, Z, remains practically constant over a fairly wide temperature range, say, from 20 to 120°C (68-248°F). According to Equation (VII-4), the temperature variation of α over the latter range is then given implicitly by the atmospheric viscosity, η_0; in fact, with varying temperature the viscosity-pressure coefficient of a given oil would then change linearly with log η_0.

It should be noted that, whilst the actual (isothermal) viscosity-pressure coefficient is usually found to change rather rapidly in the pressure range up to, say, 1,000 kgf/cm^2 (14,000 psi) - a rapid *decrease* being frequently observed -, Equation (VII-4) allows for a more gradual change. The latter feature obviously accrues from the fact that in such cases the analytically adjusted isotherms represented by the basic Equation (IV-5b) display a somewhat smoother trend - for instance in a log η-p diagram - than the experimentally determined viscosity-pressure curves.

Accordingly, the viscosity-pressure coefficient obtained from Equation (VII-4) by substituting the value p=0 will usually differ more or less (beyond the experimental inaccuracy) from the actual *atmospheric* viscosity-pressure coefficient, α_0, defined by Equation (VII-3). Whereas at first sight this might seem a drawback of Equation (VII-4), it readily turns out to constitute an advantage rather than a drawback. The reason is that, whilst the actual atmospheric viscosity-pressure coefficient, α_0, usually appears to be representative of the isothermal viscosity-pressure dependence of a given oil up to only about 200-300 kgf/cm^2 (about 3,000-4,000 psi), the value derived from Equation (VII-4) has proved to be representative of this dependence up to considerably higher pressures, normally up to at least 1,000 kgf/cm^2 (14,000 psi).

Consequently, the latter α-value may generally be considered much more appropriate than α_0. In order to distinguish between these two viscosity-pressure coefficients the former will be termed the *"initial"* viscosity-pressure coefficient, denoted by α_i. Its definition is seen to read:

$$\alpha_i = 1.151 \cdot 10^{-3} Z \, (\log \eta_0 + 1.200). \qquad \text{(VII-5)}$$

The aforementioned discrepancy between α_0 and α_i has been illustrated in the schematic Fig. VII-4, notably for the frequently observed type of a slightly concave downward log η-p isotherm. This figure clearly demonstrates that α_i may indeed be claimed representative of the viscosity-pressure dependence of the depicted oil over a considerably wider pressure range than α_0. In fact, α_i is seen to represent some averaged value of the actual viscosity-pressure coefficients, α, encountered throughout the latter pressure range.

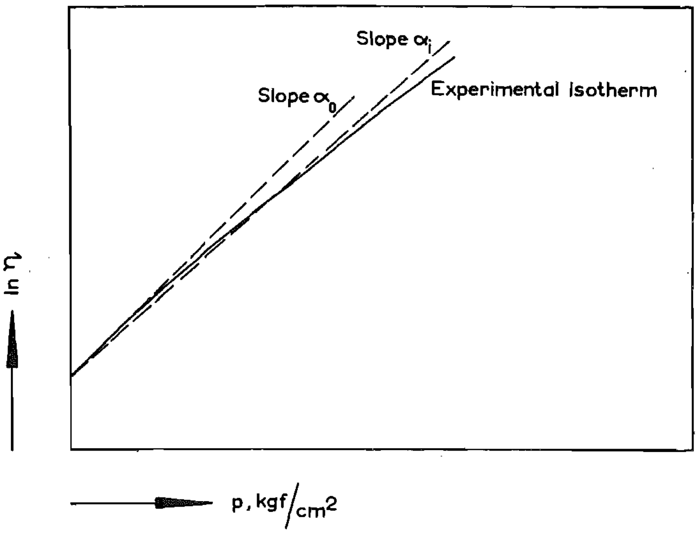

FIG. VII-4.
Schematic Representation of Atmospheric and Initial Viscosity-Pressure Coefficient.

As shown by Equation (VII-5), the new viscosity-pressure criterion, the Viscosity-Pressure Index, Z, is related very simply to the initial viscosity-pressure coefficient, α_i. The relevant relationship is particularly convenient when oils of the same viscosity grade are considered. Denoting two *isoviscous* oils by the subscripts A and B, it readily follows from Equation (VII-5) that:

$$\frac{Z_A}{Z_B} = \frac{(\alpha_i)_A}{(\alpha_i)_B} , \qquad \text{(VII-6)}$$

irrespective of the particular reference temperature. To put it into words: the ratio of the initial viscosity-pressure coefficients of oils having the same (specified) viscosity grade is given simply by the ratio of their Viscosity-Pressure Indices. Accordingly, Equation (VII-6) would be very useful in the *selection* of oils, notably in those cases where a certain viscosity grade has been prescribed and pressure varies considerably (see Section XIII. 2).

Besides in the theory of hydrodynamic lubrication, the viscosity-pressure coefficient is widely employed in theoretical studies on the viscosity-pressure characteristics of liquids. Actually, in the latter studies the use of some closely related quantity will frequently be preferred. In Eyring's theory of viscous flow the quantity V_{vis} would be representative of the isothermal viscosity-pressure dependence of liquids (see Section IV. 1). From their definitions it can readily be derived that at any (absolute) temperature T the quantity V_{vis} and the viscosity-pressure coefficient α_i would be interrelated by the expression:

$$V_{vis} = RT\alpha_i \, , \tag{VII-7}$$

where R denotes again the molar gas constant.

In accordance with the latter expression Equation (VII-6) may be rewritten in terms of V_{vis} as:

$$\frac{Z_A}{Z_B} = \frac{(V_{vis})_A}{(V_{vis})_B} \, , \tag{VII-8}$$

so that the ratio of the Viscosity-Pressure Indices of oils displaying the same viscosity grade also equals the ratio of their V_{vis}-values.

CHAPTER VIII

THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP OF MINERAL OILS: CORRELATION WITH CHEMICAL CONSTITUTION AND PHYSICAL CONSTANTS

VIII. 1. INTRODUCTION

VIII. 1. 1. *Previous Investigations*

Because of the considerable practical importance associated with the atmospheric*) viscosity-temperature relationship of mineral oils (see Chapter I), numerous investigators have attempted to elucidate its correlation with the chemical constitution as well as with various physical properties of the oil.

Most of the relevant studies have aimed at conveniently predicting the Viscosity Index**) (VI) of mineral oils either from their chemical constitution of from easily assessable physical constants. Amongst these studies two in particular have achieved very interesting results. Both started already in the early thirties in the scope of pioneering works on the chemical constitution of mineral oils, namely by Waterman's school in Holland (part A, below) and by Fenske's in the United States (part B, below).

More recently (1957), Cornelissen - likewise from Waterman's school - developed a remarkable correlation which, unlike the aforementioned ones, aims at predicting the analytically defined *kinematic* viscosity-temperature relationship of mineral oils rather than their VI (part C, below).

A. CORRELATIONS DEVELOPED BY WATERMAN AND ASSOCIATES

In the scope of their aforementioned investigations into the chemical constitution of mineral oils (see § II. 2. 2 and § XI. 4. 1) Waterman and his associates have devoted much attention to the correlation between, on the one hand, the viscosity-temperature relationship of such oils and, on the other hand, both their chemical constitution and various physical constants. These investigators considered primarily *saturated,* that is aromatic-free, mineral-oil fractions.

They succeeded in establishing a very good correlation, issued in graphical form, for estimating the VI of saturated mineral-oil fractions from their specific refraction - built up from refractive index and density - and their molecular weight 46). This correlation

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*) Throughout the present chapter the viscosity-temperature relationship invariably relates to atmospheric pressure; for convenience, however, the term "atmospheric" has usually been omitted.

**) The Viscosity Index has been discussed in § VI. 1. 2.

proved very satisfactory for the various fractions tested, covering VI's from about -40 to +130.

Afterwards[50b)], they found that the combination of specific refraction and molecular weight utilized in the latter correlation could be conveniently replaced by *one single* correlational variable, namely the total number of rings per average molecule*). This simplified version - indicating a VI-decrease with increasing ring number - is especially remarkable in that, as far as the author is aware, it constitutes the first reliable correlation that could be developed between the viscosity-temperature characteristics of saturated mineral oils and their chemical constitution. The validity of this correlation, however, has been verified only for higher ring numbers, that is from about 2.0 to 4.0; the corresponding VI's ranged again from about -40 to +130.

Waterman and his associates have further attempted to extend the applicability of the first version of their correlation - the one involving the specific refraction and molecular weight as variables - so as to include *natural*, that is aromatic-containing, mineral-oil fractions as well as *saturated* fractions for which it was originally developed[46)]. On the analogy of the idea underlying their "revised ring analysis"[50)] they achieved a tentative correlation using the aniline point as a third variable. Unfortunately, this extended correlation was stated to hold only to a rather rough approximation.

Finally, the latter investigators have tried - it would appear on the basis of the above-described correlation between the VI and the ring number of saturated mineral-oil fractions - to correlate the VI of *natural* mineral oils with their "carbon distribution". The relevant attempts, however, have remained rather unsuccessful[50b)].

B. McCLUER AND FENSKE'S CORRELATION

Whereas Waterman and his associates based their correlational attempts on *saturated* mineral oils, McCluer and Fenske started directly from *natural* mineral oils[151)]. They achieved an attractive correlation, issued in graphical form, for predicting the VI of such oils from only *two* physical constants: the kinematic viscosity at 100°F (37.8°C) and the specific gravity at 60°F (15.6°C). This correlation has been checked for over a hundred mineral-oil fractions of various compositions - including *saturated* samples - with VI's ranging from about -10 to +125 and with viscosities at 40°C (104°F) from about 20 to 600 cP [corresponding to kinematic viscosities at 210°F (98.9°C) from about 4 to 32 cS]. In all cases considered it has proved to permit safe predictions of the VI. Many mineral-oil fractions encountered in practice, however, display viscosities and/or VI's considerably below the aforementioned values. Consequently, McCluer and Fenske's otherwise attractive correlation would need at least substantial extension towards lower viscosities as well as lower VI's.

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*) It is interesting to note that in the original "ring analysis"[50)] this total number of rings per average molecule is determined from the two aforementioned quantities, that is the specific refraction and the molecular weight.

C. CORNELISSEN'S CORRELATION

In contradistinction to the preceding correlations, Cornelissen's correlation has been based on an analytical expression for the *kinematic* viscosity-temperature relationship of mineral oils, and not on their VI [40]. His correlation, which was developed exclusively for *natural* mineral oils, requires a knowledge of *three* easily measurable physical constants: kinematic viscosity, density and refractive index - all three constants being taken at a standard reference temperature of 20°C (68°F).

From the meager test results presented it would appear that Cornelissen's correlation does permit good predictions for natural mineral-oil fractions throughout the (kinematic) viscosity range for which it has been designed. Unfortunately, the latter range is comparatively small, dynamic viscosities at 40°C (104°F) extending from about 1 up to only 30 cP.

Apart from its very limited applicability, Cornelissen's correlation is afflicted with two *basic* shortcomings.

a. The first basic shortcoming concerns the analytical expression serving as a basis to this correlation. This particular expression is given by Equation (III-3) if the *kinematic* viscosity is substituted for the dynamic viscosity. Whilst the basic expression of Cornelissen's correlation thus contains *three* characteristic parameters, it has been shown in Chapter III that only *two* are really required for describing the viscosity-temperature relationship of mineral oils - and likewise any other type of liquid considered so far - with an accuracy that leaves very little to be desired. The latter statement applies the more so as the temperature range covered in Cornelissen's investigation was rather narrow, for most oils extending from 20 to 70°C (68-158°F). Consequently, the correlation based on the aforementioned three-parameter expression was bound to become unnecessarily cumbersome.

b. The second basic shortcoming of Cornelissen's correlation concerns the number of physical constants (three) employed. Indeed, as will be demonstrated in Section VIII. 3, either the density or the refractive index can be dispensed with as a correlational variable. Thus, even apart from the aforementioned inconvenience of the kinematic viscosity-temperature expression employed, Cornelissen's correlation could have been put into a substantially simplified form.

All in all, it has appeared that Cornelissen's correlation has been cast into a form that is basically too complicated and unnecessarily cumbersome, the more so as its applicability has been confined to very limited viscosity and temperature ranges.

VIII. 1. 2. *The Present Approach*

As indicated above, most of the previous correlational attempts employed the VI as a measure of the kinematic viscosity-temperature dependence of mineral oils. However, even if it is confined to mineral oils, the VI is afflicted with a few serious shortcomings, which have already been discussed in Chapter VI. In the present connection its main shortcoming consists in the use of standard reference temperatures. In fact, the VI solely defines - and yet in implicit form - the relationship between the kinematic viscosities of a given oil at its two standard reference temperatures, 100 and 210°F (37.8 and 98.9°C). Consequently, it is very inconvenient to evaluate the kinematic viscosity-temperature *relationship* of a mineral oil whose VI has been given in addition to its kinematic viscosity grade.

Obviously, a straightforward method for predicting the viscosity-temperature relationship of mineral oils should be based on some convenient analytical expression for describing the latter relationship over a wide temperature range. In this respect Cornelissen has taken a more appropriate starting-point than the other aforementioned investigators. Unfortunately, as stated above, Cornelissen's basic (kinematic) viscosity-temperature equation has proved to be insufficiently convenient in that it requires *three* characteristic parameters.

The newly developed viscosity-temperature Equation (III-6h) is very attractive in that it requires the minimum number of only *two* parameters for fully characterizing, over a very wide temperature range, the viscosity-temperature relationships of mineral oils - and likewise of all the other kinds of liquids investigated so far. In fact, apart from the viscosity grade of a given liquid, its *Slope Index* remains the only parameter to be considered.

Consequently, on the basis of Equation (III-6h) the problem of predicting the viscosity-temperature relationships of mineral oils is reduced to that of predicting their Slope Indices.

In accordance with the foregoing statements the present approach aims at achieving more satisfactory correlations than the available ones by taking the new Equation (III-6h) as a starting-point. In fact, it has been attempted to develop really satisfactory correlations for predicting the Slope Indices of mineral oils from their viscosity grade and either their chemical constitution or easily assessable physical constants.

Experimental Data

The results of the present study are based on reliable experimental data on no less than 360 mineral-oil fractions. As regards their origin and chemical composition these fractions may be considered representative of the entire range of *natural* mineral oils known so far. In addition, the fully *hydrogenated* samples of 100 natural fractions have been included.

Table VIII-1 lists the various investigations from which these basic data have been taken. Most of these oils constitute part of Waterman's collection and have been the subject of extensive investigations, of various kinds, carried out at the Laboratory for Chemical Technology of the Technological University of Delft. Of the indicated total of 247 oils taken from Waterman's collection 50 representative samples will feature below.

The viscosity grades $\eta_{40^\circ C}$ *) and the Slope Indices, S*), of the

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*) For convenience the subscript "0" - relating to atmospheric pressure - has been omitted from the viscosities and Slope Indices occurring in this chapter (compare the first footnote).

latter 50 oils from Waterman's collection and the remaining 113 oils of Table VIII-1 are compiled in Table VIII-2. All these oils have been specified already in Table II-1, where their chemical composition is characterized in terms of the n-d-M method and where several appropriate physical data are collected. For further particulars concerning the data of Table II-1 reference may be made to the relevant explanation given in Chapter II.

TABLE VIII-1

Specification of Mineral Oils Included in the Present Investigation

Investigation	Ref.	Number of Oils
Waterman et al.	38-44	247
Fenske et al.	45	73
van Westen et al.	46	17
ASME	27	16
André and O'Neal	47	7
	Total	360

As regards the Slope Indices listed in Table VIII-2 it should be pointed out that these have invariably been determined from the viscosity data available in the temperature range between 20 and 100°C (68 and 212°F) and in most cases from those measured at 100 and 210°F (37.8 and 98.9°C).

VIII. 2. CORRELATION WITH CHEMICAL CONSTITUTION

VIII. 2. 1. *Introduction*

A quantitative correlation between the viscosity-temperature relationship of mineral oils and their chemical constitution would be very desirable not only for prediction purposes but also for getting a better understanding of the underlying regularities. In fact, in the latter respect the chemical constitution of the oils may be deemed more informative than individual physical constants.

Of course, for correlational purposes "chemical constitution" must be sufficiently characterized in both convenient and significant terms. As described in § II. 2. 2, the chemical constitution of mineral oils can suitably be characterized in terms of the "Waterman analysis". For the present correlational purpose it has proved very fruitful to express their chemical constitution in terms of the carbon-type composition as determined by means of the n-d-M method. Accordingly, the percentages C_A, C_N and C_P have been employed, that is the percentages of the total number of carbon atoms that occur in aromatic-ring, naphthenic-ring and paraffinic-chain structures,

TABLE VIII-2

Experimental and Predicted Slope Indices of Representative Mineral Oils

Oil Code*)	Experimental Data		Slope Indices Predicted from η_{40^oC} Plus			
	η_{40^oC}, cP	S	C_R	d_{40^oC}	n_{40^oC}	M
W-4	2.82	1.05	1.02	1.03	1.04	1.02
W-4H	2.72	1.05	1.02	1.02	1.01	0.98
WR-7	8.79	1.12	1.12	1.13	1.14	1.10
WR-7H	7.96	1.10	1.11	1.09	1.09	1.08
WR-11	1.493	0.98	0.98	0.98	0.98	0.98
W-17	5.68	1.20	1.18	1.19	1.21	1.20
W-17H	4.86	1.14	1.15	1.13	1.11	1.17
WR-18	9.12	1.21	1.26	1.28	1.28	1.28
WR-18H	7.10	1.14	1.22	1.18	1.15	1.22
W-25	6.17	1.17	1.12	1.13	1.13	1.11
W-25H	5.52	1.14	1.11	1.08	1.08	1.09
WR-26	13.46	1.21	1.19	1.21	1.22	1.19
W-32	1.563	0.96	0.98	0.98	0.98	0.98
W-32H	1.622	0.97	0.98	0.98	0.98	0.98
WR-34	2.40	0.99	1.01	1.01	1.01	1.01
WR-41	3.30	1.02	1.04	1.04	1.05	1.04
W-43	7.59	1.09	1.11	1.12	1.14	1.10
W-43H	6.56	1.11	1.10	1.08	1.08	1.04
W-54	3.41	1.08	1.06	1.08	1.08	1.08
W-54H	3.30	1.06	1.05	1.04	1.04	1.05
WR-56	7.14	1.11	1.15	1.17	1.17	1.14
WR-56H	6.50	1.11	1.14	1.12	1.10	1.11
W-58	1.109	0.94	0.96	0.96	0.96	0.96
W-58H	1.194	0.96	0.96	0.96	0.96	0.96
W-66	4.70	1.07	1.06	1.08	1.08	1.00
W-66H	4.49	1.06	1.05	1.04	1.05	0.97
WR-67	6.58	1.06	1.07	1.08	1.11	1.01
WR-69	1.556	0.99	0.98	0.98	0.98	0.98
W-71	8.09	1.25	1.19	1.20	1.19	1.22
W-71H	6.12	1.18	1.15	1.12	1.10	1.13
W-74	1.042	0.94	0.95	0.95	0.95	0.95
W-74H	1.092	0.96	0.95	0.95	0.95	0.95
WR-76	1.683	0.99	0.99	0.99	0.99	0.99
WR-79	4.48	1.07	1.07	1.07	1.08	1.09
WR-80	5.68	1.11	1.11	1.13	1.13	1.11
WR-81	11.54	1.18	1.16	1.18	1.20	1.17
W-90	4.86	1.10	1.09	1.09	1.09	1.10
W-90H	4.49	1.09	1.08	1.06	1.06	1.04
WR-91	7.87	1.11	1.13	1.14	1.15	1.14
WR-91H	6.79	1.08	1.12	1.09	1.09	1.06
W-94	0.897	0.94	0.93	0.93	0.93	0.93
W-94H	0.895	0.93	0.93	0.93	0.93	0.93
WR-97	2.31	1.01	1.01	1.01	1.01	1.01
WR-99	3.33	1.04	1.04	1.04	1.05	1.01
W-103	8.17	1.14	1.12	1.14	1.15	1.11
W-103H	7.14	1.10	1.11	1.08	1.09	1.06

CONTINUATION OF TABLE VIII-2

Oil Code*)	Experimental Data		Slope Indices Predicted from η_{40^oC} Plus			
	η_{40^oC}, cP	S	C_R	d_{40^oC}	n_{40^oC}	M
W-107	0.834	0.94	0.93	0.93	0.93	0.93
W-108	6.58	1.16	1.11	1.13	1.14	1.09
W-109	1.021	0.95	0.94	0.94	0.94	0.94
W-110	7.38	1.16	1.11	1.14	1.15	1.09
F-1	31.0	1.22	1.20	1.21	1.25	1.20
F-2	11.62	1.18	1.15	1.18	1.18	1.10
F-3	13.71	1.19	1.16	1.18	1.19	1.14
F-4	15.81	1.20	1.17	1.18	1.19	1.15
F-5	17.50	1.20	1.17	1.18	1.20	1.16
F-6	19.01	1.20	1.17	1.19	1.20	1.16
F-7	20.5	1.21	1.18	1.19	1.21	1.18
F-8	22.0	1.21	1.18	1.19	1.22	1.18
F-9	22.9	1.21	1.17	1.19	1.22	1.17
F-10	24.9	1.21	1.18	1.19	1.22	1.18
F-11	27.0	1.22	1.18	1.19	1.23	1.19
F-12	29.2	1.22	1.19	1.20	1.24	1.20
F-13	30.8	1.22	1.19	1.20	1.25	1.20
F-14	33.5	1.23	1.19	1.21	1.18	1.21
F-15	35.6	1.23	1.20	1.21	1.26	1.21
F-16	38.2	1.23	1.19	1.21	1.26	1.22
F-17	41.0	1.24	1.20	1.21	1.27	1.22
F-18	44.7	1.24	1.20	1.21	1.28	1.23
F-19	48.5	1.24	1.21	1.21	1.28	1.23
F-20	53.1	1.24	1.20	1.21	1.28	1.23
F-21	61.0	1.25	1.21	1.22	1.28	1.23
F-22	65.8	1.24	1.21	1.22	1.29	1.22
F-23	31.1	1.23	1.22	1.23	1.27	1.20
F-24	17.95	1.21	1.20	1.22	1.23	1.16
F-25	35.5	1.24	1.22	1.23	1.27	1.20
F-26	40.8	1.24	1.22	1.24	1.29	1.21
F-27	47.2	1.25	1.23	1.25	1.30	1.21
F-28	90.0	1.37	1.38	1.39	1.41	1.37
F-29	150.3	1.43	1.41	1.43	1.43	1.42
F-30	196.8	1.43	1.42	1.44	1.45	1.44
F-31	272	1.42	1.42	1.44	1.44	1.44
F-32	327	1.40	1.41	1.42	1.43	1.44
F-33	49.8	1.31	1.29	1.32	1.36	1.30
F-34	12.50	1.23	1.24	1.25	1.24	1.27
F-35	16.48	1.25	1.26	1.27	1.26	1.26
F-36	20.3	1.27	1.25	1.28	1.28	1.26
F-37	23.3	1.28	1.26	1.28	1.29	1.26
F-38	26.4	1.28	1.27	1.28	1.30	1.27
F-39	29.5	1.29	1.26	1.29	1.31	1.27
F-40	33.3	1.30	1.27	1.30	1.31	1.27
F-41	37.2	1.31	1.27	1.30	1.32	1.28
F-42	46.7	1.32	1.29	1.32	1.34	1.30
F-43	51.5	1.33	1.30	1.32	1.35	1.30

CONTINUATION OF TABLE VIII-2

Oil Code*)	Experimental Data		Slope Indices Predicted from $\eta_{40^\circ C}$ Plus			
	$\eta_{40^\circ C}$, cP	S	C_R	$d_{40^\circ C}$	$n_{40^\circ C}$	M
F-44	56,9	1,33	1,30	1,32	1,35	1,31
F-45	62,2	1,34	1,30	1,32	1,36	1,31
F-46	69,3	1,34	1,31	1,33	1,36	1,33
F-47	75,9	1,34	1,31	1,32	1,37	1,33
F-48	84,9	1,34	1,31	1,32	1,37	1,35
F-49	94,2	1,34	1,32	1,32	1,37	1,36
F-50	104,5	1,34	1,33	1,32	1,37	1,38
F-51	67,0	1,44	1,44	1,46	1,46	1,45
F-52	6,90	1,19	1,20	1,19	1,17	1,19
F-53	163,3	1,56	1,53	1,54	1,52	1,55
F-54	273	1,60	1,56	1,59	1,55	1,57
F-55	454	1,63	1,61	1,62	1,56	1,59
F-56	14,09	1,27	1,31	1,31	1,28	1,29
F-57	18,20	1,30	1,33	1,33	1,31	1,29
F-58	23,1	1,33	1,35	1,35	1,33	1,33
F-59	29,0	1,35	1,36	1,37	1,35	1,34
F-60	33,9	1,36	1,36	1,37	1,36	1,35
F-61	39,4	1,38	1,38	1,38	1,38	1,36
F-62	45,4	1,39	1,39	1,39	1,39	1,38
F-63	52,0	1,40	1,39	1,40	1,40	1,39
F-64	60,3	1,42	1,41	1,40	1,41	1,40
F-65	70,8	1,43	1,41	1,42	1,42	1,40
F-66	83,4	1,45	1,43	1,43	1,44	1,42
F-67	100,0	1,47	1,45	1,45	1,44	1,45
F-68	122,8	1,49	1,47	1,46	1,45	1,46
F-69	150,3	1,51	1,50	1,48	1,45	1,48
F-70	188,4	1,53	1,51	1,50	1,46	1,51
F-71	231	1,55	1,54	1,52	1,47	1,53
F-72	275	1,56	1,55	1,53	1,48	1,55
F-73	316	1,56	1,57	1,54	1,48	1,56
We-1	86,9	1,18	1,21	1,24	1,29	1,22
We-1H	72,3	1,17	1,21	1,17	1,21	1,20
We-2	87,5	1,36	1,37	1,37	1,39	1,34
We-2H	55,5	1,28	1,33	1,28	1,27	1,27
We-3	252	1,63	1,62	1,68	1,66	1,61
We-3H	80,4	1,43	1,51	1,41	1,35	1,44
We-4	150,0	1,41	1,39	1,43	1,45	1,41
We-4H	71,1	1,32	1,34	1,28	1,26	1,30
We-5	69,2	1,30	1,28	1,28	1,29	1,26
We-5H	54,4	1,26	1,27	1,23	1,24	1,22
We-6	40,7	1,21	1,23	1,22	1,26	1,21
We-6H	39,9	1,22	1,23	1,20	1,21	1,28
We-7	31,8	1,18	1,17	1,16	1,19	1,13
We-8	151,0	1,44	1,39	1,46	1,50	1,43
We-9	135,2	1,40	1,38	1,42	1,45	1,40
We-10	115,1	1,38	1,35	1,36	1,37	1,36
We-11	108,5	1,37	1,34	1,34	1,36	1,33

CONTINUATION OF TABLE VIII-2

Oil Code*)	Experimental Data		Slope Indices Predicted from $\eta_{40^\circ C}$ Plus			
	$\eta_{40^\circ C}$, cP	S	C_R	$d_{40^\circ C}$	$n_{40^\circ C}$	M
A-1	25.1	1.21	1.20	1.19	1.20	1.17
A-2	7.30	1.15	1.17	1.12	1.15	1.20
A-3	41.1	1.26	1.20	1.24	1.29	1.18
A-4	129.4	1.26	1.24	1.25	1.26	1.23
A-5	438	1.28	1.29	1.32	1.33	1.30
A-6	138.7	1.25	1.25	1.24	1.25	1.23
A-7	120.5	1.25	1.26	1.28	1.31	1.25
A-8	119.7	1.21	1.20	1.22	1.23	1.21
A-9	38.9	1.26	1.19	1.23	1.28	1.17
A-10	44.7	1.39	1.37	1.37	1.37	1.34
A-11	117.5	1.49	1.47	1.47	1.44	1.45
A-12	403	1.60	1.62	1.60	1.52	1.59
A-13	119.4	1.50	1.49	1.50	1.47	1.48
A-14	117.5	1.47	1.47	1.51	1.47	1.43
A-15	58.2	1.37	1.35	1.30	1.26	1.29
A-16	501	1.77	1.76	1.78	1.76	1.72
AN-1	43.8	1.26	1.24	1.22	1.26	1.23
AN-2	43.8	1.26	1.21	1.22	1.26	1.21
AN-3	41.9	1.22	1.22	1.22	1.27	1.20
AN-4	69.5	1.36	1.35	1.31	1.30	1.32
AN-5	93.5	1.43	1.43	1.39	1.39	1.45
AN-6	31.0	1.19	1.23	1.20	1.24	1.31
AN-7	53.1	1.37	1.38	1.35	1.36	1.41

*) Refers to similarly coded oils specified in Table II-1.

respectively[*]).

The range of carbon-type compositions covered by all the various kinds of mineral oils employed in the present study has been indicated in the triangular diagram of Fig. VIII-1. In fact, these oils

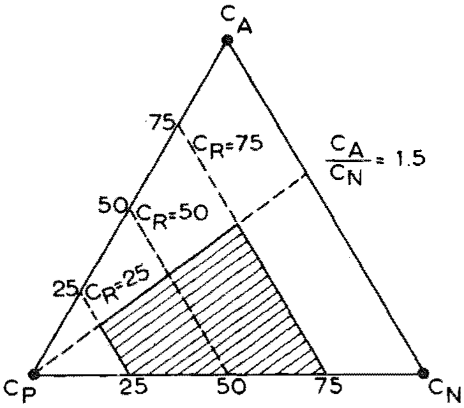

FIG. VIII-1.
Carbon-Type Composition of Mineral Oils.

cover practically the entire range where the n-d-M method may be applied. Expressed in terms of their total percentage of carbon atoms in ring structure, C_R, the compositions of the mineral oils included in the present study are seen to vary from about 25 to 75. Accordingly, the latter oils are indeed representative of the entire range of mineral oils known so far; besides, the same extensive range of C_R-values is covered by the hydrogenated samples included in this investigation.

Finally, it may be recalled that the carbon percentages employed constitute approximate - and not necessarily exact - figures (compare § II. 2. 3). The latter point should not be overlooked in criticizing the accuracy of any correlation based on them.

VIII. 2. 2. *The New Correlation*

From an extensive analysis of experimental data on the 163 mineral-oil fractions collected in Table VIII-2 the conclusion has emerged that, to a good approximation, the Slope Index belonging to a mineral-oil fraction with a given viscosity grade is fixed *uniquely* by its carbon-type composition. Moreover, it has been found that, remarkably enough, it is immaterial whether the carbon atoms present in ring structure are contained in naphthenic or aromatic rings.

Accordingly, in the relevant correlation solely the *total* percentage

---

[*]) Since the carbon percentages C_A, C_N and C_P are interrelated - their sum being of necessity 100 -, only two of them need to be taken into consideration. The author prefers to use the percentages C_A and C_N, their sum, C_R, representing the total percentage of carbon atoms in ring structure.

of carbon atoms in ring structure*), C_R, is utilized as a sufficiently accurate measure of the chemical constitution, or rather the carbon-type composition, of the mineral oils under consideration.

Plotting the Slope Indices of all the various oils considered against their viscosity functions H at the arbitrarily adopted standard reference temperature**) of 40°C (104°F) and using their percentage C_R as a parameter has yielded the correlation depicted in Fig. VIII-2. This correlation implies a straight-line relationship between the Slope Index, S, and the viscosity function $H_{40^\circ C}$ for mineral oils having a common percentage C_R. Moreover, the resulting straight lines form a *fan*. Their point of convergence, in Fig. VIII-2 denoted by K, has the coordinates $H_{40^\circ C} = 0.2000$ - corresponding to a viscosity $\eta_{40^\circ C} = 2.43$ cP - and S = 1.01.

Remarkably enough, for mineral oils with viscosity grades below this *"transitional"* viscosity $\eta_{40^\circ C} = 2.43$ cP the percentage C_R is no longer an influential quantity, their Slope Indices being a function solely of their viscosity grades (compare § VI.2.1 and particularly Fig. VI-2). The Slope Indices of such unusually fluid oils appear to be closely scattered around a single straight line. In fact, this line has proved to constitute the produced part of the bottom line of the depicted fan, that is the one referring to $C_R = 25$.

An interesting feature of the correlational diagram of Fig. VIII-2 consists in that it traces the approximate "natural boundaries" imposed on the Slope Indices encountered amongst natural mineral oils - obtained by conventional refining methods - from all the divergent sources investigated so far. Indeed, the great variety of Slope Indices found amongst the mineral oils occurring in nature may be considered to be located between the two outmost straight lines of the fan depicted, that is those relating to $C_R = 25$ and $C_R = 75$.

It stands to reason that the convergence of the various straight lines relating to constant percentages C_R does not actually proceed so abruptly as indicated in Fig. VIII-2. In fact, this convergence has so been approximated only in order that the underlying correlation may be cast into a simple mathematical form. Nevertheless, the final correlation has proved to hold good even in the vicinity of the point of convergence.

The family of straight lines depicted in Fig. VIII-2 can be represented by the following analytical expression:

$$S = 1.01 + 3.0 \cdot 10^{-2} (C_R - 7)(H_{40^\circ C} - 0.2000). \quad \text{(VIII-1a)}$$

According to Equation (VIII-1a), the slope of these straight lines varies linearly with the percentage C_R.

The expression for the straight line indicated for the range of very low viscosity grades can readily be obtained by substituting the value $C_R = 25$ into Equation (VIII-1a). The resulting expression

---

*) It stands to reason that the percentage of paraffinic carbon atoms, C_P, may be used instead of C_R, their interrelationship reading $C_R = 100 - C_P$.

**) It may already be remarked here that it would not make any essential difference if the reference temperature were fixed at another value somewhere in the conventional temperature range.

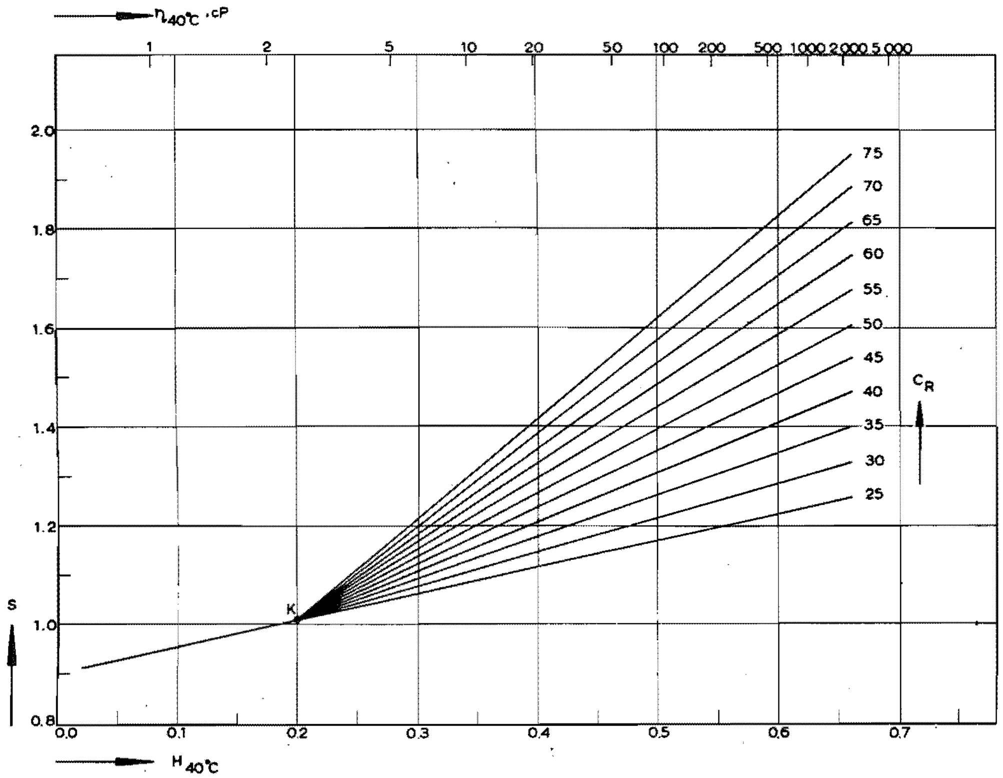

FIG. VIII-2.
Correlation Between the Viscosity-Temperature Relationship of Mineral Oils and Their Percentage of Carbon Atoms in Ring Structure.

reads:

$$S = 1.01 + 0.54\ (H_{40^\circ C} - 0.2000). \qquad \text{(VIII-1b)}$$

On the basis of its analytical Expression (VIII-1a) the new correlation may further be cast into a more *general* form. That is Expression (VIII-1a) can be generalized such that it may be directly applied at any *arbitrary* reference temperature instead of only at the adopted standard reference temperature of 40°C. This can be performed as follows. From the basic viscosity-temperature Equation (III-6h) it can readily be derived that for a given oil*):

$$H_{40^\circ C} = H - S\ (\Theta + 0.1127). \qquad \text{(VIII-2a)}$$

Substituting the latter expression for $H_{40^\circ C}$ into Equation (VIII-1a) the following *generalized* correlation for the Slope Index can be obtained:

$$S = \frac{1.01 + 3.0 \cdot 10^{-2}\ (C_R - 7)\ (H - 0.2000)}{1.00 + 3.0 \cdot 10^{-2}\ (C_R - 7)\ (\Theta + 0.1127)}. \qquad \text{(VIII-3a)}$$

The interrelationship between Correlations (VIII-1a) and (VIII-3a) may be brought out somewhat more clearly by rearranging the latter correlation as follows:

$$S = 1.01 + \frac{3.0 \cdot 10^{-2}\ (C_R - 7)}{1.00 + 3.0 \cdot 10^{-2}\ (C_R - 7)\ (\Theta + 0.1127)} \Big[H - 0.2000 - 1.01\ (\Theta + 0.1127)\Big]. \qquad \text{(VIII-3b)}$$

It is important to note that Correlations (VIII-3a) and (VIII-3b) represent the complete viscosity-temperature relationship - according to the basic Equation (III-6h) - of any mineral oil in terms of its Slope Index, S, and its percentage C_R*, the latter quantity being taken as some measure of its chemical constitution. Consequently, if only one viscosity value - at some arbitrary reference temperature - of the mineral oil is known, its percentage* C_R*, all by itself, determines its complete viscosity-temperature relationship.*

Applicability

The new correlation in the form of Equation (VIII-1a) has been checked for all the aforementioned 360 mineral-oil fractions (see § VIII. 1. 2).

For each of the 163 fractions - both natural and hydrogenated - collected in Table VIII-2 the predicted Slope Indices have been listed

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*) As stated before, throughout this chapter the subscript "0" - relating to atmospheric pressure - has been omitted.

TABLE VIII-3

Distribution of Deviations Between Experimental and Predicted Slope Indices Amongst the 360 Oils Tested

Deviation $\|\delta S\|$	Percentage of the 360 Oils Tested			
	Correlation Employing η_{40^oC} Plus ...			
	C_R	d_{40^oC}	n_{40^oC}	M
0.00	14.8	19.0	13.3	16.2
0.01	31.7	28.4	37.1	21.1
0.02	22.9	27.0	15.7	20.1
0.03	14.1	13.0	10.2	14.4
0.04	6.6	4.7	6.9	6.4
0.05	6.3	1.9	6.1	7.7
0.06	1.7	4.4	5.5	1.7
0.07	0.3	1.6	1.9	8.2
0.08	1.6		2.8	2.2
0.09				1.6
0.10				
0.11			0.5	
0.12				0.3
Average Deviation *)	0.020	0.019	0.023	0.027
Standard Deviation **)	0.026	0.025	0.032	0.036

*) Defined by $\frac{1}{n}\sum_{i=1}^{i=n}|\delta_i|$ **) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n}\delta_i^2}{n-1}}$

in that table. In addition, Table VIII-3 indicates the distribution of the deviations between experimental and predicted Slope Indices amongst the really great variety of the 360 oils tested.

The latter table shows that the ***absolute*** average and standard deviations in the Slope Index amount to no more than 0.020 and 0.026 units, respectively, which figures are only slightly beyond the accuracy inherent in the experimentally derived Slope Indices. These absolute deviations correspond to ***relative*** average and standard deviations in the predicted Slope Indices of only 1.7 and 2.2%, respectively.

It may further be pointed out that, as shown by Equation (VI-4), the ***relative*** accuracy inherent in the predicted Slope Index equals that in the corresponding viscosity-temperature coefficient, β.

In order to give some idea of the relative errors that may occur in the viscosities proper if these are calculated from the basic viscosity-temperature Equation (III-6h) by using the Slope Indices predicted from the present correlation, Table VIII-4 has been prepared. For a wide range of viscosity grades η_{40^oC} this table shows

TABLE VIII-4

Effect of a Deviation of 0.02 Units in Their Slope Index on the Predicted Viscosity $\eta_{100^\circ C}$ of a Great Variety of Oils

$\eta_{40^\circ C}$, cP	$C_R = 50$			DVI = 100 (S = 1.234)		DVI = 0 (S = 1.497)	
	S	$\eta_{40^\circ C}/\eta_{100^\circ C}$	$\lvert \%\delta\eta_{100^\circ C} \rvert$ *)	$\eta_{40^\circ C}/\eta_{100^\circ C}$	$\lvert \%\delta\eta_{100^\circ C} \rvert$	$\eta_{40^\circ C}/\eta_{100^\circ C}$	$\lvert \%\delta\eta_{100^\circ C} \rvert$
1	0.94	1.959	1.2				
2	1.00	2.41	1.5				
5	1.11	3.39	1.8				
10	1.19	4.50	2.1	4.69	2.1		
20	1.27	6.01	2.4	5.79	2.4		
50	1.35	8.93	2.7	7.66	2.7	10.86	2.6
100	1.40	12.16	3.0	9.46	3.0	13.93	2.9
200	1.45	16.60	3.2	11.70	3.4	17.82	3.2
500	1.51	25.4	3.5	15.45	3.7	24.7	3.5
1,000	1.56	35.1	3.8	19.10	4.0	31.7	3.8
2,000	1.59	48.8	4.1	21.9	4.4	40.5	4.1
5,000	1.64	76.0	4.4	31.3	4.8	56.1	4.4

*) $\lvert \%\delta\eta \rvert = 100 \dfrac{\lvert \eta_{pred} - \eta_{exp} \rvert}{\eta_{exp}}$

the percentage errors in the corresponding viscosities $\eta_{100^\circ C}$ that would result from a deviation of 0.02 units in the Slope Index of the oil considered. In addition, the appropriate Slope Indices, S, and viscosity ratios $\eta_{40^\circ C}/\eta_{100^\circ C}$ have been included in the latter table. Three distinct cases have been considered: first, the case where the percentage C_R of all the oils included amounts to 50, the appropriate Slope Indices being defined by Correlation (VIII-1a); further, the cases where the DVI[*] of all these oils amounts to 100 (S = 1.234) and to 0 (S = 1.497), respectively. Since both latter S-values are not found amongst relatively fluid mineral oils (see Fig. VIII-2), the pertinent data have been omitted from Table VIII-4.

The latter table shows that for a constant deviation between experimental and predicted Slope Indices the *relative* errors in the predicted viscosities $\eta_{100^\circ C}$ increase regularly with increasing viscosity grade of the oils. It may be added that for a given viscosity grade these relative errors increase nearly proportionally to the difference between experimental and predicted Slope Indices. For example when this difference amounts to 0.04 units, the percentage errors listed in Table VIII-4 also increase by a factor of nearly two.

As regards the percentage deviations collected in the latter table it is only fair that these be considered in connection with the really great viscosity variations involved.

For properly judging or criticizing the accuracy achieved with the present correlation it may further be useful to mention that the various viscosity deviations listed in Table VIII-4 would be fully compensated at the standard reference temperature of 100°C (212°F) by a *temperature* difference amounting to no more than about 1.0°C (1.8°F). The latter figure may well go to emphasize the wide practical usefulness of the new correlation.

Summarizing, it may be stated that the present correlation permits good viscosity predictions in a wide temperature range. For normal purposes these predictions will generally turn out satisfactory at least in the conventional temperature from, say, 20 to 150°C (68-302°F). In fact, even in the entire temperature range of general practical interest extending from, say, 0 to 200°C (32-392°F) will the results normally prove quite acceptable.

VIII.2.3. *Additional Applications*

A. THE ATMOSPHERIC ISOBAR POLE LINE

A very interesting mathematical consequence of the validity of the correlation described in the preceding § VIII.2.2 has been elaborated in Appendix VIII-1, at the end of this chapter. This mathematical consequence consists in that the atmospheric viscosity-temperature isobars of mineral oils having a common percentage C_R are depicted in the basic H-Θ chart as a *fan*.

Thus, these rectified viscosity-temperature isobars pass through a common point, which is termed the *"atmospheric isobar pole"*.

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[*] The DVI has been introduced in § VI.2.2.

Accordingly, any member of the fan of straight *lines* depicted in Fig. VIII-2 corresponds with one single *point* - the particular atmospheric isobar pole - in the basic H-Θ chart. More particularly this finding implies that all the various kinds of very fluid mineral oils, that is those oils whose viscosity grade $\eta_{40^\circ C}$ does not exceed 2.43 cP ($H_{40^\circ C} \leqslant 0.2000$), possess the same pole as the more viscous oils having a common percentage C_R of 25.

Moreover, as also shown in the aforementioned Appendix VIII-1, the various *poles* in the H-Θ chart are located on one single straight line, which is termed the *"atmospheric isobar pole line"*. Its equation reads:

$$H_a = 1.01\ \Theta_a + 0.3138, \qquad \text{(VIII-4)}$$

where H_a and Θ_a denote the coordinates of the various poles located on this pole line.

TABLE VIII-5

Atmospheric Isobar Poles for Three Typical C_R-Values

C_R	Pole Viscosity		Pole Temperature	
	H_a	η_a, cP	Θ_a	t_a, °C
25	-1.6667	0.066	-1.9607	12,000 (22,000°F)
50	-0.5814	0.115	-0.8862	900 (1,650°F)
75	-0.2941	0.203	-0.6018	405 (760°F)

As stated above, the coordinates of the atmospheric isobar poles - whose locus is defined by Expression (VIII-4) - are a function solely of the percentage C_R. The relevant simple Equations (VIII-5a) and (VIII-6a) given in Appendix VIII-1 may be rewritten as:

$$H_a = -\frac{33.7}{C_R - 7} + 0.2000 \qquad \text{(VIII-5b)}$$

and

$$\Theta_a = -\frac{33.3}{C_R - 7} - 0.1127. \qquad \text{(VIII-6b)}$$

For three typical C_R-values the coordinates of the atmospheric isobar poles are listed in Table VIII-5.

Thus, these poles are situated in the region of very low viscosities and extremely high temperatures. Therefore, they can have neither practical nor physical significance.

Apparently, the present *"pole concept"* is very useful for further elucidating the nature of the correlation achieved. In fact, the Slope Index of any mineral oil can now also be expressed in terms of the pole coordinates, H_a and Θ_a, as follows:

$$S = \frac{H - H_a}{\Theta - \Theta_a} . \qquad \text{(VIII-7)}$$

If the appropriate expressions for the pole coordinates, that is Equations (VIII-5b) and (VIII-6b), are substituted into Equation (VIII-7), the latter equation becomes identical with Correlations (VIII-3a) and (VIII-3b).

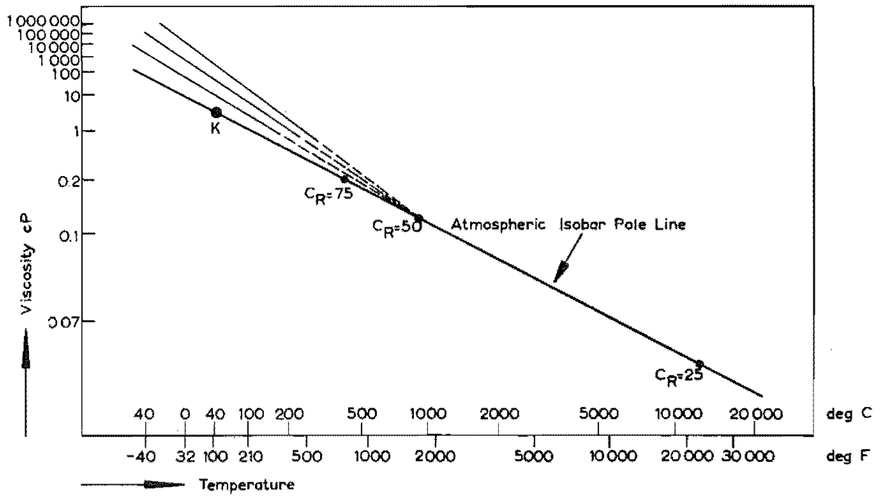

FIG. VIII-3.
The Atmospheric Isobar Pole Line of Mineral Oils.

The atmospheric isobar pole line defined by Expression (VIII-4) has been depicted in Fig. VIII-3. A few members of the fan of isobars relating to C_R = 50 have also be drawn.

For the sake of clearness, it may be added that in Fig. VIII-3 the isobars of all mineral oils whose viscosity grade $\eta_{40^\circ C}$ exceeds 2.43 cP ($H_{40^\circ C} > 0.2000$) would be located *above* the pole line. In contrast, for all mineral oils with viscosity grades smaller than the latter value the isobars would be located *below* the depicted pole line; furthermore, all these isobars would converge towards one and the same pole relating to C_R = 25.

Oils with a "transitional" viscosity $\eta_{40^\circ C}$ = 2.43 cP would display a common Slope Index, namely S = 1.01, which is identical with that of the atmospheric isobar pole line. Moreover, since their viscosity grade - denoted by point K in Fig. VIII-3 - is located on this very pole line, their isobars *coincide* with the latter line, thus satisfying the underlying Equation (VIII-4). Therefore, the transitional viscosities, η_K, for temperatures different from 40°C can readily be calculated from Equation (VIII-4). It may be recalled that these η_K-values have practical significance in that they indicate, at each temperature involved, the approximate *upper* level of the viscosity range where the chemical constitution of mineral oils has no longer

TABLE VIII-6

"Transitional" Viscosity η_K as a Function of Temperature

Temperature		Viscosity η_K, cP
deg C	deg F	
0	32	7.24
20	68	3.90
40	104	2.43
70	158	1.42
100	212	0.95
120	248	0.77
150	302	0.59
200	392	0.42

any appreciable effect on their Slope Indices.

Accordingly, for mineral oils with a given viscosity grade not exceeding the values listed in Table VIII-6 there is no longer any practical sense in specifying anything at all with respect to the differentiation as to their viscosity-temperature dependence.

B. PREDICTING THE EFFECT OF HYDROGENATION ON THE VISCOSITY-TEMPERATURE RELATIONSHIP OF NATURAL MINERAL OILS

It is a well-known fact that, as a rule, *hydrogenation* of natural mineral oils raises their Viscosity Index; or, more generally, that it affects their viscosity-temperature dependence in a favourable manner.

It has appeared that the above-described correlation lends itself very well to a nearer analysis of the consequent effect. It stands to reason that the present analysis will be confined to the effect of the so-called *analytical*, or non-destructive, hydrogenation. In that case the only change brought about in the carbon-type composition of a natural mineral oil consists in the conversion of aromatic into the corresponding naphthenic carbon atoms; or, more precisely, the *decrease* in the percentage of carbon atoms in aromatic-ring structure, C_A, equals the *increase* in the percentage of carbon atoms in naphthenic-ring structure, C_N, their sum C_R remaining constant.

From the constancy of C_R it follows that within the accuracy of the present correlation the effect of hydrogenation on the viscosity-temperature relationship of a given natural mineral oil is determined *solely* by the accompanying change in its viscosity *grade*.

Consequently, the problem of predicting the difference in Slope Index between a given natural mineral-oil fraction and its fully - or partly - hydrogenated sample has been reduced to that of predicting the difference between their viscosity grades. Besides, a fortunate circumstance consists in that the latter difference need not be predicted with great accuracy. The reason is that - as may readily be seen from Fig. VIII-2 - for any constant C_R-value the Slope Index

changes only comparatively slowly with varying viscosity grade.
It has now been attempted to estimate this difference between the viscosity grades of a natural mineral-oil fraction and its hydrogenated sample solely from the *difference* in their carbon-type composition. Since only *fully* hydrogenated, that is *saturated*, mineral-oil fractions have been taken into consideration, the latter statement means that only the C_A-value of the original sample has been used as a correlational variable.

By means of the appropriate data on a representative group of 100 natural mineral-oil fractions and their saturated samples the author has indeed succeeded in establishing a convenient correlation which permits a fairly accurate prediction of the *viscosity grade*

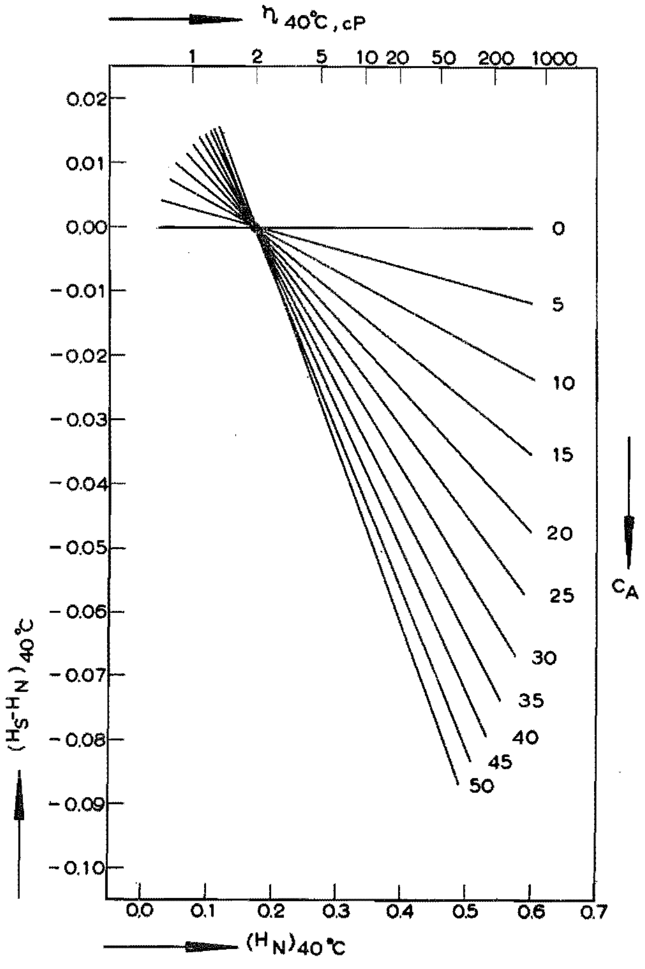

FIG. VIII-4.
Correlation Between the Viscosity Grades of Natural Mineral Oils and Their Saturated Samples.

TABLE VIII-7

Experimental and Predicted Viscosities and Slope Indices of Representative Saturated Mineral Oils

Original Fraction		Saturated Sample			
Oil Code*)	$\eta_{40^\circ C}$, cP Exp.	$\eta_{40^\circ C}$, cP		Slope Index	
		Exp.	Pred.	Exp.	Pred.
W-1	1,205	1,225	1,242	0,96	0,96
W-2	1,574	1,552	1,600	0,99	0,98
W-3	2,09	2,08	2,09	1,01	1,00
W-4	2,82	2,72	2,75	1,06	1,02
W-5	4,15	3,90	3,94	1,08	1,05
W-6	5,85	5,27	5,36	1,11	1,08
WR-7	8,79	7,74	7,67	1,10	1,10
W-8	13,24	11,12	11,24	1,18	1,13
W-9	23,3	19,06	18,66	1,18	1,16
W-10	1,242	1,306	1,256	0,94	0,96
WR-11	1,493	1,521	1,455	0,96	0,97
W-12	1,706	1,742	1,862	0,97	0,99
W-13	1,964	2,02	1,964	0,99	0,99
W-14	2,30	2,29	2,26	1,01	1,00
W-15	2,73	2,70	2,61	1,02	1,02
W-16	4,02	3,59	3,53	1,05	1,08
W-17	5,68	4,86	4,59	1,14	1,14
WR-18	9,12	6,93	6,40	1,14	1,20
W-19	20,6	12,85	11,72	1,33	1,30
W-21	1,159	1,180	1,180	0,97	0,96
W-22	1,496	1,500	1,514	0,98	0,98
W-23	2,19	2,19	2,36	1,02	1,00
W-24	3,55	3,35	3,42	1,08	1,05
W-25	6,17	5,52	5,55	1,14	1,10
WR-26	13,46	10,33	10,47	1,22	1,17
W-27	28,6	20,4	20,7	1,28	1,23
W-28	68,4	39,0	41,6	1,34	1,28
W-29	1,042	1,114	1,135	0,94	0,95
W-30	1,186	1,262	1,271	0,95	0,96
W-31	1,343	1,406	1,422	0,95	0,97
W-32	1,563	1,622	1,626	0,97	0,98
W-33	1,778	1,770	1,811	0,98	0,99
WR-34	2,40	2,28	2,26	1,00	1,00
W-36	12,47	10,05	9,22	1,09	1,14
W-37	1,038	1,064	1,076	0,95	0,95
W-38	1,306	1,343	1,340	0,96	0,97
W-40	2,32	2,27	2,29	1,00	1,00
WR-41	3,30	3,14	3,12	1,04	1,03
W-42	4,92	4,50	4,55	1,07	1,07
W-43	7,59	6,56	6,73	1,11	1,10
W-45	0,865	0,918	0,904	0,96	0,94
W-46	0,935	0,975	0,977	0,95	0,94
W-47	1,052	1,086	1,094	0,95	0,96

CONTINUATION OF TABLE VIII-7

Original Fraction		Saturated Sample			
Oil Code*)	η_{40^oC}, cP Exp.	η_{40^oC}, cP		Slope Index	
		Exp.	Pred.	Exp.	Pred.
W-48	1.188	1.225	1.230	0.96	0.96
W-49	1.358	1.390	1.400	0.98	0.97
W-50	1.567	1.596	1.596	0.98	0.98
W-51	1.866	1.854	1.875	1.00	0.99
W-52	2.19	2.18	2.17	1.01	1.00
W-53	2.66	2.60	2.57	1.03	1.02
W-54	3.41	3.30	3.20	1.06	1.05
W-55	4.70	4.38	4.23	1.10	1.08
WR-56	7.14	6.41	6.28	1.11	1.13
W-57	15.38	11.62	11.07	1.22	1.19
W-58	1.109	1.194	1.156	0.96	0.95
W-59	1.288	1.337	1.340	0.96	0.97
W-60	1.476	1.528	1.521	0.97	0.98
W-61	1.722	1.702	1.750	0.98	0.99
W-62	2.03	2.02	2.023	0.99	1.00
W-63	2.39	2.37	2.34	1.00	1.01
W-64	2.93	2.85	2.82	1.01	1.02
W-66	4.70	4.49	4.38	1.06	1.05
WR-67	6.58	6.15	5.97	1.06	1.07
W-68	9.46	8.87	8.38	1.08	1.09
WR-69	1.556	1.563	1.535	0.98	0.98
W-70	1.726	2.81	3.04	1.07	1.04
W-74	1.042	1.092	1.074	0.96	0.95
W-75	1.294	1.291	1.324	0.96	0.97
W-77	2.12	2.10	2.10	1.01	1.00
W-78	2.95	2.81	2.85	1.04	1.02
WR-80	6.68	5.69	5.77	1.12	1.10
WR-81	11.54	8.61	8.87	1.16	1.14
W-82	20.7	14.86	15.49	1.17	1.17
W-83	43.2	28.2	27.8	1.25	1.21
W-84	90.4	52.8	48.2	1.25	1.25
W-85	1.084	1.143	1.120	0.96	0.95
W-86	1.321	1.358	1.355	0.97	0.97
W-87	1.686	1.710	1.710	0.98	0.99
W-88	2.30	2.28	2.27	1.01	1.00
W-89	3.22	3.16	3.07	1.05	1.04
W-90	4.86	4.49	4.42	1.09	1.08
WR-91	7.87	6.86	6.74	1.08	1.11
W-92	13.46	11.14	10.84	1.14	1.16
W-94	0.897	0.895	0.920	0.93	0.94
W-95	1.390	1.400	1.413	0.97	0.97
W-96	1.858	1.871	1.866	0.99	0.99
WR-97	2.31	2.25	2.25	1.01	1.00
W-98	2.73	2.68	2.67	1.02	1.02
WR-99	3.33	3.05	3.15	1.04	1.03
W-100	3.98	3.85	3.82	1.06	1.05

CONTINUATION OF TABLE VIII-7

Original Fraction		Saturated Sample			
Oil Code*)	$\eta_{40^{\circ}C}$, cP Exp.	$\eta_{40^{\circ}C}$, cP		Slope Index	
		Exp.	Pred.	Exp.	Pred.
W-101	5.07	4.83	4.70	1.08	1.07
W-102	6.50	6.15	5.90	1.11	1.10
W-103	8.17	7.14	7.20	1.10	1.11
W-104	9.80	8.55	8.55	1.12	1.13
W-105	18.49	14.55	14.52	1.15	1.19
We-1	86.9	72.3	65.2	1.17	1.20
We-2	87.5	55.5	60.3	1.18	1.34
We-3	252	80.4	76.7	1.43	1.50
We-4	150.0	71.1	82.0	1.32	1.34
We-5	69.2	54.4	58.8	1.26	1.27
We-6	40.7	39.9	37.2	1.22	1.23

*) Refers to similarly coded oils specified in Table II-1.

of a given saturated mineral-oil fraction solely from the viscosity grade and the percentage C_A of the corresponding natural sample.

The viscosity grades η_{40^oC} and the Slope Indices*), S, of all these 100 natural mineral-oil fractions and their saturated samples are compiled in Table VIII-7. Further particulars on these oils can be found again in Table II-1.

The new correlation is represented in Fig. VIII-4, where the difference between the viscosity functions H_S and H_N of the saturated and natural fraction, respectively, has been plotted against the latter function, both viscosity functions being taken again at the standard reference temperature of 40 °C. By introducing the percentage C_A of the natural fraction as a parameter a *fan* of straight lines has been obtained, each line referring to a distinct C_A-value. The coordinates of the point of convergence amount to $(H_N)_{40^oC} = 0.1750$ - or $(\eta_N)_{40^oC} = 1.98$ cP - and $(H_S - H_N)_{40^oC} = 0.0000$.

It is well known that as a rule the viscosity grade of a natural mineral oil is *decreased* through hydrogenation. This rule is confirmed by the correlation depicted in Fig. VIII-4. In addition, however, the new correlation shows that a viscosity *increase* would be observed for very fluid mineral oils, that is with a viscosity grade $(\eta_N)_{40^oC}$ below the aforementioned level of 1.98 cP. Further, for natural mineral oils with viscosity grades in the vicinity of the latter value no appreciable viscosity change at all would be brought about by hydrogenation.

The correlation depicted in Fig. VIII-4 can be cast into the following analytical form:

$$(H_S)_{40^oC} = (H_N)_{40^oC} - 5.5 \cdot 10^{-3}\, C_A \left[(H_N)_{40^oC} - 0.1750\right] . \qquad \text{(VIII-8)}$$

As demonstrated by the results included in Table VIII-7, Correlation (VIII-8) does yield fairly accurate predictions of the viscosity grades $(H_S)_{40^oC}$ of saturated mineral-oil fractions solely from the viscosity grade $(H_N)_{40^oC}$ and the percentage C_A of the original samples.

At any rate, these predictions prove to be quite satisfactory for the purpose intended.

The prediction of the *Slope Indices* of saturated mineral-oil fractions can now readily be performed by substituting the value calculated for $(H_S)_{40^oC}$ from Equation (VIII-8) into Correlation (VIII-1a) or (VIII-1b). Thus, the present procedure for estimating the Slope Index of a given saturated mineral-oil fraction does require a knowledge solely of the viscosity grade and the carbon-type composition of the corresponding natural sample.

For the great variety of 100 saturated mineral-oil fractions listed in Table VIII-7 the Slope Indices estimated according to the latter procedure have been included in that table. In addition, Table VIII-8 indicates the distribution of the deviations between experimental and predicted Slope Indices amongst the various fractions tested.

It is seen from the latter table that the *absolute* average and standard deviations in the Slope Index amount to no more than 0.016 and 0.022 units, respectively, which figures are only slightly beyond the

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*) These Slope Indices have invariably been determined from the viscosity data available in the temperature range between 20 and 100 °C (68 and 212 °F).

TABLE VIII-8

Distribution of Deviations Between Experimental and Predicted Slope Indices Amongst the 100 Saturated Mineral Oils Tested

Deviation $|\delta S|$	Percentage of the 100 Oils Tested
0.00	20
0.01	46
0.02	13
0.03	10
0.04	3
0.05	4
0.06	3
0.07	1
Average Deviation*)	0.016
Standard Deviation**)	0.022

*) Defined by $\frac{1}{n}\sum_{i=1}^{i=n} |\delta_i|$

**) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} \delta_i^2}{n-1}}$

accuracy inherent in the experimentally determined Slope Indices. These absolute deviations correspond to *relative* average and standard deviations in both the predicted Slope Indices and viscosity-temperature coefficients, β, of only 1.4 and 1.9%, respectively.

From Correlation (VIII-1a) or (VIII-1b) and the present Equation (VIII-8) it follows that the Slope Index of a natural mineral-oil fraction would normally be decreased by (analytical) hydrogenation, or, in other words, its DVI would be raised. However, it also appears that one cannot uphold the point of view that this would *invariably* be the case.

In fact, according to the present findings, the Slope Index of a natural mineral-oil fraction is not appreciably altered through hydrogenation if its viscosity grade $\eta_{40^\circ C}$ approximates the aforementioned level of about 2 cP (1.98 cP). Finally, for fractions displaying still lower viscosity grades the Slope Index is even raised through hydrogenation, though to a very small extent.

Summarizing, for the great variety of saturated mineral-oil fractions tested the present procedure has proved to permit a reliable estimate of their complete viscosity-temperature relationship solely from the viscosity grade and the carbon-type composition of the corresponding natural fraction.

VIII. 2. 4. *Concluding Remarks*

The newly developed correlation has proved a valuable and convenient tool for predicting the viscosity-temperature relationship of mineral oils. In addition, this correlation may be deemed significant in that it furnishes some insight into the effect of the chemical constitution of mineral oils on the latter relationship, so that it may be very helpful in preparing oils with the desired viscosity-temperature characteristics.

According to the present correlation, the temperature effect on the specified viscosity grade of a mineral oil is determined solely by its *total* percentage of carbon atoms in ring structure, C_R. In other words, mineral oils possessing both a common viscosity grade and a common percentage C_R would display *identical* viscosity-temperature relationships irrespective of the manner in which their C_R-values are built up from the component percentages C_A and C_N. This conclusion has further been substantiated by the results obtained in trying to account for the effect of hydrogenation on the viscosity-temperature relationship of natural mineral oils.

According to a widely adopted view-point, the temperature dependence of the viscosity of mineral oils increases with their *"aromaticity"*. However, taking the rather vague concept of aromaticity as the percentage C_A, it would follow from the newly developed correlation that in its generality the latter view-point cannot be upheld, not even if it is confined to oils of comparable*) viscosity grades. Indeed, as rightly pointed out by Bondi [20a], the viscosity-temperature dependence of mineral oils and their aromaticity are basically *unrelated.*

Returning to the carbon-type composition diagram of Fig. VIII-1, the present correlation would permit the construction of straight lines of constant Slope Index in such a diagram but only for oils of comparable viscosity grade; these lines would coincide with straight lines of constant C_R.

Indeed, if the viscosity grade of the mineral oils concerned varies considerably, this is indispensable as a correlational variable. This holds the more so as the oils become less viscous. In the case of very fluid oils it is even *solely* their viscosity grade that determines their viscosity-temperature dependence, their chemical constitution having no longer any appreciable influence.

Yet, it may be useful to devote some further attention to the question as to how far the Slope Index - and also the conventional Viscosity Index (see Chapter VI) - of mineral oils would be related to their chemical constitution *proper.*

If the chemical constitution of mineral oils is expressed in terms of their carbon-type composition, it is readily seen from Fig. VIII-2 that, as already pointed out, a unique correlation with their Slope

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*) In this connection, it may be useful to emphasize that - as is well known to all those familiar with the present matter - the viscosity-temperature dependence of mineral oils (in fact, liquids in general) displaying widely different viscosity grades cannot simply be compared. Consequently, such generalized statements as, for instance, the one implying that paraffinic mineral oils would show flatter viscosity-temperature curves than naphthenic samples cannot be upheld.

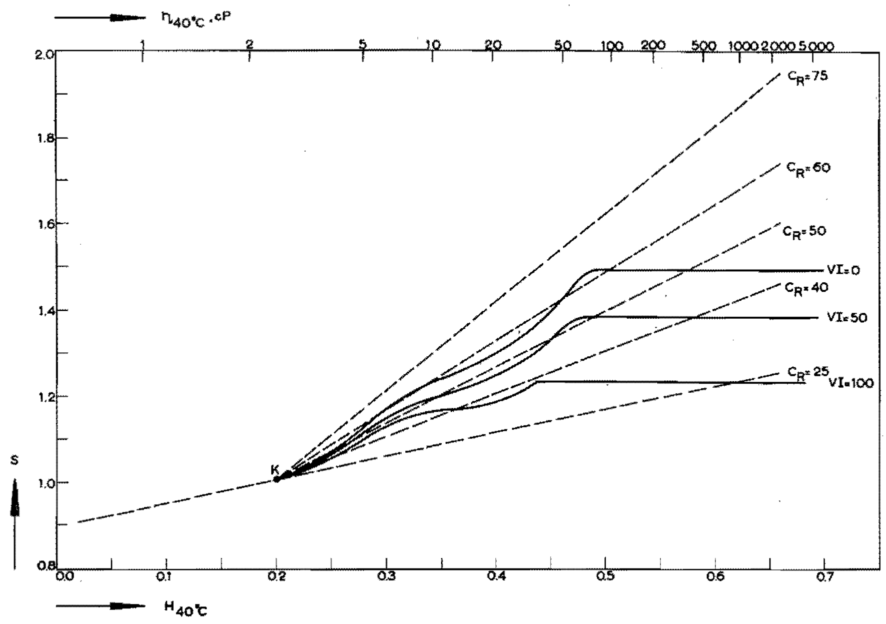

FIG.VIII-5.
Curves of Constant VI Plotted in the New Correlation of Fig.VIII-2.

Index does not exist through the entire viscosity range of practical interest. As shown by Fig. VIII-5, a similar conclusion holds with respect to the conventional Viscosity Index. It should be well realized, however, that for a given carbon-type composition - or rather a given percentage C_R - the Slope Index, and similarly the conventional Viscosity Index, changes only comparatively slowly with the viscosity grade, particularly for the more viscous oils.

For the sake of clearness, it may be mentioned that the preceding conclusion is by no means in conflict with the statement presented in Chapter VI that, except for very fluid oils, the Slope Index is substantially constant in a given *"naturally" homologous* group of mineral oils. The reason is that the members of such a naturally homologous group usually display some small, gradual change in their carbon-type composition, as implied by the validity of the correlation depicted in Fig. VIII-2.

VIII. 3. CORRELATION WITH PHYSICAL CONSTANTS

VIII. 3. 1. *Introduction*

In the preceding Section VIII. 2 it has been demonstrated that, to a good approximation, the correlation between the Slope Index of mineral oils and their viscosity grade is fixed solely by their percentage C_R. Since the latter percentage is determined from some combination of *three* suitably chosen physical constants [42], the aforementioned correlation is equally defined by any such combination. In the present context the combination of *viscosity*, *density* and *refractive index* - all three constants being taken at the same standard reference temperature - is particularly attractive as only the latter *two* physical constants enter as additional correlational variables.

Off-hand it may thus be concluded that only *two* easily assessable physical constants, namely density and refractive index, are *sufficient* for defining, to a good approximation, the correlation between the Slope Index and the viscosity grade of mineral oils. It cannot *a priori* be decided, however, whether each of these two physical constants is also really *needed* in the latter correlation.

For settling the question whether both the density and the refractive index are required as correlational variables it may first be noted that in the correlation described in the preceding Section VIII-2 only the percentage C_R (= $C_A + C_N$) occurs as a parameter and not the *individual* percentages C_A and C_N. Moreover, as is readily seen from Fig. VIII-2, the C_R-values need to be known *accurately* only for the more viscous oils. These two considerations suggest that it would certainly be worth-while to investigate further the possibility of suppressing either the refractive index or the density as a correlational variable.

Indeed, as will be shown below, it has been found that only *one* of the latter two physical constants is really necessary for defining, to a good approximation, the correlation between the Slope Index and the viscosity grade of mineral oils. The consequent reduction of the total number of variables involved in this correlation - from four to three - is significant not so much in that one easily assessable physical constant - either the refractive index or the density - need not be measured, but primarily in that the resulting correlation may thus be cast into a really simple and convenient form.

Of the two relevant correlations the one utilizing the *density* as a parameter has appeared to be somewhat more accurate than the other.

Finally, the author has succeeded in achieving a similar - though slightly less accurate - correlation employing yet another interesting quantity as a parameter, namely the (average) *molecular weight* of the oils.

All in all, it may be stated that each of the individual physical constants needed in the n-d-M method permits a good prediction of the Slope Index of a mineral-oil fraction if only its viscosity grade has been specified.

VIII. 3. 2. *Correlation With Density*

For all the various mineral oils designated in Table VIII-2 the Slope Indices, S, have again been plotted against their viscosity functions $H_{40°C}$, this time using the *density* $d_{40°C}$ as a parameter. As demonstrated by the resulting Fig. VIII-6, it appeared that more or less curved lines of constant density could be constructed.

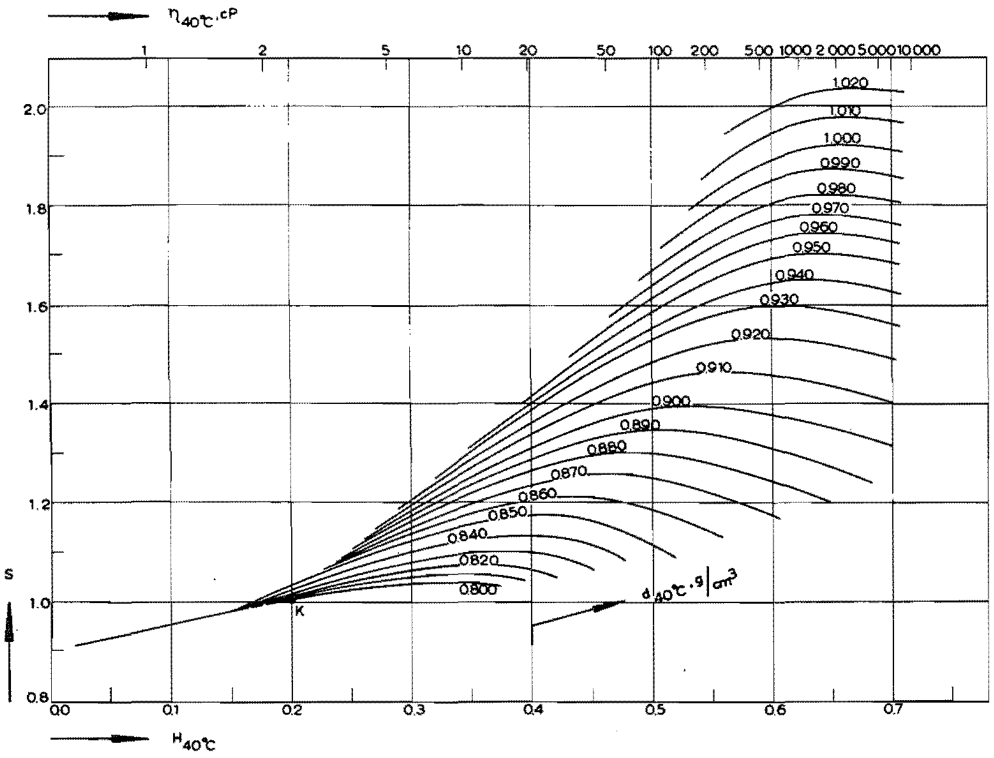

FIG. VIII-6.
Correlation Between the Viscosity-Temperature Relationship of Mineral Oils and Their Density.

The lines depicted in the latter figure relate to distinct densities $d_{40^\circ C}$ ranging from 0.800 up to 1.020 g/cm^3. Each of these constant-density lines is seen to exhibit a maximum S-value; with increasing density this maximum shifts towards higher viscosity grades. For very fluid oils the unique straight-line relationship between the Slope Index and the viscosity function $H_{40^\circ C}$ depicted in Fig. VIII-2 has been retained - for reasons of uniformity - in the present Fig. VIII-6.

A remarkable feature of the present correlation is that over fairly wide viscosity ranges the Slope Index of mineral oils is practically solely determined by their density. For the less viscous oils, however, the effect of density on the correlation between Slope Index and viscosity grade becomes considerably less pronounced; finally, for the very fluid oils with viscosities $\eta_{40^\circ C}$ not exceeding the aforementioned value of 2.43 cP (denoted by point K in Fig. VIII-6) the density has no longer any appreciable effect on the latter correlation.

Further, for mineral oils with a relatively great sulfur content the correlation depicted in Fig. VIII-6 has proved to yield on the whole somewhat better predictions if their densities are properly corrected. The relevant minor correction, however, has appeared to become really significant only in cases where the percentage by weight of sulfur present, wt.% S, amounts to at least, say, 1%. Nevertheless, for reasons of uniformity such a correction has invariably been applied to the densities of the mineral oils tested, at least in so far as their wt.% S has been specified*). In accordance with recent investigations[152] an amount of 0.006 g/cm^3 has been subtracted from the experimental density for each wt.% S present in the mineral oil under consideration.

The correlation depicted in Fig. VIII-6 has been utilized for estimating the Slope Indices of all the various kinds of mineral-oil fractions - both natural and saturated - specified in Table VIII-2. The results of the relevant readings are collected in the same table. In addition, Table VIII-3 gives the distribution of the deviations between experimental and predicted Slope Indices amongst the really great variety of the 360 mineral-oil fractions indicated in § VIII.1.2.

Table VIII-3 shows that the *absolute* average and standard deviations in the Slope Index amount to no more than 0.019 and 0.025 units, respectively, which figures are only slightly beyond the accuracy inherent in the experimentally derived Slope Indices. These absolute deviations correspond to *relative* average and standard deviations in both the predicted Slope Indices and viscosity-temperature coefficients of only 1.6 and 2.1%, respectively.

On the whole the indicated agreement between experimental and predicted Slope Indices may be considered very satisfactory, certainly so for normal practical purposes**).

*The correlational accuracy achieved by the present "density correlation" tends to be even slightly better***) than that of*

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*) As indicated in Table II-1, the sulfur content has not been specified for the mineral oils from References 27 and 45. But the minor differences that would have been observed in the predicted Slope Indices of these oils if their properly corrected densities could have been used, may be deemed practically insignificant, notably in view of the really great variety of oils employed in verifying the present correlation.

**) For further particulars on the practical significance of the deviations involved reference is made to § VIII.2.2.

***) The so-called F-test yields a statistical confidence level of about 89%.

the "chemical-constitution correlation" described in § VIII.2.2. In addition, this density correlation has the significant advantage over the latter that it constitutes a straightforward method for predicting the Slope Indices of mineral oils. Indeed, the present correlation directly employs two easily assessable physical constants, viscosity grade and density, and does not involve any derived quantities. Consequently, for practical applications the present density correlation is more attractive than the foregoing chemical-constitution correlation.

TABLE VIII-9

Approximate Density-Temperature Coefficients $\delta d/\delta t$ of Mineral Oils as a Function of Their Density $d_{40^\circ C}$

$d_{40^\circ C}$, g/cm^3	$\delta d/\delta t$, g/(cm^3 · deg C)
0.75	-7.5×10^{-4}
0.80	-7.1×10^{-4}
0.85	-6.7×10^{-4}
0.90	-6.3×10^{-4}
0.95	-5.9×10^{-4}
1.00	-5.5×10^{-4}

Finally, it may be elucidated how the present correlation can equally be applied when the density of the mineral oil considered is given only at one arbitrary temperature differing markedly from the adopted standard reference temperature of 40°C. In fact, the density at the latter temperature can be estimated very easily and with an accuracy that well suffices for the purpose intended. This accrues from the well-known facts that the temperature coefficient of the density of mineral oils is very small and, moreover, not very different from one oil to another. In addition, the density-temperature coefficient, $\partial d/\partial t$, of mineral oils shows a fair correlation with their density at some standard reference temperature. The following correlation has proved quite satisfactory for the present purpose*):

$$\frac{\partial d}{\partial t} = (8.0\ d_{40^\circ C} - 13.5)\,10^{-4}, \qquad \text{(VIII-9)}$$

where the density d has again been expressed in g/cm^3 and the temperature t in deg C. For convenience the values of the density-temperature coefficients corresponding to some distinct values of $d_{40^\circ C}$ are listed in Table VIII-9.

For estimating by means of Equation (VIII-9) the density of a given mineral oil in a wide temperature range a linear relationship

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*) If more accurate density predictions are needed, one may resort to correlations involving some additional physical constant, for instance the well-known correlation proposed by Lipkin and Kurtz[51] which, in addition to the density at some standard reference temperature, requires the molecular weight of the oil.

between density and temperature may be assumed; that is the density-temperature coefficient of the oil considered is taken independent of temperature. It may be stated that, in general, even for a temperature range of at least 60°C (108°F), the densities predicted according to the present procedure are accurate within 0.5%.

VIII. 3. 3. *Correlation With Refractive Index*

Using the *refractive index* $n_{40^{\circ}C}$ (invariably relating to the sodium-D line) instead of the density $d_{40^{\circ}C}$ of all the various mineral oils designated in Table VIII-2 has led to a correlation quite similar to the one described in the preceding § VIII. 3. 2. The resulting *"refractive-index correlation"* has been depicted in Fig. VIII-7. The curves included in this figure relate to distinct refractive indices $n_{40^{\circ}C}$ ranging from 1.440 up to 1.590.

As indicated in the preceding § VIII.3.2 for the density, it has likewise appeared for the refractive index that it is advisable to apply some slight correction to its experimental value if the oil considered contains an appreciable amount of sulfur. In accordance with the investigations cited above152) the experimental refractive indices of the oils tested have been corrected by subtracting 0.002 units for each wt.% S present (see also the relevant footnote in § VIII.3.2).

The correlation depicted in Fig. VIII-7 has been utilized for estimating the Slope Indices of all the various kinds of mineral-oil fractions - both natural and saturated - designated in Table VIII-2. These estimates are compiled in the same table. In addition, Table VIII-3 gives the distribution of the deviations between experimental and predicted Slope Indices amongst the really great variety of the 360 mineral-oil fractions indicated in § VIII. 1. 2.

Table VIII-3 shows that the *absolute* average and standard deviations in the Slope Index amount to no more than 0.023 and 0.032 units, respectively. These correspond to *relative* average and standard deviations in both the predicted Slope Indices and viscosity-temperature coefficients of only 2.0 and 2.6%, respectively.*)

*On the whole, therefore, the present refractive-index correlation also permits very satisfactory predictions of the Slope Indices of mineral oils. Yet, its correlational accuracy is slightly inferior**) to that of the foregoing correlation utilizing the density instead of the refractive index.*

Finally, it may be mentioned that like the preceding density correlation the present refractive-index correlation can equally be applied when the refractive index of the mineral oil considered is given at one *arbitrary* temperature differing considerably from the adopted standard reference temperature of 40°C. In fact, in a fairly wide temperature range some average value may be used for the temperature coefficient of the refractive index of any given mineral oil. A value of about $-3.7 \cdot 10^{-4}$ (deg C)$^{-1}$ for the latter coefficient has indeed proved acceptable for the present purpose.

A better approximation is possible when one *density* value of the

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*) For further particulars on the practical significance of the deviations involved reference is made again to § VIII. 2. 2.

**) According to the F-test, the statistical confidence level exceeds 99.9%.

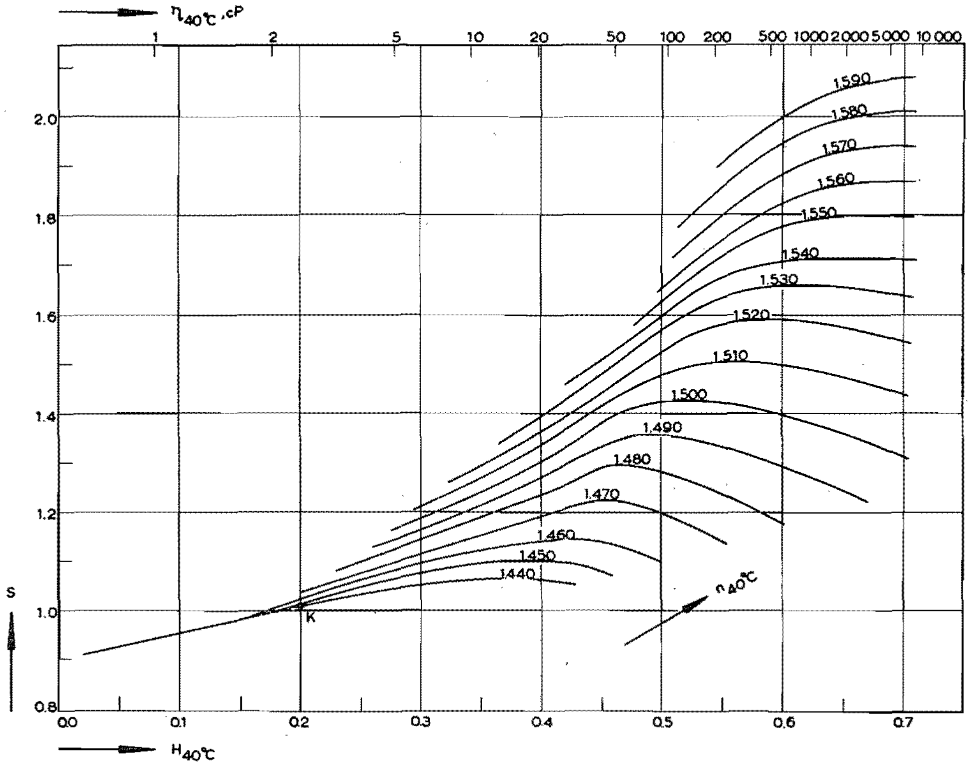

FIG. VIII-7.
Correlation Between the Viscosity-Temperature Relationship of Mineral Oils and Their Refractive Index.

oil considered is also known. In that case it is feasible to utilize the well-established correlation - already applied in § II.2.3 - that over a fairly wide temperature range the temperature coefficient of the refractive index of any given mineral oil amounts to 0.59 times its density-temperature coefficient (density again being expressed in g/cm^3), the latter quantity having been discussed already in the preceding § VIII.3.2.

VIII.3.4. *Correlation With Molecular Weight*

Since the (average) *molecular weight*, M, of mineral oils is involved in numerous correlations, either between various physical constants individually or between physical constants and their chemical constitution, it would be interesting to investigate its suitability for the present purpose of predicting their Slope Indices.

In comparison with the density and refractive index utilized in the preceding correlations the molecular weight of mineral oils may be stated to constitute a more *informative* physical constant. Moreover, it has the attractive feature that it is, of course, independent of temperature.

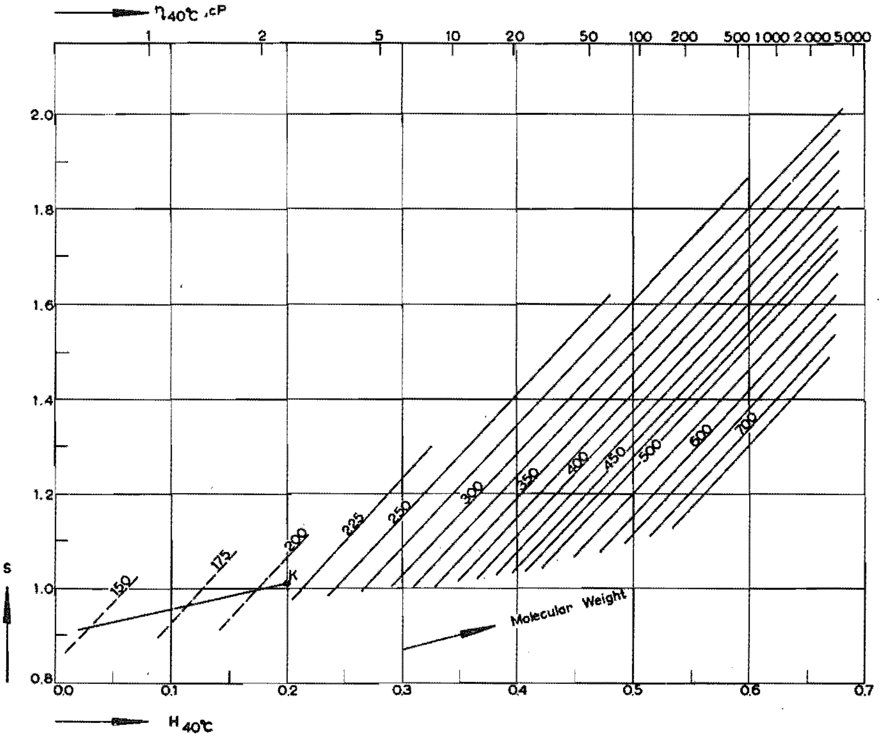

FIG. VIII-8.
Correlation Between the Viscosity-Temperature Relationship of Mineral Oils and Their Molecular Weight.

For all the various mineral oils designated in Table VIII-2 the molecular weight has indeed proved a suitable parameter for estimating their Slope Index solely from their viscosity grade. As illustrated in Fig. VIII-8, the resulting correlation is represented in an S-$H_{40^\circ C}$ diagram by a family of *parallel* straight lines, each line relating to a distinct M-value. In analytical form this correlation is defined by:

$$S = 2.63\ H_{40^\circ C} - \log(M - 100) + 2.54. \qquad \text{(VIII-10a)}$$

The molecular-weight range for which the present *"molecular-weight correlation"* has been verified extends from as low as about 150 up to nearly 750. For very fluid oils the unique straight-line relationship between the Slope Index and the viscosity function $H_{40^\circ C}$ indicated in Fig. VIII-2 has again been retained in the present Fig. VIII-8. For reasons of clearness, however, a few broken lines of constant molecular weight have been depicted in the latter viscosity range.

It may be noted that for the members of a given group of mineral oils with a common molecular weight the Slope Index increases relatively strongly with their viscosity grade. Similarly, the present correlation shows that if one considers a series of oils with a common viscosity grade, the Slope Index increases regularly with decreasing molecular weight.

Application of Correlation (VIII-10a) to all the various kinds of mineral oils - both natural and saturated - designated in Table VIII-2 has yielded the Slope Indices there included. In addition, Table VIII-3 gives the distribution of the deviations between experimental and predicted Slope Indices amongst the really great variety of the 360 mineral-oil fractions indicated in § VIII. 1. 2.

Table VIII-3 shows that the *absolute* average and standard deviations in the Slope Index amount to no more than 0.027 and 0.036 units, respectively. These correspond to *relative* average and standard deviations in both the predicted Slope Indices and viscosity-temperature coefficients of only 2.4 and 3.2%, respectively.*)

As a rule, therefore, the present molecular-weight correlation also allows quite satisfactory predictions of the Slope Indices of mineral oils.

However, the latter correlation is somewhat less reliable than the one employing the refractive index (see § VIII. 3. 3) and particularly the one using the density (see § VIII. 3. 2) of the mineral oil considered.**) Another disadvantage in the practical application of Correlation (VIII-10a) consists in that the molecular weight of mineral oils cannot be determined so easily and accurately as their density or their refractive index.

In fact, the value of the present correlation may primarily lie even more in the *inverse* purpose, that is for assessing the molecular weight of mineral oils solely from their Slope Index and vis-

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*) For further particulars on the practical significance of the deviations involved reference is made again to § VIII. 2. 2.

**) For both differences involved the F-test yields statistical confidence levels above 99.5%.

cosity grade.

Employing a diagram like Fig. VIII-8 for such assessments, any interpolation between the indicated M-values should be performed at constant Slope Index. It stands to reason that the molecular weight may also be computed from the basic Equation (VIII-10a). For the present purpose Correlation (VIII-10a) should rather be rewritten in the form:

$$M = 347 \cdot 10^{-S} (\log \eta_{40^\circ C} + 1.200)^{2.63}, \qquad \text{(VIII-10b)}$$

where the molecular weight occurs as an explicit variable.

In general, Equation (VIII-10b) has proved to permit very good estimates of the molecular weights of mineral oils. In fact, for all the divergent kinds of oils tested the average deviation amounts to only about 2.5%, whilst the experimental values may be in error by 2-5%.

Amongst the many correlations previously developed for estimating the molecular weight of mineral oils from easily assessable physical constants the most attractive one would seem to be Hirschler's correlation involving only the kinematic viscosities at 100 and 210°F [153). Essentially, therefore, the latter correlation will be very similar to the present one. Hirschler's correlation covers a molecular weight range from about 220 up to 700. The predictions have to be performed graphically. In general, these would reach the accuracy that is inherent in normal molecular-weight data available from the literature, that is from about 2 to 5%.

As regards its correlational accuracy the present Correlation (VIII-10b) appears to be at least on a par with Hirschler's. In addition, it has the advantages that it is based on *dynamic* viscosity and that the viscosities need not be known at invariably the same two arbitrary standard reference temperatures. Further, the present correlation covers the entire molecular-weight range tested, that is from about 150 up to 750. Last but not least, the new Correlation (VIII-10b) has been cast into a fairly simple analytical form.

In fact, the present Correlation (VIII-10b) for estimating the molecular weight of mineral oils would appear to be the first one that could be analytically defined, all previous correlations being based on graphical averaging.

VIII. 3. 5. *Additional Applications*

A. THE APPLICABILITY OF THE PRESENT CORRELATIONS AT SOME ARBITRARY REFERENCE TEMPERATURE

If one *viscosity* value of a given mineral oil has been specified at some arbitrary temperature differing considerably from the standard reference temperature of 40°C, the three correlations described in the preceding parts may yet be utilized for predicting its Slope Index. The following procedure may be adopted.

One relationship connecting the two unknown quantities S and $H_{40^\circ C}$ is implied by the appropriate line, either of constant density in Fig.

VIII-6 or of constant refractive index in Fig. VIII-7 or of constant molecular weight in Fig. VIII-8. A second relationship is implied by the basic viscosity-temperature Equation (III-6h), namely:

$$S = \frac{H - H_{40^\circ C}}{\Theta + 0.1127}, \qquad \text{(VIII-2b)}$$

where the specified viscosity value of a given oil should be substituted into the viscosity function H at the arbitrary reference temperature Θ.

From these two independent relationships between the two unknown quantities S and $H_{40^\circ C}$ the Slope Index S can readily be solved. This can be performed most conveniently by plotting the straight-line relationship between S and $H_{40^\circ C}$ defined by Equation (VIII-2b) in one of the pertinent Figs. VIII-6, VIII-7 or VIII-8. The point of intersection of the resulting straight line with the appropriate line of constant density, refractive index or molecular weight*), respectively, yields the Slope Index of the oil considered.

It may be recalled that, as delineated at the end of the preceding § VIII. 3. 2 and § VIII. 3. 3, respectively, the density and the refractive index of a given mineral oil need neither be known necessarily at the adopted standard reference temperature of 40°C. Consequently, the foregoing findings may indeed be summarized in the following *generalized* conclusion**):

The viscosity-temperature dependence of mineral oils can be obtained, to a good approximation, solely from their viscosity grade and one of the physical constants density, refractive index or molecular weight, irrespective of the particular reference temperatures involved.

B. CONVERSION OF KINEMATIC INTO DYNAMIC VISCOSITIES FOR MINERAL OILS WITH UNKNOWN DENSITIES

The density correlation depicted in Fig. VIII-6 may also be utilized in an *inverse* manner, that is for estimating the density $d_{40^\circ C}$ of the oil considered from its Slope Index and its viscosity grade $\eta_{40^\circ C}$. In this way density***) estimates can readily be achieved that normally prove accurate within about 1%. As seen from Fig. VIII-6, this accuracy cannot be upheld for very fluid oils, as for such oils the significance of the density as an influential quantity is comparatively small and finally even vanishing. Fortunately, the differentiation as to the densities of these very fluid oils is also comparatively small, so that fair estimates can still be made.

This "inverse" application may be particularly valuable in the

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*) Since the molecular-weight correlation of Fig. VIII-8 has also been defined analytically by Correlation (VIII-10a), the Slope Index of the oil considered can likewise be obtained by eliminating $H_{40^\circ C}$ from Equation (VIII-2b) and the latter correlation.

**) It stands to reason that this correlation will apply primarily to the conventional temperature range.

***) Similarly, Fig. VIII-7 can be employed for predicting the refractive index $n_{40^\circ C}$ of mineral oils, the deviation normally being within about 0.5%.

numerous cases where only *kinematic* viscosities have been reported. Now, these can readily be converted into the corresponding *dynamic* viscosities - which, in contrast to kinematic viscosities, are really significant in the theory and practice of lubrication - once the appropriate densities have been estimated by means of the subsequent trial-and-error method.

As a first approximation some intermediate value is assumed for the density at 40 °C, say, $d_{40^oC} = 0.900$ g/cm^3; from this value the densities at the involved temperatures are estimated by using the appropriate density-temperature coefficient listed in Table VIII-9, that is $\partial d/\partial t = -6.3 \cdot 10^{-4}$ g/(cm$^3 \cdot$ deg C). After converting the specified kinematic into the corresponding dynamic viscosities by means of the densities assumed the Slope Index and the viscosity function H_{40^oC} of a given oil are calculated from the basic viscosity-temperature Equation (III-6h).

Then, a plot of the latter two quantities in Fig. VIII-6 permits reading off a certain value for d_{40^oC}. Usually, however, the latter value will differ more or less from the arbitrarily assumed value $d_{40^oC} = 0.900$ g/cm^3. Although it might be tried to establish a still more appropriate value for d_{40^oC} by repeating the above procedure with a newly adjusted d_{40^oC}-value, it has been found that, fortunately, such further tryings need not be made. Indeed, the d_{40^oC}-value first read from Fig. VIII-6 cannot appreciably be improved along these lines*).

Finally, from the predicted value of d_{40^oC} the densities at the desired temperatures can easily be calculated according to the procedure presented at the end of § VIII. 3. 2.

Two concrete examples for illustrating the foregoing method are provided in Appendix VIII-2 at the end of this chapter.

It may be pointed out that the latter method for converting kinematic into dynamic viscosities proves to be a very rapid one. The author has frequently applied this method for evaluating numerous important kinematic-viscosity data found in the literature, which data otherwise could not have been used with sufficient reliability in the various investigations involved.

VIII. 4. DISCUSSION

VIII. 4. 1. *Comparison of the Various Correlations Developed*

The four newly developed correlations for predicting the viscosity-temperature dependence of mineral oils - both natural and saturated - have proved to combine simplicity and reliability. Thus, they are very suitable indeed for practical application. In addition, they lend themselves very well to correlational purposes.

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*) The reason for this fortunate circumstance is that, as indicated above, over comparatively wide viscosity ranges the density d_{40^oC} is practically solely determined by the Slope Index, whose value proves to be hardly affected by the involved small differences between assumed and estimated densities that have successively been used for converting kinematic into dynamic viscosities.

Two types of correlations have been advanced in the present study:

a. In Section VIII. 2 a correlation has been devised for predicting the Slope Index of mineral oils with known viscosity grade solely from their *chemical constitution.* In fact, for this particular purpose their chemical constitution has proved to be represented satisfactorily simply by the total percentage of carbon atoms in ring structure, C_R.
b. In Section VIII. 3 three correlations have been developed for estimating the Slope Index of mineral oils with known viscosity grade from *one single,* easily assessable, *physical constant.* The following physical constants have been employed successfully: *density, refractive index* and *molecular weight.*

Whilst the correlation based on the chemical constitution of the oils is very convenient for predicting their viscosity-temperature relationship, its value would lie primarily in furnishing some insight into the relevant effect of their chemical constitution proper. Thus, this correlation may be very helpful in preparing oils with the desired viscosity-temperature characteristics.

The three physical-constant correlations have the weighty advantage over the latter correlation that they constitute really *straightforward* tools. Accordingly, for practical applications these correlations with easily assessable physical constants are more attractive. The correlation involving only the density of the oil as a parameter is the most accurate one of the three; its overall accuracy tends to be even slightly better than that of the correlation based on the chemical constitution of the oils.

All in all, for practical applications the density correlation is definitely to be preferred.

VIII. 4. 2. *Further Discussion of the Validity Ranges of the New Correlations*

Besides the aforementioned total of 360 mineral oils representing a really wide variety of origins and chemical constitutions, various additional oils (not specified here) have been employed in verifying the applicability of the new correlations. The relevant results have proved to substantiate fully their applicability, even somewhat beyond the ranges of Slope Indices and viscosity grades $\eta_{40^\circ C}$ covered by the data on the aforementioned variety of 360 mineral oils.

The extensive ranges of Slope Indices and viscosity grades for which the three physical-constant correlations have been checked are approximately comprised by the two converging dashed lines in Fig. VIII-9 (see also Fig. I-1).

As indicated in Fig. VIII-9, these two dashed lines are fairly closely approximated by the outmost straight lines*) - relating to $C_R = 25$ and $C_R = 75$ - of the correlation with chemical constitution depicted in Fig. VIII-2. In this connection, it should be pointed out that the n-d-M method, which has invariably been used for determining the carbon-type composition of the oils, may not safely be applied when

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*) Further, the intermediate straight line relating to $C_R = 50$ and the straight line for very fluid oils have been replotted from Fig. VIII-2.

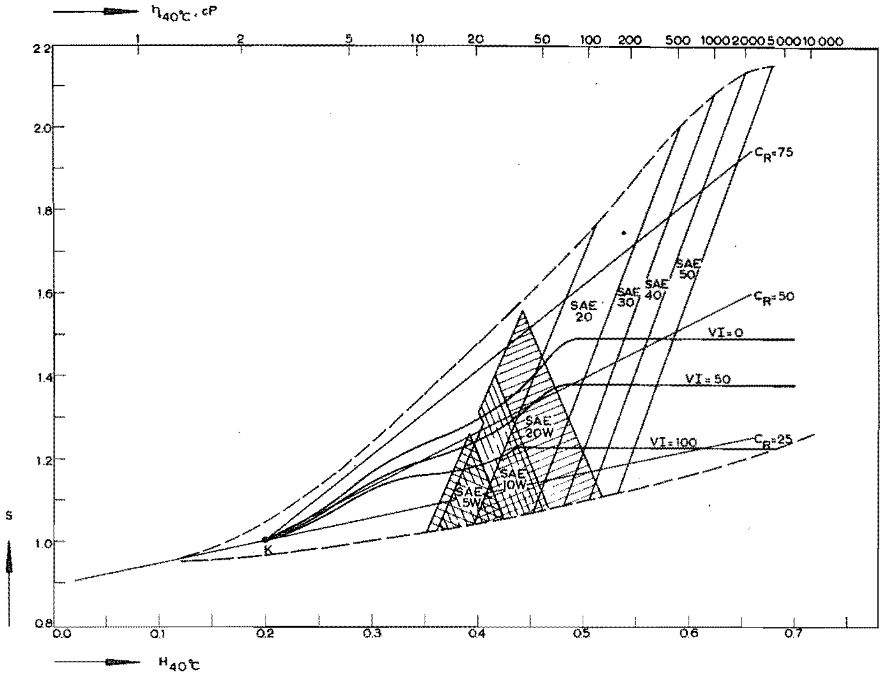

FIG. VIII-9.
Validity Ranges of the New Viscosity-Temperature Correlations at a Standard Reference Temperature of 40^{o}C.

C_R exceeds 75 or when $C_A > 1.5\ C_N$. This is the reason why the correlation based on this carbon-type composition is bound to have a somewhat narrower validity range than the three physical-constant correlations.

All in all, the applicability range indicated in Fig. VIII-9 for the three physical-constant correlations may be taken to represent practically the full range of Slope Indices and corresponding viscosity-grades η_{40^oC} *exhibited by all the divergent kinds of mineral oils known so far (excepting extremely viscous ones). These include not only mineral oils obtained by conventional refining methods - denoted as "natural" mineral oils -, but even completely hydrogenated - saturated - samples.*

Possibly, these physical-constant correlations would yield less reliable results for certain mineral oils whose "natural" character has been drastically modified by applying rather extreme refining methods - or such oils might even fall somewhat beyond the applicability range indicated in Fig. VIII-9. It should be emphasized, however, that - apart from the numerous mineral oils saturated by complete (analytical) hydrogenation - even such "extreme" products as *highly aromatic extracts* and *"hydrolubes"* obtained by *destructive* hydrogenation have proved to comply almost equally well with these physical-constant correlations.

The latter correlations have also been applied successfully to several mineral oils containing small amounts of *additives*. Indeed, their Slope Indices and - to a smaller extent - their viscosity grades are, in general, hardly affected by the presence of a few per cent (by weight) of such additives. However, when the density or the refractive index is used as a correlational variable, it may be advisable that this be properly corrected.

Of course, conspicuous deviations from the present physical-constant correlations will be observed for *polymer-blended* mineral oils; that is oils whose Slope Index has been specifically decreased by the addition of a substantial amount of some "VI-improver". The latter point will be elaborated in § VIII. 4. 6.

In order that the indicated applicability ranges of the various correlations may be grasped and memorized more easily, familiar and widely employed measures of both the (kinematic) viscosity-temperature dependence and the (kinematic) viscosity grade of mineral oils have been included in Fig. VIII-9.

The three constant-VI lines - relating to VI's of 0, 50 and 100 - have been replotted from Fig. VIII-5. It may be remarked that, indeed, this has been done merely in view of the wide-spread familiarity with the VI, which constitutes an otherwise dubious quantity (compare Chapter VI).

Fig. VIII-9 further indicates the approximate ranges of Slope Indices and viscosity grades η_{40^oC} covered by the well-known SAE standard for classifying crankcase lubricating oils in terms of their viscosity *grade*[154]. The *"SAE Viscosity Numbers"* have found almost universal use in lubrication practice; further particulars on them are given in Appendix VIII-3 at the end of this chapter.

Each of the *kinematic* viscosities - indicating the viscosity ranges covered by the various SAE Viscosity Numbers - listed in Table VIII-11 of the latter appendix corresponds to a distinct line in the S-H_{40^oC} diagram of Fig. VIII-9. The conversion of these kinematic into *dynamic* viscosities - for the various possible S-values - constitutes another interesting application of the procedure described in part B of § VIII. 3. 5. Remarkably enough, the lines indicating the ranges of S and H_{40^oC} covered by these SAE Viscosity Numbers all prove to be *straight*, at least within the accuracy of the aforementioned conversion method.

From Fig. VIII-9 it is seen that the various SAE Viscosity Numbers correspond to ranges of S and η_{40^oC} that are indeed located well within the applicability range of the correlations under discussion.

On the other hand, this diagram is very convenient for readily determining[*] the SAE Viscosity Number of a given mineral oil from its *dynamic* viscosity-temperature relationship as described by Equation (III-6h). Similarly, each of the present *correlations* is very suitable for *predicting* the SAE Viscosity Numbers of mineral oils.

Further, the following remarks may be made on the Slope Indices

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[*] Thus, one is no longer committed to the two standard reference temperatures of the relevant SAE standard, that is 0 and 210°F (-17.8 and 98.9°C).

associated with the SAE Viscosity Numbers indicated in Fig. VIII-9.

a. Each of the SAE *summer*-grade viscosities, that is SAE 20, 30, 40 and 50, covers the entire range of Slope Indices found amongst mineral oils of the pertinent viscosity grades.
b. The same holds for the *winter*-grade viscosities represented by SAE 20W, even though the lower viscosity limit at 210°F has been specified in addition to the lower and upper limits at 0°F (see Appendix VIII-3).
c. In contrast to the other SAE Viscosity Numbers, the numbers SAE 10W and particularly SAE 5W cover only part of the Slope Indices found amongst mineral oils of the pertinent viscosity grades.

Finally, a diagram quite similar to Fig. VIII-9 has been prepared for the standard reference temperature of 100°C (212°F)*).

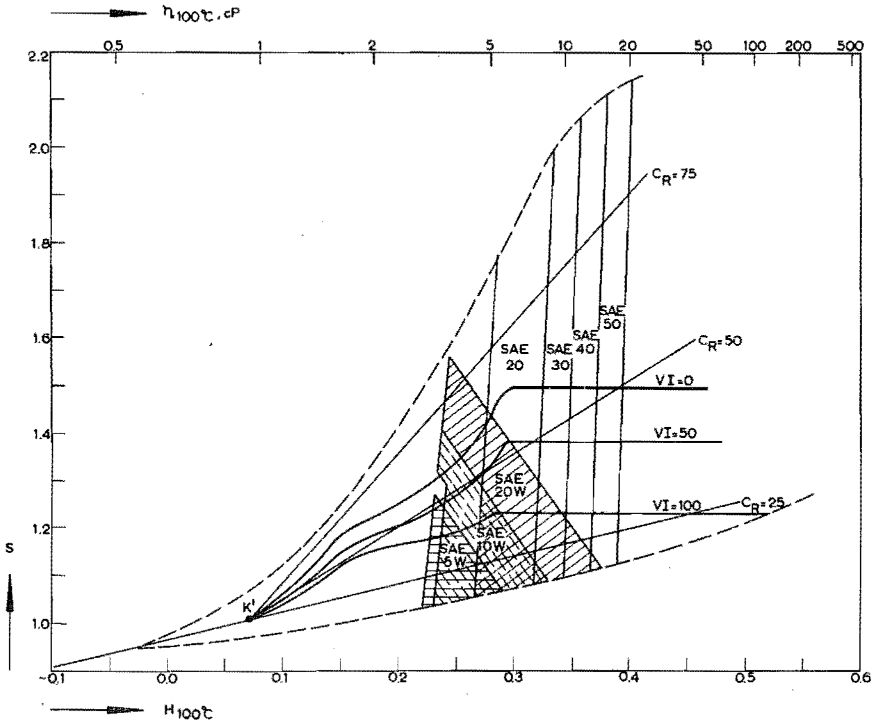


FIG. VIII-10.
Validity Ranges of the New Viscosity-Temperature Correlations at a Standard Reference Temperature of 100°C.

The resulting Fig. VIII-10 is particularly convenient in that the latter temperature is very close to 210°F, which constitutes a standard

*) The "transitional" viscosity indicated by point K' amounts to $\eta_{K'}$ = 0.947 cP.

reference temperature for both the VI-system and the SAE summer-grade viscosities.

VIII. 4. 3. *The Compatibility of Pure Hydrocarbons With the New Correlations for Mineral Oils*

The present correlations have been designed specifically for mineral oils, that is for mixtures of an enormous variety of (essentially) hydrocarbon compounds. Accordingly, the specific effect of any of these individual compounds on the physical properties of such complex mixtures will be hardly detectable. The latter feature may be so conceived that certain "averaging" effects are obtaining in mineral oils, the individual compounds tending to lose their identity. In fact, it is this very feature which permits the development of, for instance, quantitative correlations for predicting the viscosity-temperature dependence of mineral oils from their chemical constitution and/or from easily assessable physical constants.

Consequently, it may by no means be inferred that individual, *pure* hydrocarbons would likewise be compatible with the present correlations for estimating the Slope Indices of - both natural and saturated - mineral oils. On the contrary, the foregoing considerations would suggest that pure hydrocarbons might show considerable deviations from these correlations, particularly those hydrocarbons whose structure differs widely from the average chemical constitution of the normally encountered types of mineral oils.

As regards the compatibility of pure hydrocarbons with the correlation employing the percentage of carbon atoms in ring structure, C_R, as a parameter (see Section VIII. 2), it may be recalled that this percentage C_R is significant only as a *statistical* quantity indicative of the "average" chemical constitution of the component hydrocarbons of a particular mineral oil (see also § II. 2. 2). But for individual hydrocarbon compounds the percentage C_R - or any other such statistical quantity - can, by definition, no longer possess its statistical significance.

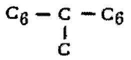
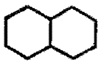
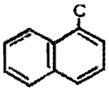
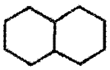
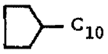
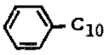
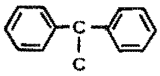
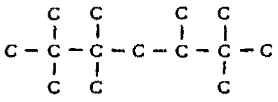
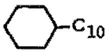
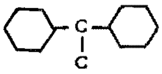
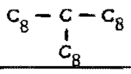
In accordance with the foregoing considerations it has indeed been found that application of the latter correlation to pure hydrocarbons may yield Slope Indices very much in error.

With respect to the conformance of pure hydrocarbons to the three physical-constant correlations of Section VIII. 3 the situation appears to be somewhat better. *A priori,* it may be stated that each of these correlations would equally apply to pure hydrocarbons if the three correlational variables involved - the viscosity function $H_{40°C}$, the Slope Index and either the density or the refractive index or the molecular weight - were strictly *additive* in pure-hydrocarbon mixtures, irrespective of the number of components involved.

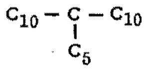
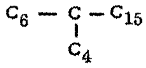
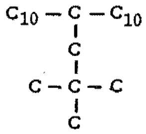
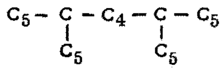
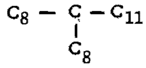
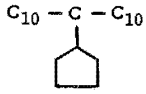
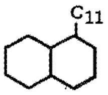
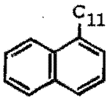
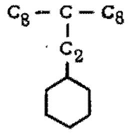
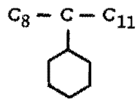
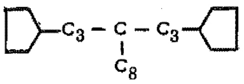
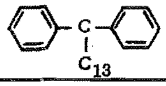
Now, the molecular weight is strictly additive in terms of molar fractions, whilst the density and the refractive index of such mixtures generally are approximately additive in terms of both weight and volume fractions. Further, the viscosity function $H_{40°C}$ and the Slope Index of pure-hydrocarbon mixtures may be taken additive in terms of either weight or volume fractions but in general only to a first

TABLE VIII-10

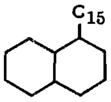
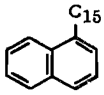
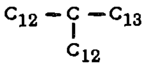
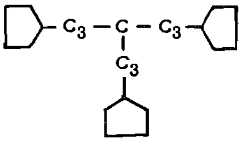
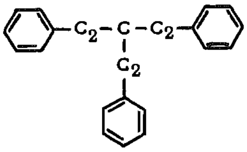
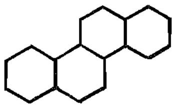
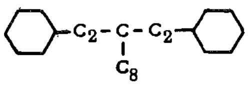
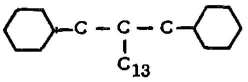
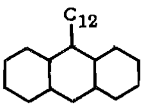
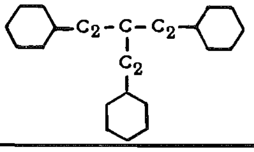
Percentage Deviations Between Experimental and Predicted Slope Indices of 40 Pure Hydrocarbons

Compound		Experimental Data			%δs*)
PSU No.	Structural Formula	$\eta_{40°C}$, cP	$d_{40°C}$, g/cm^3	Slope Index	
512	 $C_6-\underset{\displaystyle C}{\underset{\mid}{C}}-C_6$	1,455	0,749	1,03	-6
570	 trans	1,489	0,855	0,95	+2
533	$C=C-C_{13}$	1,700	0,761	1,00	-2
532	$n-C_{15}$	1,900	0,755	1,00	-1
567		2,13	1,006	0,99	+1
569	 cis	2,21	0,882	0,98	+2
573		2,37	0,797	1,00	+1
571		2,46	0,842	1,00	+3
516		2,72	0,984	0,97	+10
556	 $C-\underset{\displaystyle C}{\overset{\displaystyle C}{C}}-\underset{\displaystyle C}{\overset{\displaystyle C}{C}}-C-\overset{\displaystyle C}{C}-\underset{\displaystyle C}{\overset{\displaystyle C}{C}}-C$	2,84	0,787	1,02	-1
572		3,19	0,805	1,00	+2
540	$n-C_{20}$	4,16	0,775	1,00	+1
520		4,36	0,860	1,06	+5
518		4,62	0,879	1,07	0
25	 $C_8-\underset{\displaystyle C_8}{\underset{\mid}{C}}-C_8$	6,61	0,789	1,09	-5

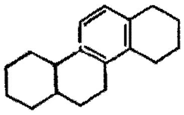
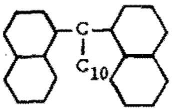
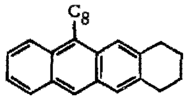
CONTINUATION OF TABLE VIII-10

Compound		Experimental Data			%δS*)
PSU No.	Structural Formula	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	Slope Index	
27	 $C_{10}-\underset{C_5}{\underset{\vert}{C}}-C_{10}$	7.45	0.791	1.08	-5
3	 $C_6-\underset{C_4}{\underset{\vert}{C}}-C_{15}$	8.20	0.791	1.09	-5
67	 $\begin{array}{c} C_{10}-C-C_{10} \\ \vert \\ C \\ \vert \\ C-C-C \\ \vert \\ C \end{array}$	8.61	0.790	1.13	-8
22	 $C_5-\underset{C_5}{\underset{\vert}{C}}-C_4-\underset{C_5}{\underset{\vert}{C}}-C_5$	8.67	0.794	1.19	-13
63	 $C_8-\underset{C_8}{\underset{\vert}{C}}-C_{11}$	8.91	0.795	1.08	-5
64		9.57	0.820	1.10	-3
544		9.95	0.860	1.10	+6
559		10.33	0.914	1.15	+10
88		11.22	0.843	1.15	-1
78		12.36	0.824	1.15	-5
111		12.59	0.845	1.12	+2
12		15.56	0.905	1.16	+12

CONTINUATION OF TABLE VIII-10

Compound		Experimental Data			%δS*)
PSU No.	Structural Formula	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	Slope Index	
175		16.00	0.855	1.10	+7
174		16.00	0.901	1.14	+13
134	 $C_{12}-\underset{\displaystyle C_{12}}{C}-C_{13}$	19.14	0.806	1.05	-1
113		20.7	0.876	1.17	+7
89		23.1	0.994	1.30	+14
575		23.3	0.968	1.26	+15
19		26.0	0.853	1.27	-7
65		30.9	0.850	1.27	-8
125		37.0	0.889	1.28	+3
90		131$^{**)}$	0.891$^{**)}$	1.52	-11

CONTINUATION OF TABLE VIII-10

Compound		Experimental Data			%δS*)
PSU No.	Structural Formula	$\eta_{40^\circ C}$, cP	$d_{40^\circ C}$, g/cm^3	Slope Index	
574		409	1.036	2.04	+2
122		615	0.919	1.70	-10
179		684	1.011	1.70	+15

$$^{*)}\ \%\delta S = 100\,\frac{S_{pred} - S_{exp}}{S_{exp}}$$

**) Extrapolated data

approximation (compare Chapter XII). All in all, when the aforementioned correlations are used to predict the Slope Indices of pure hydrocarbons, conspicuous deviations are very likely to occur in several cases.

Whilst the latter conjecture has indeed appeared to be correct, it has simultaneously been found that for the great majority of the many pure hydrocarbons tested the predicted Slope Indices were *not* considerably in error. Particularly the correlation employing the density of the oil as a parameter permits predictions of the Slope Indices of pure hydrocarbons that may be deemed at least semi-quantitative.

In order to convey an impression of the deviations involved the *density* correlation of Fig. VIII-6 has been applied to a great variety of 40 pure hydrocarbons taken at random from API Research Project 42[139,11,12]. In Table VIII-10 all these compounds are arranged in order of increasing viscosity grade $\eta_{40^\circ C}$. In addition to the experimental densities and Slope Indices, the percentage deviations between these experimental and the predicted Slope Indices have been included. On the whole, the deviations appear to remain fairly small; in fact, such predictions may well be acceptable for several (semi-quantitative) purposes.

VIII. 4. 4. *The Viscosity-Temperature Coefficients and "Activation Energies for Viscous Flow" of Mineral Oils*

A. APPLICATION OF THE NEW CORRELATIONS

As stated in § VI. 3. 1, the viscosity-temperature coefficient β - defined by Equation (VI-3) - represents the relative change of viscosity per temperature unit. It has been related to the Slope Index and the viscosity grade of a given liquid as follows:

$$\beta = 1.316 \cdot 10^{-2} \, S \, (\log \eta + 1.200). \qquad \text{(VI-5a)}$$

As also indicated in § VI. 3. 1, in theoretical studies on the viscosity-temperature characteristics of liquids the use of the closely related quantity E_{vis} is frequently preferred. In Eyring's theory of viscous flow (see § III. 1. 1) the latter quantity has been denoted as the "activation energy for viscous flow". It is important to note that essentially the same quantity has emerged from the great majority of viscosity theories irrespective of the particular model assumed for viscous flow.

The relationship between this activation energy for viscous flow and the viscosity-temperature coefficient has been shown to read:

$$E_{vis} = R\,T^2\,\beta. \qquad \text{(VI-8)}$$

On the basis of Equation (VI-5a) the viscosity-temperature coefficients of mineral oils can readily be predicted from each of the four new correlations for estimating their Slope Indices. Confining oneself again to the standard reference temperature of 40°C, the latter equation is rewritten as:

$$\beta_{40^\circ C} = 1.316 \cdot 10^{-2}\ S\ (\log \eta_{40^\circ C} + 1.200). \qquad \text{(VI-5)}$$

At the same standard reference temperature Relationship (VI-8) between E_{vis} and β becomes:

$$(E_{vis})_{40^\circ C} = 194.6\ \beta_{40^\circ C}\ , \qquad \text{(VI-8a)}$$

where E_{vis} is expressed in kcal/gmole.

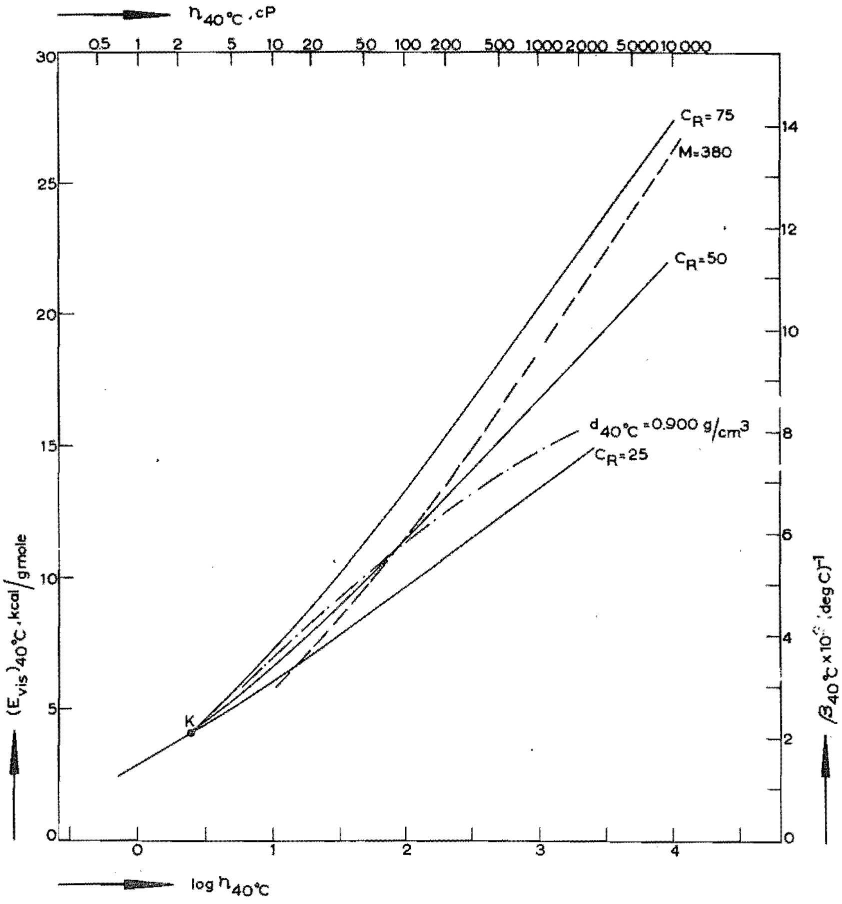


FIG. VIII-11.
Viscosity-Temperature Coefficients and "Activation Energies for Viscous Flow" of Mineral Oils According to the New Correlations.

For several groups of mineral oils characterized by a common value of the parameter used in the correlation concerned both viscosity-temperature criteria, $\beta_{40^\circ C}$ and $(E_{vis})_{40^\circ C}$, have been calculated according to the above procedure. In Fig. VIII-11 the predicted values have been plotted as a function of the viscosity grades $\eta_{40°C}$ of the oils considered.

Since for very fluid mineral oils one and the same straight-line relationship between S and $H_{40°C}$ has been upheld in each of the four correlations under consideration, these oils are depicted by a single line in Fig. VIII-11. But for oils with viscosity grades $\eta_{40°C}$ exceeding 2.43 cP - indicated by point K in the latter figure - the differentiation as to both $\beta_{40°C}$ and $(E_{vis})_{40°C}$ increases rapidly with their viscosity grade.

Fig. VIII-11 demonstrates that for the members of a group of mineral oils characterized by a common percentage C_R both viscosity-temperature criteria increase strongly with their viscosity grade, the more so the higher the particular C_R-value.

In addition to the three lines relating to C_R-values*) of 25, 50 and 75, one constant-density line has been drawn, namely for $d_{40°C} = 0.900$ g/cm^3. Whilst the lines of constant C_R are markedly convex towards the (logarithmic) viscosity axis, the constant-density line is conspicuously concave downward; a similar trend is observed for other density values.

From the underlying correlations it will be clear that the lines of constant refractive index, $n_{40°C}$, when plotted in Fig. VIII-11, are quite similar to those of constant density.

Finally, a line of constant molecular weight (M = 380) has been drawn through the intersection point of the depicted lines relating to $C_R = 50$ and to $d_{40°C} = 0.900$ g/cm^3. It may be added that similar lines would result for other M-values. Thus, within a group of mineral oils showing a common molecular weight both viscosity-temperature criteria increase very strongly with their viscosity grade.

B. MINERAL OILS WITH A COMMON RING NUMBER

Particularly in connection with the aforementioned concept of the activation energy for viscous flow it would be interesting to introduce yet another correlation for predicting the viscosity-temperature dependence of mineral oils.

This correlation employs the *total* ring number, R, of the oils for estimating their Slope Index solely from their viscosity grade. Thus, it constitutes a second correlation with their chemical constitution. The reason why it has not been included in the appropriate Section VIII. 2 consists in that its correlational accuracy is not fully on a par with that of the foregoing correlations (Sections VIII. 2 and VIII. 3) and more particularly with that of the correlation based on the carbon-type composition of the oils. Yet, it certainly constitutes a fairly accurate correlation, which may be advantageously employed for normal practical purposes. In fact, the relative average and standard deviations in the predicted Slope Indices of all the 360 mineral oils - both natural and saturated - indicated in § VIII. 1. 2 amount to no more than about 3 and 4%, respectively.

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*) It may be noted (compare § VIII. 2. 2) that the lines relating to $C_R = 25$ and $C_R = 75$ comprise nearly the entire range of values encountered for $\beta_{40°C}$ and $(E_{vis})_{40°C}$ amongst natural mineral oils.

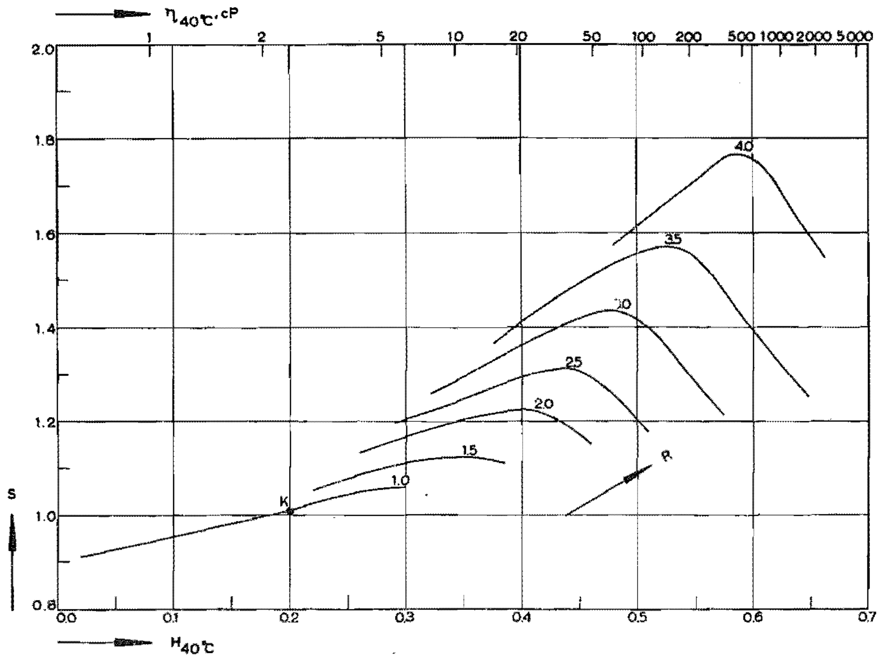

FIG. VIII-12.
Correlation Between the Viscosity-Temperature Relationship of Mineral Oils and Their Total Ring Number.

The new correlation*) has been depicted in Fig. VIII-12. The curves relating to higher ring numbers are peculiar in that they fall rather sharply for the more viscous oils.

Application of the latter correlation for calculating the activation energies for viscous flow (or the viscosity-temperature coefficients) of the members of various mineral-oil groups with a common ring number has yielded the results plotted in Fig. VIII-13.
This figure demonstrates that for the members of a mineral-oil group characterized by a particular ring number not exceeding about R = 2 the activation energy for viscous flow increases regularly with their viscosity grade. For groups with higher ring numbers, however, the most remarkable result has been achieved that the ac-

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*) The present correlation shows some resemblance to the one developed by Waterman and his associates for estimating the VI of saturated mineral oils solely from their ring number, R (see § VIII.1.1, part A). The validity of the latter correlation has been verified for ring numbers from about 2.0 to 4.0, and VI's from about -40 to +130.

According to the present correlation of Fig. VIII-12, Waterman's correlation may be upheld only for oils of comparable viscosity grades, even if it is confined to saturated samples. Indeed, it would appear that Waterman's correlation has been checked only for saturated mineral oils exhibiting relatively small variations in their viscosity grade.

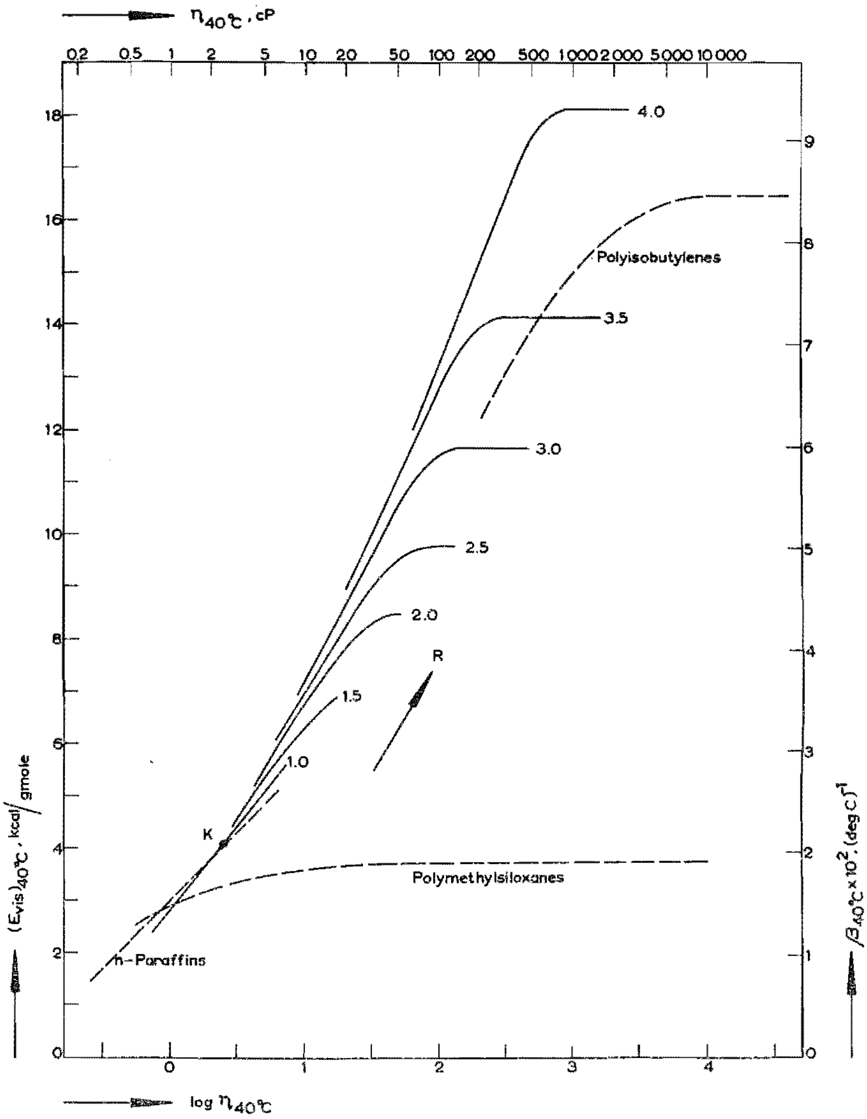

FIG. VIII-13.
Viscosity-Temperature Coefficients and "Activation Energies for Viscous Flow" of Mineral Oils According to the Correlation of Fig. VIII-12.

tivation energy for viscous flow approaches a certain limiting value, which is characteristic of the particular group.

The latter finding implies that for all the various members of such a group whose viscosity grades exceed a certain "critical" level the activation energy for viscous flow is substantially determined solely by their (average) ring complex. Or in other words, as soon as within such a group of mineral oils the (average) total length of paraffinic side chains attached to the latter ring complex has reached a certain "critical" value, it has no longer any appreciable effect on the resulting activation energy for viscous flow; but the viscosity *grade* still increases regularly with increasing chain length.

It should be realized that mineral oils naturally consist of a complexity of (essentially) hydrocarbons, so that their (apparent) activation energies for viscous flow cannot simply be compared with those of pure compounds. Nevertheless, on the basis of the concept of the "average" mineral-oil molecule (see § II. 2. 2) the observed dominating effect of the ring complex of mineral oils on their activation energy for viscous flow would seem quite plausible.

The feature that within a given series of interrelated liquids the (apparent) activation energy for viscous flow approaches a certain maximum value for the more viscous members is well known from studies on the viscosity-temperature characteristics of *long-chain polymers.* For two polymer series exhibiting this feature, namely (linear) polymethylsiloxanes[17,27,48,72,145,146)] and polyisobutylenes[75)], the activation energies for viscous flow have been included in Fig. VIII-13.

However, the reason for the constancy of E_{vis} for the more viscous members of such polymer series must be essentially different from that for the constancy of E_{vis} in the aforementioned mineral-oil series. In fact, for such polymer series the latter feature is generally attributed to the tendency of the long-chain molecules to become coiled, so that they commence to move in segments rather than as individual units. The consequent *"segmental flow"* is more pronounced according as the molecules are more flexible. Accordingly, in Fig. VIII-13 the unusually flexible polymethylsiloxanes are seen to reach their limiting value of E_{vis} at a much lower viscosity level than the rather branched polyisobutylenes.

For comparison the activation energies for viscous flow of the n-paraffins[77;139-141)] have also been depicted in Fig. VIII-13. However, since these liquids become solid already at relatively low viscosity grades, a similar constancy of their E_{vis} cannot be observed.

As compared with the two depicted series of flexible long-chain polymers the groups of mineral oils characterized by a common ring number are seen to reach their limiting value of E_{vis} at remarkably low viscosity grades. Moreover, in such mineral-oil groups the latter value is approached rather abruptly.

VIII. 4. 5. *Application of the Atmospheric-Isobar-Pole Concept to Homologous Groups of Liquids*

In part A of § VIII. 2. 3 it has been shown that, to a good approximation, the (atmospheric) viscosity-temperature isobars of all the various members of a group of mineral oils characterized by a common percentage C_R constitute a fan when these are plotted in the basic H-Θ chart. The point of convergence in the latter chart has been termed the *"atmospheric isobar pole".*

It would seem very interesting to investigate whether the relevant pole concept may also apply to truly homologous groups of pure hydrocarbons and particularly to those homologous groups of non-hydrocarbon lubricating oils that are important in modern lubrication practice.

This can conveniently be checked by plotting the Slope Indices, S, of the various members of a particular homologous group against their viscosity grades expressed in terms of H_r (at the standard reference temperature Θ_r). As elucidated in part A of the aforementioned § VIII. 2. 3, a definite atmospheric isobar pole may be assigned to a particular homologous group if the various members conform well to a straight-line relationship in such an S-H_r diagram. In accordance with preceding results on the relationship between Slope Index and viscosity grade in various homologous groups of liquids - described in Chapter VI (see in particular Figs. VI-3 and VI-5) - a standard reference temperature of 100°C (212°F) has been adopted in the present investigation.

Thus, in Fig. VIII-14 the Slope Indices of the members of several divergent homologous groups have been plotted against their viscosity grades $H_{100^\circ C}$. For comparison the straight lines for three mineral-oil groups characterized by a common percentage C_R have been depicted, namely those relating to C_R-values of 25, 50 and 75; further, the common straight line for very fluid oils, that is with viscosity grades $\eta_{100^\circ C}$ not exceeding 0.947 cP (indicated by point K'), has been included (compare Fig. VIII-10). Moreover, the straight lines indicating the SAE summer-grade viscosities, that is SAE 20, 30, 40 and 50, have been replotted from Fig. VIII-10.

Indeed, it has appeared that up to relatively high viscosity grades the various members of each homologous group considered do conform well to the straight-line relationships between S and $H_{100^\circ C}$ depicted in Fig. VIII-14. In fact, such a linear relationship may generally be taken to hold good up to at least the highest viscosity grades encountered in *mineral* lubricating-oil practice, say, up to viscosities $\eta_{100^\circ C}$ of 50-100 cP (compare Figs. VI-2 and VI-3). At the highest viscosity grades considered in Fig. VIII-14 the Slope Indices may start to vary less than indicated by the corresponding straight-line relationship; in fact, in the range of very high viscosity grades the Slope Indices of homologous groups would approximate a constant value, which is characteristic of a particular group (compare § VI. 2. 3 and Fig. VI-3).

A similar linear relationship between S and $H_{100^\circ C}$ has been found to hold good for all the other homologous groups tested so far. Consequently, the (atmospheric) viscosity-temperature isobars of the various members of such homologous groups do form a fan when these are plotted in the basic H-Θ chart.

As previously found for mineral-oil groups with a common percentage C_R, the atmospheric isobar poles of the chlorotrifluoroethylene polymers[27, 72, 142, 144] and the (meta-linked, unsubstituted) polyphenyl ethers[23b] are situated in the region of very low viscosities and extremely high temperatures[*].

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[*] Since the produced part of the straight line depicted for the chlorotrifluoroethylene polymers in Fig. VIII-14 passes through the "transitional" point K' of mineral oils, the corresponding atmospheric isobar pole happens to be located on the atmospheric isobar pole line established for mineral oils (see § VII. 2. 3, part A). In fact, the pole of these chlorotrifluoroethylene polymers would coincide with that for mineral oils having a common percentage C_R of 51.

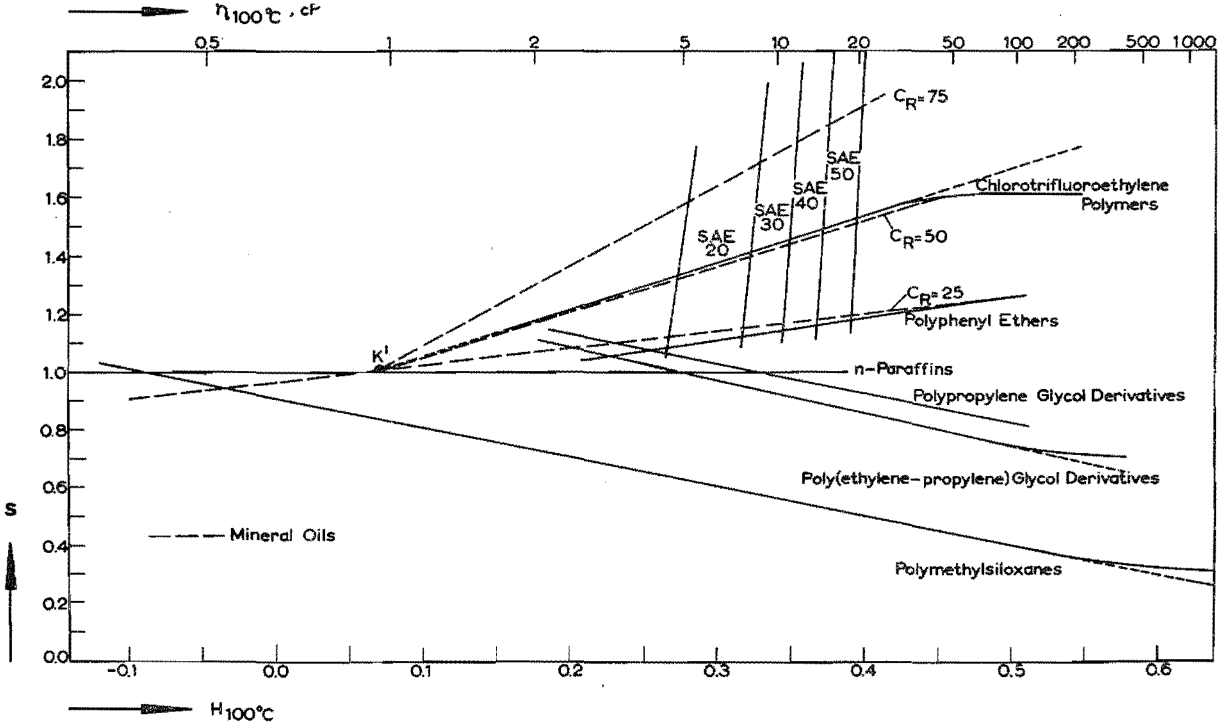

FIG. VIII-14.
Correlation Between the Slope Indices and Viscosity Grades of Various Homologous Groups of Liquids.

The atmospheric isobar poles of the other homologous groups of synthetic lubricating oils depicted in Fig. VIII-14, namely the polypropylene and poly(ethylene-propylene) glycol derivatives[72,114b] and the linear polymethylsiloxanes[17,27,48,72,145,146], are located in the opposite region of the H-Θ chart, that is the region of extremely high viscosities and very low temperatures.

As indicated already in § VI.2.1, the Slope Indices of all the n-paraffins depicted, that is from n-C_5 up to n-C_{64}, show invariably one and the same value, namely $S = 1.00$. Accordingly, in the basic H-Θ chart the viscosity-temperature isobars of all these n-paraffins constitute a family of parallel straight lines, their common slope amounting to unity. To keep in harmony with the present pole concept the homologous group of n-paraffins may thus be taken to have an atmospheric isobar pole located at infinity.

Summarizing, it has indeed proved possible to extend the applicability of the atmospheric-isobar-pole concept to any of the homologous groups of liquids considered hitherto.

VIII. 4. 6. *The Viscosity-Temperature Relationship of Polymer-Blended Mineral Oils*

A. INTRODUCTION

During the last decades, the addition of long-chain polymers to mineral base oils with the object of improving their viscosity-temperature qualities has assumed considerable practical importance. Amongst the many types of polymers proposed three have achieved wide-spread usage, namely polyisobutylenes, polymethacrylates and polyalkylstyrenes.

Besides an increase of the viscosity grade of a given base oil, such polymers bring about a *relative* flattening of its viscosity-temperature curve. The latter means that the resulting blend displays a viscosity-temperature curve which is flatter than that of a *straight* mineral oil having the same (increased) viscosity grade as the produced *blend* but the viscosity-temperature quality - normally expressed in terms of the VI - of the *base oil*. Accordingly, such polymers are commonly denoted as *"VI-improvers"*.

In order to avoid the ambiguities and irregularities inherent in the VI-system (see Chapter VI) the indicated improvement of the viscosity-temperature quality of the base oil will be treated here in terms of the new viscosity-temperature criterion, the Slope Index. It is then found that the Slope Index of the blend is smaller than that of the base oil; or, in other words, the DVI of the base oil has been raised. The aforementioned polymers will appropriately be termed *"DVI-improvers"*.

The indicated beneficial action of DVI-improvers may thus be considered to consist in that their viscosity-increasing effect ("thickening power") on a given base oil is *relatively* greater at higher than at lower temperatures, that is as compared with a straight mineral oil showing the same viscosity grade as the blend but the Slope Index of the base oil. This temperature-dependent effect of a DVI-improver on the viscosity of a given base oil is generally ascribed to a high degree of *coiling* of the polymer chain at lower temperatures and an *uncoiling* with rising temperature.

The degree of coiling of the polymer chain is primarily governed by two factors - both generally increasing with temperature -, namely the flexibility of the chain and the solubility of the polymer in a particular base oil. Thus, it becomes clear that the Slope Index of a given base oil can be decreased most effectively by using some flexible long-chain polymer which is poorly soluble in the oil at low temperatures but so soluble at high temperatures that it there assumes an almost completely uncoiled form.

B. THE VISCOSITY-TEMPERATURE COEFFICIENTS OF POLYMER-BLENDED MINERAL OILS

It should be emphasized that DVI-improvers need not necessarily lower the *viscosity-temperature coefficient* (or the activation energy for viscous flow) of the base oil. In fact, this quantity may also remain substantially constant or may even increase markedly.

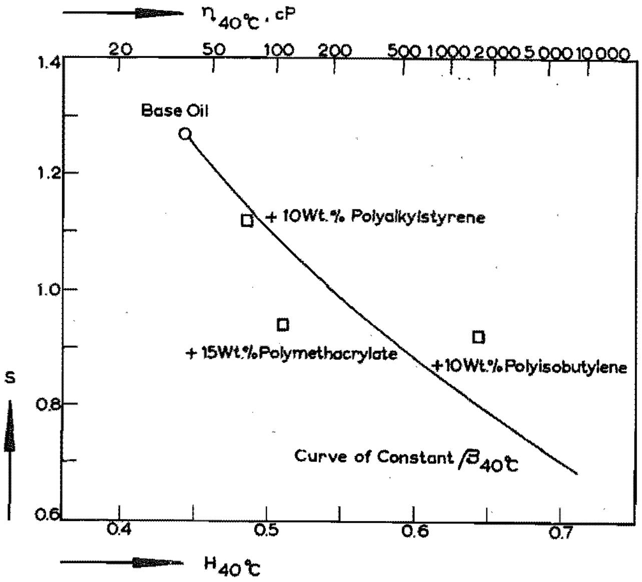

FIG. VIII-15.
Viscosity-Temperature Dependence of a Series of Polymer-Blended Mineral Oils.

These things are illustrated in Fig. VIII-15, where the Slope Indices of a given base oil and three blends prepared from it, by the addition of different types of long-chain polymers, have been plotted against the corresponding viscosity grades $H_{40^\circ C}$ [17]; moreover, this figure represents the relationship between Slope Index and viscosity grade - on the basis of Equation (VI-5) - for the various blends that would display the same viscosity-temperature coefficient $\beta_{40^\circ C}$ as the base oil. Whilst for the polyalkylstyrene-containing blend of Fig. VIII-15 the viscosity-temperature coefficient is practically identical to that of the base oil, the viscosity-temperature coefficient of the polymethacrylate-containing blend is considerably lower and that of the polyisobutylene-containing blend markedly higher than that of the base oil.

Consequently, in accordance with theory the viscosity-temperature coefficients of blends prepared from a given base oil depend rather strongly on the particular polymer employed. Similarly, as will be illustrated below, the quantitative effect of a given polymer on different base oils may vary rather widely from one oil to another.

Nevertheless, as discussed by Bondi[20,21], the viscosity-temperature coefficients of a large number of commercial polymer-blended mineral oils come fairly close to that of the base oil. Moreover, deviations from this simple behaviour would be qualitatively predictable from information on the flexibility of the polymer chain and the solubility of the polymer in the base oil employed[21].

Unfortunately, it may be deemed well-nigh impossible to predict *quantitatively* the effect of a particular polymer on a given base oil, if only because the solvent action of mineral oils is very complex. It is true that some interesting correlations for predicting the latter effect have been established - notably by Wuellner and Brannen[155] -, but these would appear to be of rather limited applicability and would not lend themselves to generalization*).

C. THE PRESENT METHOD FOR CHARACTERIZING THE EFFECT OF POLYMERS ON THE VISCOSITY-TEMPERATURE RELATIONSHIP OF A GIVEN BASE OIL

It stands to reason that the correlations developed in Sections VIII. 2 and VIII. 3 for predicting the Slope Index of mineral oils cannot be applied to polymer-blended samples (compare § VIII. 4. 2).

However, the present mathematical framework and more particularly the atmospheric-isobar-pole concept (see § VIII. 4. 5) have proved very useful for simply *characterizing* the effect of polymers on the viscosity-temperature relationship of a given base oil. The new characterization method is based on two findings now to be outlined.

a. In the first place it has been established that over a very wide concentration range the relationship between the Slope Indices and the viscosity grades H_r of a series of blends prepared from a given base oil by adding varying amounts of a particular polymer is substantially linear. Thus, like the (atmospheric) isobars of homologous groups of liquids and of mineral-oil groups characterized by a common percentage C_R, the isobars of such a series of blends constitute a fan when they are plotted in the basic H-Θ chart. In fact, the present finding represents another interesting application of the atmospheric-isobar-pole concept.

In general, the aforementioned linear relationship between S and H_r for a given polymer/base-oil combination can be upheld for blends covering the very wide concentration range from at least 2 to 30 per cent by weight of polymer. In fact, in the majority

*) This also applies to the "generalized" correlation recently proposed by Wright and Crouse[156].

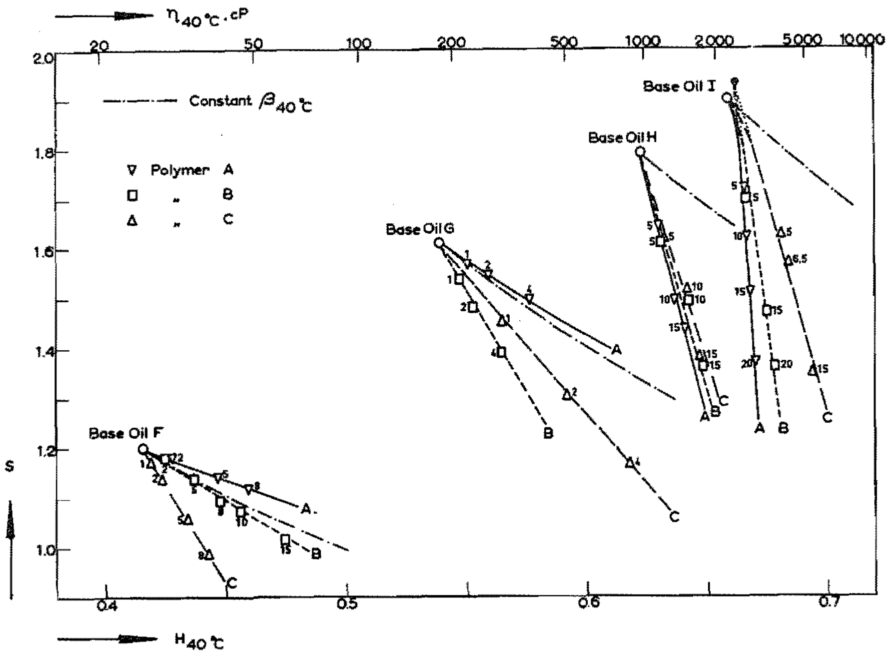

FIG. VIII-16.

Illustration of the Present Method for Characterizing the Effect of Polymers on the Viscosity-Temperature Relationship of a Given Base Oil.

Designations: A = Polyisobutylene
B = Condensation product of a highly chlorinated wax with naphthalene
C = Polycetylmethacrylate.

of systems tested the base oil itself also proved to conform very well to the straight-line relationship between S and H_r established for such a series of blends. But in certain systems the base oil was found to comply markedly less with the latter relationship.

b. In the second place it has been found that, to a good approximation, the straight lines resulting in an S-H_r diagram by adding different polymers to one and the same base oil converge towards one single point, which coincides with, or at least comes close to, the point depicting the base oil. This finding has been illustrated in Fig. VIII-16 for four very divergent kinds of mineral oils*), each oil being blended with three well-known types of polymers 157).
The latter finding can be shown to imply that in the basic H-Θ chart the (atmospheric) isobar poles of different polymers added to the same base oil would be located on one single straight line - the isobar pole line characterizing the base oil considered -, which coincides with, or at least comes close to, the (atmospheric) H-Θ isobar of the base oil.

Along the above lines a really simple method has been achieved for characterizing the effect of polymers on the viscosity-temperature relationship of a given base oil. In fact, once the location of the aforementioned point of convergence in an S-H_r diagram (such as Fig. VIII-16) has been established for a given base oil, only *one* experimental blend is required for determining, over a very wide concentration range, the relationship between the Slope Indices and the viscosity grades H_r of the series of blends obtained by adding varying amounts of a particular polymer to this base oil.
Finally, it may be stated that if one confines the present method to interrelated base oils and/or polymers, further simplifications may well be achieved.

APPENDICES

Appendix VIII-1. *The Atmospheric Isobar Pole Line*

Correlation (VIII-3a) of § VIII. 2. 2 may be rearranged to:

$$H - \left[-\frac{101}{3.0\,(C_R - 7)} + 0.2000 \right] = S \left\{ \Theta - \left[-\frac{101}{3.0\,(C_R - 7)} - 0.1127 \right] \right\} . \qquad \text{(VIII-3c)}$$

From the latter expression it is readily seen that the viscosity-temperature isobars of mineral oils characterized by a common percentage C_R are represented in the basic H-Θ chart by a family of

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*) It should be noted that base oil "H" and particularly base oil "I" represent rather extreme types of mineral oils. Accordingly, these oils may be taken to permit a severe test of the validity of the present finding.

straight lines emanating from one single point, which is termed the *"atmospheric isobar pole"*.

Denoting the coordinates of this pole by H_a and Θ_a, the relevant equations can be read from Equation (VIII-3c), namely:

$$H_a = -\frac{101}{3.0\,(C_R - 7)} + 0.2000 \qquad \text{(VIII-5a)}$$

and

$$\Theta_a = -\frac{100}{3.0\,(C_R - 7)} - 0.1127. \qquad \text{(VIII-6a)}$$

Furthermore, the percentage C_R can be eliminated from the latter two expressions. This leads to the following linear relationship between the pole viscosity H_a and the pole temperature Θ_a:

$$H_a = 1.01\,\Theta_a + 0.3138. \qquad \text{(VIII-4)}$$

Consequently, in the basic H-Θ chart the pole coordinates H_a and Θ_a are located on one single straight line, irrespective of the percentages C_R involved. This straight line, represented by Equation (VIII-4), constitutes the *"atmospheric isobar pole line"*.

Appendix VIII-2. *Examples of the Conversion of Kinematic into Dynamic Viscosities for Mineral Oils With Unknown Densities*

(see § VIII.3.5, part B)

A. KINEMATIC VISCOSITIES AT 100 AND 210°F BEING SPECIFIED

For the arbitrarily chosen Pennsylvania oil F-22 of Table VIII-2 the experimental kinematic viscosities at 100 and 210°F (37.8 and 98.9°C) are specified as: $\nu_{100°F}$ = 85.3 cS and $\nu_{210°F}$ = 9.63 cS.

As a first approximation it is assumed that its density $d_{40°C}$ amounts to 0.900 g/cm^3. Employing the density-temperature coefficient $\partial d/\partial t = -6.3 \cdot 10^{-4}$ g/(cm^3 · deg C), it would follow: $d_{100°F}$ = = 0.901 g/cm^3 and $d_{210°F}$ = 0.863 g/cm^3. Therefore, the dynamic viscosities would amount to: $\eta_{100°F}$ = 76.7 cP and $\eta_{210°F}$ = 8.32 cP. Substituting the latter viscosities into the basic viscosity-temperature Equation (III-6h), it would follow that S = 1.24 and $H_{40°C}$ = 0.48*).

Plotting the latter values of S and $H_{40°C}$ in Fig. VIII-6 yields - as a second approximation - the density value $d_{40°C}$ = 0.867 g/cm^3. As compared with the experimental value $d_{40°C}$ = 0.864 g/cm^3 the latter estimate proves to be very good indeed. According to Equation (VIII-9), the estimated density $d_{40°C}$ = 0.867 g/cm^3 corresponds to the following density values at the present reference temperatures: $d_{100°F}$ = 0.868 g/cm^3 and $d_{210°F}$ = 0.829 g/cm^3.

Using the latter density data and the aforementioned experimental kinematic viscosities, one finally arrives at the following dynamic

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*) It suffices to specify only two decimal places of the viscosity function $H_{40°C}$.

viscosities: $\eta_{100^\circ F} = 74.0$ cP and $\eta_{210^\circ F} = 8.00$ cP. The deviations from the experimental viscosities, being $\eta_{100^\circ F} = 73.8$ cP and $\eta_{210^\circ F} = 7.98$ cP, lie well within the experimental accuracy.

B. KINEMATIC VISCOSITY AT 210°F AND VISCOSITY INDEX BEING SPECIFIED

For the arbitrarily selected Gulf Coast oil F-67 of Table VIII-2 the experimental kinematic viscosity at 210°F and the Viscosity Index are specified as: $\nu_{210^\circ F} = 8.89$ cS and VI = 12. From these data its kinematic viscosity at 100°F is found, by means of the ASTM Viscosity-Index tables[128)], to amount to $\nu_{100^\circ F} = 125.9$ cS.

As described in the foregoing part A of this appendix, the density values $d_{100^\circ F} = 0.901$ g/cm^3 and $d_{210^\circ F} = 0.863$ g/cm^3 will first be tried. The corresponding dynamic viscosities would be: $\eta_{100^\circ F} = 113.5$ cP and $\eta_{210^\circ F} = 7.67$ cP. By means of the basic viscosity-temperature Equation (III-6h) these viscosities would yield the values $S = 1.47$ and $H_{40^\circ C} = 0.50$.

Applying Fig. VIII-6 then gives, as a second approximation, the density value $d_{40^\circ C} = 0.916$ g/cm^3, which proves to be in good agreement with the experimental value of 0.910 g/cm^3. According to Equation (VIII-9), the estimated density $d_{40^\circ C} = 0.916$ g/cm^3 corresponds to the following densities at the present reference temperatures: $d_{100^\circ F} = 0.917$ g/cm^3 and $d_{210^\circ F} = 0.880$ g/cm^3.

By means of the latter densities the following dynamic viscosities are finally derived from the aforementioned experimental kinematic viscosities: $\eta_{100^\circ F} = 115.4$ cP and $\eta_{210^\circ F} = 7.82$ cP. The deviations from the experimental data, that is $\eta_{100^\circ F} = 114.8$ cP and $\eta_{210^\circ F} = 7.76$ cP, are again well within the experimental accuracy.

Appendix VIII-3. *SAE Crankcase-Oil Viscosity Classification*

In practice the viscosity *grade* of crankcase lubricating oils is generally specified in terms of their "SAE Viscosity Number"[154)]. Each such number corresponds to a particular *range* of viscosity grades.

As the relevant SAE standard aims at classifying crankcase oils, in terms of their viscosity grade *only*, at temperatures near to those at which the oils are intended to operate, two standard reference temperatures are employed, namely 0°F (-17.8°C) for the so-called *winter*-grade viscosities (indicated by the suffix "W") and 210°F (98.9°C) for the *summer*-grade viscosities.

The *official* values indicating the viscosity ranges covered by the various SAE Viscosity Numbers are expressed in SUS (SAE J300). For information only, the corresponding (approximate) kinematic viscosities, in cS, have been listed in the later standard SAE J309. All the pertinent data are reproduced in Table VIII-11.

TABLE VIII-11

SAE Crankcase-Oil Viscosity Classification

SAE Viscosity Number	Viscosity Range							
	At 0°F (-17.8°C)				At 210°F (98.9°C)			
	Minimum*)		Maximum		Minimum		Maximum	
	SUS	cS	SUS	cS	SUS	cS	SUS	cS
5W	-	-	4,000	869				
10W	6,000**)	1,303	<12,000	2,606				
20W	12,000***)	2,606	48,000	10,423				
20					45	5.73	< 58	< 9.62
30					58	9.62	< 70	< 12.93
40					70	12.93	< 85	< 16.77
50					85	16.77	<110	< 22.68

*) The viscosity of oils included in this classification shall not be less than 39 SUS (3.86 cS) at 210°F.

**) Minimum viscosity at 0°F may be waived provided viscosity at 210°F is not below 40 SUS (4.18 cS).

***) Minimum viscosity at 0°F may be waived provided viscosity at 210°F is not below 45 SUS (5.73 cS).

CHAPTER IX

THE VISCOSITY-PRESSURE RELATIONSHIP OF MINERAL OILS: CORRELATION WITH CHEMICAL CONSTITUTION AND PHYSICAL CONSTANTS

IX. 1. INTRODUCTION

IX. 1. 1. *Background*

As elucidated in Chapter I of this thesis, the pressure dependence of the viscosity of oils may be of paramount importance in various engineering applications, primarily in the field of hydrodynamic lubrication. It is no wonder, therefore, that numerous investigators have attempted to establish correlations*) for estimating the viscosity-pressure relationship of lubricating oils, notably mineral oils, either through the sole use of (physical) quantities that are easily assessable at *atmospheric* pressure or directly from their chemical constitution.
In the present chapter attention will be concentrated upon the prediction of the viscosity-pressure variation of *mineral* oils.

It is well known that for correlational purposes the chemical constitution of mineral oils can suitably be expressed in terms of the "Waterman analysis", notably in terms of the carbon percentages C_A; C_N and C_P (see § II. 2. 2).
As regards the existing correlations employing atmospheric quantities it appears that most of these are based on some parameter that is claimed to be representative of the atmospheric *temperature* variation of viscosity. In addition, *straight* physical constants such as atmospheric density - taken at some standard reference temperature - are frequently utilized.
The existing correlations with chemical constitution and with straight physical constants are discussed in § IX. 1. 2. The many correlations involving the use of some quantity that would be representative of the atmospheric viscosity-temperature dependence will be considered separately in Chapter X.

Furthermore, it should be emphasized that a basic difficulty encountered in all such correlational attempts consists in casting the isothermal viscosity-pressure relationship into as simple an analytical form as possible (having a minimum number of parameters) in order to make correlation easier. Moreover, in order to cover a wide temperature range the parameters employed for characterizing the latter (isothermal) relationship should be known functions of temperature or, preferably, they should be substantially independent of temperature.

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*) Critical reviews of such correlations have been presented by Blok[84], by Hersey and Hopkins[26] and by Dow[37].

Unfortunately, nearly all formulas hitherto employed for the isothermal viscosity-pressure relationship are unsatisfactory in that simplification has gone too far. But oversimplification is bound to limit the applicability of any correlation based on these particular formulas.

In fact, the great majority of correlational attempts proves to be essentially based on the assumption that the oversimplified Barus Equation (IV-1a) would sufficiently characterize the isothermal viscosity-pressure relationship of mineral oils. Further, the viscosity-pressure coefficient, α, in the latter equation varies rather strongly with temperature, the relevant variation being very different from one oil to another.

IX. 1. 2. *Previous Investigations*

A. CORRELATION WITH CHEMICAL CONSTITUTION

From the extensive investigations carried out by Dow and associates[36,37] it has appeared that at the same standard reference temperature paraffinic mineral oils often possess a smaller viscosity-pressure coefficient, α, than naphthenic samples. This, however, appears to be no general rule. Accordingly, it is not surprising that they did not succeed in establishing some satisfactory correlation between the viscosity-pressure coefficient of mineral oils and their carbon-type composition.

In fact, in a fairly recent paper[30] Kuss clearly demonstrated that no such correlation between the viscosity-pressure coefficient and the carbon-type composition can be achieved that is *generally* applicable to mineral oils.

Moreover, from the latter finding Kuss drew the rather sweeping conclusion that characterization of the chemical constitution of mineral oils in terms of their carbon-type composition does not suffice for determining their viscosity-pressure behaviour. However, as discussed by Roelands *et al.*[44], this conclusion is overgeneralized and cannot be upheld*).

Indeed, Roelands *et al.*[44] have succeeded in establishing a really convenient correlation which permits satisfactory predictions of the effect of pressure on the atmospheric viscosity of mineral oils solely from their carbon-type composition. This correlation has been based on the mathematical framework developed in the same paper[44], the expression for the isothermal viscosity-pressure relationship being identical to the two-parameter Equation (IV-3). The corresponding *complete* viscosity-pressure equation (compare § V. 4. 2) has the desirable feature that its (three) parameters are substantially independent not only of pressure but also of temperature. Now, these three characteristic parameters have been found to be related very

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*) It should be added that, in a private discussion with the present writer, Prof. Kuss has admitted that this conclusion has indeed been intended to apply specifically to correlations based on the viscosity-pressure coefficient α, which actually constitutes the only viscosity-pressure criterion employed in his investigation[30].

simply to the carbon-type composition of the mineral oil considered, in fact to the constitutional criterion (C_A + 1.5 C_N).

The resulting correlation has been derived exclusively on the basis of original data on 20 well-defined mineral oils. It has further been checked successfully for various mineral oils for which sufficient data are available in the literature.

Although this correlation has been verified over fairly extensive ranges of atmospheric viscosity, temperature and pressure, it would be very desirable yet to extend its applicability range. In addition, in view of the expressions developed in Chapter IV for the viscosity-pressure relationship, the attractive mathematical framework employed in the latter correlation could still be simplified considerably.

B. CORRELATION WITH ATMOSPHERIC PHYSICAL CONSTANTS

In general, the many attempts to establish correlations for predicting the viscosity-pressure dependence of mineral oils from (easily measurable) atmospheric physical constants have met with only very limited success (see Dow[36,37)], Blok[84)], Kuss[29,13)] and Hersey and Hopkins[26)]). A variety of physical constants prove to have been tried out, but only a few more or less quantitative correlations could thus be achieved.

The atmospheric *density* - taken at some standard reference temperature - has been advocated by several investigators as a suitable quantity for estimating the viscosity-pressure dependence (at the same standard reference temperature) of mineral oils. The consequent correlation has been suggested by Kadmer[158)]. It has been elaborated by Grunberg[159,160)] on the basis of the extensive viscosity-pressure data compiled by Kuss[29)]. In fact, Grunberg claimed that at the adopted standard reference temperature of 25°C (77°F) a linear correlation would exist between the viscosity-pressure coefficients and the atmospheric densities of the great majority of mineral oils considered; but more or less extreme types, notably aromatic extracts, proved to deviate conspicuously from the latter correlation (compare Kuss[29)]).

A nearer analysis carried out by the present writer has led to the conclusion that the assumption of a unique correlation, at some standard reference temperature, between the viscosity-pressure coefficients and the atmospheric densities of mineral oils is generally far from adequate. This has been elucidated - in connection with new findings - in § IX.4.2.

Dow and Fink[36,37)], like most other investigators, based their correlational attempts on the assumption that mineral oils would conform to Barus's simple Equation (IV-1a). However, they did not use the viscosity-pressure coefficient α of that equation but a related quantity, which proves to be defined by $\alpha/\ln \eta_0$. They stated that, at a standard reference temperature of 100°F (37.8°C), the latter quantity would bear a close correlation to the *aniline point* of the oils. The resulting correlation - indicating a greater value of $\alpha/\ln \eta_0$ with decreasing aniline point - was put into a simple analytical form.

Further, it should be mentioned that Dow and Fink had little success in attempting to correlate their viscosity-pressure quantity $\alpha/\ln \eta_0$ with properties that they consider of more fundamental significance, for instance atmospheric density, atmospheric refractive index, molecular weight, Viscosity Index, paraffinic content, aromatic content, hydrogen-carbon ratio and rings per molecule.

As regards Dow and Fink's correlation with the aniline point of mineral oils the present author has found that for many oils this correlation does yield acceptable predictions of their viscosity-pressure coefficients, α. But for other oils, particularly the less viscous ones, the predicted α-values may be in error by 25 to 50% and even more. Consequently, Dow and Fink's correlation cannot be upheld for general application to mineral oils either.

It would appear that hitherto only Kuss[30)] has succeeded in devising a correlation between the viscosity-pressure dependence of mineral oils and atmospheric physical constants which does yield acceptable results *throughout*. Moreover, Kuss's correlation has the attractive feature of being applicable in a fairly wide temperature range.

This correlation permits predicting the viscosity-pressure coefficient, α, of a given mineral oil from its *aniline point* and its *density* (at the temperature concerned), the latter quantity being properly *corrected* for the presence of carbon atoms in aromatic-ring structure*). The relevant correction of the experimental density is performed similarly to the procedure adopted by Waterman and associates in their so-called ν-n-d method[38,42)]. Accordingly, apart from the indispensable atmospheric viscosity at the various temperatures involved, Kuss's correlation requires a knowledge not only of the aniline point and of the atmospheric density at these various temperatures, but also of three atmospheric physical constants needed for applying the aforementioned correction, namely *viscosity*, *density* and *refractive index* at the standard reference temperature of 20°C (68°F) used in the ν-n-d method**).

First of all, it should be emphasized that in general the viscosity-pressure coefficients predicted by means of Kuss's correlation for very divergent kinds of mineral oils may be deemed quite satisfactory.

Unfortunately, this correlation involves a comparatively great number of physical constants, so that it is rather cumbersome to use. Further, it has the same fundamental drawback as most of the other correlations proposed, namely that it is based on the assumption that the oils would conform to the simple Barus equation.

Kuss's very important correlation will be discussed more thoroughly - in connection with newly developed correlations - in § IX.4.5.

C. MISCELLANEOUS INVESTIGATIONS

Apparently because of the very limited success of previous attempts to correlate the viscosity-pressure variation of mineral oils

*) Thus, this corrected atmospheric density would represent that of the corresponding saturated sample.

**) Preferably, the sulfur content of the mineral oil should also be known.

with atmospheric physical quantities or with their chemical constitution, Blok[84] delineated a novel approach in which mineral oils were classified according to *"naturally" homologous* groups*). Primarily on the basis of his findings for the particular naturally homologous group of Pennsylvania oils Blok postulated that, in a viscosity-pressure diagram, the isotherms of all members of each such group would form *one single* family of non-crossing curves. This is a most remarkable result, because off-hand one might expect a *separate* family of isotherms for every individual member of the group.

As a consequence of Blok's postulate, the trend of any isotherm of any member of a naturally homologous group would be completely defined solely by its *atmospheric* viscosity. Or in other words, to the accuracy embodied into this postulate, all oils of such a group would show identical isotherms at temperatures so adjusted that their atmospheric viscosities are equal.

Particularly in view of the rather discouraging results of the many previous correlational efforts, Blok's approach should be deemed an important contribution in the present field. The really simple interrelationship disclosed between the viscosity-pressure dependences of mineral oils belonging to some naturally homologous group might be taken as a convenient starting-point in trying to achieve some *generalized* correlation. Conversely, for any naturally homologous group the validity of such a generalized correlation can readily be checked on the basis of Blok's postulate (see also § IX.3.4).

Using the extensive experimental data obtained in the scope of the well-known ASME pressure-viscosity project[27], Chu and Cameron[161] recently produced a set of three correlations for estimating the viscosity-pressure variation of mineral oils. In their investigation mineral oils are denoted as "naphthenics" if their aniline point is below 90°C (194°F), the other oils being termed "paraffinics". Whilst for the thus-defined naphthenics they advocated the use of a correlation originally proposed by Worster[162] for application to mineral oils in general, they developed two new correlations for the thus-defined paraffinics.

Irrespective of the underlying viscosity-pressure equations, Chu and Cameron's correlations imply that both in the group of paraffinics and in that of naphthenics the viscosity-pressure variation would depend only on the *atmospheric* viscosity of the oil considered; or in other words, the pressure effect on its atmospheric viscosity would be independent of its chemical constitution (compare Blok's aforementioned postulate).

However, such a sweeping assumption readily proves to be very far from adequate. Whilst Chu and Cameron's overgeneralized correlations may be of some value for qualitative or even certain semi-quantitative purposes, they obviously may not be relied upon in making *quantitative* estimates of the viscosity-pressure dependence of mineral oils.

Chu and Cameron's correlations will also be discussed more thoroughly - in connection with new findings - in § IX.3.4.

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*) Actually, Blok used the term "similar" for indicating such groups.

IX. 1. 3. *The Present Approach*

From the foregoing discussion it may be concluded that still a real need exists for more generally applicable and more convenient correlations that would permit satisfactory predictions of the pressure effect on the atmospheric viscosity of mineral oils either from their chemical constitution or from atmospheric physical constants.

The importance of a suitable *mathematical framework* for such correlations can hardly be overemphasized. Now, as elucidated in the subsequent Section IX. 2, the newly developed expressions for characterizing the viscosity-pressure relationship of mineral oils (see Chapters IV and V) would seem very feasible for correlational purposes. In fact, it could be shown that only the *Viscosity-Pressure Index*, Z, at some standard reference temperature, needs to be known in order to evaluate the pressure effect on the atmospheric viscosity of mineral oils over a wide range not only of pressure but also of *temperature*.

Accordingly, the present approach aims at devising correlations for estimating their Viscosity-Pressure Index, again at the standard reference temperature of 40°C, from their viscosity grade $\eta_{0,40^\circ C}$ and either their chemical constitution or atmospheric physical constants. It should be pointed out that the present approach to the Viscosity-Pressure Indices $Z_{40^\circ C}$ of mineral oils is rather analogous to that described in the preceding Chapter VIII for their (atmospheric) Slope Indices.

Experimental Data

The search for generalized correlations that would permit satisfactory estimates of the viscosity-pressure dependence of mineral oils has long been hampered by the lack of reliable experimental high-pressure data on representative samples. In addition, the oils tested have frequently been specified insufficiently, particularly with respect to their chemical constitution.

Fortunately, the indispensable basic data have gradually become available, notably in the scope of the famous ASME pressure-viscosity project[27] and of Kuss's extensive high-pressure investigations[29,30,13].

The results of the present study are based on reliable experimental data on 74 mineral-oil fractions. As regards their origin and chemical composition, these fractions may be considered representative of the entire range of *natural* mineral oils known so far. In addition, some fully *hydrogenated* samples have been included.

Table IX-1 lists the various investigations from which these basic data have been taken. The viscosity grades $\eta_{0,40^\circ C}$, the (atmospheric) Slope Indices, S_0, and the Viscosity-Pressure Indices $Z_{40^\circ C}$ of the various oils*) are compiled in Table IX-2. All these oils have been

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*) The author wishes to express his sincere gratitude to Prof. E. Kuss, at the Institut für Erdölforschung in Hannover, for generously placing at his disposal the complete series of accurate experimental viscosity data on the carefully selected, representative group of mineral oils coded K-1 through K-29. The author's best thanks are due also to Prof. Gg.R.Schultze, director of the latter institute, for his kind co-operation.

TABLE IX-1

Specification of Mineral Oils Included in the Present Investigation

Investigation	Ref.	Number of Oils
Kuss	29,30	31
Roelands et al.	44	20
ASME	27	16
Dow et al.	35	7
	Total	74

specified already in Table II-1, where their chemical constitution is characterized in terms of the n-d-M method and where several appropriate physical data are collected. For further particulars concerning the data of Table II-1 reference may be made to the relevant explanation given in Chapter II.

As regards the Viscosity-Pressure Indices $Z_{40^\circ C}$ listed in Table IX-2 it should be pointed out that practically all of them have been derived on the basis of experimental data for the pressure range up to about 1,000-2,000 kgf/cm^2 (14,000-28,000 psi). The corresponding atmospheric Slope Indices, S_0, have invariably been determined from the viscosity data available in the temperature range between 20 and 100°C (68 and 212°F).

IX. 2. THE MATHEMATICAL FRAMEWORK FOR THE PRESENT CORRELATIONS

As indicated already at the end of § VII. 3. 1, the complete viscosity-temperature-pressure Equation (V-1a) can be substantially simplified if its applicability is confined to *mineral* oils. This accrues from the finding - described in the same § VII. 3. 1 and illustrated by Fig. VII-3 - that for all the various kinds of mineral oils tested the temperature effect on their viscosity-pressure dependence follows one and the same simple pattern.

IX. 2. 1. *The Isotherm Pole Line*

One of the basic features incorporated into the complete viscosity-temperature-pressure Equation (V-1a) has been shown to consist in that any given liquid is characterized by a particular viscosity-pressure pole, so that its family of isotherms is depicted in an H-Π chart as a fan. Essentially the same thing is implied by saying that with varying temperature its Viscosity-Pressure Index, Z, changes linearly with its atmospheric viscosity function H_0.

For all the various kinds of *mineral* oils investigated so far it can now mathematically be deduced from the above-discussed Fig. VII-3 that in an H-Π chart their viscosity-pressure poles are located,

TABLE IX-2

Experimental and Predicted Viscosity-Pressure Indices Z_{40^oC} of Representative Mineral Oils

Oil Code*)	Experimental Data			Z_{40^oC} Predicted from $\eta_{0,40^oC}$ Plus....			
	$\eta_{0,40^oC}$, cP	S_0	Z_{40^oC}	C_R	$d_{0,40^oC}$	$n_{0,40^oC}$	$(n-d)_{0,40^oC}$
K-1	260	1.24	0.58	0.57	0.60	0.63	0.57
K-2	134.9	1.30	0.62	0.62	0.65	0.68	0.63
K-3	101.0	1.27	0.61	0.63	0.65	0.66	0.66
K-4	159.2	1.26	0.60	0.58	0.62	0.64	0.59
K-5	147.2	1.40	0.69	0.67	0.67	0.66	0.70
K-6	110.9	1.42	0.73	0.69	0.73	0.79	0.69
K-7	58.9	1.18	0.62	0.66	0.64	0.63	0.65
K-8	67.6	1.50	0.80	0.77	0.81	0.85	0.78
K-9	328	1.47	0.70	0.72	0.70	0.78	0.67
K-10	62.4	1.30	0.67	0.69	0.71	0.73	0.70
K-11	246	1.39	0.66	0.65	0.69	0.74	0.67
K-12	408	1.35	0.65	0.68	0.66	0.70	0.65
K-13	1,686	0.97	0.68		0.74	0.77	0.72
K-14	7.16	1.09	0.66	0.69	0.65	0.68	0.66
K-15	2.93	1.04	0.72	0.76	0.76	0.77	0.75
K-16	12.90	1.14	0.67	0.62	0.62	0.63	0.63
K-17	31.8	1.19	0.66	0.68	0.68	0.68	0.68
K-18	36.6	1.27	0.69	0.66	0.67	0.69	0.67
K-19	27.3	1.31	0.72	0.72	0.70	0.71	0.69
K-20	33.5	1.23	0.64	0.67	0.66	0.66	0.67
K-21	173.8	1.29	0.60	0.62	0.61	0.60	0.63
K-22	139.5	1.27	0.61	0.64	0.61	0.58	0.64
K-23	355	1.34	0.60	0.58	0.57	0.56	0.59
K-24	83.7	1.34	0.70	0.69	0.69	0.70	0.70
K-25	192.0	1.38	0.65	0.66	0.64	0.61	0.70
K-26	90.0	1.52	0.83	0.82	0.80	0.83	0.81
K-27	19.13	1.36	0.80		0.89	0.92	0.85
K-28	127.6	1.76	0.93		1.00	1.02	0.88
K-29	1,290	1.89	0.99	0.99	0.98	0.98	0.97
K-30	88.4	1.38	0.78	0.78	0.76	0.75	0.81
K-31	19.00	1.32	0.79	0.79	0.79	0.82	0.78
WR-7	8.79	1.12	0.70	0.68	0.69	0.74	0.67
WR-7H	7.96	1.10	0.72	0.68	0.65	0.66	0.68
WR-11	1,493	0.98	0.76	0.74	0.75	0.75	0.76
WR-18	9.12	1.21	0.84	0.85	0.84	0.87	0.85
WR-18H	7.10	1.14	0.86	0.84	0.78	0.77	0.83
WR-26	13.46	1.21	0.73	0.71	0.75	0.78	0.72
WR-34	2.40	0.99	0.70	0.75	0.77	0.79	0.75
WR-41	3.30	1.02	0.70	0.71	0.70	0.75	0.70
WR-56	7.14	1.11	0.75	0.74	0.76	0.80	0.75
WR-56H	6.50	1.11	0.76	0.74	0.71	0.72	0.76
WR-67	6.58	1.06	0.66	0.66	0.67	0.73	0.64
WR-69	1,556	0.99	0.76	0.74	0.74	0.75	0.75
WR-76	1,683	0.99	0.72	0.74	0.73	0.74	0.73
WR-79	4.48	1.07	0.70	0.71	0.70	0.75	0.69

CONTINUATION OF TABLE IX-2

Oil Code*)	Experimental Data			Z_{40^oC} Predicted from $\eta_{0,40^oC}$ Plus....			
	$\eta_{0,40^oC}$, cP	S_0	Z_{40^oC}	C_R	$d_{0,40^oC}$	$n_{0,40^oC}$	$(n-d)_{0,40^oC}$
WR-80	6.68	1.11	0.70	0.70	0.71	0.76	0.69
WR-81	11.54	1.18	0.69	0.69	0.72	0.77	0.69
WR-91	7.87	1.11	0.70	0.70	0.72	0.76	0.70
WR-91H	6.79	1.08	0.74	0.71	0.68	0.69	0.70
WR-97	2.31	1.01	0.71	0.72	0.71	0.74	0.70
WR-99	3.33	1.04	0.72	0.71	0.69	0.73	0.68
A-1	25.1	1.21	0.71	0.67	0.66	0.67	0.68
A-2	7.30	1.15	0.79	0.76	0.75	0.77	0.76
A-3	41.1	1.26	0.67	0.64	0.67	0.69	0.65
A-4	129.4	1.26	0.60	0.60	0.62	0.60	0.63
A-5	438	1.28	0.60	0.57	0.62	0.64	0.64
A-6	138.7	1.25	0.60	0.60	0.61	0.59	0.62
A-7	120.5	1.25	0.63	0.61	0.64	0.65	0.64
A-8	119.7	1.21	0.61	0.57	0.60	0.58	0.63
A-9	38.9	1.26	0.66	0.62	0.67	0.69	0.66
A-10	44.7	1.39	0.83	0.78	0.78	0.79	0.82
A-11	117.5	1.49	0.84	0.81	0.79	0.79	0.86
A-12	403	1.60	0.90	0.87	0.82	0.79	0.90
A-13	119.4	1.50	0.87	0.83	0.82	0.81	0.88
A-14	117.5	1.47	0.85	0.81	0.82	0.81	0.89
A-15	58.2	1.37	0.79	0.75	0.70	0.64	0.79
A-16	501	1.77	1.02	1.02	0.98	0.97	1.01
D-1	157.8	1.42	0.76	0.75	0.75	0.76	0.78
D-2	78.5	1.37	0.77	0.74	0.73	0.73	0.76
D-3	30.1	1.29	0.78	0.73	0.75	0.77	0.75
D-4	427	1.35	0.63	0.62	0.62	0.63	0.65
D-5	19.19	1.29	0.81	0.80	0.82	0.85	0.80
D-6	382	1.58	0.87	0.83	0.84	0.84	0.87
D-7	1,334	1.61	0.81	0.79	0.85	0.86	0.85

*) Refers to similarly coded oils specified in Table II-1.

to a good approximation, on one single straight line, which is termed the *"isotherm pole line"*. Its equation can readily be shown to read:

$$H_p = 0.74\,\Pi_p + 0.1400 . \qquad \text{(IX-1)}$$

It may be noted that the slope (0.74) and the intercept (0.1400) of this pole line are identical to the coordinates of the point of convergence in Fig. VII-3.

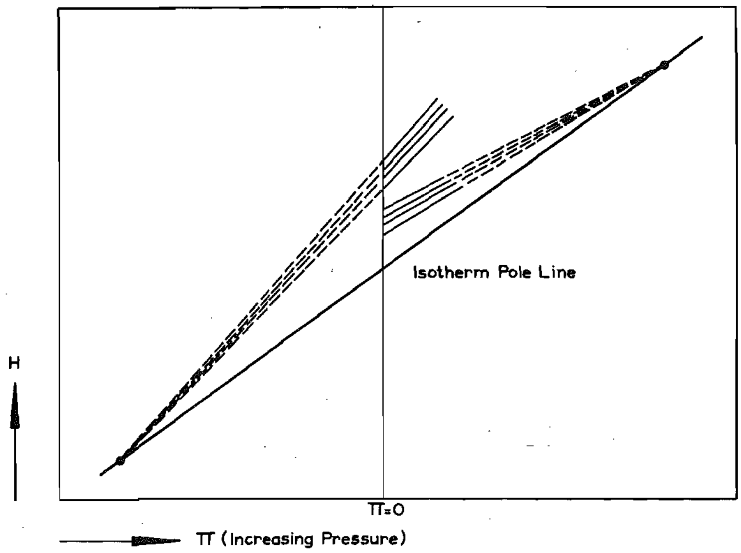

FIG. IX-1.
The Isotherm Pole Line of Mineral Oils.

Further, this slope value of 0.74 found for the isotherm pole line happens to be identical to the value established for the standard reference liquids in the classification system described in Chapter VII, that is the series of mineral oils characterized by a common percentage C_R of 48. Thus, the isotherms of all the members of this particular series would be parallel to the isotherm pole line (in an H-Π chart); nevertheless, their viscosity-pressure poles may be conceived still to be located on the isotherm pole line, although at infinity.

The concept of the isotherm pole line has been illustrated in the schematic Fig. IX-1. The families of isotherms for two arbitrary mineral oils have also been depicted. For the sake of clearness, it may be recalled that the viscosity-pressure poles are located very far beyond the ranges of viscosity and pressure that may assume practical significance.

In the space model of Fig. V-3 the isotherm pole line would be represented by a *plane* parallel to the Θ-axis. Accordingly, the viscosity-pressure pole line of any given mineral oil would be situated in the latter plane, which is termed the *"isotherm pole plane"*; obviously, its viscosity-temperature-pressure pole would likewise be situated in this plane.

IX. 2. 2. *The Complete Viscosity-Temperature-Pressure Equation for Mineral Oils*

Restating the complete viscosity-temperature-pressure Equation (V-1a):

$$H = S_0\Theta + C\Theta\Pi + D\Pi + \log G_0, \qquad \text{(V-1a)}$$

it may be recalled that the viscosity-temperature-pressure relationship of a given liquid is fully characterized by *four* parameters, G_0, S_0, C and D. The parameters C and D have further been defined in terms solely of the two atmospheric quantities G_0 and S_0, and the coordinates of the viscosity-pressure pole, H_p and Π_p, as follows:

$$C = -\frac{S_0}{\Pi_p} \qquad \text{(V-2)}$$

and

$$D = \frac{H_p - \log G_0}{\Pi_p}. \qquad \text{(V-3)}$$

Now, by suitable combination with Equation (IX-1) for the isotherm pole line of mineral oils and with Equation (V-3), Expression (V-2) for the parameter C can be transformed into:

$$C = S_0\left(\frac{D - 0.74}{\log G_0 - 0.1400}\right). \qquad \text{(IX-2)}$$

Consequently, it has been derived that for *mineral* oils the parameter C is a function solely of the other three parameters occurring in the basic viscosity-temperature-pressure Equation (V-1a). For such oils the latter equation may therefore be simplified into:

$$H = S_0\Theta + S_0\left(\frac{D - 0.74}{\log G_0 - 0.1400}\right)\Theta\Pi + D\Pi + \log G_0. \qquad \text{(IX-3)}$$

According to Equation (IX-3), only *three* parameters, G_0, S_0 and D, suffice for describing the complete viscosity-temperature-pressure relationship of mineral oils. This simplified equation has generally proved reliable over a temperature range extending from about 0 to 150°C (32-302°F) and up to pressures of at least 3,000 kgf/cm^2 (43,000 psi).

Further, the level parameter G_0 may be eliminated from Equation (IX-3) by substituting the viscosity grade $H_{0,r}$. This leads to:

$$H - H_{0,r} = S_0(\Theta - \Theta_r) + S_0\left(\frac{D - 0.74}{H_{0,r} - S_0\Theta_r - 0.1400}\right)\Theta\Pi + D\Pi. \quad \text{(IX-4)}$$

It is seen that Equation (IX-4) requires only *two* parameters - definitely the *minimum* number conceivable -, namely S_0 and D, for fully characterizing the effect of both temperature and pressure on the viscosity *grade* of a given mineral oil.

IX.2.3. *Application in the New Correlations*

Turning more particularly to the effect of pressure on the atmospheric viscosity-temperature relationship of mineral oils, it readily follows by combination of Equations (V-6a) and (IX-2) that this effect is satisfactorily characterized by the following expression for the Viscosity-Pressure Index, Z:

$$Z = D + S_0\left(\frac{D - 0.74}{\log G_0 - 0.1400}\right)\Theta \,. \quad \text{(IX-5)}$$

Since G_0 and S_0 are atmospheric quantities, the quantity D (= $Z_{0^\circ C}$) constitutes the *only* parameter that is required for fully characterizing the effect of pressure on the atmospheric viscosity-temperature relationship of mineral oils.

Consequently, it may be stated that the *complete* viscosity-temperature-pressure relationship of a mineral oil with known values for the atmospheric parameters G_0 and S_0 is determined solely by the pressure parameter D. The relevant Equation (IX-3) has been claimed to hold over a very wide temperature range and up to very high pressures.

In practice the parameter D (= $Z_{0^\circ C}$) of Equation (IX-5) may be conveniently replaced by the corresponding Z-value at some more appropriate standard reference temperature, for instance 40°C. For this purpose Equation (IX-5) may be advantageously transformed into Expression (VII-1a) of § VII.3.1. At the adopted standard reference temperature of 40°C the latter expression reads:

$$Z = Z_{40^\circ C} - (Z_{40^\circ C} - 0.74)\left(\frac{H_{0,40^\circ C} - H_0}{H_{0,40^\circ C} - 0.1400}\right) \quad \text{(VII-1c)}$$

In accordance with Equation (VII-1c) the correlations to be developed in the subsequent parts of this chapter aim at predicting the Viscosity-Pressure Index $Z_{40^\circ C}$ *of mineral oils from their viscosity grade* $H_{0,40^\circ C}$ *and either their chemical constitution or easily assessable physical constants. Once a suitable correlation for predicting* $Z_{40^\circ C}$ *has been established, the temperature effect on* $Z_{40^\circ C}$ *can easily be determined on the basis of Equation (VII-1c) solely from their atmospheric viscosity-temperature relationship.*

IX. 3. CORRELATION WITH CHEMICAL CONSTITUTION

IX. 3. 1. *Introduction*

A quantitative correlation between the viscosity-pressure relationship of mineral oils and their chemical constitution would be very desirable not only for prediction purposes but also for getting a better understanding of the underlying regularities. In fact, in the latter respect the chemical constitution of the oils may be deemed more informative than individual physical constants.

For the present correlational purpose it has again proved very fruitful to express the chemical constitution of the oils in terms of their carbon-type composition as determined by means of the n-d-M method (compare § VIII. 2. 1). Amongst the total of 74 mineral oils included in Table IX-2, 3 samples (K-13, K-27 and K-28) had to be left out of consideration since their composition appears to fall beyond the scope of the latter method.

The chemical constitution of the 71 remaining oils covers practically the entire range where the n-d-M method may be applied. Expressed in terms of their total percentage of carbon atoms in ring structure, C_R, the compositions of the mineral oils utilized in the present study are seen to vary from about 25 to 75 (compare Fig. VIII-1).

IX. 3. 2. *The New Correlation*

From an extensive analysis of experimental data on the aforementioned 71 mineral-oil fractions collected in Table IX-2 the conclusion has been obtained that, to a good approximation, the Viscosity-Pressure Index belonging to a mineral-oil fraction with a given viscosity grade is fixed *uniquely* by its carbon-type composition. Moreover, it has appeared that, remarkably enough, it is immaterial whether the carbon atoms present in ring structure are contained in naphthenic or aromatic rings.

Accordingly, in the relevant correlation solely the *total* percentage of carbon atoms in ring structure*), C_R, is utilized as a sufficiently accurate measure of the chemical constitution, or rather the carbon-type composition, of the mineral oils under consideration.

Plotting at the arbitrarily adopted standard reference temperature**) of 40°C (104°F) the Viscosity-Pressure Indices, Z, of all the various oils considered against their atmospheric viscosity functions H_0 and using their percentage C_R as a parameter has yielded the correlation depicted in Fig. IX-2 (compare Fig. VII-1). This correlation implies a straight-line relationship between the Viscosity-Pressure Index $Z_{40^\circ C}$ and the viscosity function $H_{0,40^\circ C}$ for mineral oils hav-

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*) It stands to reason that the percentage of paraffinic carbon atoms, C_P, may be used instead of C_R, their interrelationship reading $C_R = 100 - C_P$.

**) It may already be remarked here that it would not make any essential difference if the reference temperature were fixed at another value somewhere in the conventional temperature range (compare § IX. 2. 3).

ing a common percentage C_R. Moreover, the resulting straight lines form a *fan*. Their point of convergence, in Fig. IX-1 denoted by L, has the coordinates $H_{0,40°C} = 0.1400$ - corresponding to a viscosity $\eta_{0,40°C} = 1.51$ cP - and $Z_{40°C} = 0.74$.

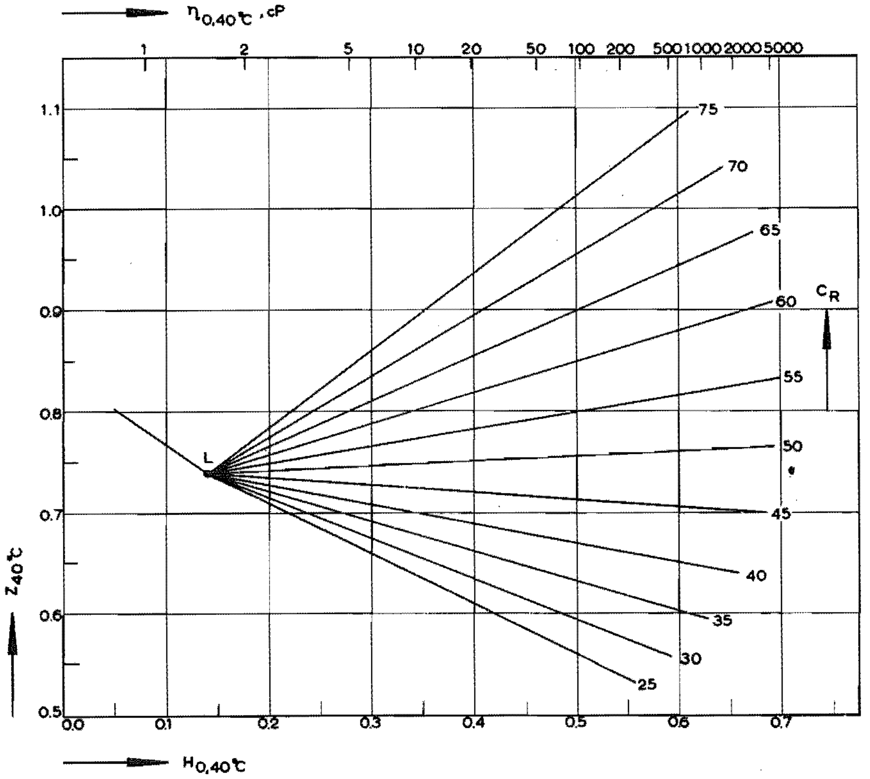

FIG. IX-2.
Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and Their Percentage of Carbon Atoms in Ring Structure.

Remarkably enough, for mineral oils with viscosity grades below this *"transitional"* viscosity $\eta_{0,40°C} = 1.51$ cP the percentage C_R is no longer an influential quantity, their Viscosity-Pressure Index $Z_{40°C}$ being a function solely of their viscosity grade (compare § VII. 2. 1 and particularly Fig. VII-1). The $Z_{40°C}$-values of such unusually fluid oils appear to be closely scattered around a single straight line.

An interesting feature of the correlational diagram of Fig. IX-2 consists in that it traces the approximate "natural boundaries" imposed on the $Z_{40°C}$-values encountered amongst natural mineral oils - obtained by conventional refining methods - from all the divergent sources investigated so far. Indeed, the great variety of Viscosity-

Pressure Indices $Z_{40^\circ C}$ found amongst the mineral oils occurring in nature may be considered to be located between the two outmost straight lines of the fan depicted, that is those relating to $C_R = 25$ and $C_R = 75$.

It stands to reason that the convergence of the various straight lines relating to constant percentages C_R does not actually proceed so abruptly as indicated in Fig. IX-2. In fact, this convergence has been so approximated only in order that the underlying correlation may be cast into a simple mathematical form. Nevertheless, the final correlation has proved to hold good even in the vicinity of the point of convergence.

The family of straight lines depicted in Fig. IX-2 can be represented by the following mathematical expression:

$$Z_{40^\circ C} = 0.74 + \left(\frac{800}{230 - C_R} - 4.40\right)(H_{0,40^\circ C} - 0.1400) \; . \qquad \text{(IX-6a)}$$

The expression for the single line indicated for the range of very low viscosity grades proves to read*):

$$Z_{40^\circ C} = 0.74 - 0.7(H_{0,40^\circ C} - 0.1400) \; . \qquad \text{(IX-6b)}$$

On the basis of the mathematical Expression (IX-6a) the new correlation may also be cast into a more *general* form. That is Expression (IX-6a) can be generalized such that it may be directly applied at any *arbitrary* reference temperature instead of only at the adopted standard reference temperature of 40°C. By combination of Expression (IX-6a) with Equation (VII-1c) presented at the end of § IX. 2. 3 the following *generalized* correlation is readily deduced:

$$Z = 0.74 + \left(\frac{800}{230 - C_R} - 4.40\right)(H_0 - 0.1400). \qquad \text{(IX-7a)}$$

The present Correlation (IX-7a) is extremely convenient in that at any arbitrary temperature the Viscosity-Pressure Index, Z, of a given mineral oil can be estimated directly from its atmospheric viscosity and its percentage C_R.

Similarly, Expression (IX-6b) can be cast into the following generalized form:

$$Z = 0.74 - 0.7(H_0 - 0.1400), \qquad \text{(IX-7b)}$$

which applies to the unusually fluid mineral oils with viscosity grades $\eta_{0,40^\circ C}$ not exceeding 1.51 cP ($H_{0,40^\circ C} \leq 0.1400$).

Applicability

The new correlation in the form of Equation (IX-6a) has been

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*) This expression is obtained from Equation (IX-6a) by substituting the hypothetical value $C_R=14$.

checked for all the aforementioned 71 mineral-oil fractions designated in Table IX-2. For each of these fractions - including some saturated samples - the predicted Viscosity-Pressure Indices $Z_{40^{\circ}C}$ have been listed in that table. In addition, Table IX-3 indicates the distribution of the deviations between experimental and predicted Viscosity-Pressure Indices amongst the really great variety of the 71 oils tested.

The latter table shows that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to only 0.021 and 0.026 units, respectively, which figures are hardly beyond the accuracy inherent in the experimentally derived values. These absolute deviations correspond to *relative* average and standard deviations of no more than 3.1 and 3.6%, respectively. Moreover, for all the divergent kinds of oils tested the absolute deviation *invariably* remains within 0.05 units.

TABLE IX-3

Distribution of Deviations Between Experimental and Predicted Viscosity-Pressure Indices $Z_{40^{\circ}C}$ Amongst the Various Oils Tested

Deviation	Percentage of the Oils Tested			
	Correlation Employing $\eta_{0,40^{\circ}C}$ Plus....			
$\lvert\delta Z_{40^{\circ}C}\rvert$	C_R	$d_{0,40^{\circ}C}$	$n_{0,40^{\circ}C}$	$(n-d)_{0,40^{\circ}C}$
0.00	16.9	12.2	9.5	17.6
0.01	19.7	27.0	10.8	27.0
0.02	24.0	18.9	9.5	16.2
0.03	18.3	12.2	12.2	20.3
0.04	15.5	9.5	16.2	12.2
0.05	5.6	8.1	17.6	6.7
0.06		2.7	9.5	
0.07		4.0	1.3	
0.08		2.7	4.1	
0.09		2.7	5.4	
0.11			1.3	
0.12			1.3	
0.15			1.3	
Average Deviation*)	0.021	0.027	0.042	0.020
Standard Deviation**)	0.026	0.036	0.052	0.025

*) Defined by $\frac{1}{n}\sum_{i=1}^{i=n}\left|\delta_i\right|$

**) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n}\delta_i^2}{n-1}}$

It may further be pointed out that, as shown by Equation (VII-5), the *relative* accuracy inherent in the predicted Viscosity-Pressure Index equals that in the corresponding initial viscosity-pressure coefficient, α_i (see Section VII.4). Therefore, it follows from the preceding data that the relative average and standard deviations achieved for the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ of all the divergent kinds of mineral oils tested also amount to only 3.1 and 3.6%, respectively.

In order to give some idea of the relative errors that may occur in the viscosities proper when these are calculated from the basic viscosity-pressure Equation (IV-5e) by using the Viscosity-Pressure Indices $Z_{40^\circ C}$ predicted from the present correlation, Table IX-4 has been prepared. For a wide range of viscosity grades $\eta_{0,40^\circ C}$ this table shows the percentage errors in the corresponding viscosities at pressures of 500, 1,000, 1,500 and 2,000 kgf/cm^2 (7,000, 14,000, 21,000 and 28,000 psi, respectively) that would result from a deviation of 0.02 units in the Viscosity-Pressure Index $Z_{40^\circ C}$ of the oil considered. For this Viscosity-Pressure Index an intermediate value of $Z_{40^\circ C} = 0.75$ has invariably been employed; accordingly, the assumed relative error in the latter $Z_{40^\circ C}$-value amounts to 2.7%. Besides the percentage errors in the various viscosities, the appropriate viscosity ratios $(\eta_p/\eta_0)_{40^\circ C}$ at each reference pressure have been included.

TABLE IX-4

Effect of a Deviation of 0.02 Units in Their Viscosity-Pressure Index $Z_{40^\circ C}$ on the Predicted Elevated-Pressure Viscosities of Oils With a Common $Z_{40^\circ C} = 0.75$ and Varying Viscosity Grades $\eta_{0,40^\circ C}$

$\eta_{0,40^\circ C}$, cP	Reference Pressure, kgf/cm^2							
	500		1,000		1,500		2,000	
	$(\eta/\eta_0)_{40^\circ C}$	$\lvert \% \delta\eta_{40^\circ C} \rvert$ *)	$(\eta/\eta_0)_{40^\circ C}$	$\lvert \% \delta\eta_{40^\circ C} \rvert$	$(\eta/\eta_0)_{40^\circ C}$	$\lvert \% \delta\eta_{40^\circ C} \rvert$	$(\eta/\eta_0)_{40^\circ C}$	$\lvert \% \delta\eta_{40^\circ C} \rvert$
2	1.879	2	3.41	3.5	6.07	8	10.57	8
10	2.52	2.5	6.04	5.5	14.03	9	31.6	12
100	3.84	4	13.71	8	46.7	13	152.1	17
1,000	5.81	5	31.0	10.5	154.2	17	730	23
5,000	7.80	6	55.0	12	357	20	2,190	27

*) $$\lvert \% \delta\eta \rvert = 100\,\frac{\lvert \eta_{pred} - \eta_{exp} \rvert}{\eta_{exp}}$$

Table IX-4 shows that for a constant deviation between experimental and predicted Viscosity-Pressure Indices the *relative* errors in the predicted viscosities increase regularly with increasing viscosity grade of the oils. It may be added that for a given viscosity grade these relative errors increase nearly proportionally to the difference between experimental and predicted Viscosity-Pressure Indices. For example, when this difference amounts to 0.04 units, the percentage errors listed in Table IX-4 also increase by a factor of nearly two.

As regards the percentage deviations collected in the latter table it is only fair that these be considered in connection with the really great viscosity variations involved.

For properly judging or criticizing the accuracy achieved with the present correlation it may further be useful to report both the pressure and temperature*) differences that at the reference pressures of Table IX-4 would fully compensate the various viscosity deviations listed in that table. The relevant pressure and temperature differences have been collected in Table IX-5. The smallness of these differences convincingly demonstrates the wide practical usefulness of the present correlation.

TABLE IX-5

Pressure and Temperature Differences Compensating the Various Viscosity Deviations Listed in Table IX-4

Differences	Reference Pressure, kgf/cm²			
	500	1,000	1,500	2,000
Pressure, kgf/cm²	15	30	50	75
Temperature, deg C	0.5 - 0.8	0.9 - 1.4	1.2 - 2.0	1.5 - 2.4

IX. 3. 3. *The Isotherms and Isobars for Mineral Oils With a Common Percentage* C_R

A. THE RELATIONSHIP BETWEEN THE ISOTHERMS OF ISO-C_R OILS

It may be recalled that the family of isotherms characterizing a given mineral oil - or any other liquid - is depicted in an H-Π chart as a fan. Now, it can readily be shown from the correlation developed in the preceding § IX.3.2 - for instance from Equation (IX-7a) - that for a group of oils characterized by a common percentage C_R the individual families of isotherms - one family for every member of the group - are depicted in an H-Π chart as *one single* fan. In other words, oils having a common percentage C_R also possess a common viscosity-pressure pole. The position of this pole is *uniquely* determined by the C_R-value concerned and is therefore characteristic of an entire group of iso-C_R oils.

Expressions for the pole viscosity H_P and the pole pressure Π_P as a function of the percentage C_R can be deduced on the basis of the new Correlation (IX-7a) and Equation (IX-1) for the isotherm pole line. By simple algebra one arrives at the following expressions:

$$H_P = - \frac{592}{C_R - 48} + 0.3080 \qquad \text{(IX-8)}$$

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*) The compensating temperature variations have been estimated on the basis of the new correlational Fig. X-1 yet to be discussed.

and

$$\Pi_P = -\frac{800}{C_R - 48} + 0.227 . \qquad \text{(IX-9)}$$

It should be noted, however, that very fluid oils, that is with viscosity grades $H_{0,40^\circ C}$ not exceeding 0.1400 ($\eta_{0,40^\circ C} \leqslant 1.51$ cP), possess one and the same viscosity-pressure pole, regardless of their chemical constitution. The position of this pole can be obtained from Equations (IX-8) and (IX-9) by substituting the aforementioned hypothetical value $C_R = 14$.

B. THE RELATIONSHIP BETWEEN THE ISOBARS OF ISO-C_R OILS

On the basis of the viscosity-temperature pole concept expounded in part B of § III. 2. 2 the *atmospheric* viscosity-temperature relationship of a given liquid can be described by:

$$H_0 - H_P = S_0 (\Theta - \Theta_P), \qquad \text{(IX-10)}$$

where the pole viscosity H_P displays the same value for its viscosity-temperature and its viscosity-pressure pole. Thus, confining oneself to *mineral* oils, the pole viscosity H_P in Equation (IX-10) is determined, according to Formula (IX-8), solely by their percentage C_R. But the other coordinate of the viscosity-temperature pole, the pole temperature Θ_P, turns out to be *not* a function solely of their percentage C_R. This may be demonstrated as follows.

It has been shown in part A of § VIII. 2. 3 that, to a good approximation, the *atmospheric* isobars of iso-C_R oils constitute a fan when these are plotted in an H-Θ chart; in addition, the resulting atmospheric isobar poles of all the various kinds of mineral oils tested were found to be located on one single straight line, the atmospheric isobar pole line. Further, after introducing the coordinates H_a and Θ_a of the atmospheric isobar pole of a given mineral oil its atmospheric Slope Index has been defined by Equation (VIII-7). Now, substitution of the latter equation*) for S_0 into Equation (IX-10) yields:

$$\frac{\Theta - \Theta_P}{\Theta - \Theta_a} = \frac{H_0 - H_P}{H_0 - H_a} \qquad \text{(IX-11a)}$$

or at some standard reference temperature Θ_r, where $H_0 = H_{0,r}$:

$$\frac{\Theta_r - \Theta_P}{\Theta_r - \Theta_a} = \frac{H_{0,r} - H_P}{H_{0,r} - H_a} . \qquad \text{(IX-11b)}$$

The quantities H_P, H_a and Θ_a in Equations (IX-11a) and (IX-11b) are *uniquely* determined by the percentage C_R of the mineral oil considered. Consequently, the pole temperature Θ_P is found to

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*) It may be recalled that throughout Chapter VIII the subscript "0" - relating to atmospheric pressure - has been omitted.

depend not only on its percentage C_R but also on its viscosity *grade**). Therefore, within a group of iso-C_R oils the pole temperature Θ_P, in contrast to the pole pressure Π_P, is still dependent on the particular member considered.

Accordingly, whereas all members of a group of iso-C_R oils have a common viscosity-pressure pole, they do not show a common viscosity-temperature pole, their Θ_P-values varying from one member to another. Thus, plotting the isobars of the various members of such a group in an H-Θ chart yields a set of fans, one fan for every member of the group.

Further, an interesting relationship has proved to exist between the individual isobar fans of the various members of a group of iso-C_R oils.

It may be recalled that the *atmospheric* isobars of all members of such a group also constitute a fan when plotted in the H-Θ chart. Now, a similar relationship between the isobars of these members has been found to hold at *any* specified reference pressure.

In order to show up the latter relationship one may conveniently start from Equation (IV-7a). Replacing the atmospheric viscosity H_0 in that equation by the appropriate expression implied by Formula (VIII-7), one easily arrives at the following equation for the viscosity-temperature-pressure relationship of mineral oils:

$$H - \left[H_a + \left(\frac{H_a - H_P}{-\Pi_P}\right)\Pi\right] = S_0\left(1 - \frac{\Pi}{\Pi_P}\right)(\Theta - \Theta_a). \qquad \text{(IX-12)}$$

For all members of a given group of iso-C_R oils the coordinates of their viscosity-pressure pole, H_P and Π_P, and of their atmospheric isobar pole, H_a and Θ_a, assume the same value throughout; accordingly, for all these members only *one* parameter occurs in Equation (IX-12), namely the atmospheric Slope Index, S_0. Indeed, it then follows from the latter equation that at any specified reference pressure the isobars of all members of such a group are depicted in an H-Θ chart as a fan, as found above for their atmospheric isobars specifically.

Denoting the viscosity and the temperature coordinate of the relevant *elevated*-pressure isobar poles by H_e and Θ_e, respectively, these quantities are seen to be defined by:

$$H_e = H_a + \left(\frac{H_a - H_P}{-\Pi_P}\right)\Pi \qquad \text{(IX-13)}$$

and

$$\Theta_e = \Theta_a \qquad \text{(IX-14)}$$

---

*) An analytical expression relating the pole temperature Θ_P of mineral oils to their percentage C_R and their viscosity grade $H_{0,r}$ is readily obtained by substituting the appropriate Equations (IX-8), (VIII-5b) and (VIII-6b) for the quantities H_P, H_a and Θ_a, respectively, into the present Equation (IX-11b).

Therefore, the viscosity coordinate H_e varies linearly with the reference pressure Π. Remarkably enough, the temperature coordinate Θ_e is independent of pressure, thus being equal to that of the atmospheric isobar pole, Θ_a, of the group of iso-C_R oils considered.

The expounded convergence of the isobars of the members of a group of iso-C_R oils has been illustrated in the schematic Fig. IX-3. In this figure the isobars of three iso-C_R oils have been depicted in an H-Θ chart for atmospheric pressure and for two arbitrary reference pressures, p_1 and p_2. It should be noted that, in contrast to their isotherms, the isobars of different members of such a group may well *intersect*, even in the viscosity and temperature ranges which assume practical significance.

Further, it may be added that in the space model of Fig. V-3 the elevated-pressure isobar poles of the various members of a group of iso-C_R oils would be located on one single straight line parallel to the H-Π plane, the temperature coordinate being $\Theta = \Theta_a$.

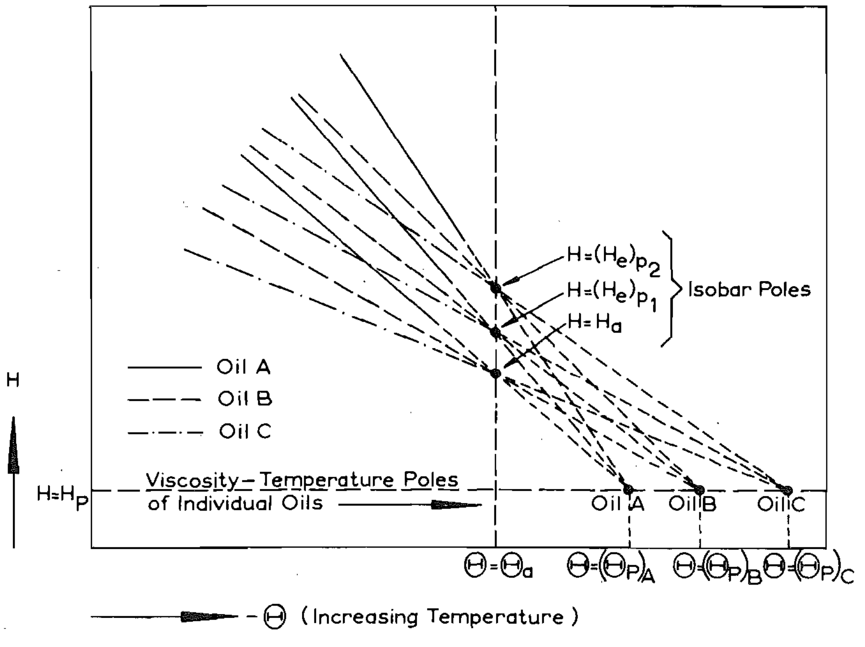

FIG. IX-3.
Schematic Representation of the Relationship Between the Isobars of Mineral Oils With a Common Percentage of Carbon Atoms in Ring Structure.

In conclusion it may be useful to point out that the convergence of the elevated-pressure isobars of iso-C_R oils as defined by Equation (IX-12) and illustrated in Fig. IX-3 is a purely mathematical consequence of the aforementioned convergences of all their *isotherms* and of their *atmospheric isobars*.

C. THE COMPLETE VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP FOR ISO-C_R OILS

Considering the complete viscosity-temperature-pressure relationship for a given liquid in the form of Equation (V-14):

$$\frac{H - H_p}{H_{0,r} - H_p} = \frac{\Theta - \Theta_p}{\Theta_r - \Theta_p} \cdot \frac{\Pi - \Pi_p}{-\Pi_p}, \qquad \text{(V-14)}$$

it has been demonstrated that for *mineral* oils the coordinates H_p and Π_p of their viscosity-temperature-pressure pole would be uniquely related to their percentage C_R and would thus be the same for all members of a given group of iso-C_R oils. The third pole coordinate, Θ_p, however, would be dependent not only on the percentage C_R but also on the viscosity *grade*, $H_{0,r}$ (or $\eta_{0,r}$), of the particular member under consideration.

Therefore, in the space model of Fig. V-3, which represents the complete viscosity-temperature-pressure Equation (V-14), all members of a given group of iso-C_R oils would possess a common viscosity pole plane ($H = H_p$) and a common viscosity-pressure pole line ($H = H_p$, $\Pi = \Pi_p$), but the viscosity-temperature pole line ($H = H_p$, $\Theta = \Theta_p$) would differ from oil to oil.

Essentially, within a given group of iso-C_R oils only one *parameter is required for fully characterizing the viscosity-temperature-pressure relationship of any individual member of the group, namely its viscosity grade, $\eta_{0,r}$.*

In consequence, the effects of both temperature and pressure on the specified viscosity grade of an arbitrary mineral oil can be sufficiently defined solely by indicating the group to which it belongs, that is solely by giving its percentage C_R.

IX. 3. 4. *Concluding Remarks*

A. The newly developed correlation has proved a valuable and convenient tool for estimating the viscosity-pressure relationship of mineral oils. In addition, this correlation may be deemed significant in that it furnishes some insight into the effect of the chemical constitution of mineral oils on the latter relationship, so that it may be very helpful in preparing oils with the desired viscosity-pressure characteristics.

According to the present correlation, the effect of pressure on the atmospheric viscosity - at any arbitrary temperature - of a given mineral oil is determined solely by its *total* percentage of carbon atoms in ring structure, C_R. In other words, mineral oils possessing a common viscosity grade and a common percentage C_R would display *identical* isotherms at the standard reference temperature involved, irrespective of the manner in which their C_R-values are built up from the component percentages C_A and C_N.

B. The new correlation is substantially simpler and more generally applicable than the aforementioned correlation (see part A of § IX.1.2) recently published by Roelands *et al.*[14]. The relevant simplification primarily concerns the mathematical framework employed; further, the constitutional criterion ($C_A + 1.5\ C_N$) utilized in the previous correlation could be replaced simply by C_R ($= C_A + C_N$).

Indeed, in the new correlation the percentage C_R has been found definitely superior to the former criterion ($C_A + 1.5\ C_N$), according to which carbon atoms in naphthenic-ring structure should have a somewhat greater influence than those in aromatic-ring structure. In this connection it should be pointed out that the previous correlation has been based on 20 mineral oils with rather low viscosity grades, whilst the newly developed correlation has been derived on the basis of a great variety of mineral oils covering a really extensive viscosity range.

C. It should be emphasized that the present correlation for predicting the Viscosity-Pressure Index of mineral oils solely from their viscosity grade and their percentage C_R is quite analogous to the correlation described in Chapter VIII for estimating their atmospheric Slope Index. Indeed, both the Viscosity-Pressure Index (at any arbitrary temperature) and the atmospheric Slope Index of mineral oils of known viscosity grade have proved to be fixed, to a good approximation, solely by their percentage C_R. This opens up very interesting possibilities for correlating the viscosity-pressure relationship of mineral oils with their atmospheric viscosity-temperature relationship. These possibilities will be thoroughly exploited in Chapter X.

D. Returning to the carbon-type composition diagram of Fig. VIII-1, it follows from the present correlation that at any standard reference temperature straight lines of constant Viscosity-Pressure Index may be constructed in such a diagram, but only for oils of comparable viscosity grade; these lines would coincide with straight lines denoting constant percentages C_R. Indeed, if the viscosity grade of the oils considered varies considerably, this is generally*) indispensable as an additional parameter. This holds to a greater extent as the oils become less viscous. In the case of very fluid oils ($\eta_{0,40^\circ C} \leqslant 1.51$ cP) it is even *solely* their viscosity grade that determines their Viscosity-Pressure Index, their chemical constitution having no longer any appreciable influence.

Accordingly, the present correlation corroborates Kuss's aforementioned conclusion (see part A of § IX.1.2) that no overall correlation would exist between the viscosity-pressure coefficient, α, of mineral oils and their carbon-type composition proper.

At the same time, however, the newly developed correlation clearly invalidates Kuss's second conclusion: that characterization of the chemical constitution of mineral oils in terms of their carbon-type composition would not suffice for determining their viscosity-pressure behaviour (compare part A of § IX.1.2). In fact, it has now been proved that the pressure effect on the atmospheric viscosity of mineral oils is sufficiently characterized solely by the constitutional criterion C_R.

*) Excepting oils whose percentage C_R lies in the vicinity of 48.

E. From the preceding § IX. 3. 3 it follows that in a viscosity-pressure diagram - irrespective of the particular viscosity and pressure scale employed - the *isotherms* of all members of a given group of iso-C_R oils would constitute one single family of non-crossing curves, each isotherm thus being determined solely by the corresponding atmospheric viscosity. In contrast, in a viscosity-temperature diagram the *isobars* of different members of such a group may well intersect.

It should be noted that these two features have previously been indicated by Blok[84) for *naturally homologous* groups of mineral oils (see part C of § IX. 1. 2). This qualitative agreement between Blok's findings for naturally homologous groups and the present findings for groups of iso-C_R oils is not so surprising, since in general the constitutional criterion C_R would not tend to vary considerably within a given naturally homologous group, the variation proceeding fairly regularly with the viscosity grade of the members of such a group at that (compare the final remarks of § VIII. 2. 4).

F. Finally, Chu and Cameron's set of three correlations indicated in part C of § IX. 1. 2 has been compared with the present correlation.

As stated above, these authors employed the aniline point of mineral oils as a (very arbitrary) criterion for distinguishing between "paraffinics" and "naphthenics". For the thus-defined naphthenics - for which they considered Barus's equation adequate - they advocated the use of a correlation originally proposed by Worster[162) for application to mineral oils in general; at any temperature involved this correlation implies a linear relationship between the viscosity-pressure coefficient, α, and the logarithm of the atmospheric viscosity. For the thus-defined paraffinics - for which Barus's equation was deemed too rough - two new correlations were developed on the basis of two distinct equations for their viscosity-pressure relationship. Both equations contain *two* parameters, one of them being given a common value for all paraffinics. The other parameter was expressed in the first equation - which proves to be identical to Blok's Equation (IV-4) - as a function of the atmospheric viscosity of the oil concerned and the prevailing temperature, whilst in the second equation it was defined solely in terms of its atmospheric viscosity.

In Fig. IX-4 the Viscosity-Pressure Indices Z_{40^oC} predicted from each of the three correlations*) proposed by Chu and Cameron have been plotted against the corresponding viscosity grades $H_{0,40^oC}$**). The curve labelled "Paraffinics I" relates to the correlation based on Blok's Equation (IV-4), the curve labelled "Paraffinics II" referring to the second correlation for the above-defined paraffinics. For comparison the straight lines for C_R-values of

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*) The plotted Z_{40^oC}-values have been calculated by means of the basic Equation (IV-5e) from the given viscosities at atmospheric pressure and those predicted for 1,000 kgf/cm^2 (14,220 psi).

**) It should be added that, although a standard reference temperature of 40°C has been adopted in Fig. IX-4, both the correlation for naphthenics and the second correlation for paraffinics would apply irrespective of the particular temperature involved, the Viscosity-Pressure Index, Z, being a function solely of the atmospheric viscosity, η_0.

25, 50 and 75 and the straight line for very fluid mineral oils have been replotted from the correlational Fig. IX-2.

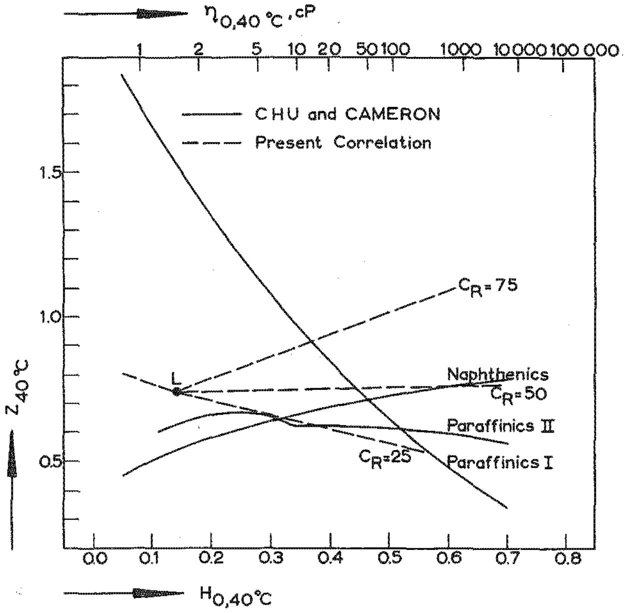

FIG. IX-4.
Chu and Cameron's Correlations in Comparison With the New Correlation of Fig. IX-2.

Fig. IX-4 constitutes a convincing quantitative substantiation of the indicated roughness of Chu and Cameron's correlations. Particularly the first correlation for paraffinics will normally yield very poor predictions (compare also the discussion on the aforementioned paper by Roelands *et al.*[44]).

IX. 4. CORRELATION WITH ATMOSPHERIC PHYSICAL CONSTANTS

IX. 4. 1. *Introduction*

In the preceding Section IX. 3 it has been demonstrated that, to a good approximation, the correlation between the Viscosity-Pressure Index $Z_{40°C}$ of mineral oils and their viscosity grade $\eta_{0,40°C}$ is fixed solely by the constitutional criterion C_R. As the latter quantity is determined from some combination of *three* suitably chosen atmospheric physical constants[42], the present correlation is equally fixed by any such combination.

The reasoning presented in § VIII. 3. 1 with respect to the estimation of the Slope Index of mineral oils leads up to the conclusion that in the correlation discussed the percentage C_R may be conveniently replaced by *two* simple atmospheric physical constants, namely the *density* and the *refractive index* of the oils, these two quantities being taken at the same standard reference temperature as their viscosity grade. Furthermore, just as in the case of the Slope Index it would be worth-while to investigate the possibility of suppressing either the refractive index or the density as a correlational variable.

Indeed, as will be shown below, it has been found that only *one* of the latter two atmospheric physical constants is really needed for defining, to a good approximation, the correlation between the Viscosity-Pressure Index Z_{40^oC} of mineral oils and their viscosity grade $\eta_{0,40^oC}$. But the *density* has proved to permit an appreciably stricter correlation than the *refractive index*.

Finally, a particularly satisfactory correlation has been achieved using the *difference* between the refractive index and the density (in g/cm^3) of the oils as a correlational variable.

IX.4.2. *Correlation With Density*

For all the various mineral oils designated in Table IX-2 the Viscosity-Pressure Indices Z_{40^oC} have again been plotted against their viscosity grade $H_{0,40^oC}$, this time using the atmospheric *density* $d_{0,40^oC}$ as a parameter. As demonstrated by the resulting Fig. IX-5, it appeared that more or less curved lines of constant density could be constructed.

The lines depicted in the latter figure relate to distinct densities $d_{0,40^oC}$ ranging from 0.800 up to 1.000 g/cm^3. For very fluid oils the unique straight-line relationship between Z_{40^oC} and $H_{0,40^oC}$ depicted in Fig. IX-2 has been retained - for reasons of uniformity - in the present Fig. IX-5.

As indicated in § VIII.3.2 for the analogous correlation which aims at predicting the Slope Index of mineral oils, it has likewise appeared for the present correlation that it is advisable to apply some slight correction to the experimental density value when the oil considered contains an appreciable amount of sulfur. In accordance with the procedure outlined in the aforementioned § VIII.2.3 the experimental densities of the oils tested have been corrected by subtracting an amount of 0.006 g/cm^3 for each wt.% S present*).

The correlation depicted in Fig. IX-5 has been utilized for estimating the Viscosity-Pressure Indices Z_{40^oC} of all the various kinds of mineral-oil fractions designated in Table IX-2. For each of these 74 fractions - including some saturated samples - the predicted values of Z_{40^oC} have been included in the same table. In addition, Table IX-3 indicates the distribution of the deviations between experimental and predicted Viscosity-Pressure Indices amongst the really great variety of the 74 oils tested.

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*) As indicated in Table II-1, the sulfur content has not been specified for the mineral oils from References 27 and 35. But the minor differences that would have been observed in the predicted Viscosity-Pressure Indices of these oils if their properly corrected densities could have been used, may be deemed practically insignificant, notably in view of the really great variety of oils utilized in verifying the present correlation.

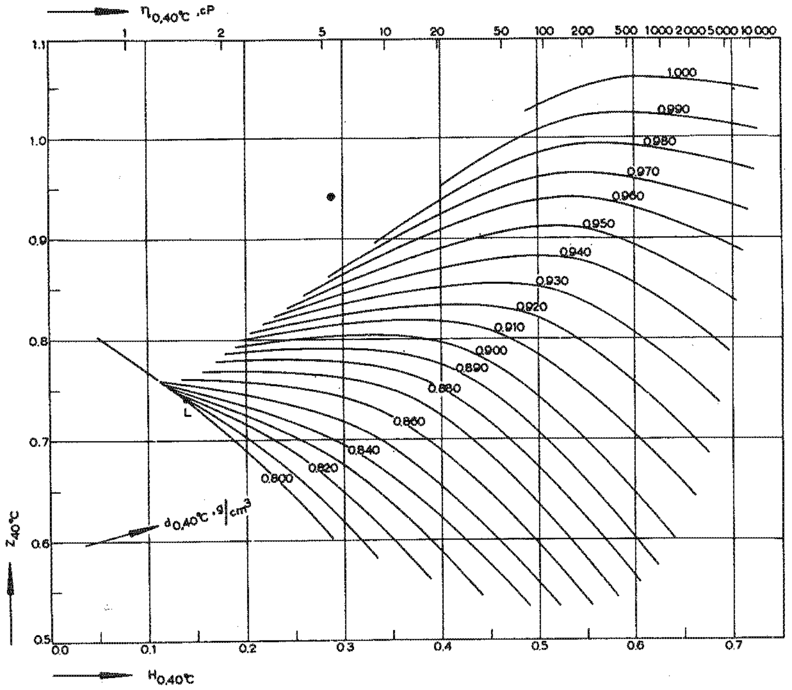

FIG. IX-5.
Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and Their Density.

The latter table shows that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to no more than 0.027 and 0.036 units, respectively, which figures are only slightly beyond the accuracy inherent in the experimentally derived values. These absolute deviations correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices $Z_{40°C}$ and initial viscosity-pressure coefficients $\alpha_{i,40°C}$ of only 3.6 and 4.7%, respectively.

On the whole, the indicated agreement between experimental and predicted Viscosity-Pressure Indices may be considered very satisfactory, certainly so for normal practical purposes*).

*The correlational accuracy achieved by the present "density correlation" appears to be somewhat inferior**) to that of the "chemical-constitution correlation" described in § IX. 3. 2. However, the present correlation has the significant advantage over the latter that it constitutes a really straightforward method for*

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*) For further particulars on the practical significance of the deviations involved reference may be made to § IX.3.2, notably to Tables IX-4 and IX-5.

**) The F-test yields a statistical confidence level exceeding 99%.

predicting the Viscosity-Pressure Indices of mineral oils.

The present correlation also permits depicting the initial viscosity-pressure coefficient $\alpha_{i,40^\circ C}$ - defined by Equation (VII-5) - of mineral oils as a function of their density $d_{0,40^\circ C}$, using their viscosity grade $\eta_{0,40^\circ C}$ as a parameter. For a few distinct values of the viscosity grade this derived correlation has been shown in Fig. IX-6, the ranges of $\alpha_{i,40^\circ C}$ and $d_{0,40^\circ C}$ being those covered by the basic correlation of Fig. IX-5.

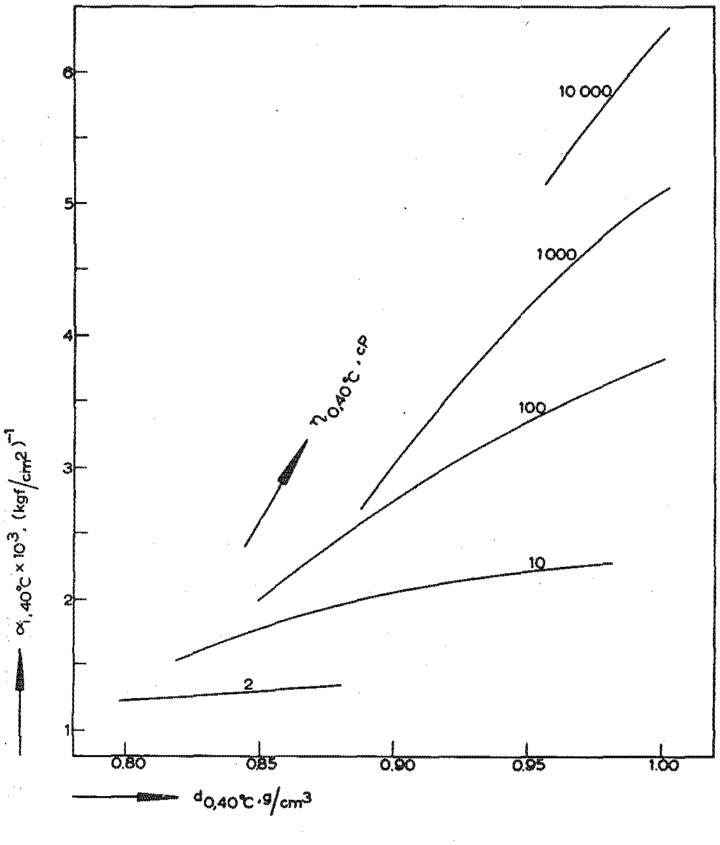

FIG. IX-6.
Initial Viscosity-Pressure Coefficients of Mineral Oils According to the Correlation of Fig. IX-5.

It should be pointed out (compare Section VII.4) that the initial viscosity-pressure coefficient, α_i, is very well comparable with the widely employed "average" viscosity-pressure coefficient, that is the value of α averaged over the lower pressure range, say, the range up to 1,000-2,000 kgf/cm^2 (14,000-28,000 psi). Consequently, Fig. IX-6 clearly invalidates the assumption - discussed already in part B of § IX.1.2 - that, at constant temperature, the (average) viscosity-pressure coefficients and the atmospheric densities of mineral oils would be uniquely correlated.

IX. 4. 3. *Correlation With Refractive Index*

Using the (atmospheric) *refractive index* $n_{0,40°C}$ (invariably relating to the sodium-D line) instead of the density $d_{0,40°C}$ of all the various mineral oils designated in Table IX-2 has yielded a correlation quite similar to the one described in the preceding § IX. 4. 2 (compare also § VIII. 3. 3). The resulting *"refractive-index correlation"* has been depicted in Fig. IX-7. The curves included in this figure relate to distinct refractive indices $n_{0,40°C}$ varying from 1.440 up to 1.570.

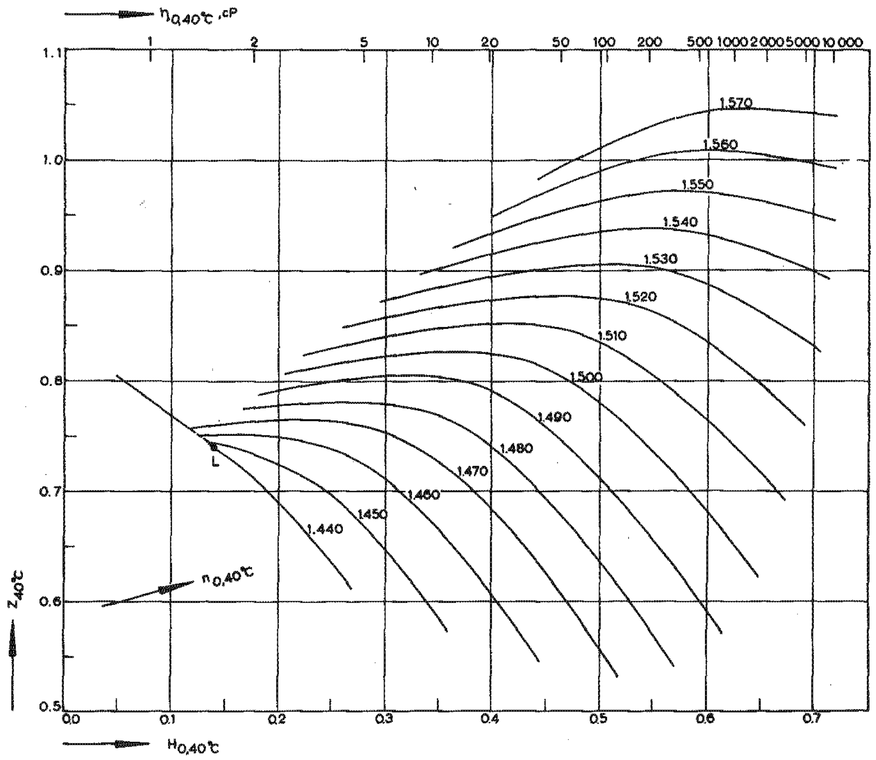

FIG. IX-7.
Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and Their Refractive Index.

A slight correction should preferably be applied also to the experimental value of the refractive index when the oil considered has an appreciable sulfur content. In accordance with the procedure outlined in § VIII.3.3 the experimental refractive indices of the oils tested have been corrected by subtracting 0.002 units for each wt.% S present (see also the relevant footnote in the preceding § IX.4.2).

The correlation depicted in Fig. IX-7 has been employed for estimating the Viscosity-Pressure Indices Z_{40^oC} of all the various kinds of mineral-oil fractions designated in Table IX-2. For each of these 74 fractions - including some saturated samples - these estimates are compiled in the same table. In addition, Table IX-3 gives the distribution of the deviations between experimental and predicted Viscosity-Pressure Indices amongst the really great variety of the 74 oils tested.

The latter table shows that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to 0.042 and 0.052 units, respectively. These correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices Z_{40^oC} and initial viscosity-pressure coefficients $\alpha_{i,40^oC}$ of 5.7 and 7.0%, respectively*).

*On the whole, therefore, the present refractive-index correlation permits satisfactory predictions of the Viscosity-Pressure Indices of mineral oils. However, its correlational accuracy is inferior**) to that of the foregoing correlation utilizing the density instead of the refractive index.*

IX.4.4. *Correlation With the Difference Between Refractive Index and Density*

It has appeared that the accuracy inherent in the above-described correlations utilizing either the density or the refractive index of the oil can still be substantially improved by employing a linear combination of these two quantities. In fact, by using simply the *difference* between the refractive index and the density - provided that the latter is expressed in g/cm^3 - a particularly satisfactory correlation for predicting the Viscosity-Pressure Indices of mineral oils has been achieved.

The latter correlation, which has again been derived from the data on the 74 mineral oils designated in Table IX-2, has been depicted in Fig. IX-8. The curves included in this figure relate to distinct values of the difference $(n\text{-}d)_{0,40^oC}$, with d in g/cm^3, ranging from 0.570 to 0.660. The present correlation is seen to be quite similar to the two preceding ones employing the density and the refractive index, respectively.

Likewise, a slight correction should preferably be applied to the difference $(n\text{-}d)_{0,40^oC}$ for the sulfur content of the oil considered. Of course, this can be performed by correcting the density and the refractive index individually according to the procedures outlined in § IX.4.2 and § IX.4.3, respectively; but the same correction can be applied at once by adding 0.004 units to the experimentally found difference $(n\text{-}d)_{0,40^oC}$ for each wt.% S present.

The correlation depicted in Fig. IX-8 has been utilized for reading the Viscosity-Pressure Indices Z_{40^oC} of all the various kinds of mineral-oil fractions designated in Table IX-2. For each of these 74 fractions - including some saturated samples - these readings are collected in the latter table. In addition, Table IX-3 gives again

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*) For further particulars on the practical significance of the deviations involved reference is made again to § IX.3.2, notably to Tables IX-4 and IX-5.

**) According to the F-test, the statistical confidence level exceeds 99.9%.

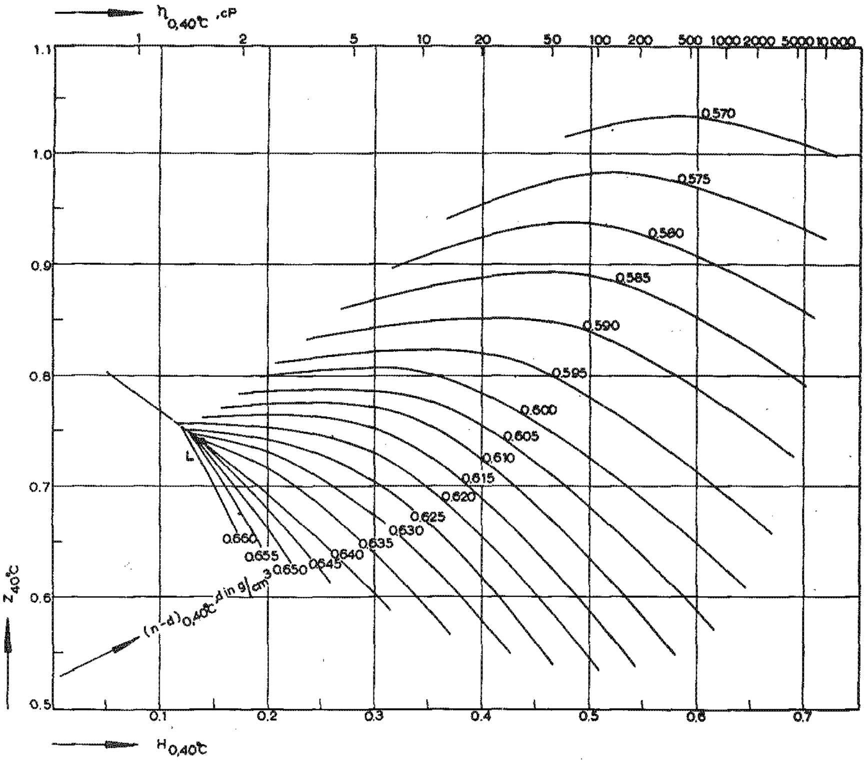

FIG. IX-8.

Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and the Difference Between Their Refractive Index and Density.

the distribution of the deviations between experimental and predicted Viscosity-Pressure Indices amongst the really great variety of the 74 oils tested.

Table IX-3 indicates that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to no more than 0.020 and 0.025 units, respectively, which figures are hardly beyond the accuracy inherent in the experimentally derived values. These absolute deviations correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices Z_{40^oC} and initial viscosity-pressure coefficients $\alpha_{i,40^oC}$ of only 2.9 and 3.6%, respectively. Moreover, for all the divergent kinds of mineral oils tested the absolute deviations observed in their predicted Viscosity-Pressure Indices *invariably* remain within 0.05 units*).

Summarizing, the present correlation has proved really satisfactory for estimating the Viscosity-Pressure Indices of mineral

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*) For further particulars on the practical significance of the deviations involved reference is made once again to § IX.3.2, notably to Tables IX-4 and IX-5.

oils. Its correlational accuracy is substantially better than that of the preceding density correlation (see § IX.4.2), let alone that of the refractive-index correlation (see § IX.4.3). In fact, the correlation depicted in Fig.IX-8 is fully on a par with the chemical-constitution correlation described in § IX.3.2.

IX.4.5. *Concluding Remarks*

A. THE APPLICABILITY OF THE PRESENT CORRELATIONS AT SOME ARBITRARY REFERENCE TEMPERATURE

If one atmospheric *viscosity* value of a given mineral oil has been specified at some temperature differing considerably from the standard reference temperature of 40°C, the three correlations described in the foregoing parts of this section may yet be utilized for predicting its Viscosity-Pressure Index $Z_{40^\circ C}$. To that end, first its atmospheric Slope Index is estimated from the given atmospheric-viscosity value and either the atmospheric density $d_{0,40^\circ C}$ or refractive index $n_{0,40^\circ C}$ by applying the procedure outlined in part A of § VIII.3.5; then, the desired viscosity grade $\eta_{0,40^\circ C}$ can readily be computed.

Further, the three aforementioned correlations employing the atmospheric density and/or refractive index of the oils at the standard reference temperature of 40°C can also be applied when the values of these physical constants are given only at one temperature which differs markedly from 40°C. Indeed, according to the procedures delineated at the ends of § VIII.3.2 and § VIII.3.3, respectively, the values of both physical constants at this standard reference temperature can be estimated sufficiently accurately from the single specified value.

Finally, it may be recalled that, as elucidated in § IX.2.3, the temperature variation of $Z_{40^\circ C}$ may easily be estimated solely from the - specified or predicted - atmospheric viscosity-temperature relationship of the oils.

The foregoing findings may be summarized in the following *generalized* conclusion*):

> *The viscosity-pressure dependence of mineral oils can be obtained, to a good approximation, solely from their viscosity grade and their atmospheric density and/or refractive index, irrespective of the particular reference temperatures involved.*

B. THE ANALOGY BETWEEN THE PRESENT CORRELATIONS AND THOSE FOR PREDICTING THE ATMOSPHERIC SLOPE INDEX OF MINERAL OILS

It is seen that the two correlations described in § IX.4.2 and § IX.4.3 for predicting the Viscosity-Pressure Index $Z_{40^\circ C}$ of mineral oils with known viscosity grade $\eta_{0,40^\circ C}$ solely from their at-

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*) It stands to reason that this conclusion will apply primarily to the conventional temperature range.

mospheric density $d_{0,40^oC}$ or refractive index $n_{0,40^oC}$, respectively, are quite analogous to the ones developed in Chapter VIII for estimating their atmospheric Slope Index.

Furthermore, a correlation analogous to the one employing the difference between atmospheric refractive index and density (see § IX. 4. 4) for predicting the Viscosity-Pressure Index Z_{40^oC} of mineral oils has proved very satisfactory also for estimating their atmospheric Slope Indices. The reason why it has not been included in the appropriate Chapter VIII is that the latter correlation did not turn out stricter than the corresponding - simpler - correlation using only the atmospheric density (see § VIII. 3. 2).

The indicated analogy between the present physical-constant correlations*) for predicting the Viscosity-Pressure Index Z_{40^oC} of mineral oils and those for estimating their atmospheric Slope Index opens up very interesting possibilities for conveniently correlating the viscosity-pressure relationship of such oils with their atmospheric viscosity-temperature relationship (compare point C of § IX. 3. 4). These possibilities will be thoroughly exploited in the subsequent Chapter X.

C. COMPARISON WITH KUSS'S CORRELATION

As stated already in part B of § IX. 1. 2, Kuss's correlation[30)] would appear to be the only one published so far that does permit generally satisfactory predictions of the viscosity-pressure dependence of mineral oils solely from atmospheric physical constants. It would therefore be very interesting to compare the accuracy of Kuss's correlation with that of the newly developed correlations which also utilize only atmospheric physical constants, notably the density and/or refractive index of the oils.

However, a considerable number of the 74 mineral oils designated in Table IX-2 could not be included in this comparison because their aniline points - which are required in Kuss's correlation - have not been determined. The comparison has been confined to the oils K-1 through K-29 (Table IX-2), on which Kuss's correlation was primarily based, plus 11 oils from the ASME pressure-viscosity project[27)] which were used by Kuss for further verifying his correlation. Altogether, a representative group of 40 mineral oils have thus been considered.

For this great variety of mineral oils it has been found that the overall accuracy of Kuss's correlation is superior to that of the present refractive-index correlation (see § IX. 4. 3) but slightly inferior to that of the present density correlation (see § IX. 4. 2). This conclusion also implies that the newly developed correlation employing the difference between refractive index and density of the oils

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*) It may be added that a tentative correlation analogous to the one employing the molecular weight of mineral oils for estimating their atmospheric Slope Index (see § VIII. 3. 4) was deemed too rough for predicting their Viscosity-Pressure Index Z_{40^oC}. In this connection, it may be significant to recall that the molecular-weight correlation of Chapter VIII proved substantially less accurate than the aforementioned correlations utilizing the atmospheric density and/or refractive index of the oils for estimating their atmospheric Slope Index.

(see § IX.4.4) is substantially stricter than Kuss's.

The improved overall accuracy inherent in two of the three newly developed correlations should be deemed most remarkable, since these require a smaller number of atmospheric physical constants than Kuss's correlation.

In fact, chiefly owing to the comparatively great number of atmospheric physical constants involved, the latter correlation is rather cumbersome to use. In contrast, the newly developed correlations excel in simplicity. Last but not least, the present correlations yield predictions that, owing to the underlying mathematical framework (see Section IX.2), are essentially more significant and more widely usable than Kuss's.

IX.5. DISCUSSION

IX.5.1. *Comparison of the Various Correlations Developed*

The four newly developed correlations for predicting the viscosity-pressure dependence of mineral oils - both natural and saturated - have proved to combine simplicity and reliability. Thus, they are very suitable indeed for practical application. In addition, they lend themselves very well to correlational purposes.

Two types of correlations have been advanced in the present study:

a. In Section IX.3 a correlation has been devised for predicting the Viscosity-Pressure Index of mineral oils with known viscosity grade solely from their *chemical constitution*. In fact, for this particular purpose their chemical constitution has proved to be represented satisfactorily simply by the total percentage of carbon atoms in ring structure, C_R.
b. In Section IX.4 two correlations have been established for estimating the Viscosity-Pressure Index of mineral oils with known viscosity grade from *one single*, easily measurable, *atmospheric physical constant*. The atmospheric *density* and *refractive index* have been employed successfully. In addition, the *difference* between these two quantities has permitted a particularly satisfactory correlation.

Whilst the correlation based on the chemical constitution of the oils is very convenient for predicting their viscosity-pressure relationship, its value would lie primarily in furnishing some insight into the relevant effect of their chemical constitution proper. Thus, this correlation may be very helpful in preparing oils with the desired viscosity-pressure characteristics.

The three physical-constant correlations have the weighty advantage over the latter correlation that they constitute really *straightforward* tools for easily estimating the viscosity-pressure dependence of mineral oils. Accordingly, for practical applications these correlations with simple atmospheric physical constants are more attractive. The correlation involving the difference between refractive index and density is the most accurate one of the three; in fact, its accuracy proves to be fully on a par with that of the correlation based on the chemical constitution of the oils.

All in all, for practical applications the correlation employing the difference between refractive index and density as a parameter is definitely to be preferred.

IX. 5. 2. *Further Discussion of the Validity Ranges of the New Correlations*

The extensive ranges of Viscosity-Pressure Indices and viscosity grades for which the three new physical-constant correlations (see Section IX. 4) have been checked are approximately comprised by the two converging dashed lines in Fig. IX-9 (see also Fig. I-2).

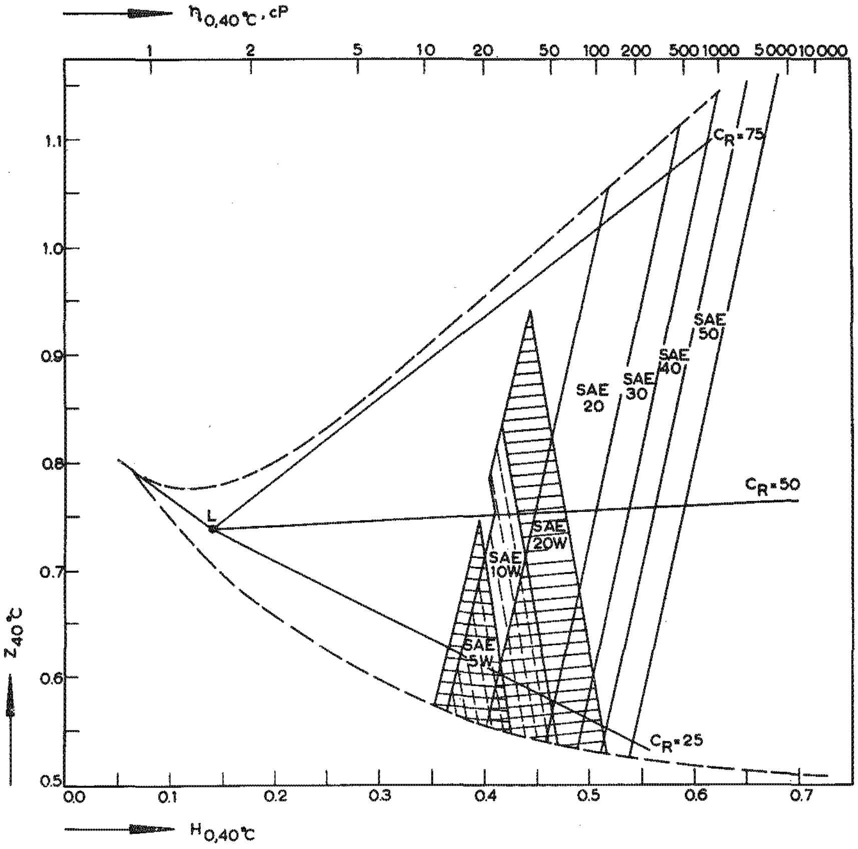

FIG. IX-9.
Validity Ranges of the New Viscosity-Pressure Correlations.

As indicated in Fig. IX-9, these two dashed lines are fairly closely approximated by the outmost straight lines*) - relating to $C_R = 25$ and $C_R = 75$ - of the correlation with chemical constitution depicted in Fig. IX-2. In this connection it should be pointed out that the n-d-M method, which has invariably been used for determining the carbon-type composition of the oils, may not safely be applied when C_R exceeds 75 or when $C_A > 1.5\ C_N$. This is the reason why the correlation based on this carbon-type composition is bound to have a somewhat narrower validity range than the three physical-constant correlations.

In order that the indicated applicability ranges of the various correlations may be grasped and memorized more easily the *approximate* ranges of Z_{40^oC} and $H_{0,40^oC}$ covered by the well-known SAE Viscosity Numbers for classifying crankcase lubricating oils in terms of their viscosity grade (see § VIII.4.2) have also been depicted in Fig. IX-9. The latter ranges have been estimated on the basis of the preceding Fig. VIII-9 and the correlational Fig. X-1 yet to be discussed. Remarkably enough, the lines indicating these various ranges all prove to be *straight*, at least within the accuracy of the latter two figures.

All in all, the applicability range depicted in Fig. IX-9 for the three physical-constant correlations may be taken to represent practically the full range of Viscosity-Pressure Indices Z_{40^oC} *and corresponding viscosity grades* $\eta_{0,40^oC}$ *exhibited by all the divergent kinds of mineral oils known so far (excepting extremely viscous ones). These include not only mineral oils obtained by conventional refining methods - denoted as "natural" mineral oils - but even completely hydrogenated - saturated - samples.*

Possibly, the present physical-constant correlations would yield less reliable results for certain mineral oils whose "natural" character has been drastically modified by applying rather extreme refining methods - or such oils might even fall somewhat beyond the applicability range indicated in Fig. IX-9. It should be emphasized, however, that - apart from several mineral oils saturated by complete hydrogenation - even such "extreme" products as *highly aromatic extracts* have proved to comply almost equally well with these correlations.

The latter correlations have also been applied successfully to several mineral oils containing small amounts of *additives*. Indeed, their Viscosity-Pressure Indices and - to a smaller extent - their viscosity grades are, in general, hardly affected by the presence of a few per cent (by weight) of such additives. It may be advisable, however, to apply a small correction to their density and/or refractive index if these are used as correlational variables (compare § VIII.4.2).

Finally, it should be pointed out that *polymer-blended* mineral oils do not conform to the present physical-constant correlations. Nevertheless, as will be elucidated in § X.4.2, the Viscosity-Pressure Index of such oils can also be predicted very conveniently.

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*) Further, the intermediate straight line relating to $C_R = 50$ and the straight line for very fluid oils have been replotted from Fig. IX-2.

IX.5.3. *The Compatibility of Pure Hydrocarbons With the New Correlations for Mineral Oils*

The present correlations have been designed specifically for mineral oils, that is for mixtures of an enormous variety of (essentially) hydrocarbon compounds. Thus, it may by no means be inferred that individual, *pure* hydrocarbons would likewise be compatible with these correlations.

On the contrary, considerations similar to those presented in § VIII.4.3 with respect to the estimation of the atmospheric Slope Indices of pure hydrocarbons lead to the conjecture that conspicuous deviations are very likely to occur in several cases, particularly for pure hydrocarbons whose structure differs widely from the average chemical constitution of the normally encountered types of mineral oils.

Whilst this conjecture has indeed appeared to be correct, it has simultaneously been found that the three physical-constant correlations of Section IX.4 yield predictions of the Viscosity-Pressure Indices of pure hydrocarbons which may be deemed reasonable in many cases. In other cases, however, such predictions are useful only as a first - rather rough - approximation.

In order to convey an impression of the deviations involved the *density* correlation depicted in Fig. IX-5 has been applied to a variety of 15 pure hydrocarbons tested by Schiessler and associates in the scope of API Research Project 42[11,12]. In Table IX-6 all these compounds are arranged in order of increasing viscosity grade $\eta_{0,40^\circ C}$. Besides the experimental densities $d_{0,40^\circ C}$, the experimental and predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ have been included. Indeed, whilst several predictions may be considered fair, other ones turn out to be rather rough, notably for the highly aromatic compounds.

It may be added that similar deviations result when the other two correlations of Section IX.4 are applied.

IX.5.4. *The Initial Viscosity-Pressure Coefficients of Mineral Oils According to the Present Correlations*

In Section VII.4 the *initial* viscosity-pressure coefficient, α_i, has been defined by:

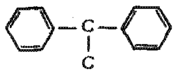
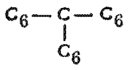
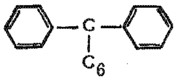
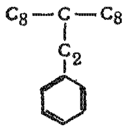
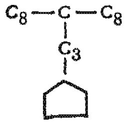
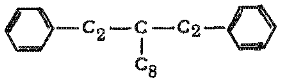
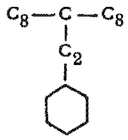
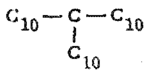
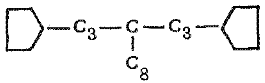
$$\alpha_i = 1.151 \cdot 10^{-3} \, Z \, (\log \eta_0 + 1.200). \qquad \text{(VII-5)}$$

On the basis of this equation the initial viscosity-pressure coefficients of mineral oils can readily be estimated from any of the four newly developed correlations for predicting their Viscosity-Pressure Indices, Z. For several groups of mineral oils characterized by a common value of the parameter used in the correlation concerned the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ have thus been estimated and plotted in Fig. IX-10 as a function of their viscosity grades $\eta_{0,40^\circ C}$ (compare § VIII.4.4).

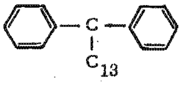
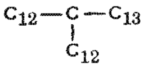
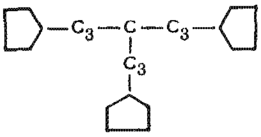
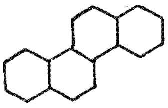
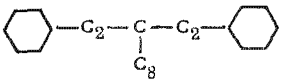
Since for very fluid mineral oils one and the same straight-line relationship between $Z_{40^\circ C}$ and $H_{0,40^\circ C}$ has been upheld in each of the four correlations under consideration, these oils are depicted

TABLE IX-6

Experimental and Predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ of 15 Pure Hydrocarbons

Compound		Experimental Data		$Z_{40^\circ C}$	
PSU No.	Structural Formula	$\eta_{0,40^\circ C}$, cP	$d_{0,40^\circ C}$, g/cm^3	Exp.	Pred.
516		2.72	0.984	0.59	0.82
500	 $C_6-\underset{\substack{\vert \\ C_6}}{C}-C_6$	3.33	0.774	0.67	0.60
25	 $C_8-\underset{\substack{\vert \\ C_8}}{C}-C_8$	6.61	0.789	0.60	0.54
503		7.41	0.936	0.66	0.84
87		7.41	0.820	0.61	0.63
110		8.59	0.816	0.59	0.61
18		10.64	0.908	0.58	0.81
88		11.22	0.843	0.64	0.67
8	 $C_{10}-\underset{\substack{\vert \\ C_{10}}}{C}-C_{10}$	11.27	0.799	0.57	0.52
111		12.59	0.845	0.62	0.67

CONTINUATION OF TABLE IX-6

	Compound	Experimental Data		$Z_{40°C}$	
PSU No.	Structural Formula	$\eta_{0,40°C}$, cP	$d_{0,40°C}$, g/cm^3	Exp.	Pred.
12		15.56	0,905	0.63	0.81
134	 $C_{12}-\underset{C_{12}}{\underset{\vert}{C}}-C_{13}$	19.14	0.806	0.52	0.49
113		20.7	0.876	0.64	0.74
575		23.3	0.968	1.15	0.91
19		26.0	0.853	0.71	0.65

by a single line in Fig. IX-10. But for oils with viscosity grades $\eta_{0,40°C}$ exceeding 1.51 cP - indicated by point L in the latter figure - the differentiation as to $\alpha_{i,40°C}$ increases repidly with their viscosity grade.

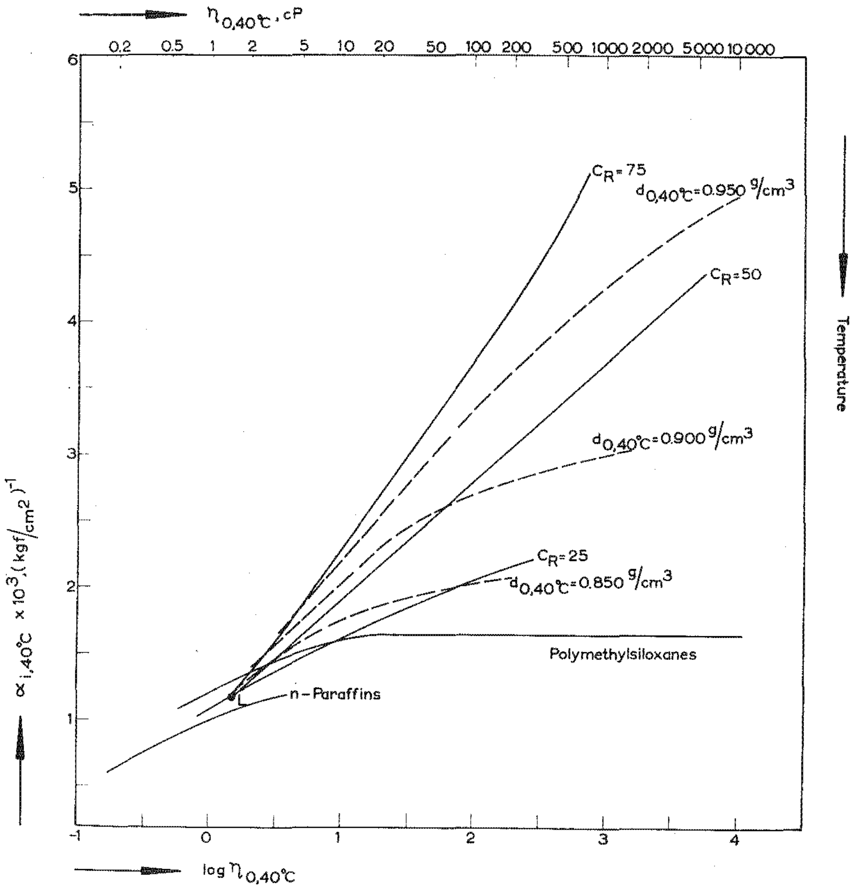


FIG. IX-10.
Initial Viscosity-Pressure Coefficients of Mineral Oils According to the Present Correlations.

Fig. IX-10 demonstrates that for iso-C_R oils the initial viscosity-pressure coefficients increase strongly with their viscosity grade, the more so the higher their particular C_R-value*).

Further, three lines of constant atmospheric density $d_{0,40°C}$ have been drawn in Fig. IX-10. It is seen that within groups of iso-den-

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*) It may be noted (compare § I[illegible]) that the lines relating to $C_R = 25$ and $C_R = 75$ comprise nearly the entire range of initial viscosity-pressure coefficients encountered amongst natural mineral oils.

sity oils the initial viscosity-pressure coefficients increase to a much smaller extent than within comparable groups of iso-C_R oils. In fact, for the more viscous members of groups of oils characterized by some rather low density the initial viscosity-pressure coefficients would even tend to approach a constant value characteristic of the particular group.

From the underlying correlations it will be clear that lines relating to constant atmospheric refractive index $n_{0,40^oC}$ and of constant difference $(n-d)_{0,40^oC}$ are quite similar to those depicted in Fig. IX-10 for constant density $d_{0,40^oC}$.

It may be remarked that a correlation analogous to the one utilizing the *total ring number* of mineral oils for estimating their atmospheric Slope Index (see part B of § VIII. 4. 4) solely from their viscosity grade proved too rough for predicting their Viscosity-Pressure Index. In this connection it may be significant to recall that the ring-number correlation of Chapter VIII has been found substantially less accurate than the other correlations produced in that chapter.

Nevertheless, on the analogy of the feature - described in § VIII. 4. 4 - that for the more viscous members of mineral-oil groups characterized by a common, sufficiently high ring number the viscosity-*temperature* coefficient approaches a constant value, it could be shown at least qualitatively that their initial viscosity-pressure coefficients would likewise tend to become constant.

Using experimental data from the investigations cited in § VII. 2. 2, the initial viscosity-pressure coefficients $\alpha_{i,40^oC}$ of the homologous group of (linear) polymethylsiloxanes have also been included in Fig. IX-10. Remarkably enough, already at comparatively low viscosity grades these initial viscosity-pressure coefficients reach a substantially constant level.

From Equation (VII-7) it follows that at any constant temperature the volume V_{vis} entering into Eyring's theory of viscous flow (see Section IV. 1) is proportional to the present quantity α_i. Accordingly, the volume V_{vis} likewise assumes a constant value for the higher members of the series of polymethylsiloxanes depicted. Just like the aforementioned constancy of their activation energy for viscous flow the present feature is generally attributed to the phenomenon of *segmental flow* displayed by such flexible long-chain polymers (see § VIII. 4. 4).

For comparison the initial viscosity-pressure coefficients of the homologous series of n-paraffins (compare § VII. 2. 2) have also been depicted in Fig. IX-10. However, since these liquids become solid already at relatively low viscosity grades, a similar constancy of their α_i (and V_{vis}) cannot be observed.

CHAPTER X

CORRELATION BETWEEN THE VISCOSITY-PRESSURE RELATIONSHIP OF MINERAL OILS AND THEIR ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP

X. 1. INTRODUCTION

X. 1. 1. *Previous Investigations*

As pointed out already in § IX. 1. 1, many attempts have been made to predict the pressure variation of the viscosity of mineral oils solely from some parameter that is claimed to be representative of their *temperature* variation at atmospheric pressure. Indeed, since the publication, in 1929, of Kiesskalt's well-known correlation 163,164) it has widely been recognized that at least a rough parallelism would exist between the easily assessable atmospheric temperature effect on the viscosity of mineral oils and the corresponding pressure effect.

In the course of time, therefore, various correlations more or less similar to Kiesskalt's original one have been proposed, notably by Cameron 60), Sanderson 109, 110), Bradbury *et al.* 28), Clark 165), Anderson 166) and Appeldoorn 124). Unfortunately, all these correlations show considerable scatter, thus indicating that the basic assumption that for all mineral oils*) approximately the same equivalence would be observed between the effects of temperature and pressure on their atmospheric viscosity is oversimplified and may be upheld only as a first approximation.

Besides the aforementioned correlations - which essentially employ only some atmospheric viscosity-temperature criterion for estimating the viscosity-pressure dependence of mineral oils -, a few correlations have been designed which utilize their viscosity *grade* as an additional parameter. These are the correlations proposed by Matteson and Vogt 167), Weber 168) and Hartung 169).

Off-hand, the use of the viscosity grade in addition to some atmospheric viscosity-temperature criterion would seem to offer much better possibilities for establishing a reasonable correlation**). Indeed, the soundness of the latter conjecture has more or less been substantiated by Weber's and particularly by Hartung's correlation. Unfortunately, Weber's correlation has been devised for such a small range of viscosity grades that it has only minor practical significance. Hartung's correlation constitutes by far the best one available in that it generally yields quite acceptable predictions for the normal types of mineral oils. However, it is af-

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*) As will be elucidated in part B of § X. 2. 2, Clark's aforementioned correlation takes a somewhat different form according as the oils are classified as "paraffinic" or "naphthenic".

**) Some suggestive thoughts on this conjecture have been expressed by Hersey and Hopkins 26) in their discussion of Kiesskalt's correlation.

flicted with the serious shortcoming that it still covers only a moderate part of the entire range of viscosity-temperature-pressure relationships encountered amongst all the various kinds of mineral oils known so far. Moreover, Hartung's correlation proves to be rather unwieldy and lacks any mathematical framework for the viscosity-temperature-pressure relationships contemplated.

All in all, it may be stated that, notwithstanding the many correlational attempts carried out in this field, the present situation with respect to the interrelationship between the viscosity-pressure dependence of mineral oils and their atmospheric viscosity-temperature dependence is still rather obscure.

X.1.2. *The Present Approach*

The foregoing discussion emphasizes the desirability of throwing more light upon the interrelationship between temperature and pressure effects on the viscosity of mineral oils. In the first place, the possibilities for establishing more generally applicable and more convenient correlations should be exploited more thoroughly. In the second place, more quantitative information should be gained on the accuracy of available correlations, some of which have been, and are still, employed rather frequently.

In the preceding Chapter IX various correlations for predicting the Viscosity-Pressure Index of mineral oils have been developed which prove to be quite analogous to the new correlations described in Chapter VIII for estimating their atmospheric Slope Index. In fact, all these correlations permit predicting the Viscosity-Pressure Index and the atmospheric Slope Index, respectively, solely from the viscosity grade of the oils and one easily assessable quantity. As such quantities have been used: the percentage of carbon atoms in ring structure, C_R - representing a measure of the chemical constitution of the oils -, their atmospheric density (in g/cm^3), their atmospheric refractive index and also the difference between the latter two physical constants (taken at the standard reference temperature of 40°C).
As stated already in Chapter IX (see point C of § IX.3.4 and part B of § IX.4.5), the indicated analogy opens up very interesting possibilities for correlating the viscosity-pressure relationship of mineral oils directly with their atmospheric viscosity-temperature relationship. Indeed, by combining any such analogous correlations - employing the same parameter in addition to the viscosity grade of the oils - a new correlation may readily be obtained which would permit predicting the Viscosity-Pressure Index of mineral oils with known viscosity grade solely from their atmospheric Slope Index.
Instead of combining two such analogous correlations - which constitute approximations already by themselves - it has been preferred to make a fresh approach simply by plotting the Viscosity-Pressure Indices of all the various kinds of oils under consideration against their viscosity grades, using their atmospheric Slope Indices as a parameter. This has again been done at the standard reference temperature of 40°C (104°F). But it should be recalled that the

- comparatively small - temperature effect on the Viscosity-Pressure Index Z_{40^oC} can easily be determined, by means of the mathematical framework outlined in Section IX.2, solely from the atmospheric viscosity-temperature relationship.

Thus, the present approach has produced a really satisfactory correlation for estimating the Viscosity-Pressure Index of mineral oils, in a wide temperature range, solely from their viscosity grade and their atmospheric Slope Index. More generally, it may be stated that the newly developed correlation does permit predicting, to a good approximation, the complete viscosity-temperature-pressure relationship of mineral oils solely from their atmospheric viscosity-temperature relationship.

Further, the considerable inaccuracies inherent in the various correlations hitherto proposed have been quantitatively revealed on the basis of the present correlation.

Experimental Data

The results of the present study are based on reliable experimental data on 113 mineral-oil fractions. As regards their origin and chemical composition these fractions may be considered representative of the entire range of natural mineral oils known so far. In addition, some fully hydrogenated samples have been included.

TABLE X-1

Specification of Mineral Oils Included in the Present Investigation

Investigation	Ref.	Number of Oils
Kuss	29, 30	59
Roelands et al.	44	20
Dow et al.	31-35; 25	18
ASME	27	16
	Total	113

Table X-1 lists the various investigations from which these basic data have been taken. The viscosity grades $\eta_{0,40^oC}$, the atmospheric Slope Indices, S_0, and the Viscosity-Pressure Indices Z_{40^oC} of the various oils are compiled in Table X-2. It may be noted that all the 74 mineral oils collected in Table IX-2 of the preceding chapter have also been included in the present study. The additional 39 oils here considered are designated in Table X-3. The latter oils have not been employed in the foregoing Chapter IX because their atmospheric density and refractive index are not known with the desired accuracy.

For further details on the present basic data reference is made to § IX.1.3.

TABLE X-2

Experimental and Predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ of Representative Mineral Oils

Oil Code*)	Experimental Data				$Z_{40^\circ C}$ Predicted from $\eta_{0,40^\circ C}$ Plus	
	$\eta_{0,40^\circ C}$, cP	s_0	s_0^*	$Z_{40^\circ C}$	s_0	s_0^*
K-1	260	1.24	1.23	0.58	0.59	0.57
K-2	134.9	1.30	1.29	0.62	0.65	0.63
K-3	101.0	1.27	1.27	0.61	0.64	0.63
K-4	159.2	1.26	1.25	0.60	0.62	0.60
K-5	147.2	1.40	1.40	0.69	0.72	0.73
K-6	110.9	1.42	1.40	0.73	0.75	0.74
K-7	58.9	1.18	1.18	0.62	0.61	0.61
K-8	67.6	1.50	1.48	0.80	0.84	0.84
K-9	328	1.47	1.44	0.70	0.73	0.73
K-10	62.4	1.30	1.29	0.67	0.69	0.68
K-11	246	1.39	1.37	0.66	0.69	0.67
K-12	408	1.35	1.34	0.65	0.64	0.62
K-13	1.686	0.97	0.93	0.68	0.68	0.66
K-14	7.16	1.09	1.09	0.66	0.70	0.70
K-15	2.93	1.04	1.04	0.72	0.76	0.75
K-16	12.90	1.14	1.14	0.67	0.67	0.68
K-17	31.8	1.19	1.19	0.66	0.65	0.64
K-18	36.6	1.27	1.27	0.69	0.70	0.70
K-19	27.3	1.31	1.31	0.72	0.75	0.77
K-20	33.5	1.23	1.23	0.64	0.67	0.67
K-21	173.8	1.29	1.29	0.60	0.63	0.62
K-22	139.5	1.27	1.28	0.61	0.63	0.62
K-23	355	1.34	1.34	0.60	0.64	0.63
K-24	83.7	1.34	1.34	0.70	0.70	0.70
K-25	192.0	1.38	1.39	0.65	0.69	0.70
K-26	90.0	1.52	1.50	0.83	0.84	0.84
K-27	19.13	1.36	1.30	0.80	0.84	0.81
K-28	127.6	1.76	1.65	0.93	0.99	0.96
K-29	1,290	1.89	1.82	0.99	1.00	1.03
K-30	88.4	1.38	1.38	0.78	0.73	0.74
K-31	19.00	1.32	1.31	0.79	0.80	0.82
K-32	306	1.53		0.76	0.79	
K-33	785	1.64		0.85	0.84	
K-34	10.10	1.20		0.74	0.78	
K-35	104.0	1.42		0.74	0.75	
K-36	14.10	1.22		0.77	0.74	
K-37	36.7	1.31		0.70	0.73	
K-38	86.0	1.36		0.72	0.72	
K-39	134.8	1.36		0.69	0.69	
K-40	7.12	1.13		0.80	0.78	
K-41	68.3	1.27		0.62	0.66	
K-42	29.5	1.27		0.69	0.71	
K-43	74.0	1.30		0.65	0.68	
K-44	200	1.23		0.60	0.59	
K-45	8.35	1.16		0.73	0.77	

CONTINUATION OF TABLE X-2

Oil	Experimental Data				Z_{40^oC} Predicted from $\eta_{0,40^oC}$ Plus ...	
Code*)	$\eta_{0,40^oC}$, cP	S_0	S_0^*	Z_{40^oC}	S_0	S_0^*
K-46	11.15	1.22		0.77	0.78	
K-47	10.20	1.20		0.74	0.77	
K-48	57.7	1.34		0.74	0.73	
K-49	75.0	1.38		0.78	0.74	
K-50	10.10	1.16		0.71	0.72	
K-51	8.60	1.16		0.75	0.76	
K-52	9.70	1.20		0.75	0.79	
K-53	19.70	1.35		0.78	0.83	
K-54	39.7	1.38		0.76	0.78	
K-55	124.0	1.52		0.75	0.82	
K-56	43.7	1.25		0.61	0.67	
K-57	60.0	1.25		0.61	0.65	
K-58	316	1.26		0.54	0.59	
K-59	35.4	1.25		0.68	0.68	
WR-7	8.79	1.12	1.11	0.70	0.70	0.70
WR-7H	7.96	1.10	1.11	0.72	0.70	0.71
WR-11	1.493	0.98	0.99	0.76	0.74	0.74
WR-18	9.12	1.21	1.18	0.84	0.82	0.80
WR-18H	7.10	1.14	1.16	0.86	0.79	0.82
WR-26	13.46	1.21	1.20	0.73	0.73	0.75
WR-34	2.40	0.99	0.97	0.70	0.66	0.67
WR-41	3.30	1.02	1.01	0.70	0.68	0.69
WR-56	7.14	1.11	1.10	0.75	0.74	0.72
WR-56H	6.50	1.11	1.13	0.76	0.76	0.79
WR-67	6.58	1.06	1.05	0.66	0.66	0.67
WR-69	1.556	0.99	0.99	0.76	0.76	0.75
WR-76	1.683	0.99	0.99	0.72	0.75	0.74
WR-79	4.48	1.07	1.06	0.70	0.75	0.72
WR-80	6.68	1.11	1.10	0.70	0.75	0.73
WR-81	11.54	1.18	1.17	0.69	0.72	0.73
WR-91	7.87	1.11	1.10	0.70	0.71	0.70
WR-91H	6.79	1.08	1.09	0.74	0.69	0.71
WR-97	2.31	1.01	1.01	0.71	0.73	0.73
WR-99	3.33	1.04	1.04	0.72	0.73	0.73
D-1	157.8	1.42	1.41	0.76	0.73	0.73
D-2	78.5	1.37	1.37	0.77	0.73	0.74
D-3	30.1	1.29	1.29	0.78	0.73	0.73
D-4	427	1.35	1.35	0.63	0.64	0.63
D-5	19.19	1.29	1.27	0.81	0.77	0.77
D-6	382	1.58	1.56	0.87	0.82	0.84
D-7	1,334	1.61	1.57	0.81	0.80	0.81
D-8	74.5	1.22		0.63	0.62	
D-9	99.5	1.44		0.83	0.77	
D-10	30.6	1.23		0.69	0.68	
D-11	27.7	1.20		0.71	0.66	

CONTINUATION OF TABLE X-2

Oil	Experimental Data				$Z_{40^\circ C}$ Predicted	
Code*)	$\eta_{0,40^\circ C}$, cP	S_0	S_0^*	$Z_{40^\circ C}$	from $\eta_{0,40^\circ C}$ Plus	
					S_0	S_0^*
D-12	82.8	1.43		0.74	0.77	
D-13	35.4	1.24		0.59	0.58	
D-14	31.2	1.24		0.64	0.68	
D-15	23.8	1.23		0.67	0.69	
D-16	21.3	1.22		0.64	0.70	
D-17	18.36	1.16		0.65	0.66	
D-18	13.06	1.21		0.68	0.74	
A-1	25.1	1.21	1.22	0.71	0.67	0.69
A-2	7.30	1.15	1.15	0.79	0.80	0.79
A-3	41.1	1.26	1.25	0.67	0.68	0.67
A-4	129.4	1.26	1.27	0.60	0.62	0.62
A-5	438	1.28	1.27	0.60	0.59	0.57
A-6	138.7	1.25	1.25	0.60	0.61	0.60
A-7	120.5	1.25	1.25	0.63	0.62	0.61
A-8	119.7	1.21	1.22	0.61	0.59	0.59
A-9	38.9	1.26	1.26	0.66	0.68	0.68
A-10	44.7	1.39	1.39	0.83	0.78	0.80
A-11	117.5	1.49	1.49	0.84	0.80	0.82
A-12	403	1.60	1.60	0.90	0.83	0.87
A-13	119.4	1.50	1.50	0.87	0.81	0.82
A-14	117.5	1.47	1.47	0.85	0.78	0.80
A-15	58.2	1.37	1.39	0.79	0.75	0.78
A-16	501	1.77	1.72	1.02	0.96	0.98

*) Refers to similarly coded oils specified in Tables II-1 and X-3.

TABLE X-3

Designations to the Additional Mineral Oils Tested

Code	Experimenters' Designation	$\eta_{0,40^\circ C}$, cP
	KUSS29)	
	Group Low	
K-32	Low E	306
K-33	Low F	785
	Group Medium	
K-34	Medium P	10.10
K-35	Medium Q	104.0
K-36	B.1	14.10
K-37	B.2	36.7
K-38	B.3	86.0
K-39	B.4	134.8
	Group High	
K-40	High H	7.12
K-41	High I	68.3
K-42	High L	29.5
K-43	High M	74.0
K-44	High N	200
	Group W.B.Lub.	
K-45	Lub.1, White Oil	8.35
K-46	Lub.1, Raffinate	11.15
K-47	Lub.1, Distillate	10.20
K-48	Lub.2, Raffinate	57.7
K-49	Lub.2, Raffinate 8	75.0
K-50	Lub.1, White Oil	10.10
K-51	Lub.1, Raffinate	8.60
K-52	Lub.1, Distillate	9.70
K-53	Lub.1, Extract	19.70
K-54	Lub.2, Distillate	39.7
K-55	Lub.3, Distillate	124.0
	Group SAE	
K-56	SAE 20, Dewaxed	43.7
K-57	SAE 30, Dewaxed	60.0
K-58	SAE 70, Dewaxed	316
K-59	SAE 20, Waxy Raffinate	35.4
	DOW et al.31-34;25)	
D-8	Pennsylvania Oil	74.5
D-9	California Oil	99.5
D-10	Pennsylvania 180 Neutral	30.6
D-11	Raffinate from D-10	27.7
D-12	Extract from D-10	82.8

CONTINUATION OF TABLE X-3

Code	Experimenters' Designation	$\eta_{0,40^{\circ}C}$, cP
	DOW et al. (Cont.)	
	Pennsylvania Oils	
D-13	Commercial Bright Stock (High M)	35.4
D-14	Commercial Neutral (Low M)	31.2
D-15	High-Boiling-Point Fraction from D-16	23.8
D-16	Solvent-Refined Oil	21.3
D-17	Medium-Boiling-Point Fraction from D-16	18.36
D-18	Low-Boiling-Point Fraction from D-16	13.06

X.2. THE PRESENT CORRELATION

X.2.1. *The Basic Correlation*

For all the various mineral oils designated in Table X-2 the Viscosity-Pressure Indices $Z_{40^\circ C}$ have been plotted against their viscosity grades $H_{0,40^\circ C}$, using their atmospheric Slope Indices, S_0, as a parameter. As demonstrated by the resulting Fig.X-1, it appeared that more or less curved lines of constant Slope Index could indeed be constructed.

It is seen that, according to this new correlation, the Viscosity-Pressure Indices $Z_{40^\circ C}$ of mineral oils characterized by a common Slope Index S_0 decrease fairly regularly with increasing viscosity grade $\eta_{0,40^\circ C}$. For very fluid mineral oils the unique straight-line relationship between $Z_{40^\circ C}$ and $H_{0,40^\circ C}$ depicted in the correlational figures of Chapter IX has been retained - for reasons of uniformity - in the present Fig.X-1.

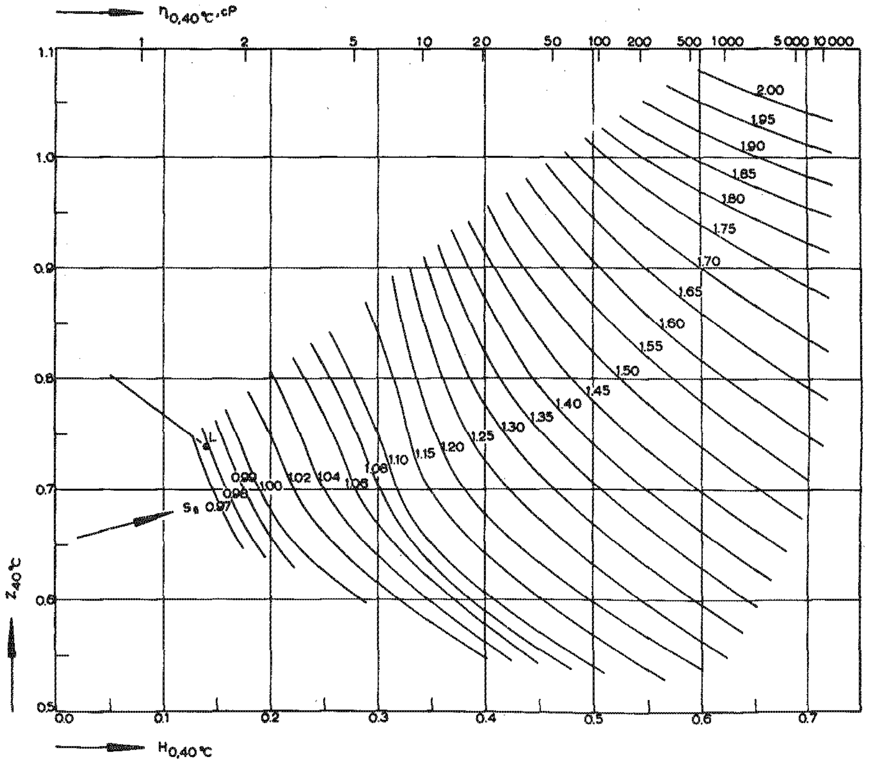

FIG.X-1.
Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and Their Atmospheric Slope Index.

The correlation depicted in Fig. X-1 has been applied to all the various kinds of mineral-oil fractions designated in Table X-2. For each of these 113 fractions - including some saturated samples - the predicted values of $Z_{40^\circ C}$ have been included in the same table. In addition, Table X-4 indicates the distribution of the deviations between experimental and predicted Viscosity-Pressure Indices amongst the really great variety of the 113 oils tested.

TABLE X-4

Distribution of Deviations Between Experimental and Predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ Amongst the Various Oils Tested

Deviation	Percentage of the Oils Tested	
	Correlation Employing $\eta_{0,40^\circ C}$ Plus	
$\lvert \delta Z_{40^\circ C} \rvert$	s_0	s_0^*
0.00	9.7	12.2
0.01	25.6	23.0
0.02	14.2	20.3
0.03	15.1	24.3
0.04	16.8	13.5
0.05	8.9	6.7
0.06	6.2	
0.07	3.5	
Average Deviation*)	0.027	0.022
Standard Deviation**)	0.033	0.027

*) Defined by $\frac{1}{n} \sum_{i=1}^{i=n} \lvert \delta_i \rvert$

**) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} \delta_i^2}{n-1}}$

The latter table shows that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to no more than 0.027 and 0.033 units, respectively, which figures are only slightly beyond the accuracy inherent in the experimentally derived values. These absolute deviations correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ and the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ (see Section VII.4) of only 3.8 and 4.6%, respectively.

The indicated accuracy of the basic correlation may be considered very satisfactory throughout. Its wide practical usefulness may be emphasized by referring to the last part of § IX.3.2, notably to Tables IX-4 and IX-5.

X.2.2. *Derived Correlations*

A. REFINEMENT OF THE BASIC CORRELATION

A nearer analysis has been made of the aforementioned deviations in the Viscosity-Pressure Indices predicted by means of the new correlation. This analysis has led to the finding that the - otherwise very satisfactory - overall accuracy of the basic correlation can still be further improved by taking the well-known *refractivity intercept*, r_i, of the oils into account*). It may be recalled that the latter quantity, introduced by Kurtz and Ward [170, 50], is given by $r_i = n - \frac{1}{2}d$, where n denotes again the (atmospheric) refractive index and where the atmospheric density d - taken at the same standard reference temperature - must be expressed in g/cm^3 (compare § XI.4.6).

The resulting *refined* correlation uses, instead of the experimental atmospheric Slope Index, S_0, a *"corrected"* atmospheric Slope Index S_0^*, defined by:

$$S_0^* = \left\{1 + 2\left[1.045 - (r_i)_{40^\circ C}\right]\right\} S_0, \qquad (X\text{-}1)$$

where the figure 1.045 represents some average value for the refractivity intercepts $(r_i)_{40^\circ C}$ of mineral oils. It may be mentioned that for all the various kinds of mineral oils included in the present analysis the values of $(r_i)_{40^\circ C}$ range from 1.034 to 1.078.

This refined correlation, which is very similar to the basic correlation of Fig.X-1, has been depicted in Fig.X-2. The latter figure has been based on the data of those 74 mineral oils from Table X-2 which have also been used in Chapter IX and have been included already in Table IX-2.

Application of the correlational Fig.X-2 to all the aforementioned 74 mineral oils - including some saturated samples - has yielded the Viscosity-Pressure Indices $Z_{40^\circ C}$ collected in Table X-2. Further, Table X-4 indicates the distribution of the deviations between these predicted Viscosity-Pressure Indices and the experimental values amongst the really great variety of the 74 oils tested.

The latter table shows that the *absolute* average and standard deviations in the Viscosity-Pressure Index amount to only 0.022 and 0.027 units, respectively, which figures are hardly beyond the accuracy inherent in the experimentally derived values. These deviations correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ and the initial viscosity-pressure coefficients $\alpha_{i,\,40^\circ C}$ of no more than 3.0 and 3.6%, respectively. Moreover, for all the divergent kinds of oils tested the absolute deviation *invariably* remains within 0.05 units.

Accordingly, the correlation depicted in Fig.X-2 does possess a

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*) A similar improvement could not be achieved by means of the other quantities tried, that is the atmospheric density and refractive index individually, as well as their difference (compare Section IX.4).

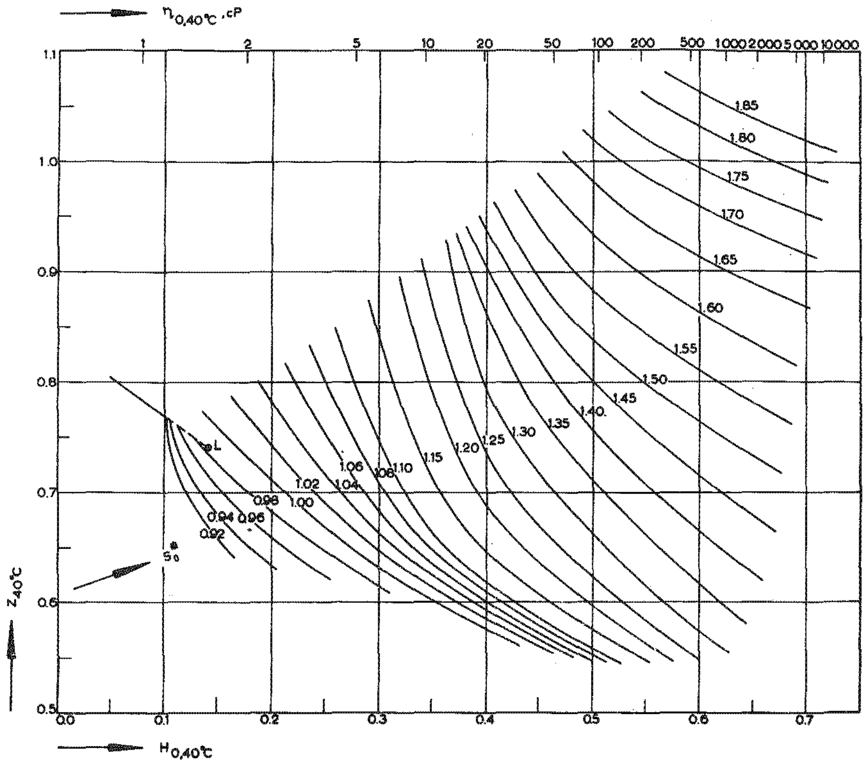

FIG.X-2.

Correlation Between the Viscosity-Pressure Relationship of Mineral Oils and Their "Corrected" Atmospheric Slope Index.

somewhat better*) overall accuracy than the basic correlation of Fig.X-1. However, the refined correlation involves two additional physical constants, namely the atmospheric density and refractive index of the oils.

B. THE VISCOSITY-PRESSURE INDEX OF MINERAL OILS AS A FUNCTION OF THEIR ATMOSPHERIC SLOPE INDEX

On the basis of the correlational Fig.X-1 the Viscosity-Pressure Index $Z_{40°C}$ of mineral oils has been plotted, in Fig.X-3, against their atmospheric Slope Index, S_0, using their viscosity grade $\eta_{0,40°C}$ as a parameter. The various lines of constant viscosity grade prove to be nearly straight over considerable ranges of both indices. For the very fluid oils with viscosity grades $\eta_{0,40°C}$ below about 1.5 cP the values of $Z_{40°C}$ and S_0 are scattered closely around the single straight line depicted in Fig.X-3.

Moreover, a solid straight line has been drawn corresponding to

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*) The F-test yields a statistical confidence level of 98%.

a constant ratio of the two indices over their entire ranges, namely $Z_{40^\circ C}/S_0 = 0.55$. The two adjacent dashed lines comprise the ranges where the Viscosity-Pressure Indices $Z_{40^\circ C}$ of mineral oils would be predicted within 10% by means of the depicted straight-line relationship:

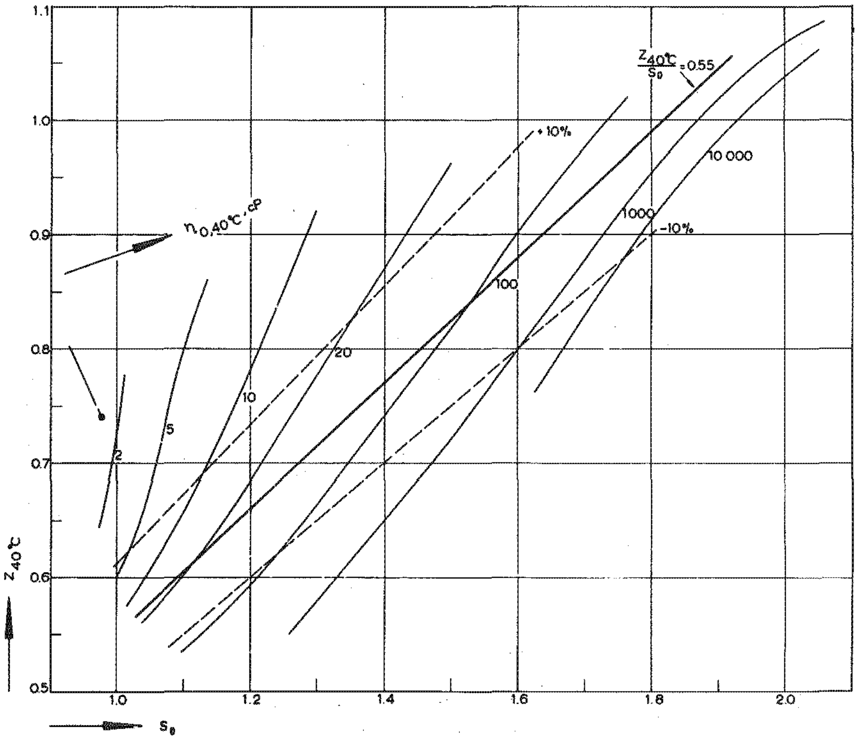

FIG.X-3.
The Viscosity-Pressure Index of Mineral Oils as a Function of Their Atmospheric Slope Index.

$$Z_{40^\circ C} = 0.55\ S_0. \qquad \text{(X-2)}$$

Although for mineral oils with low S_0-values - excepting those very fluid ones with $\eta_{0,40^\circ C}$ below about 1.5 cP - the deviations from the latter relationship may sometimes become as high as nearly 30%, it is seen that in many cases - particularly in the region of high S_0-values - Relationship (X-2) permits fair predictions of the Viscosity-Pressure Indices solely from the atmospheric Slope Indices. All in all, Expression (X-2) may be upheld as a *semi-quantitative* correlation between both indices, irrespective of the viscosity grades involved.

From the definitions of the viscosity-temperature coefficient, β, and the initial viscosity-pressure coefficient, α_i, that is Equations (VI-5) and (VII-5), respectively, it follows that for any given liquid:

$$\frac{\beta_{0,40^\circ C}}{\alpha_{i,40^\circ C}} = 11.43 \frac{S_0}{Z_{40^\circ C}} . \qquad \text{(X-3)}$$

Combination of this identity with Expression (X-2) would yield for all mineral oils:

$$\frac{\beta_{0,40^\circ C}}{\alpha_{i,40^\circ C}} = 20.8 \text{ (kgf/cm}^2\text{)/deg C.} \qquad \text{(X-4)}$$

This may be taken to mean that in the conventional temperature range and up to moderate pressures a pressure increase of about 20 kgf/cm^2 (280 psi) would have roughly the same effect on the viscosity of any given mineral oil as a temperature decrease of 1°C (1.8°F). In various cases this rule of thumb may render good services.

The present Fig.X-3 will be employed in the following Section X.3 for quantitatively discussing the accuracy of various previously proposed correlations between the viscosity-pressure dependence of mineral oils and their atmospheric viscosity-temperature dependence.

C. INITIAL VISCOSITY-PRESSURE COEFFICIENTS AND ATMOSPHERIC VISCOSITY-TEMPERATURE COEFFICIENTS OF MINERAL OILS

Again on the basis of Fig. X-1 the initial viscosity-pressure coefficient $\alpha_{i,40^\circ C}$ of mineral oils has been plotted against their viscosity grade $\eta_{0,40^\circ C}$ (on a logarithmic scale), using their atmospheric viscosity-temperature coefficient $\beta_{0,40^\circ C}$ as a parameter. The resulting Fig.X-4 is particularly interesting in that it directly indicates the correlation, at low pressures and in the vicinity of 40°C, between the relative viscosity changes per kgf/cm^2 and per deg C, respectively, for any mineral oil with known viscosity grade $\eta_{0,40^\circ C}$.

Fig.X-4 demonstrates the great differentiation as to both initial viscosity-pressure coefficients and atmospheric viscosity-temperature coefficients encountered amongst mineral oils, in comparison with their Viscosity-Pressure Indices and atmospheric Slope Indices, respectively, depicted in the basic Fig.X-1. In fact, whilst the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ of mineral oils assume values from about $1 \cdot 10^{-3}$ to $6 \cdot 10^{-3}$ (kgf/cm^2)$^{-1}$, their Viscosity-Pressure Indices range only from about 0.6 to 1.0; similarly, their atmospheric viscosity-temperature coefficients $\beta_{0,40^\circ C}$ cover values from about $2 \cdot 10^{-2}$ to $14 \cdot 10^{-2}$ (deg C)$^{-1}$, the corresponding atmospheric Slope Indices, S_0, extending only from about 1.0 to 2.0. This remarkable feature is of practical interest in that it permits the use of some constant, overall value for both the Viscosity-Pressure Indices and the atmospheric Slope Indices of mineral oils in various cases where only small pressure and temperature

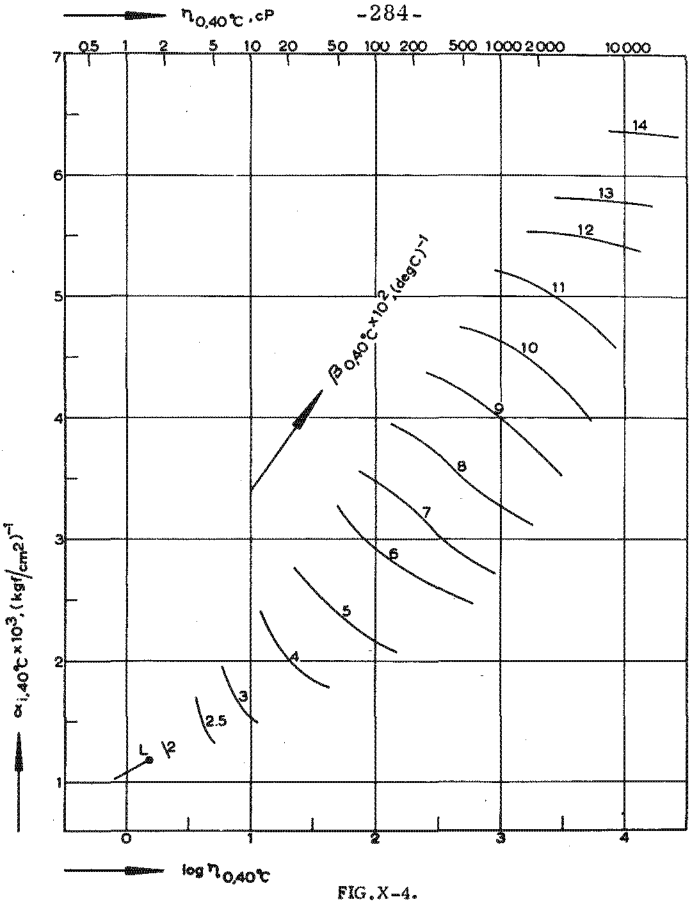

FIG.X-4.

Initial Viscosity-Pressure Coefficients and Atmospheric Viscosity-Temperature Coefficients of Mineral Oils According to the New Correlation of Fig.X-1.

changes have to be taken into consideration. More generally, such average values are convenient for orientation and may further be useful in semi-quantitative calculations, for instance in hydrodynamic lubrication.

X.2.3. *Discussion*

The validity range indicated for the correlation of Fig.X-1 may be taken to represent practically the full range of Viscosity-Pressure Indices, atmospheric Slope Indices and corresponding viscosity grades exhibited by all the divergent kinds of mineral oils known so far (excepting extremely viscous ones). These include not only mineral oils obtained by conventional refining methods - denoted as "natural" mineral oils - but even completely hydrogenated - saturated - samples.

Possibly, the present correlation would yield less reliable results for certain mineral oils whose "natural" character has been drastically modified by applying rather extreme refining methods - or such oils might even fall somewhat beyond the applicability range indicated in Fig. X-1. It should be emphasized, however, that - apart from several mineral oils saturated by complete hydrogenation - even such "extreme" products as *highly aromatic extracts* have proved to conform almost equally well to the present correlation. This correlation has also been applied successfully to several mineral oils containing substantial amounts of *additives*.

It stands to reason, however, that *polymer-blended* mineral oils cannot comply with the present correlation. Nevertheless, as will be elucidated in § X.4.2, the Viscosity-Pressure Indices of such oils can be estimated by a convenient method which takes the latter correlation as its starting-point.

The extensive ranges of Viscosity-Pressure Indices and corresponding viscosity grades where the basic correlation has been verified, are seen to be practically identical to those indicated in Fig. IX-9 for the various physical-constant correlations developed in Section IX.4.

As regards its overall accuracy the basic correlation is found to be fully on a par with the density correlation of § IX.4.2 and substantially superior to the refractive-index correlation of § IX.4.3; but it cannot equal the correlation, described in § IX.4.4, employing the difference between refractive index and density as a parameter. In fact, with respect to its overall accuracy the latter correlation is practically on a par with the refined version, outlined in part A of the preceding § X.2.2, of the basic correlation depicted in Fig. X-1.

It should be properly realized, however, that amongst all the various correlations developed in Chapter IX as well as in the present Chapter X the correlation of Fig. X-1 has the unique feature that it does not involve any physical or chemical data in addition to the atmospheric viscosities - at two, or more, representative temperatures - of the oils.

Thus, unlike the other aforementioned correlations, the present correlation may be considered significant not merely as a convenient tool for predicting the viscosity-pressure relationship of mineral oils; primarily, its value would lie in that it essentially simplifies their complete viscosity-temperature-pressure relationship (see Section IX.2).

Indeed, for all the various kinds of mineral oils tested only *two* parameters - the *minimum* mumber conceivable - have now proved sufficient for characterizing, within the accuracy of the present correlation, their complete viscosity-temperature-pressure relationship. This also implies that *one single* parameter, for instance the atmospheric Slope Index, suffices for viscometrically characterizing such oils completely if only their viscosity grade is known.

In more general terms, it can be stated that mineral oils with identical atmospheric isobars would also display, again within the accuracy of the present correlation, identical families of isotherms, *and vice versa*[*].

In view of the wide applicability and simplicity of the new correlation, it is thought that the possibility of gaining a more profound insight into its physical background may not be precluded. On the other hand, the new correlation may be very helpful in more theoretically directed attempts to clarify the viscosity-pressure behaviour of liquids in general, and hydrocarbon oils in particular.

X.3. DISCUSSION OF PREVIOUS CORRELATIONS ON THE BASIS OF THE PRESENT CORRELATION

X.3.1. *Introduction*

The present section attempts to discuss quantitatively the accuracy inherent in available correlations on the basis of the new correlation depicted in Fig.X-1. For reasons of simplicity, the relevant comparison will be confined to the standard reference temperature of 40°C adopted in the latter correlation. But it should be emphasized that by utilizing the mathematical framework outlined in Section IX.2 the comparison may easily be extended to other temperatures as well.

The correlations involving some criterion of the isothermal viscosity-pressure dependence of the oils invariably employ the viscosity-pressure coefficient, α, its numerical value being determined from measurements in the *lower* pressure range. Such viscosity-pressure coefficients constitute somewhat loose criteria in that they represent average values over miscellaneous and frequently unspecified pressure ranges. As a rule, however, they are very well comparable with the corresponding *initial* viscosity-pressure coefficients, α_i, which are exactly defined by Equation (VII-5). Anyhow, for the present comparative analysis it would certainly be justified to identify the "average" α-values occurring in several previous correlations with the newly introduced α_i-values.

Although the subsequent discussion of previous correlations is essentially based on the new correlation as depicted in Fig.X-1, it has appeared that certain correlations may be treated more conveniently by replotting them in one of the derived correlational diagrams, notably Fig.X-3, rather than in the basic Fig.X-1.

§ X.3.2 deals with the various correlations which only employ some atmospheric viscosity-temperature criterion for estimating the viscosity-pressure dependence of mineral oils. The correlations using the viscosity *grade* as an additional parameter, and which are therefore essentially based on the complete atmospheric viscosity-temperature relationship of the oils, are discussed in § X.3.3.

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[*] As demonstrated in Chapter VIII, such mineral oils - excepting the very fluid ones, which assume hardly any practical importance - also exhibit nearly the same values for the various physical constants contemplated (density, refractive index and molecular weight) and, accordingly, also possess approximately identical carbon-type compositions.

X.3.2. *Correlations Only Employing Some Atmospheric Viscosity-Temperature Criterion*

A. KIESSKALT'S CORRELATION

Kiesskalt's well-known correlation - already mentioned in § X.1.1 - was the first one to indicate a certain degree of correlation between the viscosity-pressure dependence of mineral*) oils and their viscosity-temperature variation at atmospheric pressure 163, 164). This correlation has been extensively applied and is still used to some extent.

Plotting the (average) viscosity-pressure coefficients, α, of a moderate number of mineral oils against their values for the atmospheric viscosity-temperature criterion $-\partial\eta_0/\partial t$ (taken at the same temperature), Kiesskalt found that for all these oils both quantities would be interrelated, to a fair approximation, by one single equation, which can be rewritten as:

$$10^3\,\alpha = 0.674 \cdot \log\left(-\frac{\partial\eta_0}{\partial t}\right) + 1.91, \qquad \text{(X-5a)}$$

where the viscosity-pressure coefficient, α, and the atmospheric viscosity, η_0, have again been expressed in $(\mathrm{kgf/cm^2})^{-1}$ and in cP, respectively. It should be pointed out that the validity of Correlation (X-5a) has not been restricted to some particular standard reference temperature; in fact, Kiesskalt's correlation has been derived from experimental data in the temperature range from 20 to 100°C (68-212°F).

In later years Hersey and Hopkins 26) checked Kiesskalt's correlation for a considerably greater number and variety of oils than originally considered. They found a somewhat improved overall agreement with the following expression:

$$10^3\,\alpha = 0.60 \cdot \log\left(-\frac{\partial\eta_0}{\partial t}\right) + 2.00, \qquad \text{(X-5b)}$$

which can easily be derived from Fig.22 of their paper. As shown in Fig.23 of the same paper, the revised Correlation (X-5b) corresponds very closely with Kiesskalt's original Correlation (X-5a).

From the Definition (VI-3) of the viscosity-temperature coefficient, β, it is readily seen that at any temperature the rather peculiar viscosity-temperature criterion $-\partial\eta_0/\partial t$ is identical to the product $\beta_0 \cdot \eta_0$. Further, the "average" viscosity-pressure coefficient, α, is identified with the initial viscosity-pressure coefficient, α_i (compare § X.3.1). Accordingly, the revised Correlation (X-5b) may be rewritten in the form:

$$10^3\,\alpha_i = 0.60 \cdot \log(\beta_0 \cdot \eta_0) + 2.00. \qquad \text{(X-5c)}$$

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*) Kiesskalt proposed a similar correlation for fatty oils.

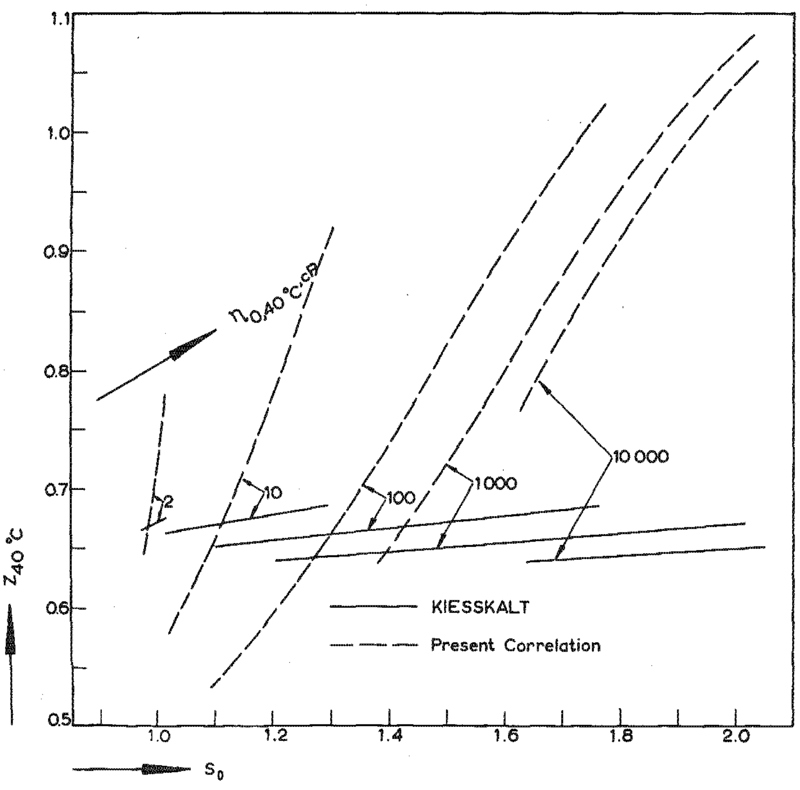

FIG. X-5.
Kiesskalt's Correlation in Comparison With the Present Correlation.

Substituting Equations (VII-5) and (VI-5) for α_i and $\beta_{0,40°C}$, respectively, into Correlation (X-5c) leads to the following equivalent expression for the present standard reference temperature of 40°C:

$$Z_{40°C} = \frac{0.521 \cdot \log\left[1.316 \cdot 10^{-2} S_0 \cdot \eta_{0,40°C}(\log \eta_{0,40°C} + 1.200)\right] + 1.737}{\log \eta_{0,40°C} + 1.200} \tag{X-5d}$$

For a few distinct values of the viscosity grade $\eta_{0,40°C}$ the derived Correlation (X-5d) has been represented in Fig. X-5. For comparison the corresponding curves of constant viscosity grade have been replotted from Fig. X-3. It should be noted that the practically straight lines according to Correlation (X-5d) have been depicted over the same ranges of the two indices $Z_{40°C}$ and S_0 as the latter curves, even though these ranges are only partly covered by Kiesskalt's original Correlation (X-5a) or its revised Form (X-5b).

Fig. X-5 leads to the rather surprising conclusion that the Vis-

cosity-Pressure Indices $Z_{40°C}$ *predicted from Kiesskalt's correlation are practically independent of both the viscosity grade and the atmospheric viscosity-temperature dependence of the oil considered. In fact, the predicted Viscosity-Pressure Indices invariably prove to come very close to the value 0.65.*

All in all, it may be stated that Kiesskalt's correlation constitutes a very crude tool for estimating the viscosity-pressure dependence of mineral oils.

B. THE CORRELATIONS OF SANDERSON, BRADBURY et al., CLARK AND ANDERSON

These four correlations are very similar in that each of them appears to be essentially based on the assumption that some constant *ratio* would exist between the viscosity-pressure coefficient, determined for the lower pressure range, and the atmospheric viscosity-temperature coefficient (taken at the same temperature) of all mineral oils. Thus, confining oneself again to the standard reference temperature of 40°C, the ratio $\alpha_{i,40°C}/\beta_{0,40°C}$ would invariably be the same for all mineral oils (compare § X.3.1). According to Identity (X-3), the latter equally applies to the ratio $Z_{40°C}/S_0$.

a. Sanderson[109, 110] established some overall equivalence between the effects of isothermal compression and atmospheric cooling on the *kinematic* viscosity of mineral oils. Although Sanderson's correlation, as it stands, was derived from data on only four *pure* hydrocarbons in the light lubricating-oil range, it was claimed to be at least approximately applicable also to the rather restricted number of mineral lubricating oils tested.

Sanderson advocated the use of the ASTM chart (see part B of § III.1.2) for representing the kinematic viscosity-temperature dependence of the oils at atmospheric pressure. Now, by placing an "equivalent" pressure scale - relating to some standard reference temperature - alongside the *temperature* scale of the latter chart the isothermal effect of pressure might be estimated graphically. Such an equivalent pressure scale has been defined for the standard reference temperature of 100°F (37.8°C).

In the present discussion it will be assumed that Sanderson's correlation would hold with nearly the same accuracy for the *dynamic* viscosity of mineral oils. Considering that the accompanying density changes are practically negligible against the viscosity changes involved, the latter assumption proves to be well justified. Further, the equivalence between temperature and pressure effects indicated for 100°F may be upheld for the present standard reference temperature of 40°C without appreciably affecting the accuracy involved.

Using again Equation (III-6h) for the atmospheric viscosity-temperature relationship of the oils and Equation (IV-5e) for their isothermal viscosity-pressure relationship, it is readily seen that a straight line should be obtained if Sanderson's equivalent temperatures and pressures are plotted against each other according to a Θ-scale and a Π-scale, respectively. Indeed, in the considered pressure range of over 1,000 kgf/cm^2 (14,000 psi) the resulting line appears to be substantially straight. Further, it can be shown that the slope of this Θ-Π line defines the aforementioned constant ratio of the Viscosity-Pressure Index $Z_{40^\circ C}$ to the atmospheric Slope Index, S_0, of mineral oils. It has thus been derived that, according to Sanderson's correlation, the ratio $Z_{40^\circ C}/S_0$ invariably amounts to 0.47.

b. Bradbury *et al.*[28)] indicated an approximate constancy of the ratio of the *atmospheric* viscosity-pressure coefficient, α_0, to the corresponding atmospheric viscosity-temperature coefficient, β_0, of all mineral oils. Their correlation may be cast into the form:

$$\frac{\alpha_0}{\beta_0} = 4.83 \cdot 10^{-7}\, T^2, \qquad \text{(X-6a)}$$

where α_0 and β_0 have again been expressed in (kgf/cm^2)$^{-1}$ and in (deg C)$^{-1}$, respectively, and where T denotes the absolute temperature, in deg K.

As pointed out in Section VII.4, the values found for the atmospheric viscosity-pressure coefficient, α_0, of mineral oils frequently prove to be appreciably smaller than those of their initial viscosity-pressure coefficients, α_i. Nevertheless, provided that the involved pressures amount to no more than two or three hundred kgf/cm^2, it does not make any appreciable difference whether the viscosity-pressure dependence of the oils is evaluated in terms of either α_0 or α_i. With this proviso it readily follows from Identity (X-3) that at the present standard reference temperature of 40°C Correlation (X-6a) may be transformed into:

$$\frac{Z_{40^\circ C}}{S_0} = 0.54\ . \qquad \text{(X-6b)}$$

c. On the basis of experimental data from the ASME pressure-viscosity project[27)] Clark[165)] developed a correlation along the line of approach first adopted by Sanderson (see the above point a). However, using one single "equivalent" pressure scale placed alongside the temperature scale of the ASTM chart*), Clark observed marked differences between "paraffinic" and "naphthenic" oils. Therefore, he devised separate pressure scales for both kinds of mineral oils. Such scales were constructed for two temperatures, namely 100 and 210°F (37.8 and 98.9°C).

Following the above procedure employed in transforming Sanderson's correlation, it can be derived that, according to Clark's correlation, the ratio $Z_{40^\circ C}/S_0$ amounts to 0.46 for "paraffinic" oils and to 0.55 for "naphthenic" oils.

d. On the basis of experimental data on both *pure*, high-molecular-

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*) Thus, like Sanderson's, Clark's correlation has been designed for kinematic viscosity.

weight hydrocarbons and commercial oils (including some non-mineral oils) Anderson 166) developed a temperature-pressure chart containing a family of constant-viscosity curves. The location of the latter curves would be independent not only of the particular oil considered but also of the atmospheric viscosity involved.

Following again the transformation method used for Sanderson's correlation (see the above point a), it appears that, according to Anderson, the ratio $Z_{40^\circ C}/S_0$ invariably amounts to 0.55.

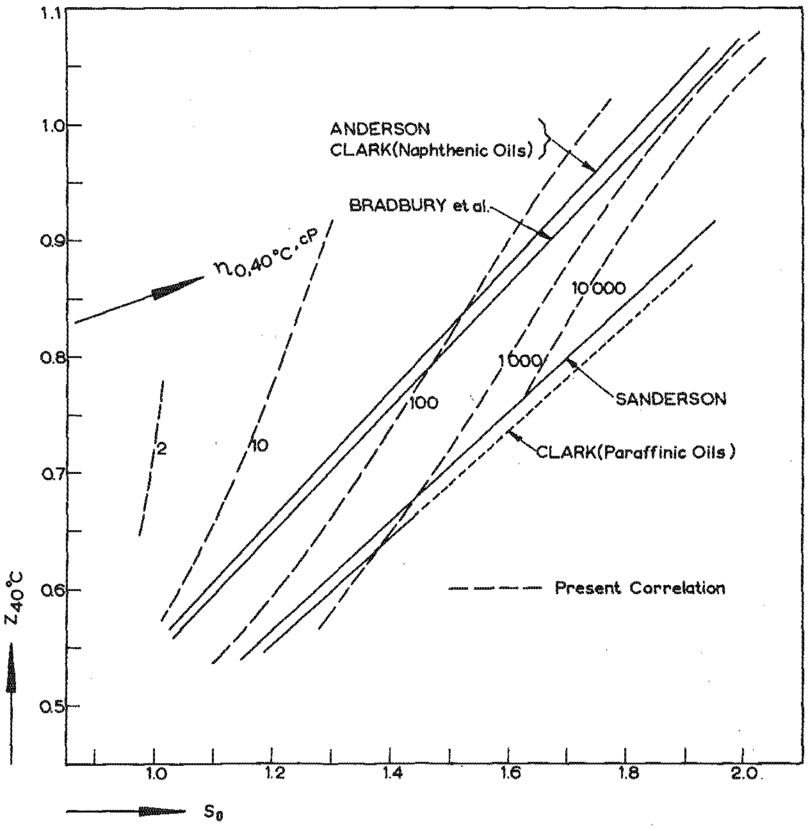

FIG.X-6.
The Correlation of Sanderson, Bradbury et al., Clark and Anderson in Comparison With the Present Correlation.

In Fig.X-6 the various correlations discussed in the present part B have been represented by straight lines*).

*) The upper straight line, relating to $Z_{40^\circ C}/S_0 = 0.55$, is identical to the solid line depicted in Fig.X-3 and defined by Correlation (X-2).

The few curves of constant viscosity grade $\eta_{0,40^\circ C}$ replotted from Fig.X-2 clearly demonstrate the oversimplified nature of the latter correlations. Nevertheless, in contrast to Sanderson's correlation and Clark's correlation for "paraffinic" oils, the remaining three correlations may be upheld as semi-quantitative approximations (compare part B of § X.2.2).

C. CAMERON'S AND APPELDOORN'S CORRELATIONS

Just like the correlations discussed in the preceding part B, Cameron's and Appeldoorn's correlations appear to be essentially based on the assumption that one and the same relationship would exist between the viscosity-pressure coefficients and the atmospheric viscosity-temperature coefficients (taken at the same temperature) of all mineral oils. Unlike these foregoing correlations, however, Cameron's and Appeldoorn's correlations do not amount to a simple proportionality between both coefficients.

a. Identifying again the initial viscosity-pressure coefficient, α_i, with the "average" viscosity-pressure coefficient used by Cameron[60] his correlation can be transformed into:

$$\frac{1}{\alpha_i} = \left[-4.20 \cdot 10^{-3}(t+95)^2 \beta_0 + 9.00\right](t+52), \qquad \text{(X-7a)}$$

where the various variables are expressed in the same units as above. At the standard reference temperature of 40°C the latter correlation takes the form:

$$\frac{1}{10^3 \, \alpha_{i,40^\circ C}} = -7.05\, \beta_{0,40^\circ C} + 0.828. \qquad \text{(X-7b)}$$

b. Appeldoorn's recent correlation[124] can be shown to amount to a common straight-line relationship between the viscosity-pressure coefficients and the corresponding atmospheric viscosity-temperature coefficients of all mineral oils. Like Cameron's, Appeldoorn's correlation would also account for the effect of temperature on the latter relationship. At the standard reference temperature of 40°C Appeldoorn's correlation can be reduced to:

$$10^3 \alpha_{i,40^\circ C} = 36.2\, \beta_{0,40^\circ C} + 0.38, \qquad \text{(X-8)}$$

where both coefficients are expressed again in the same units as above.

It may be mentioned that Appeldoorn's correlation has been derived from data on a great variety of about 100 mineral oils, most of them being identical to those used in developing the new correlation depicted in Fig.X-1 (see Table X-2). Further, Appeldoorn has considered various *pure* hydrocarbons of high molecular weight.

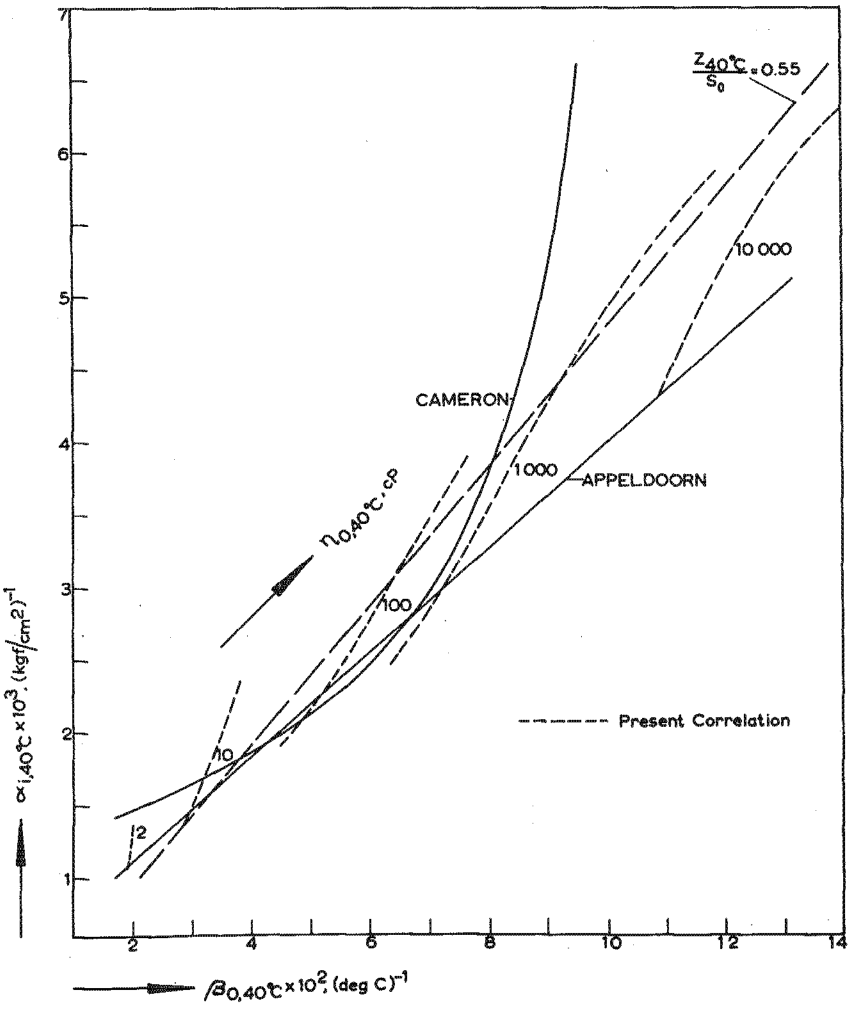

FIG. X-7.
Cameron's and Appeldoorn's Correlations in Comparison With the Present Correlation.

Correlations (X-7b) and (X-8) have been plotted in Fig. X-7*). For comparison a few curves of constant viscosity grade $\eta_{0,40°C}$ have been depicted, these being readily derivable from the basic Fig. X-1 (compare also Fig. X-4). In addition, the straight line defined by Correlation (X-4) has been included (compare Fig. X-3).

Fig. X-7 indicates that the viscosity-pressure coefficients predicted

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*) It may be noted that in a $Z_{40°C}-S_0$ chart both correlations would be depicted as a family of curves, each curve relating to some distinct viscosity grade $\eta_{0,40°C}$.

from Appeldoorn's correlation would be consistently too low over nearly the entire range of the variables covered by the present Fig.X-1. Whilst Cameron's correlation may yield predictions of a semi-quantitative nature for the range up to fairly high atmospheric viscosity-temperature coefficients, say, up to $\beta_{0,40^\circ C} = 8\cdot 10^{-2}$ (deg C)$^{-1}$, it fails completely for appreciably higher values.

On the whole, both Cameron's and Appeldoorn's correlation*) would yield rather rough predictions. In fact, as regards their overall accuracy both correlations would be markedly inferior even to the oversimplified Correlation (X-4) represented in Fig.X-7 by the straight dashed line.

X.3.3. *Correlations Based on the Atmospheric Viscosity-Temperature Relationship*

The three correlations discussed below utilize the viscosity grade of mineral oils in addition to some criterion of their atmospheric viscosity-temperature dependence. Thus, like the new correlation described in Section X.2, these correlations are essentially based on the complete atmospheric viscosity-temperature relationship of the oils.

Unlike the new correlation, however, the latter three correlations involve *kinematic* viscosities. Actually, therefore, the *densities* of the oils are also required for evaluating the pressure effect on the viscosity that really counts in lubrication, that is the *dynamic* viscosity.

A. MATTESON AND VOGT'S CORRELATION

Matteson and Vogt's correlation[167)] would appear to be the first one accounting explicitly for the effect of the viscosity grade of mineral oils on their viscosity-pressure dependence. Besides the viscosity grade, Matteson and Vogt used the Viscosity Index as a criterion which would be indicative of the "chemical type" of the oils.

Their correlational diagram represents the (average) viscosity-pressure coefficient of mineral oils as a function of their atmospheric viscosity (taken at the same temperature) for three distinct values of their Viscosity Index, namely -70, 0 and 100. The three relevant curves converge towards an atmospheric viscosity of about 2.5 cP.

Identifying again the initial viscosity-pressure coefficient, α_i, with the "average" viscosity-pressure coefficient used by Matteson and Vogt, the latter three curves of constant VI can readily be depicted in a Z-H_0 diagram. In the relevant Fig.X-8, however, a standard reference temperature of 40°C has been adopted in order to include, for each of the three aforementioned VI-values, the interrelationship between the Viscosity-Pressure Indices $Z_{40^\circ C}$ and the viscosity

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*) Recently Kouzel[171)] derived a correlation, based on data plotted in the aforementioned ASME report[27)], which proves to come quite close to Appeldoorn's.

grades $\eta_{0,40°C}$ which would follow from the new correlation of Fig.X-1*). In contrast to Matteson und Vogt's curves, the constant-VI curves derived from the new correlation show a rather capricious trend in the range of lower viscosity grades. It should further be noted that Matteson and Vogt's correlation covers only a small part of the extensive validity range of the new correlation of Fig.X-1.

Fig.X-8 indicates that, in general, Matteson and Vogt's curves would yield rough predictions. In fact, they would permit reasonable predictions only for certain oils with high viscosity grades.

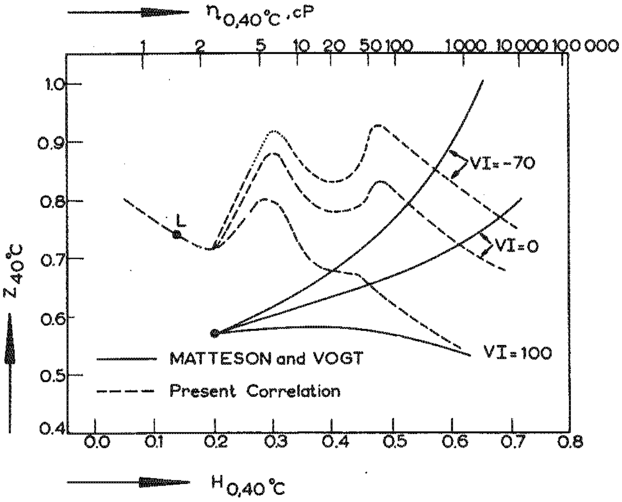

FIG.X-8.
Matteson and Vogt's Correlation in Comparison With the Present Correlation.

B. WEBER'S CORRELATION

Weber[168)] employed Walther and Ubbelohde's so-called Viscosity Pole Height[66)] as a criterion of the atmospheric *kinematic* viscosity-temperature dependence of mineral oils. For distinct values of their atmospheric (dynamic) viscosity Weber's correlational diagrams (his Figs.4 and 5) depict the (average) viscosity-pressure coefficient (taken at the same temperature) of the oils as a function of their Viscosity Pole Height.

Whilst Weber's Fig.4 contains curves of constant atmospheric viscosities ranging from 10 to 1,000 cP, his Fig.5 depicts only two such curves, namely for 250 and 1,000 cP. Unfortunately, the former figure has been derived from experimental viscosity data up to no more than 200 kgf/cm^2 (2,800 psi). Therefore, only Weber's correlational Fig.5, which has been based on experimental da-

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*) On the basis of the interrelationship between the Slope Indices, S_0, and the viscosity grades $\eta_{0,40°C}$ implied by a given Viscosity Index (compare Fig.VIII-9) the corresponding Viscosity-Pressure Indices $Z_{40°C}$ can readily by read from Fig.X-1.

ta for the pressure range up to 1,000 kgf/cm^2 (14,000 psi) and for the temperature range from 20 to 60°C (68-140°F), will be discussed.

Identifying again the initial viscosity-pressure coefficient with the "average" viscosity-pressure coefficient used by Weber, the corresponding Viscosity-Pressure Indices can easily be computed for each given atmospheric viscosity; once more, a standard reference temperature of 40°C has been adopted. Further, for any combination of viscosity grade $\eta_{0,40^\circ C}$ and Viscosity Pole Height the corresponding atmospheric Slope Index can be calculated with good accuracy if only the appropriate density is approximately known. For the involved conversion of kinematic into dynamic viscosities the densities*) of the oils have been estimated from their Viscosity-Pressure Indices $Z_{40^\circ C}$ and their viscosity grades $\eta_{0,40^\circ C}$, that is by means of Fig. IX-9.

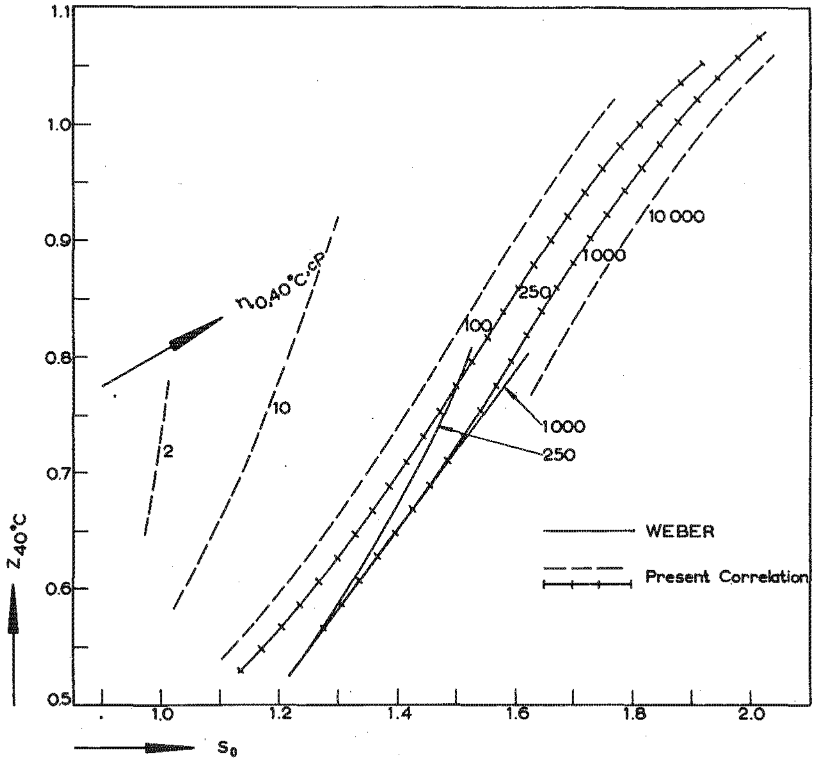

FIG. X-9.
Weber's Correlation in Comparison With the Present Correlation.

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*) The temperature variation of the density of mineral oils can easily be estimated from the correlation given in § VIII.3.2.

In Fig.X-9 the Viscosity-Pressure Indices $Z_{40^\circ C}$ thus calculated from Weber's correlational Fig.5 have been represented as a function of the atmospheric Slope Index, S_0, for the two aforementioned viscosity grades $\eta_{0,40^\circ C}$, namely 250 and 1,000 cP. The resulting two curves are seen to converge towards the range of low Viscosity-Pressure Indices and atmospheric Slope Indices. For comparison, various curves of constant viscosity grade $\eta_{0,40^\circ C}$ have been replotted from Fig.X-3*).

Fig.X-9 indicates that Weber's correlation would yield good predictions in the range considered. Unfortunately, the latter range is so small that this correlation has only very limited practical significance.

C. HARTUNG'S CORRELATION

Hartung's correlation$^{169)}$ amounts to predicting the (isothermal) relative viscosity increase, η/η_0, for several standard reference pressures and for the two standard reference temperatures of 100 and 210°F (37.8 and 98.9°C), from the atmospheric *kinematic* viscosity-temperature relationship of the oils. The latter relationship is accounted for by the kinematic viscosity grade $\nu_{0,210^\circ F}$ and the temperature interval required to change the (atmospheric) kinematic viscosity of a given oil from 20 to 10 cS; this rather unwieldy kinematic viscosity-temperature criterion is estimated by means of the ASTM chart (see part B of § III.1.2).

In Hartung's correlational diagrams - each diagram relating to some standard reference pressure and to either 100 or 210°F - the aforementioned relative viscosity increase has been depicted as a function of the above-defined temperature interval of the oils for distinct values of the kinematic viscosity grade $\nu_{0,210^\circ F}$.

Hartung derived his correlation exclusively on the basis of extensive data from the ASME pressure-viscosity project$^{27)}$. Although he considered primarily mineral oils, various other types of lubricating oils were also included. All these oils - and likewise oils from other investigations - were claimed to show reasonable conformity with his correlation, provided only that their kinematic viscosity grade $\nu_{0,210^\circ F}$ was not below about 4 cS. Further, the deviations generally turned out greater for non-mineral oils.

Before discussing the applicability of Hartung's correlation to mineral oils specifically it may already be stated that its fair applicability to certain non-mineral oils should be deemed rather fortuitous. In fact, as will be elucidated in § X.4.3, *any* such correlation designed primarily for mineral oils would, as a rule, show very large scatter when applied to other types of oils.

Hartung's correlational diagram relating to a standard reference pressure of 20,000 psi (1,406 kgf/cm^2) and a standard reference temperature of 100°F (his Fig.6) has been taken as a basis to the following discussion.

For any combination of the kinematic viscosity grade $\nu_{0,210^\circ F}$

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*) However, the curve relating to $\eta_{0,40^\circ C}$ = 250 cP has not been depicted in the preceding Fig.X-3.

and the aforementioned temperature interval required to change the oil's kinematic viscosity from 20 to 10 cS the corresponding viscosity grade $\eta_{0,40^\circ C}$ and the atmospheric Slope Index, S_0, can be estimated with good accuracy*). For the calculation of the corresponding Viscosity-Pressure Indices $Z_{40^\circ C}$ the relative viscosity increase (relating to 20,000 psi) that would be observed at the present standard reference temperature of 40°C has been taken identical to that given by Hartung for the very close temperature of 100°F (37.8°C).

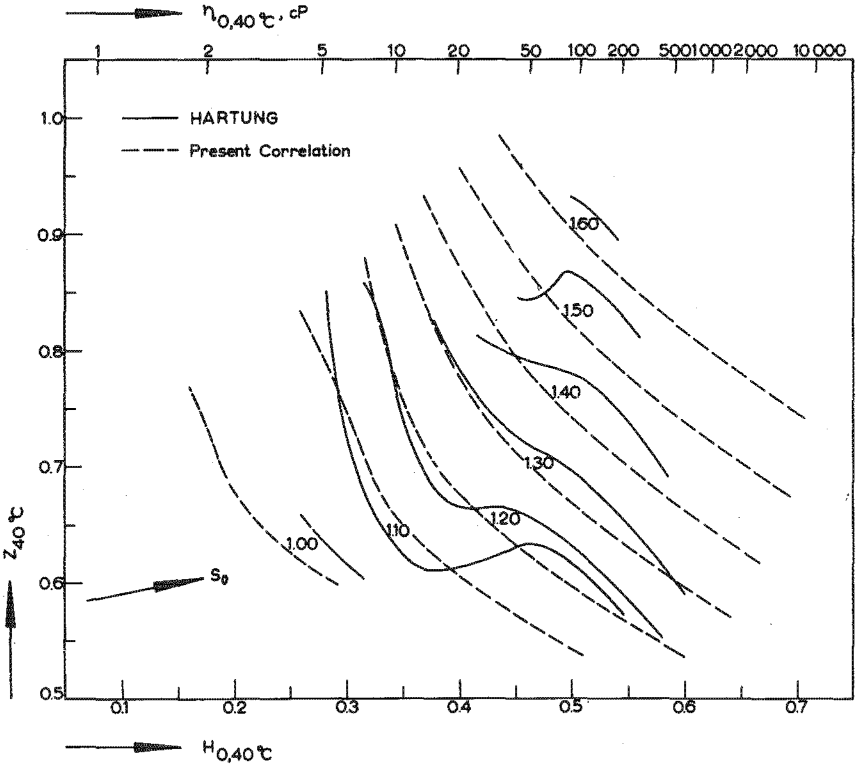

FIG. X-10.
Hartung's Correlation in Comparison With the Present Correlation.

The Viscosity-Pressure Indices $Z_{40^\circ C}$ thus calculated from Hartung's correlational diagram have been depicted in Fig. X-10 as a function of the viscosity grades $\eta_{0,40^\circ C}$ for a few distinct values of the atmospheric Slope Index, S_0. The resulting family of curves proves to display a rather capricious trend; this is not so surprising in view of the form of the curves (of constant $\nu_{0,210^\circ F}$)

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*) The involved conversion of kinematic into dynamic viscosities has again been performed by means of the procedure described in part B of § VIII.3.5.

in Hartung's original diagram. For comparison the corresponding curves of constant atmospheric Slope Index according to the new correlation have been replotted from Fig.X-1.

It should be added that the relevant curves in Fig.X-10 comprise nearly the entire range for which Hartung's correlation has been derived. Consequently, the latter range represents only a small part of the extensive validity range of the new correlation depicted in Fig.X-1.

Fig.X-10 shows that in the range of viscosity-temperature-pressure relationships covered by Hartung's correlation it would usually permit good predictions of the viscosity-pressure dependence of mineral oils. In fact, Hartung's correlation constitutes by far the best one available in that it generally yields quite acceptable predictions for the normal types of mineral oils.

However, it is afflicted with the serious shortcoming that it is far from generally applicable to all the various types of mineral oils encountered. Moreover, as elucidated above, Hartung's correlation proves to be rather unwieldly, partly because it involves both dynamic and kinematic viscosities. Last but not least, Hartung's correlation - as it stands - suffers from the basic drawback that it lacks any mathematical background for the viscosity-temperature-pressure relationships contemplated.

X.3.4. *Conclusions*

The correlations discussed have been shown to vary considerably with respect to overall accuracy, validity range and convenience. But apart from Weber's and Hartung's correlations, they have proved rather crude tools for estimating the viscosity-pressure dependence of mineral oils.

Whilst Weber's correlation has only minor practical significance in that it has been confined to a very limited range of viscosity grades, Hartung's correlation generally yields quite acceptable predictions for the normal types of mineral oils. However, the latter correlation still leaves much to be desired with respect to its validity range, practical convenience and analytical significance.

X.4. ADDITIONAL APPLICATIONS

X.4.1. *The Viscosity-Pressure Indices and Initial Viscosity-Pressure Coefficients of Mineral Oils Characterized by a Common Atmospheric Slope Index*

It would seem interesting to devote some nearer attention to both the Viscosity-Pressure Indices and the initial viscosity-pressure coefficients of mineral oils characterized by a common atmospheric Slope Index. It may be recalled that, as outlined in Chapter VI, mineral oils belonging to a given naturally homologous group - excepting the least viscous members - do display substantially the same Slope Index.

A. VISCOSITY-PRESSURE INDICES

As regards the *Viscosity-Pressure Indices* exhibited by iso-S_0 oils of various viscosity grades, Fig.X-1 indicates that these would decrease fairly regularly with increasing viscosity grade (at the standard reference temperature of 40°C). Further, it is seen from that figure that for the members of any group of mineral oils with a common S_0-value not below about 1.40 the Viscosity-Pressure Indices $Z_{40^\circ C}$ would decrease nearly linearly with increasing viscosity grade $H_{0,40^\circ C}$. But for smaller S_0-values the relevant decrease would become more pronounced for the very fluid members, that is with viscosity grades $\eta_{0,40^\circ C}$ lower than about 20 cP*).

Thus, when plotted in an H-Π chart the isotherms relating to 40°C of all the various members of any group of iso-S_0 oils would nearly constitute a *fan*, although those of the aforementioned very fluid oils would more or less stand out. It should be added, however, that up to the highest pressures explored with the underlying correlation, that is up to more than 2,000 kgf/cm^2 (28,000 psi), the latter isotherms would *not* intersect those of the more viscous members.

Finally, it may be noted that as long as the (atmospheric) Slope Index and the *Viscosity Index* of mineral oils show a unique relationship (see Chapter VI) essentially the same correlation between the Viscosity-Pressure Index and the viscosity grade as indicated in Fig.X-1 would naturally hold for mineral oils characterized by a common value of the Viscosity Index. But in the comparatively low viscosity range where the unique relationship between both viscosity-temperature criteria breaks down (see Chapter VI) the Viscosity-Pressure Index of mineral oils with a common Viscosity Index would be rather capriciously related to their viscosity grade. For three distinct Viscosity Indices these things are illustrated in the preceding Fig.X-8.

B. INITIAL VISCOSITY-PRESSURE COEFFICIENTS

On the basis of the new correlation of Fig.X-1 the *initial viscosity-pressure coefficients* $\alpha_{i,40^\circ C}$ of iso-S_0 oils can readily be represented as a function of their viscosity grades $\eta_{0,40^\circ C}$ (compare § IX.5.4). For some distinct values of the atmospheric Slope Index the resulting curves have been depicted in Fig.X-11.

For the members of any group of mineral oils with a common S_0-value not below about 1.40 the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ would increase nearly linearly with rising viscosity grade expressed in terms of log $\eta_{0,40^\circ C}$. But for smaller S_0-values the initial viscosity-pressure coefficients would tend to become constant for the very fluid members, that is with viscosity grades $\eta_{0,40^\circ C}$ lower than about 20 cP (compare the preceding part A and the relevant footnote). Remarkably enough, in the latter viscosity range the initial viscosity-pressure coefficients would pass through a small minimum.

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*) As indicated in Fig.X-1, such low viscosity grades would not be encountered amongst the aforementioned mineral oils with atmospheric Slope Indices higher than about 1.40.

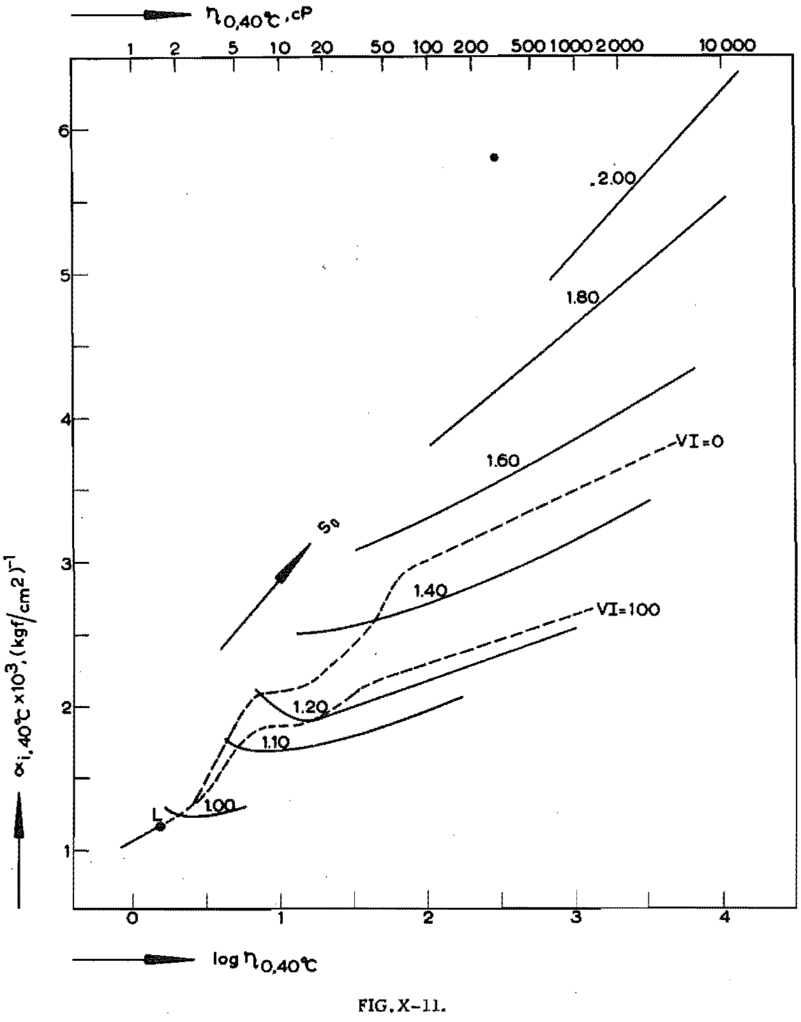

FIG. X-11.
Initial Viscosity-Pressure Coefficients of Mineral Oils With a Common Atmospheric Slope Index According to the Correlation of Fig. X-1.

When plotted in a log η-p diagram, the isotherms, relating to 40°C, of all the various members of any group of iso-S_0 oils would constitute one single family of non-crossing curves. Indeed, it can be shown that up to the highest pressures explored with the underlying correlation, that is up to more than 2,000 kgf/cm^2 (28,000 psi), the isotherms of the very fluid members would *not* intersect those of the more viscous members (compare the preceding part A).

Further, it may be noted that as long as the (atmospheric) Slope Index and the *Viscosity Index* of mineral oils display a unique relationship (see Chapter VI) essentially the same correlation between the initial viscosity-pressure coefficient and the viscosity grade as indicated in Fig.X-11 would naturally hold for mineral oils characterized by a common value of the latter index. But in the comparatively low viscosity range where the unique relationship between both indices breaks down (see Chapter VI) the initial viscosity-pressure coefficient of mineral oils with a common Viscosity Index would be rather capriciously related to their viscosity grade. For VI-values of 0 and 100 these things are illustrated in Fig.X-11*).

Finally, it should be pointed out that the present findings are closely connected with Blok's remarkable postulate (discussed in part C of § IX.1.2) that all the isotherms of the various members of a given naturally homologous group of mineral oils would be depicted, in a viscosity-pressure diagram, as one single family of non-crossing curves.

X.4.2. *The Viscosity-Pressure Relationship of Polymer-Blended Mineral Oils*

As discussed in § VIII.4.6, the (atmospheric) Slope Index of a given mineral oil can be lowered considerably by the addition of some long-chain polymer. Measurements of the pressure effect on the viscosity of such polymer-blended mineral oils indicate that their Viscosity-Pressure Index likewise decreases conspicuously. But as will be stated more precisely below, the Viscosity-Pressure Index is lowered to a relatively smaller extent than the (atmospheric) Slope Index.

As regards the viscosity-pressure coefficient of a given polymer-blended mineral oil, this would, to a first approximation, equal that of the base oil[21,17,22]; in fact, the same would apply to its (atmospheric) viscosity-*temperature* coefficient (compare part B of § VIII.4.6). As pointed out by Bondi[21], the viscosity-pressure coefficients of a large number of commercial polymer-blended mineral oils do come fairly close to that of the base oil.

In general, however, the viscosity-pressure coefficients of blends prepared from a given base oil may depend rather strongly on the particular polymer employed. This may be illustrated by Fig.X-12, which relates to the *initial* viscosity-pressure coefficient, α_i, rather than the somewhat loosely defined "viscosity-pressure coefficient", α. In this figure the Viscosity-Pressure Indices $Z_{40^\circ C}$ of a given base oil and three blends**) prepared from it, by the addition of different types of long-chain polymers, have been plotted against the corresponding viscosity grades $H_{0,40^\circ C}$[17]. Moreover, the depicted curve represents the relationship between Viscosity-Pressure Index and viscosity grade - on the basis of Equation (VII-5) - for the various blends that would display the same initial viscosity-pressure coefficient $\alpha_{i,40^\circ C}$ as the base oil. It is seen that, whilst the initial viscosity-pressure coefficients of the polyalkylstyrene- and polymethacrylate-containing blends do prove practically identical

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*) These two constant-VI curves have been calculated from the corresponding curves of Fig.X-8.

**) The (atmospheric) Slope Indices of the same base oil and its blends have been depicted in Fig.VIII-15.

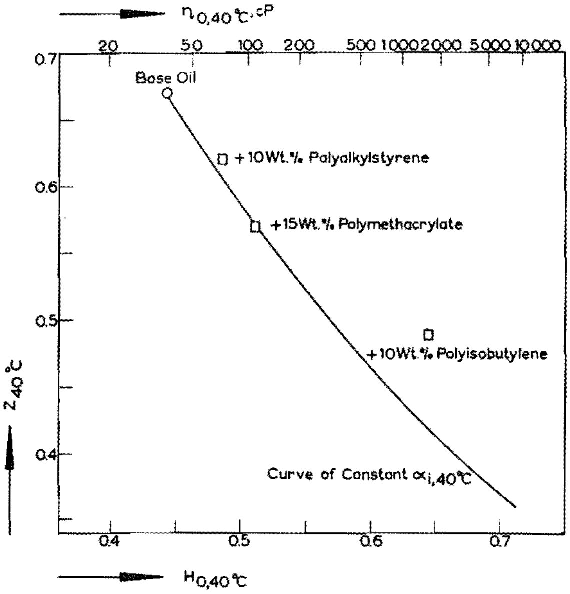

FIG.X-12.
Viscosity-Pressure Dependence of a Series of Polymer-Blended Mineral Oils.

to that of the base oil, the value exhibited by the polyisobutylene-containing blend is conspicuously higher.

Such deviations from the depicted curve would be predictable by accounting for the effect of pressure on the solubility of the polymer in the base oil and on the flexibility of the polymer chain[21]. However, quantitative predictions would appear very difficult.

As indicated already in § X.2.3, the new correlation of Fig.X-1 does not hold for mineral oils containing substantial amounts of some long-chain polymer. In fact, applying this correlation - in the form of Fig.X-1 or rather appropriately extended to include lower S_0-values, which are frequently encountered amongst polymer-blended mineral oils - to such blends yields Viscosity-Pressure Indices considerably below the experimental values. This means that the actual Viscosity-Pressure Index of a given polymer-blended mineral oil is much higher than that of a *straight* mineral oil with the same (atmospheric) Slope Index and viscosity grade. Thus, as noted above, the polymer may indeed be taken to decrease the Viscosity-Pressure Index relatively less than the (atmospheric) Slope Index of the mineral oil. But it would be far from correct to state - as done sometimes in the literature - that the polymer decreases the temperature dependence of the viscosity of the mineral oil, leaving its pressure dependence practically unchanged.

Nevertheless, the new correlational Fig.X-1 may serve as a convenient basis for estimating the Viscosity-Pressure Indices of polymer-blended mineral oils as well. The consequent procedure requires a knowledge solely of the atmospheric viscosity-temperature relationship of the blend and of the Viscosity-Pressure Index of the base oil.

For the latter purpose the basic Fig.X-1 has been extended to include lower (atmospheric) Slope Indices, which are frequently encountered amongst polymer-blended mineral oils; the extended correlation is represented by Fig.X-13. Remarkably enough, it has been found that the decrease in Viscosity-Pressure Index actually effected by the polymer is related very simply to the decrease that would be predicted from Fig.X-13. In fact, the following proportionality has been found to hold really good for the various oils considered:

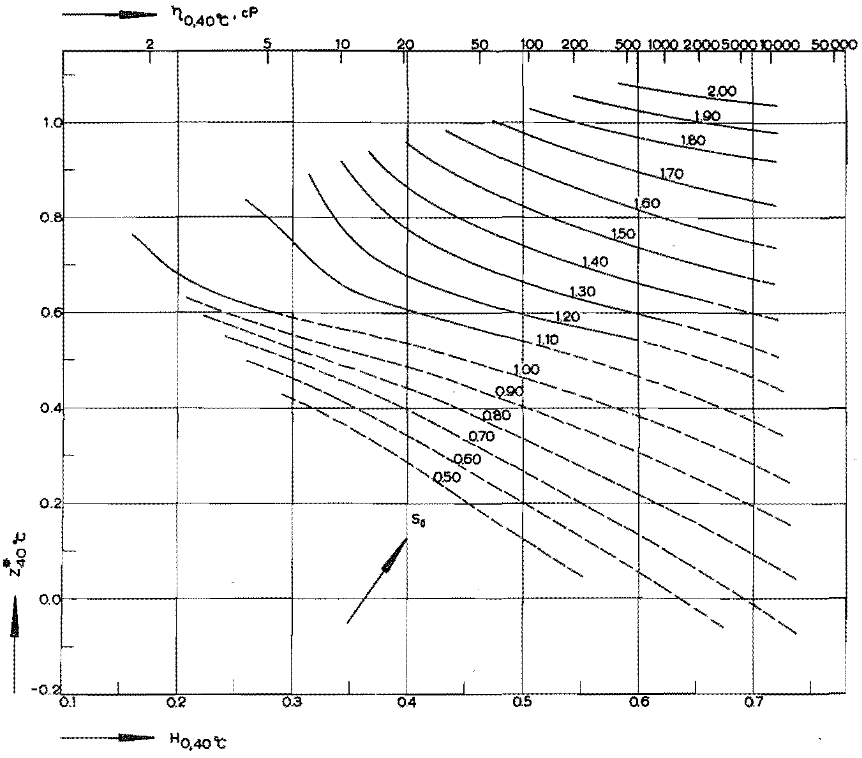

FIG.X-13.

Correlation Between Hypothetical Viscosity-Pressure Indices of Polymer-Blended Mineral Oils and Their Atmospheric Viscosity-Temperature Relationships.

$$(Z_{Or} - Z_{Bl})_{40^\circ C} = 0.4\,(Z_{Or} - Z^*_{Bl})_{40^\circ C}\,, \qquad \text{(X-9a)}$$

where Z_{Or} and Z_{Bl} denote the Viscosity-Pressure Indices of the base oil and the blend, respectively, and where Z^*_{Bl} stands for the *hypothetical* Viscosity-Pressure Index of the blend read from Fig.X-13. Correlation (X-9a) may be simplified into:

$$Z_{Bl} = 0.6\ Z_{Or} + 0.4\ Z^{*}_{Bl}. \qquad \text{(X-9b)}$$

For the time being the described correlation should be considered *tentative* in that it has been based on comparatively few data. Indeed, viscosity-pressure data on sufficiently defined polymer-blended mineral oils would still appear very scarce. The included blends and their base oils are designated in Table X-5.

TABLE X-5

Experimental and Predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ of Typical Polymer-Blended Mineral Oils

No.	Experimenters' Designation	Experimental Data		$Z_{40^\circ C}$	
	Base Oils	$\eta_{0,40^\circ C}$, cP	S_0	Exp.	Pred.
1	Paraffinic Oil[17] (Depicted in Fig.X-12)	37.2	1.27	0.67	
2	Heavy Gas-Oil Fraction[27], coded 25-E; Oil A-2 of Table II-1	7.30	1.15	0.79	
3	Paraffinic Oil[27], coded 31-G; Oil A-3 of Table II-1	41.1	1.26	0.67	
	Blends				
1	Oil No.1 + 10 Wt.% Polyisobutylene (Depicted in Fig.X-12)	1,592	0.92	0.49	0.51
2	Oil No.1 + 15 Wt.% Polymethacrylate (Depicted in Fig.X-12)	109.4	0.94	0.57	0.57
3	Oil No.1 + 10 Wt.% Polyalkylstyrene (Depicted in Fig.X-12)	73.1	1.12	0.62	0.63
4	Oil No.2 + 10.2 Wt.% Polymethacrylate (Low M) Blend[27] coded 26-E; API Oil No.103	27.4	0.87	0.66	0.66
5	Oil No.2 + 4.7 Wt.% Polymethacrylate (High M) Blend[27] coded 27-E; API Oil No.104	26.4	0.84	0.66	0.65
6	Oil No.3 + "Paratone"*) Blend[27] coded 44-G	120.5	1.11	0.62	0.62
7	Oil No.3 + 4.5 Wt.% "Acryloid 710"**) Blend[27] coded 45-G	123.9	0.99	0.58	0.58

*) Mineral-oil solution of polyisobutylene

**) Oil-soluble polymethacrylate

As shown by the last column of this table, the Viscosity-Pressure Indices $Z_{40^\circ C}$ thus predicted for the various blends are in excellent agreement with the experimental values.

Finally, it should be added that the Viscosity-Pressure Indices of polymer-blended mineral oils - just as those of straight mineral oils - may either increase or decrease somewhat with rising temperature or may remain substantially constant. But, at any rate, the temperature variation of the Viscosity-Pressure Indices of polymer-blended mineral oils generally does not follow the simple pattern described in § VII.3.2 for *straight* mineral oils. In other words, the viscosity-pressure *poles* of such blends are generally not located on the isotherm pole line established for straight mineral oils (see § IX.2.1).

Fortunately, the Viscosity-Pressure Indices of polymer-blended mineral oils may again be taken constant in a fairly wide temperature range (compare § V.2.3).

X.4.3. *The Viscosity-Pressure Indices and Atmospheric Slope Indices of Synthetic Lubricating Oils and Miscellaneous Liquids*

In Fig.X-14 the Viscosity-Pressure Indices $Z_{40^\circ C}$ of a great variety of synthetic lubricating oils and further liquids have been plotted against their atmospheric Slope Indices, S_0.

First of all, three homologous groups of, commercially available, synthetic lubricating oils have been depicted. These groups - being the only ones for which the author could gather sufficient data - are represented by the technologically important (linear) polymethylsiloxanes, polyglycols and polybutenes. In addition, the truly homologous group of pure n-paraffins - having invariably the same Slope Index $S_0 = 1.00$ - has been included*).

Furthermore, individual points have been depicted in Fig.X-14 for 18 miscellaneous liquids, including several important types of synthetic lubricating oils. The latter liquids are identical to the similarly numbered ones of Fig.VII-2 and have already been specified in Table VII-1.

For comparison, the range of Viscosity-Pressure Indices $Z_{40^\circ C}$ and atmospheric Slope Indices comprised by all the various kinds of mineral oils investigated so far has been indicated approximately by dashed lines. More particularly, the group of mineral oils characterized by a common percentage C_R of 48 - and displaying a common Viscosity-Pressure Index $Z_{40^\circ C} = 0.74$ - has been represented by a (horizontal) solid line.

Finally, the straight line relating to the aforementioned constant ratio $Z_{40^\circ C}/S_0$ of 0.55 - representing some overall value for mineral oils (see part B of § X.2.2) - has been constructed.

For all the synthetic lubricating oils and further liquids comprised by Fig.X-14 the *ratio* of the Viscosity-Pressure Index $Z_{40^\circ C}$ to the atmospheric Slope Index, S_0, has been plotted in Fig.X-15 as a function of their viscosity grade $\eta_{0,40^\circ C}$. On the basis of Equation (X-3) the corresponding ratio between "equivalent" pressure and temperature changes, expressed in terms of $(kgf/cm^2)/deg\ C$, has also been indicated (see part B of § X.2.2).

The range covered in Fig.X-15 by all the various kinds of mineral oils investigated so far is comprised approximately by the two converging dashed lines. Further, four distinct series of iso-S_0 mineral oils have been depicted, namely for S_0-values of 1.00, 1.20, 1.50 and 1.80.

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*) The experimental data on these four homologous groups derive from the investigations already cited in § VII.2.2 (see also Fig.VII-2).

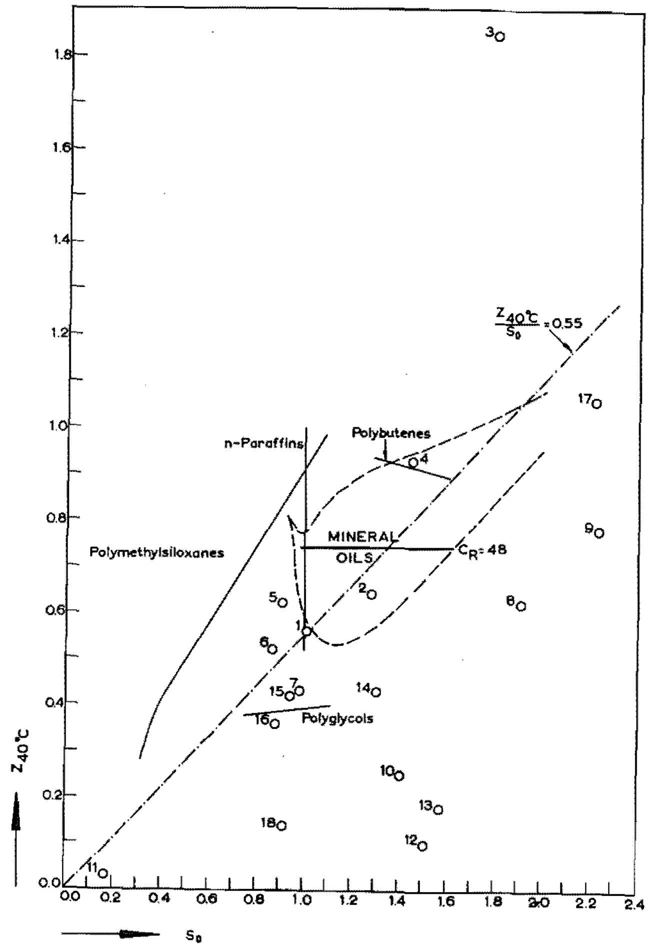

FIG. X-14.

Viscosity-Pressure Indices and Atmospheric Slope Indices of Synthetic Lubricating Oils and Miscellaneous Liquids.

Designations:

1. Diester
2. ditto
3. Fluorocarbon
4. Chlorofluorocarbon
5. Silicate Ester
6. Polyalkylstyrene
7. Polymethacrylate
8. Chloroparaffin
9. ditto
10. Triethanol Amine
11. Mercury
12. Water
13. Glycerol
14. Castor Oil
15. Rapeseed Oil
16. Whale Oil
17. Bitumen
18. Water-Glycol Fluid

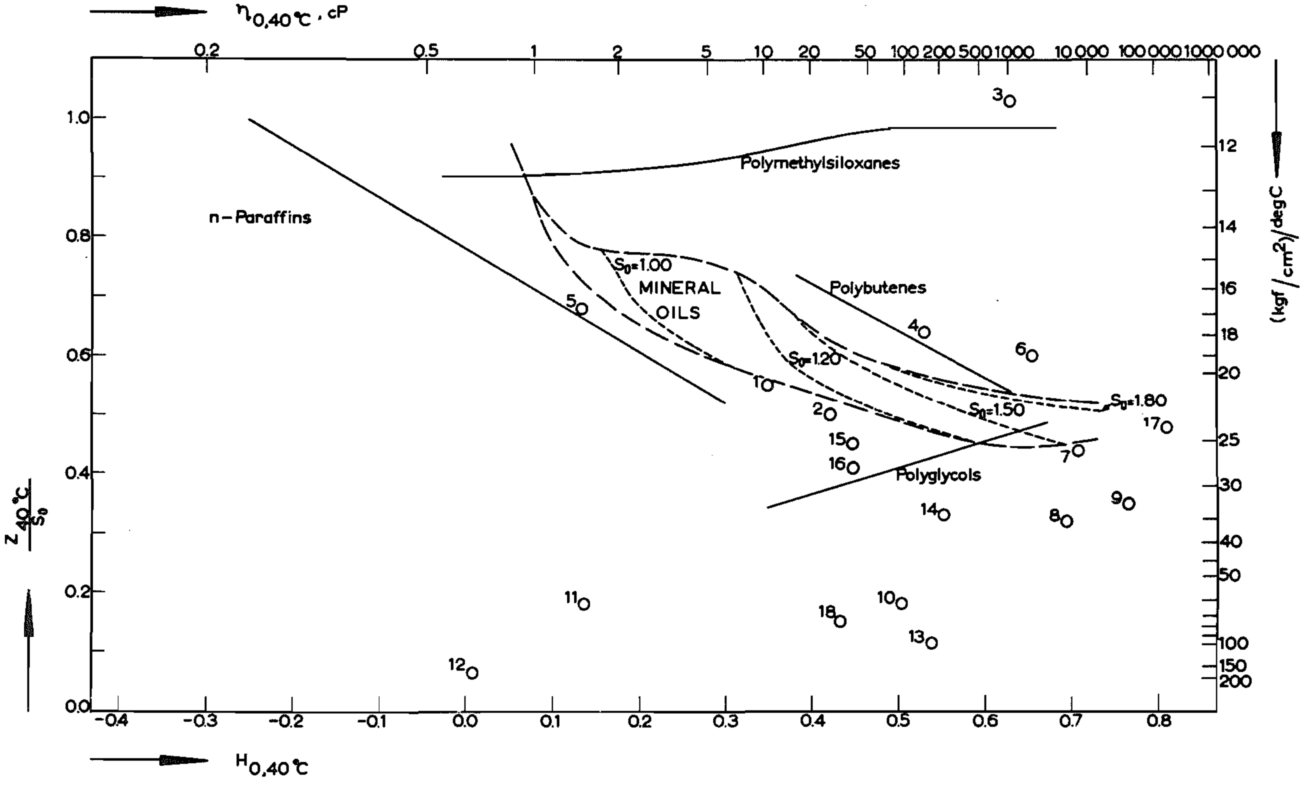

FIG.X-15.
Ratio of Viscosity-Pressure Indices to Atmospheric Slope Indices of Synthetic Lubricating Oils and Miscellaneous Liquids as a Function of Their Viscosity Grade. For designations see Fig.X-14.

Fig. X-14 and particularly Fig. X-15 clearly show that the ratio $Z_{40^\circ C}/S_0$ may differ very widely from one liquid to another. As seen from Fig. X-15, this holds primarily for the more viscous liquids. Indeed, in the range of rather low viscosity grades the differentiation as to the ratios $Z_{40^\circ C}/S_0$ between the divergent types of liquids under consideration, including the mineral oils, becomes much less and would even tend to vanish*).

Fig. X-15 further shows that the ratio $Z_{40^\circ C}/S_0$ of mineral oils would usually be located within a comparatively small range. In fact, as stated already in part B of § X. 2. 2 (see also Fig. X-3), this ratio normally comes fairly close to the value 0.55. Consequently, the applicability of any more or less satisfactory correlation for predicting the viscosity-pressure dependence of *mineral* oils from their atmospheric viscosity-temperature relationship is bound to be restricted to such oils specifically. It is true that such a correlation may yield reasonable predictions also for certain non-mineral oils, but this should be deemed rather fortuitous (compare the discussion of Hartung's correlation, in part C of § X. 3. 3).

Pure Hydrocarbons

Even when the present correlation for mineral oils is applied to individual, *pure* hydrocarbons, conspicuous deviations are very

TABLE X-6

Experimental and Predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ of 15 Pure Hydrocarbons

Compound	Experimental Data		$Z_{40^\circ C}$	
PSU No.	$\eta_{0,40^\circ C}$, cP	S_0	Exp.	Pred.
516	2.72	0.97	0.59	0.61
500	3.33	1.12	0.67	0.90
25	6.61	1.09	0.60	0.71
503	7.41	1.22	0.66	0.90
87	7.41	1.09	0.61	0.69
110	8.59	1.11	0.59	0.69
18	10.64	1.14	0.58	0.69
88	11.22	1.15	0.64	0.69
8	11.27	1.08	0.57	0.63
111	12.59	1.12	0.62	0.65
12	15.56	1.16	0.63	0.67
134	19.14	1.05	0.52	0.57
113	20.7	1.17	0.64	0.66
575	23.3	1.26	1.15	0.73
19	26.0	1.27	0.71	0.72

---

*) Obviously, water and mercury are outstanding in the latter respect. In fact, a similar exceptional behaviour of these liquids has previously been observed with regard to their atmospheric Slope Index and Viscosity-Pressure Index individually (see Figs. VI-3 and VII-2, respectively).

likely to occur in several cases, notably for pure hydrocarbons whose structure differs widely from the average chemical constitution of the normally encountered types of mineral oils (compare § IX.5.3).

Whilst this conjecture has indeed appeared to be correct, it has simultaneously been found that the present correlation yields predictions of the Viscosity-Pressure Indices of pure hydrocarbons which may be considered reasonable in many cases. In other cases, however, such predictions are useful only as a first - rather rough - approximation.

In order to convey an impression of the deviations involved the present correlation has been applied to a variety of 15 pure hydrocarbons, which have already been designated in Table IX-6. Besides their viscosity grades $\eta_{0,40^\circ C}$ and their atmospheric Slope Indices, the experimental and predicted Viscosity-Pressure Indices $Z_{40^\circ C}$ have been listed in Table X-6. Indeed, whilst several predictions may be considered fair, other ones are seen to be rather rough.

X.5. THEORETICAL CONSIDERATIONS ON THE CORRELATION BETWEEN THE TEMPERATURE AND PRESSURE DEPENDENCE OF THE VISCOSITY OF LIQUIDS

X.5.1. *Correlation of Viscosity With Volume*

As early as 1882 Warburg and von Babo[172)] conjectured that the viscosity of liquids would be a unique function of their specific *volume* (or their density). The first investigator, however, who has particularly advocated - around the year 1913 - the assumption of pure volume dependence of viscosity was Batschinski[85)]. In later years this assumption was frequently resorted to and many empirical equations aiming at its quantitative formulation were proposed.

The aforementioned assumption implies that simultaneous variation of temperature and pressure such that the specific volume is kept constant would also leave the viscosity substantially unchanged; or more generally, changes in viscosity brought about by varying either temperature or pressure would be caused solely by the accompanying volume changes.

As a consequence, this assumption would offer the very alluring possibility of assessing the isothermal effect of pressure on the viscosity of a given liquid from the isobaric (notably atmospheric) effect of temperature solely on the basis of its equation of state.

Indeed, for simple, non-associated liquids the assumption of pure volume dependence of their viscosity generally proves to hold rather good. Unfortunately, for more complicated liquids, notably lubricating oils, this assumption can by no means be upheld. It was Bridgman[8)] who first demonstrated for a great variety of such more complicated liquids the breakdown of the latter assumption.

The basic reason for the breakdown of the assumption of pure volume dependence of viscosity consists in that, rigorously speaking, *two* of the three variables of state, temperature, pressure and specific volume, are needed for completely defining the viscosity

- which constitutes a real quantity of state - of a Newtonian liquid. Consequently, any efforts to account for the effects of temperature and pressure on its viscosity in terms solely of its specific volume are, in general, foredoomed to fail more or less.

In fact, it is physically clear that when temperature and pressure are increased such that the specific volume of a given liquid remains the same, the *thermal mobility* of its molecules is bound to increase also. Accordingly, it may *a priori* be expected that, even though its volume is kept constant, the viscosity of a given liquid will become smaller, at least to some extent, with increasing temperature (and pressure).

Now, experimental data have proved that for simple, non-associated liquids the indicated effect of increased thermal mobility of their molecules on the resulting viscosity value generally is very small or even completely negligible. But this effect may become quite pronounced for more complicated liquids. For the very complex mixtures represented by mineral oils, for example, the *isochoric* viscosity-temperature effect, at normal temperatures, turns out to be of the order of no less than 50% of that at constant pressure.

X.5.2. *The Correlation Between the Temperature and Pressure Dependence of Viscosity in Terms of Eyring's Theory*

A. THE ISOBARIC VISCOSITY-TEMPERATURE EFFECT

A suggestive interpretation of the viscosity-temperature effect at constant volume has been provided by Eyring and his associates in terms of their general theory of viscous flow (see § III.1.1 and § IV.1.1). According to their view, the total isobaric "activation energy for viscous flow", E_{vis}, may be separated into two parts, namely:

$$E_{vis} = E_{vis}^{h} + E_{vis}^{j}, \tag{X-10}$$

where the volume-dependent part E_{vis}^{h} represents the energy - like E_{vis} and E_{vis}^{j}, taken per gmole of the liquid - required for the *formation of a hole* large enough to permit a molecular jump, whilst the isochoric part E_{vis}^{j} denotes the additional energy required for *performing such a jump*. Whereas E_{vis}^{h} reflects an *indirect* effect of temperature, that is the effect due to thermal expansion of the liquid, the isochoric activation energy E_{vis}^{j} reflects the accompanying *direct* effect of temperature, that is the effect due to an increased thermal mobility of its molecules.

In later years Eyring's interpretation was particularly advocated and elaborated by Bondi; in fact, Bondi has presented an extensive analysis of available viscosity data on a very great variety of liquids, including various types of lubricating oils[173,20,174]. According to Bondi's view, the total activation energy E_{vis} of a liquid with a given molecular configuration is governed by the obtaining *intermolecular forces* and the *flexibility* (*intra*molecular forces) of its molecules. More particularly, whilst the quantity E_{vis}^{h} would be a measure of its intermolecular forces, the isochoric quantity E_{vis}^{j} would be predominantly determined by its molecular flexibility.

In accordance with the viscosity-temperature Equation (III-1b) the *isobaric* activation energy E_{vis} is defined by:

$$E_{vis} = R\left[\frac{\delta \ln \eta}{\delta(1/T)}\right]_p , \qquad \text{(X-11)}$$

where R denotes again the molar gas constant. Analogously, the *isochoric* activation energy E_{vis}^{j} can be written as:

$$E_{vis}^{j} = R\left[\frac{\delta \ln \eta}{\delta(1/T)}\right]_v . \qquad \text{(X-12)}$$

In harmony with Bondi's view the isochoric activation energy E_{vis}^{j} assumes relatively small values for liquids composed of very flexible molecules, but relatively large values for liquids composed of rather rigid molecules. For the latter liquids, particularly if association effects also interfere with the flow process, the contribution of the isochoric activation energy E_{vis}^{j} to the total isobaric activation energy E_{vis} may easily amount, at least at normal temperatures, to some 50% or even more. Further, since molecular flexibility is bound to increase strongly with rising temperature, the aforementioned contribution will be considerably less at relatively high temperatures. All in all, whereas the isochoric activation energy E_{vis}^{j} may largely determine the flow process at moderate temperatures, the quantity E_{vis}^{h} will be the governing factor at very high temperatures (excepting extremely high pressures).

B. CORRELATION WITH THE ISOTHERMAL VISCOSITY-PRESSURE EFFECT

In order to complete the above picture Bondi also considered the isothermal viscosity-pressure effect, this being characterized by the quantity V_{vis}, the size of the holes (per gmole) required for molecular jumps. This quantity V_{vis} would be essentially determined by the molecular configuration and flexibility of the liquid considered.

Further, Bondi emphasized the important finding that the viscosity-pressure characteristic V_{vis} of a given liquid could generally be related to its volume-dependent part of the isobaric activation energy E_{vis}^{h} by the simple expression:

$$E_{vis}^{h} = p_i V_{vis} , \qquad \text{(X-13)}$$

where the quantity p_i denotes its *internal pressure*. The internal pressure (or cohesive pressure) is a direct measure of the attractive forces between the molecules of a particular liquid. As will be elucidated hereafter, p_i is completely defined by the equation of state of the liquid considered.

Relationship (X-13) expresses that the energy E_{vis}^{h} required for the formation of a hole of size V_{vis} (taken again per gmole) is equal to the work that has to be performed against the internal pressure, p_i, for creating such a hole.

By combining Equations (X-10) and (X-13) it readily follows that the ratio of the isothermal viscosity-pressure characteristic V_{vis} to the total isobaric activation energy, E_{vis}, of a particular liquid would be given by the correlation:

$$\frac{V_{vis}}{E_{vis}} = \frac{1-\dfrac{E_{vis}^{j}}{E_{vis}}}{p_i}. \qquad \text{(X-14)}$$

This correlation implies that for those simple liquids whose isochoric activation energy is negligibly small in comparison with their total isobaric activation energy the ratio V_{vis}/E_{vis} would be a unique function of their internal pressure, p_i, so that it may be derived solely from their equation of state.

X. 5. 3. *The Present Contribution*

A. THE ISOCHORIC VISCOSITY-TEMPERATURE COEFFICIENT

Elaborating a tentative statistical-physical model of the mobility of molecules in a liquid the following viscosity expression has been achieved in Section III. 3:

$$\ln\frac{\eta}{\eta_e} = \left[\frac{v_f^*}{v_f}\,\Gamma\left(1+\frac{1}{n}\right)\right]^n . \qquad \text{(III-15)}$$

In harmony with experimental data this expression implies that, in general, the viscosity of a given liquid cannot be fully described by its specific volume, v, alone. In fact, it would be a unique function of the ratio of its minimum required specific free volume, v_f^*, to its specific free volume, v_f.

From Equation (III-15) a quantitative expression can be deduced for the *isochoric* viscosity-temperature coefficient, β_v, defined as:

$$\beta_v = -\frac{1}{\eta}\left(\frac{\delta\eta}{\delta T}\right)_v = -\left(\frac{\delta \ln\eta}{\delta T}\right)_v . \qquad \text{(X-15)}$$

The relevant expression can readily be shown to read:

$$\beta_v = -\,n\cdot\ln\frac{\eta}{\eta_e}\left[\frac{\delta\ln(v_f^*/v_f)}{\delta T}\right]_v , \qquad \text{(X-16a)}$$

or, in extended form:

$$\beta_v = n \cdot \ln\frac{\eta}{\eta_e}\left\{\left[\frac{1}{v_f}\left(\frac{\delta v_f}{\delta T}\right)_p - \frac{1}{v_f^*}\left(\frac{\delta v_f^*}{\delta T}\right)_p\right] + \left(\frac{\delta p}{\delta T}\right)_v \left[\frac{1}{v_f}\left(\frac{\delta v_f}{\delta p}\right)_T - \frac{1}{v_f^*}\left(\frac{\delta v_f^*}{\delta p}\right)_T\right]\right\}. \qquad \text{(X-16b)}$$

Further, the specific free volume, v_f, may be conveniently rewritten as:

$$v_f = v - v_{oc}\,, \qquad \text{(X-17)}$$

where v_{oc} denotes the specific *"occupied"* volume, to be regarded as a kind of van der Waals volume. This occupied volume should be of the order of the minimum required specific free volume, v_f^*, and may likewise depend somewhat on temperature and pressure.

Equation (X-16b) can then be transformed into the expression:

$$\beta_v = -n \cdot \ln\frac{\eta}{\eta_e}\left\{\left[\frac{1}{v_f}\left(\frac{\delta v_{oc}}{\delta T}\right)_p + \frac{1}{v_f^*}\left(\frac{\delta v_f^*}{\delta T}\right)_p\right] + \left(\frac{\delta p}{\delta T}\right)_v \left[\frac{1}{v_f}\left(\frac{\delta v_{oc}}{\delta p}\right)_T + \frac{1}{v_f^*}\left(\frac{\delta v_f^*}{\delta p}\right)_T\right]\right\}. \qquad \text{(X-16c)}$$

According to this equation, the isochoric viscosity-temperature coefficient, β_v, should generally assume some positive value, becoming zero only for those liquids whose specific occupied volume, v_{oc}, and minimum required specific free volume, v_f^*, are both independent of temperature and pressure. The latter would be the case only for simple liquids with a considerable degree of *flexibility*.

All in all, Equation (X-16c) may be claimed to give quantitative expression to the experimental observations, discussed in the preceding parts of this section, concerning the direct effect of temperature on the viscosity of liquids at temperatures and pressures so adjusted that their specific volume, v, remains constant.

Further, Equations (III-16) and (IV-8) have been proposed to account explicitly for the effects of temperature and pressure, respectively, on the involved ratio v_f^*/v_f. On the basis of these equations Expression (X-16a) for the isochoric viscosity-temperature coefficient, β_v, can be cast into the following more specific formulation:

$$\beta_v = n \cdot \ln\frac{\eta}{\eta_e}\left[\frac{r}{T-T_0} - \left(\frac{\delta p}{\delta T}\right)_v \frac{w}{p+p_0}\right], \qquad \text{(X-18a)}$$

where the various parameters have the same meaning as defined in the relevant Sections III. 3 and IV. 5.

In the latter sections it has further been shown that the empirically developed Equations (III-10a) and (IV-5a') may be deemed good approximations to the aforementioned more general Equations (III-17) and (IV-9), respectively. On the strength of this finding Relationship (X-18a) may finally be reduced to the empirical form:

$$\beta_v = \ln\frac{\eta}{\eta_\infty}\left[\frac{S}{T-138}-\left(\frac{\delta p}{\delta T}\right)_v\frac{Z}{p+2,000}\right]. \qquad \text{(X-18b)}$$

In general, the form between parentheses on the right-hand side of this equation proves to be positive*), so that the isochoric viscosity-temperature coefficient, β_v, is also positive. In addition, Equation (X-18b) indicates that, at least at moderate pressures, the coefficient β_v of any liquid will approximate to zero when the temperature becomes very high.

B. CORRELATION BETWEEN TEMPERATURE AND PRESSURE EFFECT

For Newtonian liquids the viscosity - being a real quantity of state - is a function solely of temperature and pressure. Consequently, the following correlation**) can rigorously be derived for any such liquid:

$$\left(\frac{\delta\ln\eta}{\delta p}\right)_T\left(\frac{\delta p}{\delta T}\right)_v = -\left(\frac{\delta\ln\eta}{\delta T}\right)_p + \left(\frac{\delta\ln\eta}{\delta T}\right)_v. \qquad \text{(X-19a)}$$

Introducing the isothermal viscosity-pressure coefficient, α, and the isobaric viscosity-temperature coefficient, β, this correlation can be rewritten as:

$$\alpha\left(\frac{\delta p}{\delta T}\right)_v = \beta-\beta_v \qquad \text{(X-19b)}$$

or

$$\frac{\alpha}{\beta} = \left(\frac{\delta T}{\delta p}\right)_v\left(1-\frac{\beta_v}{\beta}\right). \qquad \text{(X-19c)}$$

The latter three expressions are important in that they *rigorously* define the correlation between the viscosity-temperature-pressure relationship and the equation of state of any given liquid.

It should be mentioned that, as pointed out by Bondi[20,21], the isochoric pressure-temperature coefficients, $(\delta p/\delta T)_v$, at any given temperature and pressure, should be nearly constant within a particular *family* of liquids. As a consequence of Correlation (X-19c) the ratios α/β, at any fixed conditions of temperature and pressure, of all the members of such a family would then, to a first approximation, display a unique linear relationship with their corresponding ratios

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*) As indicated in the subsequent part, the isochoric pressure-temperature coefficient, $(\delta p/\delta T)_v$, normally assumes values of the order of some 10 (kgf/cm^2)/deg K (140 psi/deg K).

**) Essentially the same correlation has previously been presented by Rumpf[175] and also by Gee[176].

β_v/β. In addition, in families of simple liquids exhibiting ratios β_v/β negligibly smaller than unity the ratios α/β, at any given temperature and pressure, of the various members would be approximately the same.

Correlation (X-19c) can be put into yet another useful form by utilizing the purely mathematical identity:

$$\frac{\alpha}{\beta} = \left(\frac{\delta T}{\delta p}\right)_\eta . \tag{X-20}$$

This identity expresses that any particular *isoviscid* is defined simply by the ratio between the corresponding viscosity-pressure and viscosity-temperature coefficients.

Substituting Identity (X-20) into Correlation (X-19c) leads to the expression:

$$\left(\frac{\delta T}{\delta p}\right)_\eta = \left(\frac{\delta T}{\delta p}\right)_v \left(1 - \frac{\beta_v}{\beta}\right), \tag{X-21}$$

which constitutes a *rigorous* correlation between the *isoviscids* and *isochors* of a given liquid. It is readily seen that for those simple liquids whose isochoric viscosity-temperature coefficient, β_v, is negligibly smaller than their total isobaric viscosity-temperature coefficient, β, any given isoviscid would completely coincide with one particular isochor.

Returning to Equations (X-19b) and (X-19c), it follows that the correlation between, on the one hand, the isothermal viscosity-pressure coefficient and, on the other hand, the isobaric and isochoric viscosity-temperature coefficients of any given liquid is completely defined by its *isochoric pressure-temperature coefficient*, $(\delta p/\delta T)_v$. As regards the significance of the latter quantity, the following comments may be useful.

The thermodynamic equation of state for any liquid reads:

$$p_i = T\left(\frac{\delta p}{\delta T}\right)_v - p, \tag{X-22}$$

where p_i represents the *internal* pressure (compare the preceding part B), p standing again for the *external* (gauge) pressure; further, the quantity $T(\delta p/\delta T)_v$ is denoted as the *thermal* pressure. As long as the external pressure, p, assumes only moderate values this is entirely negligible in comparison with the thermal pressure, which usually amounts to 2,000-8,000 kgf/cm^2 (28,000-114,000 psi). Therefore, one may normally set the internal pressure, p_i, equal to this thermal pressure, $T(\delta p/\delta T)_v$, so that:

$$\left(\frac{\delta p}{\delta T}\right)_v = \frac{p_i}{T}. \tag{X-23}$$

In accordance with the aforementioned values of their internal pressures the isochoric pressure-temperature coefficients, $(\delta p/\delta T)_v$, under discussion will normally vary from, say, 5-30 $(\mathrm{kgf/cm^2})/\mathrm{deg\ K}$ (about 70-400 psi/deg K).

Substituting Identity (X-23) into Correlations (X-19b) or (X-19c) yields the expression:

$$\frac{\alpha}{\beta T} = \frac{1 - \frac{\beta_v}{\beta}}{p_i}. \qquad \text{(X-24)}$$

It can readily be shown that this expression is essentially identical to Bondi's Correlation (X-14), thus confirming that, at least at moderate pressures, the latter correlation is basically correct.

The isochoric pressure-temperature coefficient of liquids involved in Equations (X-19b) and (X-19c) can also be rigorously correlated with their isobaric *thermal-expansion coefficient*, ϵ, and their isothermal *compressibility coefficient*, κ, which are defined by, respectively:

$$\epsilon = \frac{1}{v}\left(\frac{\delta v}{\delta T}\right)_p \qquad \text{(X-25)}$$

and

$$\kappa = \frac{1}{v}\left(\frac{\delta v}{\delta p}\right)_T. \qquad \text{(X-26)}$$

The relevant correlation is readily achieved by substituting the latter expressions into the purely mathematical identity:

$$\left(\frac{\delta p}{\delta T}\right)_v = -\left(\frac{\delta v}{\delta T}\right)_p \bigg/ \left(\frac{\delta v}{\delta p}\right)_T, \qquad \text{(X-27a)}$$

which leads to:

$$\left(\frac{\delta p}{\delta T}\right)_v = \frac{\epsilon}{\kappa}. \qquad \text{(X-27b)}$$

Combining the latter identity with Equations (X-19b) or (X-19c) yields the *rigorous* correlation:

$$\frac{\alpha}{\beta} = \frac{\kappa}{\epsilon}\left(1 - \frac{\beta_v}{\beta}\right), \qquad \text{(X-28a)}$$

or also:

$$\frac{\alpha/\kappa}{\beta/\epsilon} = 1 - \frac{\beta_v}{\beta}. \qquad \text{(X-28b)}$$

Correlations (X-28a) and (X-28b) lead to the interesting conclusion that for those simple liquids whose ratios β_v/β are negligibly smaller than unity the ratio of their isothermal viscosity-pressure coefficient, α, to their isothermal compressibility coefficient, κ, is identical to the ratio of their isobaric viscosity-temperature coefficient, β, to their isobaric thermal-expansion coefficient, ϵ.

Finally, the ratio α/β of liquids can be expressed in terms of the isobaric viscosity-temperature Equation (III-17) and the isothermal viscosity-pressure Equation (IV-9), which have been achieved from the tentative statistical-physical basis for their molecular mobility elaborated in Sections III. 3 and IV. 5. The resulting expression proves to read:

$$\frac{\alpha}{\beta} = \frac{w}{r} \cdot \frac{T-T_0}{p+p_0}. \qquad \text{(X-29a)}$$

By using the empirically developed Equations (III-10a) and (IV-5a') instead of the aforementioned Equations (III-17) and (IV-9), respectively, Correlation (X-29a) can be reduced to the more specific form:

$$\frac{\alpha}{\beta} = \frac{Z}{S} \cdot \frac{T - 138}{p + 2,000}. \qquad \text{(X-29b)}$$

Correlations (X-29a) and (X-29b) lead to the very interesting result that the various conclusions reached above for the ratio α/β of liquids would, at any fixed temperature and pressure, equally apply to their ratio w/r and, more specifically, to their ratio Z/S.

C. SPECIFIC CORRELATIONS FOR MINERAL OILS

For *mineral oils* specifically the following semi-quantitative correlation between their Viscosity-Pressure Index $Z_{40^\circ C}$ and their atmospheric Slope Index, S_0, has been devised:

$$Z_{40^\circ C} = 0.55\ S_0. \qquad \text{(X-2)}$$

In accordance with Expression (X-29b), Correlation (X-2) implies that the ratio of their *initial* viscosity-pressure coefficient $\alpha_{i,40^\circ C}$ to their atmospheric viscosity-temperature coefficient $\beta_{0,40^\circ C}$ should be semi-quantitatively defined by the correlation:

$$\frac{\alpha_{i,40^\circ C}}{\beta_{0,40^\circ C}} = 0.048 \text{ deg C/(kgf/cm}^2\text{)}. \qquad \text{(X-4a)}$$

Another semi-quantitative correlation has proved to exist for the ratio of the isochoric to the isobaric viscosity-temperature coefficient of all the various kinds of mineral oils investigated so far. In fact, as indicated already by Bondi[173,20], this ratio may at normal conditions of temperature and pressure, be approximated by the simple equation:

$$\frac{\beta_v}{\beta} = 0.50. \qquad \text{(X-30)}$$

In Table X-7 the validity of Correlation (X-30) has been exemplified for three mineral oils of very divergent chemical constitution.

TABLE X-7

Viscosity-Temperature-Pressure-Volume Data on Three Mineral Oils of Divergent Chemical Constitution

Mineral Oil		Experimental Data at Atmospheric Pressure and 40°C (104°F)			
Code*)	Experimenters' Designation	η, cP	$\frac{\beta_v}{\beta}$	$(\delta p/\delta T)_v$, $(kgf/cm^2)/deg\ K$	p_i, kgf/cm^2
A-4	Paraffinic Oil	129.4	0.52	11.5	3,600
A-11	Naphthenic Oil	117.5	0.47	10.8	3,400
A-16	Aromatic Extract	501	0.50	9.9	3,100

*) Refers to similarly coded oils specified in Table II-1.

Substitution of the semi-quantitative Correlations (X-4a) and (X-30) into the rigorous Correlation (X-19c) leads to the result that, at least at atmospheric pressure and at a standard reference temperature of 40°C, the isochoric pressure-temperature coefficients of mineral oils would invariably be given by the equation*):

$$\left[\left(\frac{\delta p}{\delta T}\right)_v\right]_{0,40^\circ C} = 10.4\ (kgf/cm^2)/deg\ K. \qquad \text{(X-31)}$$

The approximate validity of the latter correlation has also been illustrated in the aforementioned Table X-7.

The involved approximate constancy of the isochoric pressure-temperature coefficients of mineral oils implies that their internal pressures, p_i, should also be nearly the same. In fact, combination of Expression (X-23) with Correlation (X-31) leads to the related expression:

$$(p_i)_{0,40^\circ C} = 3,300\ kgf/cm^2. \qquad \text{(X-32)}$$

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*) It should be noted that Correlation (X-4a) contains the initial viscosity-pressure coefficient $\alpha_{i,40^\circ C}$, whilst an expression for the atmospheric viscosity-pressure coefficient $\alpha_{0,40^\circ C}$ should have been substituted into the rigorous Correlation (X-19c). In view of the approximative nature of the involved Correlations (X-4a) and (X-30), however, the present substitution may be justified.

As exemplified again in Table X-7 for three mineral oils of very divergent chemical constitution, the indicated average value of 3,300 kgf/cm^2 (47,000 psi) does prove to be representative of their actually observed internal pressures. It may be added that, in general, the internal pressures of paraffinic mineral oils tend to be somewhat higher than those for naphthenic/aromatic ones.

Further, the rigorous Idendity (X-27b) implies that the aforementioned approximate constancy of the isochoric pressure-temperature coefficient of mineral oils should also apply, to exactly the same degree and extent, to the ratio of their isobaric thermal-expansion to their isothermal compressibility coefficient. The relevant correlation reads:

$$\left(\frac{\epsilon}{\kappa}\right)_{0,40^{\circ}\mathrm{C}} = 10.4\ (\mathrm{kgf/cm^2})/\mathrm{deg\ K}. \qquad \text{(X-33)}$$

It may be noted that the approximate constancy resulting for the ratio ϵ/κ of mineral oils is not so surprising, since it is a well-known fact that both coefficients involved do not vary considerably from one oil to another.

CHAPTER XI

THE VISCOSITY GRADE OF MINERAL OILS AND PURE HYDROCARBONS: CORRELATION WITH CHEMICAL CONSTITUTION AND PHYSICAL CONSTANTS

XI. 1. INTRODUCTION

XI. 1. 1. *Background*

All the various correlations developed in the preceding chapters for predicting the temperature and pressure dependence of the viscosity of lubricating oils, notably mineral oils, invariably involve the use of their viscosity *grade*, that is the viscosity at atmospheric pressure and at some standard reference temperature*). In fact, the use of the viscosity grade of the oils constitutes the most simple and straightforward starting-point in designing such correlations.

As a consequence, the aforementioned correlations cannot yield any information on the viscosity (grade) *itself* of the oils considered. For various purposes, however, especially for correlational studies (see below), such information would be highly desirable. Accordingly, in the present chapter ample attention will be paid to the correlation of the viscosity grade of lubricating oils, notably mineral oils and pure hydrocarbons, with their chemical constitution and easily assessable physical constants.

In fact, an overwhelming amount of work - predominantly of an empirical nature - has been devoted so far to the correlation of the viscosity grade of liquids with their chemical constitution and physical constants. The validity of the conclusions reached, however, usually proves to be very limited[173,177,178a].

In this connection it should be realized that the search for regularities between the viscosities of series of chemically interrelated compounds is seriously hampered by the difficulty of choosing conditions under which these viscosities may be feasibly compared. In particular this holds for the reference temperature to be adopted, since for most liquids the viscosity-temperature dependence is quite considerable and may vary widely for different compounds. For the latter reasons some standard reference temperature certainly cannot be regarded as a suitable *"corresponding"* temperature for different liquids. For want of something better, however, many previous investigators have simply compared the viscosities at some arbitrarily selected temperature. Others have followed the procedure - first adopted by Thorpe and Rodger in their classical viscosity studies - of comparing the viscosities at equal viscosity-temperature gradients.

Presumably, a more convenient and more generally valid evaluation

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*) It may be recalled that in the aforementioned correlations a standard reference temperature of 40°C (104°F) has arbitrarily been adopted.

of the aforementioned correlation would be possible if a reasonably *additive* function of viscosity and, notably, density were available.

Before delving more deeply into the problem in question some characteristics and possibilities of such additive functions will be elucidated.

XI. 1. 2. *Additive Functions of Physical Constants*

The concept of the additivity of certain functions formed from physical constants has proved very fruitful for studying the correlation between the physical properties involved and the chemical constitution of substances. In addition, additive functions may be highly convenient for investigating how a particular physical constant depends on other interesting properties within a group of chemically interrelated compounds.

The usefulness of this simple concept applies both to *individual compounds* and to their *mixtures*, even if these are of considerable complexity. Thus, certain additive functions rank as important tools in the statistical constitution analysis of complex mixtures such as *mineral oils* and *coal*.

During many years additive functions have found particular application in the field of hydrocarbon liquids. Since pure hydrocarbons constitute relatively simple liquids representing a great variety of systematically changing structures, these have served as model compounds in numerous investigations into additivity. These investigations have greatly contributed to gaining a more profound insight into the correlation between the properties of individual hydrocarbons and their mixtures, including the natural mixtures represented by mineral oils of divergent origin and chemical constitution.

An additive function of physical constants may be defined as: *a function which for a given compound can be calculated by summation of the atomic contributions*. Accordingly, for a given *molar* additive function F the following equation holds:

$$F = \sum_j n_j \varphi_j, \qquad (XI\text{-}1)$$

where φ_j denotes the contribution, per gmole, of atom j and n_j represents the number of these atoms j per molecule. At least for fixed conditions of temperature and pressure the atomic increment φ_j is considered independent of the configuration of the constituent atom in the molecule.

Instead of such *atomic* increments, *group* or *bond* increments are frequently employed. For more complicated molecules, in particular, it is advantageous to consider larger structural units rather than all the atoms individually. These units should be taken as large as practical in order to include certain constitutive effects which, in cases where very small units - such as the constituent atoms - are being considered, may cause appreciable discrepancies from the particular additivity rule.

Indeed, in general the increments φ_j are not fully insensitive to the effect of neighbouring atoms in a particular molecule. Nevertheless, additivity has proved to hold to a good approximation for well-known functions of physical constants such as molar volume, molar refraction and parachor, and also for several thermodynamic functions.

It is possible even to improve the accuracy of additivity rules by applying corrections for certain constitutive effects. For many purposes, however, such corrections are not necessary at all. This is most important as they may undo - or will at least jeopardize - the practical usefulness of an otherwise attractive additive function. Therefore, in general such complicating corrections should be avoided. On the other hand, for constitution analysis deviations from the additivity rules as established for certain model compounds are significant in that they may furnish additional information concerning their structure.

As a rule an additive function as defined by Equation (XI-1) for a given compound is additive on *mixing* as well; that is for a given mixture its value can be calculated by summation of the contributions of the components. Therefore, for a given mixture we have:

$$F = \sum_j X_j F_j, \qquad \text{(XI-2)}$$

where F_j represents the molar additive function of component j and X_j denotes its *molar* fraction. It should be noted, however, that Equation (XI-2) is not necessarily implied by Equation (XI-1). In fact, on mixing components of strongly different chemical constitution considerable deviations from Equation (XI-2) may be observed as a result of the interaction of the divergent molecules.

Instead of the molar function F the corresponding *specific* function $f = F/M$, where M is the molecular weight, is frequently employed. If Equation (XI-2) is valid, it can readily be derived that for a given mixture f can be calculated from the equation:

$$f = \sum_j x_j f_j, \qquad \text{(XI-3)}$$

where f_j represents the specific function of component j and x_j its *weight* fraction. An important advantage of Equation (XI-3) over Equation (XI-2) is that the molecular weight is not involved.

Such specific functions f are often of the form:

$$f = \frac{f'}{d}, \qquad \text{(XI-4)}$$

where d represents the density and f' denotes a simple function of a particular physical constant (or this physical constant itself). For a given mixture it can be shown that, provided no volume changes ensue from mixing, f' satisfies the equation:

$$f' = \sum_j y_j f'_j, \qquad \text{(XI-5)}$$

where f'_j relates to component j and y_j denotes its *volume* fraction. It would seem that so far the volume additivity of such simple quantities f' has hardly attracted the attention of investigators in this field. In the author's opinion, however, this volume additivity opens up particularly interesting possibilities.

XI. 1. 3. *Previous Investigations*

In view of the foregoing considerations, it is no wonder that numerous painstaking efforts have been carried out to establish a reasonably additive function of viscosity and, notably, density of liquids. Unfortunately, owing to the reputedly complex nature of the viscosity of liquids, unusual difficulties are encountered in trying to establish a viscosity-density function that would be fairly additive[173]. Two interesting studies in this field may be mentioned.

A. SOUDERS'S FUNCTION

Souders's so-called *viscosity-constitutional constant*, I, may be written as[179]:

$$I = M\,\frac{\log\log(10\,\eta) + 2.9}{d}\,, \qquad \text{(XI-6)}$$

where viscosity η is expressed in cP and density d in g/cm^3; further, M denotes again the molecular weight and log stands for the common or Briggsian logarithm, $\log_{10}$. The originator of this empirical function has given a variety of atomic and structural increments for calculating I from the constitution of a particular compound. If the density is known at the temperature involved, the viscosity can be obtained from the calculated I-value.

Souders's study may be considered the first fairly successful attempt to establish a reasonably additive viscosity-density function. His method has revealed some interesting possibilities in this field. For low-viscosity compounds of simple structure it may permit not too rough viscosity predictions. Unfortunately, it has some obvious shortcomings, the most serious one being that it is not reliable enough[81b].

All in all, Souders's method would not seem to offer more than a first approximation to the problem under discussion.

B. THE RHEOCHOR

On the analogy of Sugden's well-known parachor Friend and Hargreaves[180] proposed the *rheochor*, Rh, as an empirical viscosity-density function with additive properties:

$$Rh = M\,\frac{(10\,\eta_b)^{1/8}}{d_b + 2d'_b}\,. \qquad \text{(XI-7)}$$

In this function η_b represents the viscosity, again in cP, at the normal boiling point; d_b and d'_b denote the densities, again in g/cm^3, of the liquid and the vapour, respectively, both taken also at the normal boiling point.

The fact that Friend and Hargreaves had to confine the applicability of the rheochor to the boiling point - where the viscosities are quite low and not very divergent - forms a good indication of the difficulties encountered in trying to develop an additive viscosity-density function. These authors have also provided a list of increments for calculating rheochor values from the constitution of the liquids involved. If the appropriate densities of the liquid and the vapour*) are known, a fair estimate of the boiling-point viscosities can thus be made.

But actually the rheochor constitutes an even rougher approximation to the present problem than Souders's function[81b]. Last but not least, the practical - and possibly theoretical - usefulness of the rheochor is very limited by the proviso that it be employed only at the normal boiling-point temperature.

Notwithstanding the merits of the two aforementioned and many further attempts to derive a satisfactorily additive viscosity-density function, it is only fair to say that as yet much work remains to be done.

XI. 1. 4. *The Present Approach*

From the above considerations it will be clear that the present approach to the correlation of the viscosity grade of liquids, notably mineral oils and pure hydrocarbons, with their chemical constitution and physical constants has been concentrated primarily on the search for a satisfactorily *additive viscosity-density function.*

Some preliminary trials suggested that this search could be suitably based on a kind of *reduced* viscosity rather than on the viscosity (grade) itself. It is important to note that the particular form of reduced viscosity utilized in the further trials is identical to the one - defined in § III. 1. 3 - which has already proved highly fruitful for evaluating both the temperature and pressure dependence of the viscosity of liquids, especially the lubricating oils most frequently employed in current practice.

Although the present approach should be deemed only a first cautious step on somewhat slippery ground, the author believes that along the above lines he has indeed succeeded in establishing a really sufficiently additive viscosity-density function. The new, empirically derived, function is denoted as the *"viscochor"*. It is thought to be at least on a par with most of the well-known additive functions devised for physical properties such as density and refractive index which have proved to lend themselves much better to such an approach.

Various applications - particularly in the field of hydrocarbon liquids, including the complex mixtures represented by mineral oils - are described to testify to the convenience and versatility of the viscochor concept.

XI. 2. THE VISCOCHOR - AN ADDITIVE VISCOSITY-DENSITY FUNCTION

As a result of various attempts the following relationship between

*) Actually, the density of the vapour may well be neglected against that of the liquid.

viscosity η, in cP, and density d, in g/cm^3, has finally been established as a really satisfactory additive viscosity-density function:

$$\Psi = M\,\frac{(\log\eta + 1.200)^{1/8}}{d}\,. \qquad \text{(XI-8)}$$

It is suggested to call this new function the (molar) *"viscochor"*. It has the dimension of a molar volume and is expressed in cm^3/gmole.

Accordingly, the quantity:

$$\psi = \frac{(\log\eta + 1.200)^{1/8}}{d} \qquad \text{(XI-9a)}$$

represents the *specific* viscochor. It has the dimension of a specific volume and is expressed in cm^3/g.

The dimensionless function (log η + 1.200)$^{1/8}$ is thus seen to constitute the appropriate volume-additive quantity denoted by f' in Equation (XI-4). For simplicity the latter function will be represented below by the symbol h, so that we may write:

$$\psi = \frac{h}{d}\,. \qquad \text{(XI-9b)}$$

The viscochor has been derived for the aforementioned standard reference temperature of 40 °C (104 °F). Throughout this chapter viscochor values invariably refer to the latter standard condition, although, for convenience, this has usually not been indicated in the relevant expressions. After all, just like many other additive functions, the viscochor normally proves to depend only very little on temperature.

It is important to note that the viscochor has been based on the viscosity function (log η + 1.200), the same function that has been shown to be highly fruitful for evaluating both the temperature and pressure dependence of the viscosity of liquids, notably lubricating oils, in terms of the minimum number of characteristic parameters. Thus, the quantity (log η + 1.200) may well be regarded as a kind of *universal* viscosity function.

As stated in § III.1.3, the constant 1.200 may analytically be put equal to the symbolic expression -log η_∞, where η_∞ represents the viscosity, also in cP, that would be reached when extrapolating analytically to infinite temperature. Accordingly, this fictitious viscosity, amounting to η_∞ = = 0.0631 cP, would be common to all liquids. The viscosity function (log η + 1.200) may therefore be rewritten as log (η/η_∞), so that actually it involves a kind of reduced viscosity, namely the ratio of the viscosity η, at an arbitrary temperature, to the viscosity at infinite temperature, η_∞.

The regularities between viscosity and density observed in homologous series of *hydrocarbons* have given birth to the above-defined viscochor expression. Accurate data on the following series have been taken as a starting-point: n-paraffins, n-α-alkenes, n-alkylcyclopentanes, n-alkylcyclohexanes and n-alkylbenzenes.

Besides a characteristic *basic* structure, denoted by RH, these series have a straight chain of methylene (CH$_2$-) groups. Schematically their structure may thus be represented by:

$$R - (CH_2)_k - H, \qquad \text{(XI-10)}$$

where k denotes the number of methylene groups in a given molecule. For the n-paraffins, for example, R stands for a terminal methyl (CH_3-) group.

For hydrocarbons which possess a common number of methylene groups (common k-value) but belong to different homologous series (different terminal group R) conforming to the above Scheme (XI-10), the properties become more similar the longer their methylene chain. In the limiting case of an infinitely long methylene chain, that is for $M = \infty$, the members of all such series would display identical properties.

For any member of a homologous series conforming to Scheme (XI-10) the molar additive function Ψ - and likewise any other molar additive function - may be represented by:

$$\Psi = M\psi = k\Psi_{CH_2} + \Psi_{RH}\,, \qquad \text{(XI-11)}$$

where Ψ_{CH_2} and Ψ_{RH} denote the increments of the methylene group and the basic structure RH, respectively. Thus, Ψ_{RH} comprises the contributions of all atoms or groups that are not incorporated into the methylene chain.

The corresponding molecular weights M can be written as:

$$M = 14.026\ k + M_{RH}, \qquad \text{(XI-12)}$$

where 14.026 represents the group weight of a CH_2-group and M_{RH} the group weight of the RH-group. Combination of Equations (XI-11) and (XI-12) leads to the following expression for the specific viscochor of the members of the homologous hydrocarbon series considered:

$$\psi = \frac{\Psi_{CH_2}}{14.026} + \frac{\Psi_{RH} - M_{RH}\left(\dfrac{\Psi_{CH_2}}{14.026}\right)}{M}\,. \qquad \text{(XI-13a)}$$

For the members of a particular series Equation (XI-13a) may be rewritten as:

$$\psi = \psi_i + \frac{C_\psi}{M}\,. \qquad \text{(XI-13b)}$$

In the latter expression ψ_i denotes the limiting value of ψ, that is the viscochor that would be obtained by extrapolating analytically to $M = \infty$, or $1/M = 0$; it should be noted that ψ_i has one single value for all the series conforming to Scheme (XI-10). Further, the parameter C_ψ, expressed in $cm^3/gmole$, assumes a characteristic value for each particular series.

Consequently, plotting ψ against $1/M$ for all the members of these various homologous series yields a family of straight lines - one straight line for every series - converging towards the point where $1/M = 0$ ($M = \infty$) and, thus, $\psi = \psi_i$. The slopes of these lines are defined by the parameter C_ψ.

TABLE XI-1

Data on Pure Hydrocarbons

Hydrocarbon Compound	Physical Constants			Derived Quantities		
	$\eta_{40°C}$, cP	$d_{40°C}$, g/cm^3	M, calc	$h_{40°C}$	$\psi_{40°C}$, cm^3/g	$10^3/M$
n-Paraffins						
C_{15}	1,900	0,7545	212,406	1,0501	1,3917	4,71
C_{16}	2,25	0,7597	226,432	1,0563	1,3906	4,42
C_{17}	2,65	0,7643	240,458	1,0624	1,3899	4,16
C_{18}	3,09	0,7684	254,484	1,0678	1,3896	3,93
C_{19}	3,59	0,7720	268,510	1,0728	1,3897	3,72
C_{20}	4,16	0,7754	282,536	1,0777	1,3899	3,54
n-α-Alkenes						
C_{15}	1,70	0,7623	210,390	1,0457	1,3719	4,75
C_{16}	2,02	0,7671	224,416	1,0524	1,3718	4,45
C_{17}	2,38	0,7712	238,442	1,0586	1,3726	4,19
C_{18}	2,79	0,7749	252,468	1,0643	1,3736	3,96
C_{19}	3,26	0,7781	266,494	1,0697	1,3748	3,75
C_{20}	3,77	0,7812	280,520	1,0744	1,3752	3,56
n-Alkylcyclo-pentanes						
C_{15}	2,37	0,7968	210,390	1,0584	1,3285	4,75
C_{16}	2,81	0,7994	224,416	1,0645	1,3315	4,75
C_{17}	3,29	0,8018	238,442	1,0699	1,3343	4,19
C_{18}	3,83	0,8039	252,468	1,0750	1,3372	3,96
C_{19}	4,43	0,8058	266,494	1,0796	1,3399	3,75
C_{20}	5,08	0,8076	280,520	1,0839	1,3422	3,56
C_{21}	5,80	0,8092	294,546	1,0880	1,3444	3,40
n-Alkylcyclo-hexanes						
C_{15}	2,68	0,8027	210,390	1,0628	1,3239	4,75
C_{16}	3,19	0,8052	224,416	1,0689	1,3275	4,45
C_{17}	3,76	0,8073	238,442	1,0744	1,3309	4,19
C_{18}	4,38	0,8091	252,468	1,0793	1,3340	3,96
C_{19}	5,08	0,8108	266,494	1,0839	1,3369	3,75
C_{20}	5,85	0,8124	280,520	1,0882	1,3394	3,56
C_{21}	6,69	0,8138	294,546	1,0992	1,3422	3,40
C_{22}	7,61	0,8151	308,572	1,0959	1,3446	3,24
n-Alkylbenzenes						
C_{15}	2,08	0,8414	204,342	1,0535	1,2521	4,90
C_{16}	2,46	0,8412	218,368	1,0598	1,2591	4,58
C_{17}	2,89	0,8411	232,394	1,0655	1,2669	4,30
C_{18}	3,37	0,8411	246,420	1,0708	1,2732	4,06
C_{19}	3,91	0,8411	260,446	1,0757	1,2790	3,84
C_{20}	4,51	0,8411	274,472	1,0802	1,2844	3,64
C_{21}	5,18	0,8410	288,498	1,0845	1,2895	3,47
C_{22}	5,92	0,8410	302,524	1,0886	1,2944	3,31

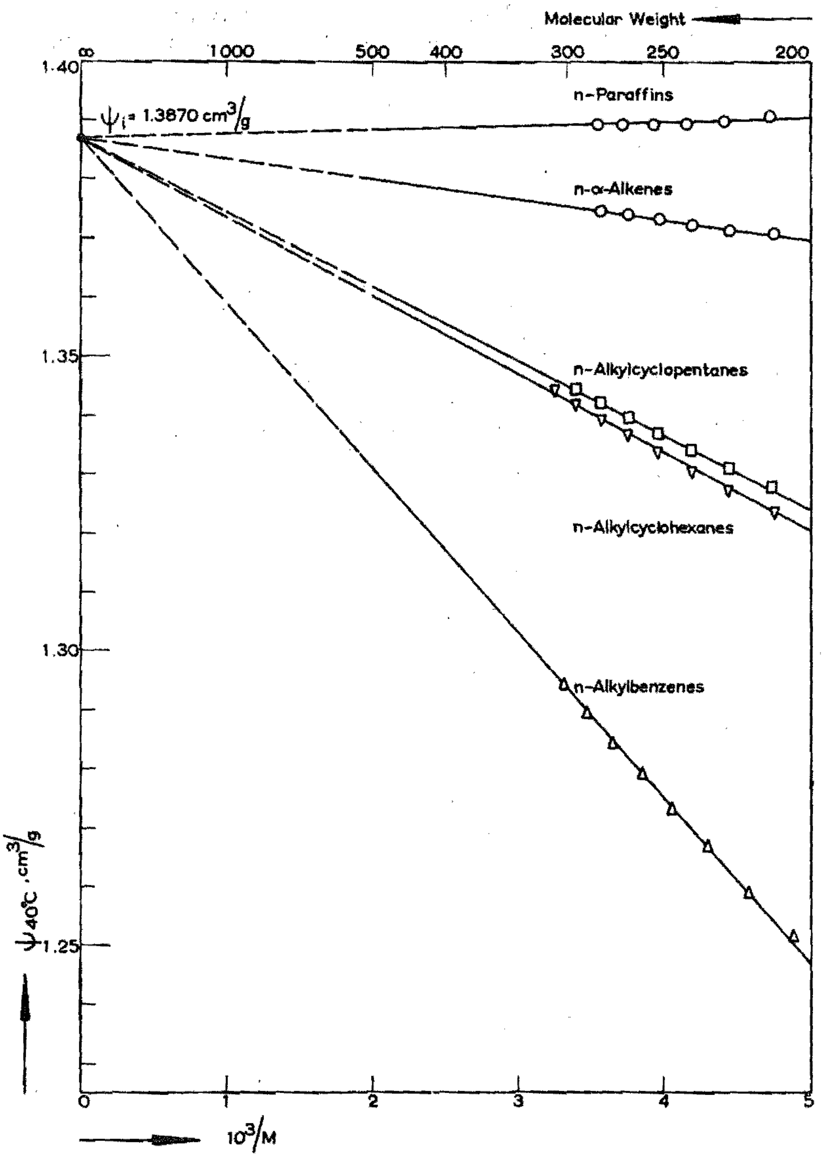

FIG. XI-1.
Specific Viscochors of Homologous Series of n-Alkylhydrocarbons.

Once the values of ψ_i and C_ψ have been determined, the values of the increments Ψ_{CH_2} and Ψ_{RH} can readily be obtained from the following equations, respectively:

$$\Psi_{CH_2} = 14.026\ \psi_i \tag{XI-14}$$

and

$$\Psi_{RH} = C_\psi + M_{RH}\ \psi_i . \tag{XI-15}$$

In accordance with the preceding considerations the ψ-values of various members of the five aforementioned homologous series have been plotted in Fig. XI-1 against their reciprocal molecular weights. In fact, in so far as their molecular weights exceed the value 200 (see below) all members on which accurate data are available[77] have been included in the latter figure; the pertinent data*) are compiled in Table XI-1. Fig. XI-1 demonstrates that all these data do conform very well to Equation (XI-13b). The limiting value of the specific viscochor has been found to amount to $\psi_i = 1.3870$ cm^3/g.

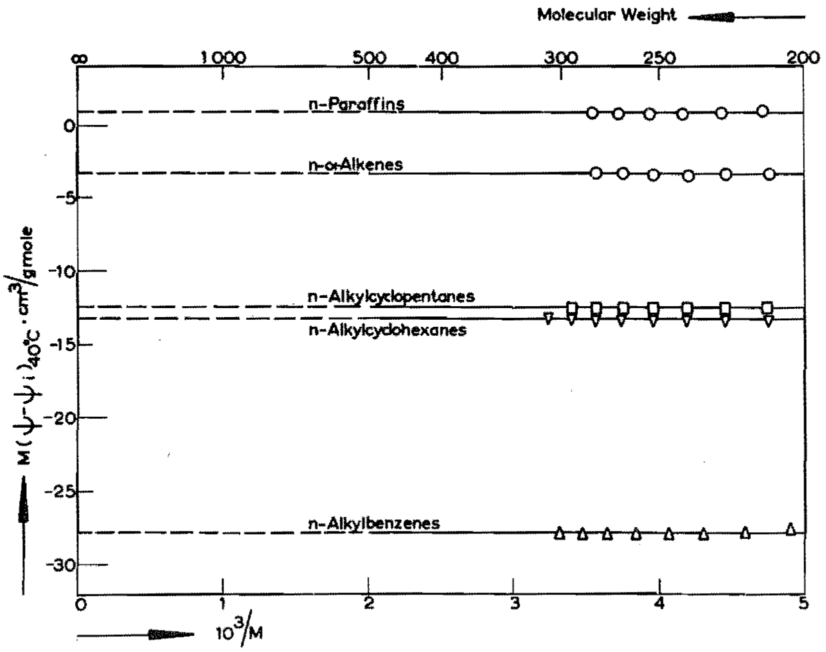

FIG. XI-2.
Specific Viscochor and Molecular Weight in Homologous Hydrocarbon Series According to Fig. XI-1.

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*) For the n-alkylcyclopentanes, n-alkylcyclohexanes and n-alkylbenzenes the densities at 40°C listed in Table XI-1 have been obtained by linearly extrapolating from the experimental values at 20 and 25°C.

Of particular importance - primarily with a view to possible analytical applications - is the relatively wide spread of ψ-values between the various series depicted. The latter feature is brought out even more clearly by Fig. XI-2, where for all the hydrocarbons included in Fig. XI-1 the values of the quantity $M(\psi - \psi_i)$ have been plotted against the reciprocal values of their molecular weights. In accordance with Equation (XI-13b) the relationships depicted in Fig. XI-2 are substantially independent of the molecular weight, so that they are represented by horizontal lines. Further, it is seen that the characteristic ordinates of these horizontal lines must be identical to the slopes, C_ψ, of the corresponding straight lines depicted in Fig. XI-1. The values determined for the slope C_ψ of the five homologous hydrocarbon series under consideration are listed in Table XI-2.

TABLE XI-2

Numerical Values for C_ψ and C_v of Pure-Hydrocarbon Series at 40°C

Series	C_ψ, $cm^3/gmole$	C_v, $cm^3/gmole$
n-Paraffins	0.84	29.00
n-α-Alkenes	-3.30	25.95
n-Alkylcyclopentanes	-12.44	14.20
n-Alkylcyclohexanes	-13.20	12.20
n-Alkylbenzenes	-27.86	0.33

Furthermore, a most remarkable feature of the viscochor consists in that it can reproduce the involved viscosities with a relatively great accuracy. The subsequent data on the series of the n-paraffins may be considered representative examples for illustrating this accuracy. First, their ψ-values have been computed from Equation (XI-13b), utilizing the aforementioned values for ψ_i and C_ψ. Next, their viscosities have been calculated from the latter ψ-values by substituting the appropriate experimental densities. The results of these calculations are collected in Table XI-3 (all data taken again at 40°C).

Table XI-3 shows that the average deviation between calculated and experimental viscosities amounts to less than 1%, which is excellent. For the remaining series the deviations are of the same order of magnitude.

The latter feature is the more striking since the viscosity differences between the various members of such a homologous series are really gigantic as compared with the differences observed for other physical properties, such as density (compare Table XI-1) and refractive index. *Consequently, the viscochor is promising also for predicting viscosities directly from the chemical constitution of a given liquid.*

As stated above, only hydrocarbons with molecular weights above 200, that is those containing more than 14 carbon atoms in their molecules, have been employed in the development of the viscochor.

TABLE XI-3

Experimental and Calculated Specific Viscochors and Viscosities of n-Paraffins at 40°C

n-Paraffin	ψ_{exp}, cm^3/g	ψ_{calc}, cm^3/g	η_{exp}, cP	η_{calc}, cP	$\%\delta\eta$*)
C_{15}	1.3917	1.3910	1.900	1.875	-1.4
C_{16}	1.3906	1.3907	2.25	2.24	-0.2
C_{17}	1.3899	1.3905	2.65	2.68	1.4
C_{18}	1.3896	1.3903	3.09	3.14	1.6
C_{19}	1.3897	1.3901	3.59	3.62	0.7
C_{20}	1.3899	1.3900	4.16	4.17	0.2

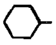
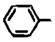
*) $\%\delta\eta = 100 \dfrac{\eta_{calc} - \eta_{exp}}{\eta_{exp}}$

The basic reason is that for lower members of the various series considered the deviations from the straight-line relationships depicted in Fig. XI-1 may become quite appreciable. After all, similar deviations are normally observed for other additive properties, such as the specific volume.

Nevertheless, with some minor changes in the location of the straight lines depicted in Fig. XI-1 several members with molecular weights considerably below 200 could still have been included. It has been preferred, however, to evaluate the numerical constants in the viscochor Equation (XI-13b) on the basis of the higher members of the various homologous series considered in order to obtain a better concurrence with the observations made on important hydrocarbon products encountered in practice, notably mineral oils in the lubricating-oil range[50].

TABLE XI-4

Tentative Viscochor Increments for Hydrocarbons

Atom or Group	Formula	$\Psi_{40^\circ C}$, $cm^3/gmole$
Methylene Group	$-CH_2-$	19.454
Terminal Hydrogen Atom	H-	1.82
Terminal Methyl Group	CH_3-	21.27
Terminal Ethylene Group	$CH_2=CH-$	33.91
Terminal Cyclopentyl Group		83.01
Terminal Cyclohexyl Group		101.70
Terminal Phenyl Group		78.66

Finally, Table XI-4 shows a few tentative viscochor increments derived by means of Equations (XI-14) and (XI-15). The calculations are based on the value $\psi_i = 1.3870$ cm³/g and the C_ψ-values listed in Table XI-2 for the five series under consideration.

Viscochors of Dimethylsiloxanes

It has just been shown how the viscochor expression could be derived from appropriate data on members of homologous series of hydrocarbons. Members of the very interesting class of the dimethylsiloxanes may serve to illustrate that the applicability of the viscochor - like that of other additive functions - is not at all confined to hydrocarbons. Members of both the *linear* and the *cyclic* series of dimethylsiloxanes have been included.

The usual system of abbreviation is employed for representing the structures of these compounds. The monofunctional terminal group $(CH_3)_3SiO_{\frac{1}{2}}$ is termed an M-unit, whilst the difunctional repetitive group $(CH_3)_2SiO$ is termed a D-unit. In this notation linear and cyclic dimethylsiloxanes have the formulas M_2D_n (or MD_nM) and D_n, respectively, where the subscript n denotes the number of D-units occurring in a given compound.

TABLE XI-5

Data on Linear and Cyclic Dimethylsiloxanes

Dimethylsiloxane Compound	Physical Constants			Derived Quantities	
	$\eta_{40°C}$, cP	$d_{40°C}$, g/cm³	M, calc	$\psi_{40°C}$, cm³/g	10³/M
Linear Series					
M_2D_2	1.050	0.8333	310.58	1.2304	3.22
M_2D_3	1.439	0.8552	384.71	1.2148	2.60
M_2D_4	1.875	0.8709	458.84	1.2051	2.18
M_2D_5	2.30	0.8821	532.96	1.1986	1.88
M_2D_6	2.77	0.8909	607.09	1.1943	1.65
Cyclic Series					
D_5	2.83	0.9358	370.64	1.1377	2.70
D_6	4.84	0.9447	444.77	1.1458	2.25
D_7	7.19	0.9503	518.90	1.1515	1.93

In Fig. XI-3 are plotted the ψ-values against the reciprocal molecular weights for some members of both series for which reliable data are available in the literature146); the pertinent data*) are compiled in Table XI-5. Just as with the homologous hydrocarbon series of Fig. XI-1, the data of both siloxane series plotted in Fig. XI-3 conform very well to the straight lines depicted. However, in contrast to these hydrocarbon series - which have a straight methylene chain

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*) The densities at 40°C listed in Table XI-5 have been calculated from the experimental values at 20°C, using the thermal-expansion coefficients reported in Reference 181.

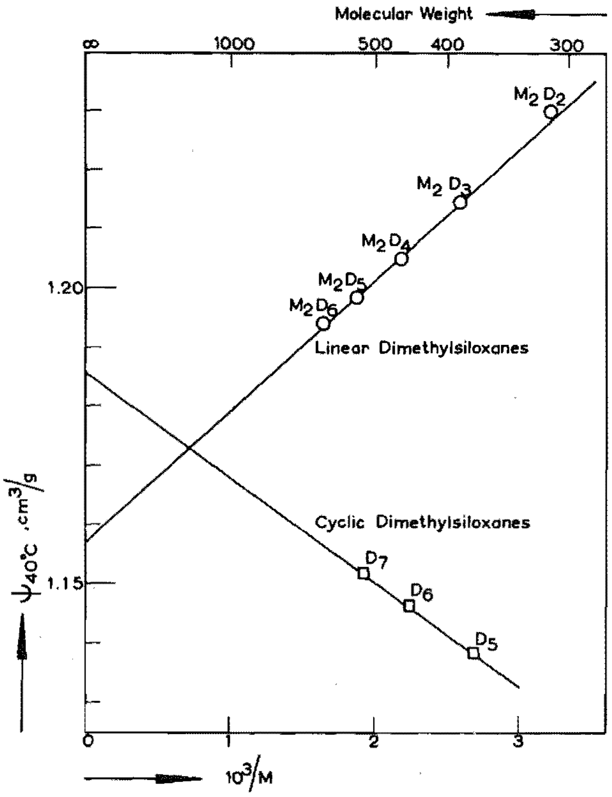

FIG. XI-3.
Specific Viscochors of Linear and Cyclic Dimethylsiloxane Series.

in common -, the linear and cyclic dimethylsiloxane series display different values for ψ_i, the limiting value of ψ. This accrues from the fact that for the linear series ψ_i relates to a D-unit in *chain* structure but for the cyclic series to a D-unit in *ring* structure.

For the *linear* dimethylsiloxanes Equation (XI-13b) has been found to read:

$$\psi = 1.1569 + \frac{22.28}{M}. \qquad \text{(XI-13c)}$$

For the *cyclic* series quite different numerical constants have been obtained, namely:

$$\psi = 1.1856 - \frac{17.75}{M}. \qquad \text{(XI-13d)}$$

On the basis of Equations (XI-13c) and (XI-13d) a few tentative viscochor increments, listed in Table XI-6, have been calculated according to the above-specified procedure.

TABLE XI-6

Tentative Viscochor Increments for Dimethylsiloxanes

Group	$\Psi_{40^\circ C}$, cm^3/gmole
Terminal M-Unit	105.03
D-Unit in Chain Structure	85.76
D-Unit in Ring Structure	87.89

XI. 3. DERIVED RELATIONSHIPS BETWEEN VISCOSITY AND OTHER PHYSICAL CONSTANTS

XI. 3. 1. *Introduction*

An interesting feature of additive functions, applying to both their molar and their specific version, consists in that in a given homologous series they are linearly interrelated. This holds for any homologous series, irrespective of the particular type, as long as the functions considered are indeed satisfactorily additive. Therefore, by combining functions of various physical constants useful relationships between the involved physical constants can readily be obtained.

These things will be exemplified for the homologous series of hydrocarbons conforming to the particular Scheme (XI-10), by combining the newly developed viscochor with one of the best-known additive functions, the molar volume, V. In this case the resulting combination offers particularly interesting possibilities, since the molar volume is contained already in the expression for the viscochor.

For any member of such series of hydrocarbons the molar volume, V, in cm^3/gmole, may be expressed by an equation similar to Equation (XI-11) for the viscochor, namely:

$$V = kV_{CH_2} + V_{RH} , \qquad \text{(XI-16)}$$

where V_{CH_2} and V_{RH} denote the increments of the methylene group and the basic structure RH, respectively. Now, by eliminating the constant k from Equations (XI-11) and (XI-16) one arrives at the following linear relationship between Ψ and V in a given homologous series:

$$\Psi = \frac{\Psi_{CH_2}}{V_{CH_2}} V + \left(\Psi_{RH} - \frac{\Psi_{CH_2}}{V_{CH_2}} V_{RH} \right) . \qquad \text{(XI-17)}$$

It may be repeated that similar linear relationships between additive functions can be derived for *any* homologous series as long as their functions behave satisfactorily additive. For convenience, however, the derivation of the particular linear relationship between Ψ and V has been confined to hydrocarbons conforming to the widely valid structural Scheme (XI-10).

Likewise it can easily be proved that equations of the type of Formula (XI-13b), representing the relationship between a particular *specific* additive function and the molecular weight of the members of a homologous series, are generally applicable. Accordingly, for the specific volume v, in cm^3/g, one may write:

$$v = v_i + \frac{C_v}{M}, \qquad \text{(XI-18)}$$

where v_i denotes the limiting value of v, that is the specific volume that would be reached by extrapolating analytically to $M = \infty$; further, C_v, in $cm^3/gmole$, is a parameter characteristic of a given series.
It is readily seen that by eliminating M from Equations (XI-13b) and (XI-18) the following linear relationship - analogous to the preceding Relationship (XI-17) for the *molar* functions Ψ and V - between the *specific* functions ψ and v can be derived:

$$\psi = \frac{C_\psi}{C_v} v + \left(\psi_i - \frac{C_\psi}{C_v} v_i\right). \qquad \text{(XI-19)}$$

XI. 3. 2. *Viscosity and Density in Homologous Series*

Equation (XI-19) can readily be rewritten as a linear expression between the viscosity function h and *density*, d:

$$h = \left(\psi_i - \frac{C_\psi}{C_v} v_i\right) d + \frac{C_\psi}{C_v}. \qquad \text{(XI-20)}$$

In order to obtain numerical values for the parameters v_i and C_v of Equation (XI-18) the specific volumes of all the hydrocarbons included in Table XI-1 have been plotted against their reciprocal molecular weights. From the resulting plot the limiting specific volume v_i was found to amount to $v_i = 1.1875$ cm^3/g ($d_i = 0.8421$ g/cm^3); the C_v-values derived for the various series are listed, together with their C_ψ-values, in the preceding Table XI-2.
From the value established for ψ_i in Section XI. 2 it follows that $h_i v_i$ $(=\psi_i) = 1.3870$ cm^3/g. Using the value just derived for v_i, it is found that $h_i = 1.1680$. Consequently, for the hydrocarbons considered the viscosity at infinite molecular weight should amount to $\eta_i = 183.7$ cP.
Finally, substitution of the aforementioned values for the various parameters of Equation (XI-20) has led to the numerical relationships between h and d defined in Table XI-7 (again at the standard reference

temperature of 40 °C).

TABLE XI-7

Numerical Constants for the Viscosity-Density Relationship of Pure-Hydrocarbons Series

Series	Numerical Constants of Equation (XI-20) at 40°C	$VDQ_{40°C}$, g/cm^3
n-Paraffins	h = 1.3526 d + 0.0290	0.7393
n-α-Alkenes	h = 1.5380 d - 0.1272	0.6502
n-Alkylcyclopentanes	h = 2.4274 d - 0.8761	0.4120
n-Alkylcyclohexanes	h = 2.6719 d - 1.0820	0.3743
n-Alkylbenzenes	h = 101.64 d - 84.42	0.0098

Fig. XI-4 depicts the latter relationships as a family of straight lines emanating from the point where $d = d_i = 0.8421$ g/cm^3 and $h = h_i = 1.1680$. The experimental data are seen to fit these lines excellently, even though the underlying Equation (XI-20) has been derived by combining two equations which constitute approximations already by themselves.

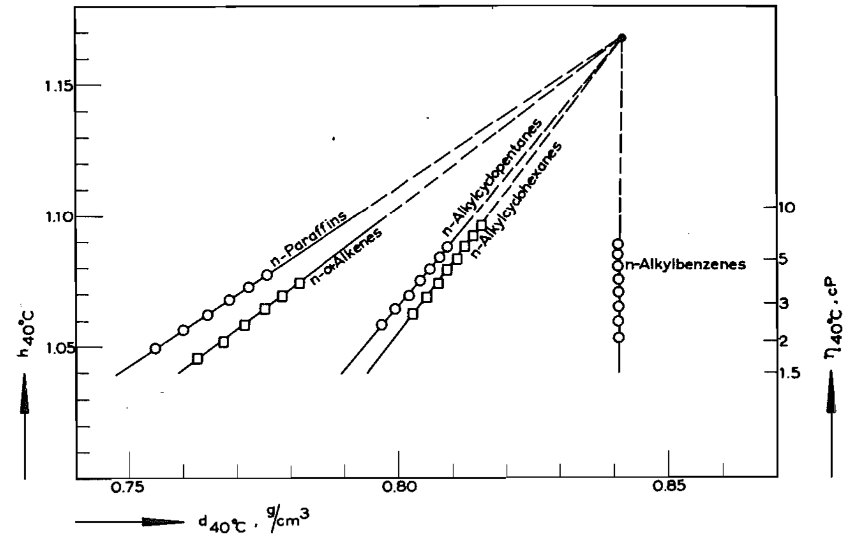

FIG. XI-4.
Viscosity-Density Relationships in Homologous Series of n-Alkylhydrocarbons.

The *slopes* of the lines depicted in Fig. XI-4 are characteristic of a given homologous series. For practical reasons it is preferred to consider the reciprocal values of these slopes. It is suggested to call the consequent function the *"Viscosity-Density Quotient"*, abbreviated by VDQ. This is seen to be defined by:

$$\mathrm{VDQ} = \frac{\Delta d}{\Delta h} = \frac{d_i - d}{h_i - h}. \qquad \text{(XI-21)}$$

For the five homologous series under discussion the VDQ's are listed in Table XI-7.

XI. 3. 3. *Viscosity and Molecular Weight in Homologous Series*

The relationship between the viscosity grade and the *molecular weight* of members of homologous series has been studied by many investigators. A chronological record of the more important analytical expressions for describing this relationship has been given by, amongst others, Doolittle[182].

Amongst the expressions defining the viscosity grade, η_r, directly in terms of the molecular weight the best-known is probably that proposed, as early as 1909, by Dunstan and Thole:

$$\log \eta_r = c_1 M + c_2, \qquad \text{(XI-22)}$$

where c_1 and c_2 are parameters characteristic of a given series. Although this empirical equation has been very widely employed, its quantitative applicability has proved very limited.

A more recent equation has been developed - likewise empirically - by Doolittle[182]:

$$\log \eta_r = k_1 e^{(k_2/M^{\frac{1}{4}})} + k_3, \qquad \text{(XI-23)}$$

where the *three* parameters k_1, k_2 and k_3 are characteristic of a given series. Equation (XI-23) is claimed to fit the data much better than the conventional equations. However, it has the serious drawback that it is rather unwieldy for practical applications.

Now, by eliminating the specific volume, v, from the preceding Equations (XI-13b) and (XI-18) a comparatively simple relationship between the viscosity function h and the molecular weight can readily be obtained, namely:

$$h = h_i + \frac{\dfrac{C_\psi}{v_i} - \dfrac{h_i}{v_i} C_v}{M + \dfrac{C_v}{v_i}} \qquad \text{(XI-24a)}$$

or, in abbreviated form:

$$h = h_i - \frac{A_h}{M + B_h}, \qquad \text{(XI-24b)}$$

where the two parameters A_h and B_h are characteristic of a given homologous series.

Confining oneself to the five homologous hydrocarbon series under consideration, the aforementioned values of the quantities h_i and v_i can be substituted into Equation (XI-24a). Thus, for these series Equations (XI-24a) and (XI-24b) may be reduced to, respectively:

$$h = 1.1680 + \frac{0.8421\ C_\psi - 0.9836\ C_v}{M + 0.8421\ C_v} \qquad \text{(XI-25a)}$$

and

$$h = 1.1680 - \frac{A_h}{M + B_h}\ . \qquad \text{(XI-25b)}$$

Furthermore, by substituting the above-specified values for the parameters C_ψ and C_v (see Table XI-2) into Equation (XI-25a) the quantities A_h and B_h appear to assume the values listed, for the five series considered, in Table XI-8.

TABLE XI-8

Numerical Values for A_h and B_h of Pure-Hydrocarbon Series at 40°C

Series	A_h, g/gmole	B_h, g/gmole
n-Paraffins	-27.82	24.42
n-α-Alkenes	-28.30	21.85
n-Alkylcyclopentanes	-24.44	11.96
n-Alkylcyclohexanes	-23.12	10.27
n-Alkylbenzenes	-23.79	0.28

Rewriting Equation (XI-25b) in the form:

$$\frac{1}{1.1680 - h} = \frac{M}{A_h} + \frac{B_h}{A_h}\ , \qquad \text{(XI-25c)}$$

it is seen that in a chart provided with a viscosity scale proportional to the left-hand side of Equation (XI-25c) and with a linear molecular-weight scale the viscosities and molecular weights of the various members of each of the five hydrocarbon series considered should be located on a straight line. This has been demonstrated in Fig. XI-5. The experimental data prove to conform very well to the straight lines constructed in accordance with Equation (XI-25c), using the values of Table XI-8 for the parameters A_h and B_h of each series.

It may be noted that an even somewhat improved degree of correlation could be achieved by employing newly adjusted, and thus slightly different, values for A_h and B_h. However, in order not to lose the connection with the underlying relationships the above-specified values have been maintained in Fig.XI-5. It is important to realize that the latter values have been derived directly from the *constitution* of the hydrocarbons.

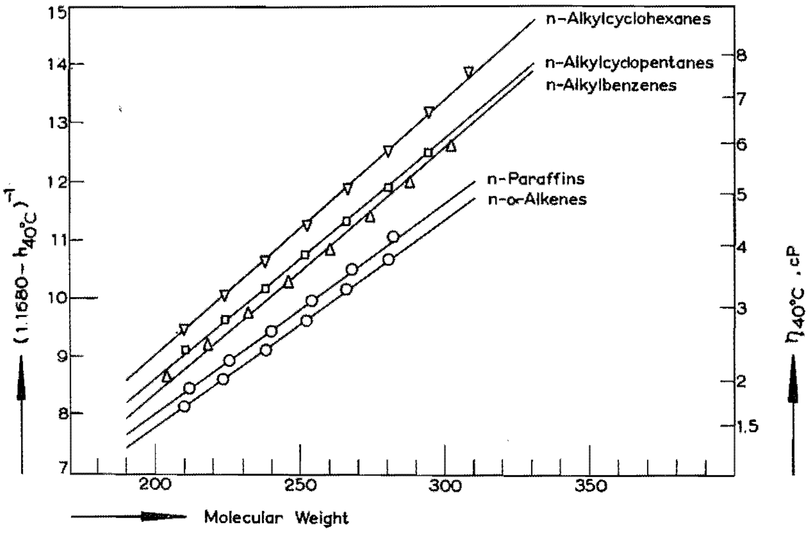

FIG.XI-5.
Viscosity-Molecular Weight Relationships in Homologous Series of n-Alkylhydrocarbons.

It is not the author's intention to present in this context a detailed study of the applicability of the new Equation (XI-24b) to types of liquids quite different from the hydrocarbons here considered, notably to various types of high-polymer compounds. For the time being it may suffice to state that this equation has proved to hold very good for the restricted number of homologous series investigated; it should be added that the latter series include divergent types of liquids and cover a very extensive molecular-weight range.

First of all, the new Equation (XI-24b) is deemed remarkable in that it represents a special case of the well-known *Smittenberg formula*.

Smittenberg, in collaboration with Mulder, has derived the following formula to describe the relationship between a particular physical constant g and the molecular weight, or chain length, of the members of an arbitrary homologous series[183]:

$$g = g_i + \frac{A_g}{M + B_g} , \qquad \text{(XI-26)}$$

where g_i represents the limiting value of g, that is its fictitious value at $M = \infty$. Whilst the parameters A_g and B_g are characteristic of a given series, the value to be assigned to g_i is common to homologous series with the same repetitive unit, such as the n-alkylhydrocarbons comprised by Scheme (XI-10). Except for the lower members, Equation (XI-26) has proved to achieve an excellent concurrence with experimental data for various physical properties, including density, refractive index and ultrasonic sound velocity[50,184,185]. Smittenberg's attractive formula has gained the reputation of combining high reliability with wide applicability. Moreover, it may be deemed very important that it has proved to be closely related to certain theoretically founded expressions. In this connection it should be mentioned that Hubert and Schultze[186] have succeeded in providing a theoretical interpretation of Smittenberg's formula for the densities and refractive indices in the same series of n-alkylhydrocarbons which have been dealt with above.

In view of such previous experiences with Smittenberg's formula for various physical constants, it is considered significant that in the present investigation a similar expression could be derived for a rather complex property as the viscosity. It is especially noteworthy that this expression constitutes only one of the simple outcomes of the newly established viscochor concept.

All in all, it would certainly be worthwhile to exploit further the possibilities and limitations of the new Equation (XI-24b), also for various other types of liquids. In particular the correlation between the values of the characteristic parameters in the latter equation and the constitution of the liquids would deserve nearer investigation.

XI. 4. APPLICATIONS TO MINERAL OILS

XI. 4. 1. *Introduction*

Quite a lot of the liquid products encountered in nature or produced by modern technology represent mixtures of great complexity. The identification of the components is extremely laborious and difficult, if not completely impossible. Obviously, a *practical* characterization of such complex mixtures can no longer be based on all the individual component molecules.

Fortunately, it has proved feasible to treat a mixture built up from molecules with strongly resembling structures as consisting of identical *"average"* molecules representing the average chemical constitution of the mixture. As regards the identification of the average molecule, it is usually sufficient to confine oneself to certain structural groups.

The concept of the average molecule forms the basis of the *"statistical constitution analysis"* introduced by Waterman and his associates (see § II. 2. 2). This is also referred to as, for instance, "graphical-statistical analysis" or "structural-group analysis"[50,42].

Statistical constitution analyses may be carried out most conveniently by utilizing easily measurable physical constants. Besides physical constants as such, in many cases *functions* of physical constants may be used more advantageously. *Additive* functions in particular have proved their value in statistical constitution analysis. Therefore, it will be interesting to exploit some of the possibilities that are opened up in this field by the newly developed additive function of viscosity and density, the viscochor.

In this section attention will be devoted to the very important group of liquids represented by *mineral oils*. These constitute extremely complex mixtures of a great variety of essentially hydrocarbon compounds. Vlugter, Waterman and van Westen have ingeniously solved the problem of characterizing such complex mixtures, in both convenient and significant terms, by considering only three basic structural groups, that is paraffinic chains, naphthenic rings and aromatic rings.

Fully hydrogenated or *saturated* mineral oils represent a somewhat simpler average constitution than natural samples in that the aromatic components of the latter have been converted - through a chemical process - into the corresponding naphthenes. The absence of aromatics renders the saturated mineral oils excellently suitable for serving as basic oils in the development of reliable methods for carrying out a convenient statistical constitution analysis[50,42].

Accordingly, in the present section the application of the viscochor concept will be elucidated primarily for *saturated* mineral oils. It will be demonstrated below how the viscochor concept can be conveniently used for determining the number of naphthenic rings per average molecule, R_N, and the percentage of carbon atoms in naphthenic-ring structure, C_N. Moreover, this concept will be shown to allow good estimates of the average molecular weight of saturated mineral oils.

To include *natural* mineral oils as well as saturated samples it has proved necessary to introduce a *third* physical constant in addition to the viscosity and density contained in the viscochor expression[50,42]. One very convenient way in which this can be performed will be expounded in principle. Again, the methods developed for saturated mineral oils serve as a basis to the scheme applying to natural samples.

Experimental Data

The present findings with saturated mineral oils are based on reliable experimental data on 112 fractions representing a wide variety of origin and chemical constitution. These fractions are designated in Table XI-9*). For further particulars on the oils reference may be made to Chapter II, notably to Table II-1.

Practically all the latter mineral-oil fractions - 105 of them - constitute part of Waterman's collection and have been the subject of extensive investigations of various kinds carried out by Waterman and associates at the Laboratory for Chemical Technology of the Technological University of Delft. The data on the 7 remaining oils derive from Reference 46.

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*) It should be noted that, since these fractions contain no aromatic rings, the quantity R_N is equal to R, the total number of rings per average molecule; further, the quantity C_N is equal to C_R, the total percentage of carbon atoms in ring structure.

TABLE XI-9

Data on Saturated Mineral-Oil Fractions Tested

Oil Code*)	Experimental Data			n-d-M Method		Viscochor Method		
	$\eta_{40^\circ C}$, cP	$\psi_{40^\circ C}$, cm^3/g	M	C_R	R	C_R	R	M
W-1H	1,225	1,3165	166	43	0,9	39	0,8	175
W-2H	1,552	1,3134	185	42	1,0	40	0,9	190
W-3H	2,08	1,3155	201	42	1,1	39	1,0	210
W-4H	2,72	1,3198	235	36	1,1	37	1,0	225
W-5H	3,90	1,3241	247	37	1,2	35	1,1	255
W-6H	5,27	1,3259	275	36	1,3	34	1,2	275
WR-7H	7,96	1,3236	304	34	1,4	35	1,3	305
W-8H	11,12	1,3293	344	33	1,6	33	1,5	335
W-9H	19,06	1,3302	381	34	1,8	33	1,7	380
W-10H	1,306	1,2659	174	62	1,5	62	1,4	170
W-11H	1,521	1,2609	181	63	1,6	64	1,6	170
W-12H	1,742	1,2559	184	64	1,7	67	1,7	175
W-13H	2,02	1,2520	186	67	1,8	68	1,8	180
W-14H	2,29	1,2498	192	67	1,8	69	1,9	185
W-15H	2,70	1,2467	195	69	1,9	71	2,0	190
W-16H	3,59	1,2458	216	67	2,1	71	2,1	200
W-17H	4,86	1,2401	226	70	2,4	74	2,4	210
WR-18H	7,10	1,2400	238	70	2,5	74	2,5	225
W-19H	12,85	1,2429	266	70	2,9	73	2,9	250
W-20H	35,6	1,2516	310	70	3,4	69	3,5	295
W-21H	1,180	1,3218	179	34	0,8	36	0,8	175
W-22H	1,500	1,3168	198	36	0,9	39	0,9	190
W-23H	2,19	1,3103	221	40	1,1	42	1,1	210
W-24H	3,35	1,3059	239	43	1,4	44	1,3	230
W-25H	5,52	1,3035	263	44	1,6	45	1,6	255
W-26H	10,33	1,3054	301	44	1,9	44	1,9	295
W-27H	20,4	1,3066	342	45	2,3	43	2,2	340
W-28H	39,0	1,3107	395	44	2,6	41	2,6	395
W-29H	1,114	1,2986	164	51	1,0	47	1,0	165
W-30H	1,262	1,2936	168	54	1,2	49	1,1	170
W-31H	1,406	1,2877	173	57	1,2	52	1,2	175
W-32H	1,622	1,2835	178	57	1,3	54	1,3	180
W-33H	1,770	1,2797	186	56	1,4	56	1,4	185
W-34H	2,28	1,2798	197	56	1,5	56	1,5	195
W-35H	3,13	1,2893	217	51	1,5	51	1,5	215
W-36H	10,05	1,3014	310	42	1,9	46	1,9	290
W-37H	1,064	1,3314	164	34	0,7	32	0,7	170
W-38H	1,343	1,3259	175	37	0,8	34	0,8	185
W-39H	1,718	1,3210	199	36	0,9	37	0,9	200
W-40H	2,27	1,3195	219	37	1,0	37	1,0	215
W-41H	3,14	1,3219	240	36	1,1	36	1,0	240
W-42H	4,50	1,3231	277	35	1,2	36	1,2	265
W-43H	6,56	1,3222	300	35	1,4	36	1,3	290
W-44H	18,88	1,3199	380	36	2,0	37	1,9	360
W-45H	0,918	1,3119	170	38	0,8	41	0,8	160

CONTINUATION OF TABLE XI-9

Oil Code*)	Experimental Data			n-d-M Method		Viscochor Method		
	$\eta_{40^\circ C}$, cP.	$\psi_{40^\circ C}$, cm^3/g	M	C_R	R	C_R	R	M
W-46H	0,975	1,3107	179	37	0,8	41	0,8	160
W-47H	1,086	1,3062	176	42	0,9	43	0,9	165
W-48H	1,225	1,3018	179	45	1,0	45	1,0	170
W-49H	1,390	1,2987	185	48	1,1	47	1,1	180
W-50H	1,596	1,2962	193	49	1,2	48	1,2	185
W-51H	1,854	1,2928	200	51	1,3	50	1,3	190
W-52H	2,18	1,2911	209	49	1,4	50	1,3	200
W-53H	2,60	1,2898	219	49	1,5	51	1,4	210
W-54H	3,30	1,2894	227	50	1,6	51	1,5	220
W-55H	4,38	1,2895	251	48	1,7	51	1,7	235
WR-56H	6,50	1,2870	269	49	1,9	52	1,9	250
W-57H	11,62	1,2849	292	52	2,3	53	2,3	280
W-58H	1,194	1,3212	175	37	0,8	37	0,8	175
W-59H	1,337	1,3153	188	37	0,9	39	0,9	180
W-60H	1,528	1,3144	196	37	0,9	40	0,9	190
W-61H	1,702	1,3111	202	40	1,0	41	1,0	195
W-62H	2,02	1,3098	215	40	1,1	42	1,1	205
W-63H	2,37	1,3136	224	39	1,1	40	1,1	215
W-64H	2,85	1,3196	243	35	1,1	37	1,0	230
W-65H	3,52	1,3273	263	32	1,0	34	1,0	250
W-66H	4,49	1,3306	291	29	1,1	32	1,0	270
W-67H	6,15	1,3303	321	30	1,2	32	1,2	290
W-68H	8,87	1,3323	353	30	1,3	31	1,3	320
W-69H	1,563	1,2940	176	55	1,2	49	1,2	185
W-70H	2,81	1,2834	205	55	1,5	54	1,6	210
W-71H	6,12	1,2823	255	53	2,0	54	1,9	245
W-72H	11,17	1,2840	303	50	2,3	54	2,3	280
W-73H	37,2	1,2981	351	50	2,7	47	2,8	365
W-74H	1,092	1,3298	170	32	0,7	33	0,7	175
W-75H	1,291	1,3274	186	31	0,8	34	0,7	185
W-76H	1,377	1,3160	193	35	0,9	39	0,9	185
W-77H	2,10	1,3210	213	36	1,0	37	0,9	210
W-78H	2,81	1,3189	225	39	1,1	38	1,0	230
W-80H	5,69	1,3173	274	39	1,5	38	1,5	270
W-81H	8,61	1,3170	301	39	1,6	39	1,6	300
W-82H	14,86	1,3188	340	38	1,9	38	1,8	340
W-83H	28,2	1,3186	377	40	2,2	38	2,2	385
W-84H	52,8	1,3211	426	41	2,6	37	2,6	445
W-85H	1,143	1,3172	165	42	0,9	38	0,8	170
W-86H	1,358	1,3134	180	41	0,9	40	0,9	180
W-87H	1,710	1,3111	192	43	1,0	41	1,0	195
W-88H	2,28	1,3093	212	44	1,2	42	1,1	210
W-89H	3,16	1,3104	225	45	1,3	42	1,2	230
W-90H	4,49	1,3133	260	40	1,4	40	1,3	250
WR-91H	6,79	1,3113	294	39	1,6	41	1,5	280
W-92H	11,14	1,3121	330	39	1,8	41	1,8	310
W-93H	40,5	1,3159	415	41	2,6	39	2,5	405

CONTINUATION OF TABLE XI-9

Oil Code*)	Experimental Data			n-d-M Method		Viscochor Method		
	η_{40^oC}, cP	ψ_{40^oC}, cm^3/g	M	C_R	R	C_R	R	M
W-94H	0.895	1.3061	149	47	0.9	44	0.9	155
W-95H	1.400	1.3105	196	36	0.9	41	0.9	180
W-96H	1.871	1.3158	206	38	1.0	39	1.0	200
W-97H	2.25	1.3188	219	36	1.0	38	1.0	215
W-98H	2.68	1.3203	222	38	1.1	37	1.0	225
W-99H	3.05	1.3286	240	31	0.9	33	0.9	240
W-100H	3.85	1.3251	255	35	1.1	35	1.1	255
W-101H	4.83	1.3216	277	36	1.3	36	1.2	265
W-102H	6.15	1.3144	285	38	1.5	40	1.4	275
W-103H	7.14	1.3225	301	36	1.5	36	1.4	290
W-104H	8.55	1.3216	309	38	1.5	36	1.5	305
W-105H	14.55	1.3076	322	43	2.0	43	2.0	320
W-106H	15.74	1.3188	400	33	1.9	38	1.8	340
We-1H	72.5	1.3428	513	30	2.5	27	2.4	565
We-2H	55.5	1.3062	417	47	3.0	44	3.0	410
We-3H	80.4	1.2712	350	64	3.6	60	3.8	355
We-4H	71.7	1.3145	430	45	2.9	40	3.0	450
We-5H	54.4	1.3242	450	39	2.7	35	2.6	460
We-6H	39.9	1.3278	425	37	2.4	34	2.3	440
We-7	31.8	1.3381	447	30	1.8	29	1.8	450

*) Refers to similarly coded oils specified in Table II-1.

XI. 4. 2. *Viscochor and Carbon-Type Composition of Saturated Mineral Oils*

In Fig. XI-6 the percentages of carbon atoms in ring structure, C_R, of all the various oils included in Table XI-9 have been plotted against their specific viscochors ψ (still expressed in cm^3/g and taken at the standard reference temperature of 40°C). The resulting figure has led to the very interesting finding that, to a good approximation, the percentage C_R is fixed solely by ψ, the resulting correlation simply being a linear one, namely:

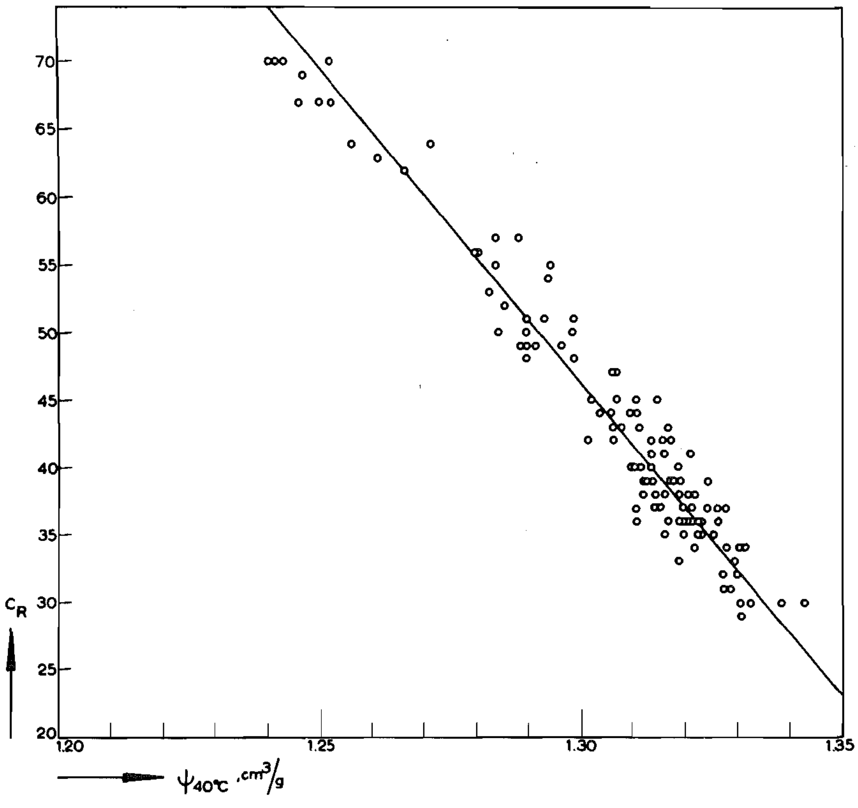

FIG. XI-6.
Correlation Between Carbon-Type Composition and Specific Viscochor of Saturated Mineral Oils.

$$C_R = -463\ (\psi - 1.4000). \qquad \text{(XI-27)}$$

Fig. XI-6 demonstrates the validity of the depicted Correlation (XI-27) in the extensive range of percentages C_R covered by the present oils, that is from about C_R = 25 up to C_R = 75.

The C_R-values of all the various mineral-oil fractions under consideration have been read from a diagram like Fig. XI-6. The readings are collected in the preceding Table XI-9 under the heading "Viscochor Method". In general, the agreement with the listed C_R-values determined by means of the n-d-M method*) may be deemed very good, the average and standard deviations amounting to only 2.0 and 2.4 C_R-units, respectively. Consequently, the specific viscochor permits very simple and reliable estimates of the carbon-type composition of saturated mineral oils.

With most of the previously established specific additive functions, such as the specific refraction, the C_R-values of saturated oils can be determined only if their ***molecular weights*** are also known. The specific viscochor, however, has the basic advantage that it is ***uniquely*** related to these C_R-values.

It should further be mentioned that, owing to the very small temperature dependence of ψ, Correlation (XI-27) may equally be applied at temperatures differing markedly from the present standard reference temperature of 40°C.

Finally, it may be pointed out that, like the n-d-M method, the present method does not allow for any possible effect of branchings in the oil molecules on the resulting composition figures. The following remarks may go to justify this procedure.

For a variety of pure hydrocarbons it was found that, like the introduction of rings, the introduction of simple side-chains generally lowers the viscochor; more complex side-chains, however, may exhibit an opposite effect. Now, the smallness of the observed effects suggests that in the case of mineral oils - which exhibit about the same small degree of branching - the presence of side-chains would hardly affect the differences between the C_R-values predicted by means of the n-d-M and the viscochor method. In fact, this conjecture is directly corroborated by the very good overall agreement between these two independent prediction methods.

The same remarks apply to the estimation of the ring number, R, of mineral oils by means of the related methods to be outlined below.

XI.4.3. *Viscochor and Ring Number of Saturated Mineral Oils*

Assuming six-membered and kata-condensed rings (see § II.2.2), the molecular weight, M, determines the relationship between the percentage C_R and the ring number R of saturated mineral oils. Two equations are required for defining this relationship[50,42]:

$$C_R = 2800\,\frac{3R}{M}\,, \quad \text{for} \quad R \leqslant 1; \qquad \text{(XI-28a)}$$

and

$$C_R = 2800\,\frac{2R+1}{M}\,, \quad \text{for} \quad R \geqslant 1. \qquad \text{(XI-28b)}$$

Combination of the latter two equations with Equation (XI-27) leads

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*) In this connection it may be useful to recall that the n-d-M method is bound to yield approximate - and not necessarily exact - values. Although it is impossible to give exact data for the deviations from the true values, it seems reasonable to allow for deviations of at least 2 C_R-units[50].

to the formulas:

$$\psi = 1.4000 - 6.048 \frac{3R}{M}, \quad \text{for} \quad R \leqslant 1; \qquad \text{(XI-29a)}$$

and

$$\psi = 1.4000 - 6.048 \frac{2R + 1}{M}, \quad \text{for} \quad R \geqslant 1. \qquad \text{(XI-29b)}$$

Consequently, for series of oils with a common ring number the specific viscochor (taken again at 40°C and expressed in cm^3/g) displays a linear relationship with their reciprocal molecular weight, just as found in Section XI.2 for homologous series of pure hydrocarbons (see Fig. XI-1).

Fig. XI-7 depicts the straight lines obtained on plotting ψ against $1/M$, according to Equations (XI-29a) and (XI-29b), for a few distinct R-values. The resulting fan shows a limiting specific viscochor $\psi_l = 1.4000$ cm^3/g, which comes fairly close to the value 1.3870 cm^3/g found above for homologous series of pure hydrocarbons with a straight methylene chain in common (see Fig. XI-1). In addition, Fig. XI-7 has been provided with a linear C_R-scale parallel to the ψ-axis as defined by Equation (XI-27).

XI.4.4. *Derived Viscosity-Density Relationships and Chemical Constitution of Saturated Mineral Oils*

A. CARBON-TYPE COMPOSITION

By substituting Identity (XI-9b) into Equation (XI-27) it follows that for saturated mineral oils characterized by a common percentage C_R the viscosity function h is proportional to their density, d. The resulting equation reads (still at 40°C):

$$h = (-2.160 \cdot 10^{-3}\ C_R + 1.4000)\ d. \qquad \text{(XI-30)}$$

In an h-d chart Equation (XI-30) is depicted as a family of straight lines - each line relating to a distinct C_R-value - emanating from the origin ($d = 0$; $h = 0$). The part of this fan which assumes practical importance - corresponding to C_R-values from 25 to 75 - has been constructed in Fig. XI-8; for comparison broken lines have been included for the (hypothetical) series of oils characterized by $C_R = 0$ and $C_R = 100$.

As regards the suitability of this figure for estimating C_R-values, reference may be made to the aforementioned data on the applicability of the basic Equation (XI-27).

B. RING NUMBER

It will next be elucidated how an h-d chart such as Fig. XI-8 can be conveniently employed also for estimating the ring number, R,

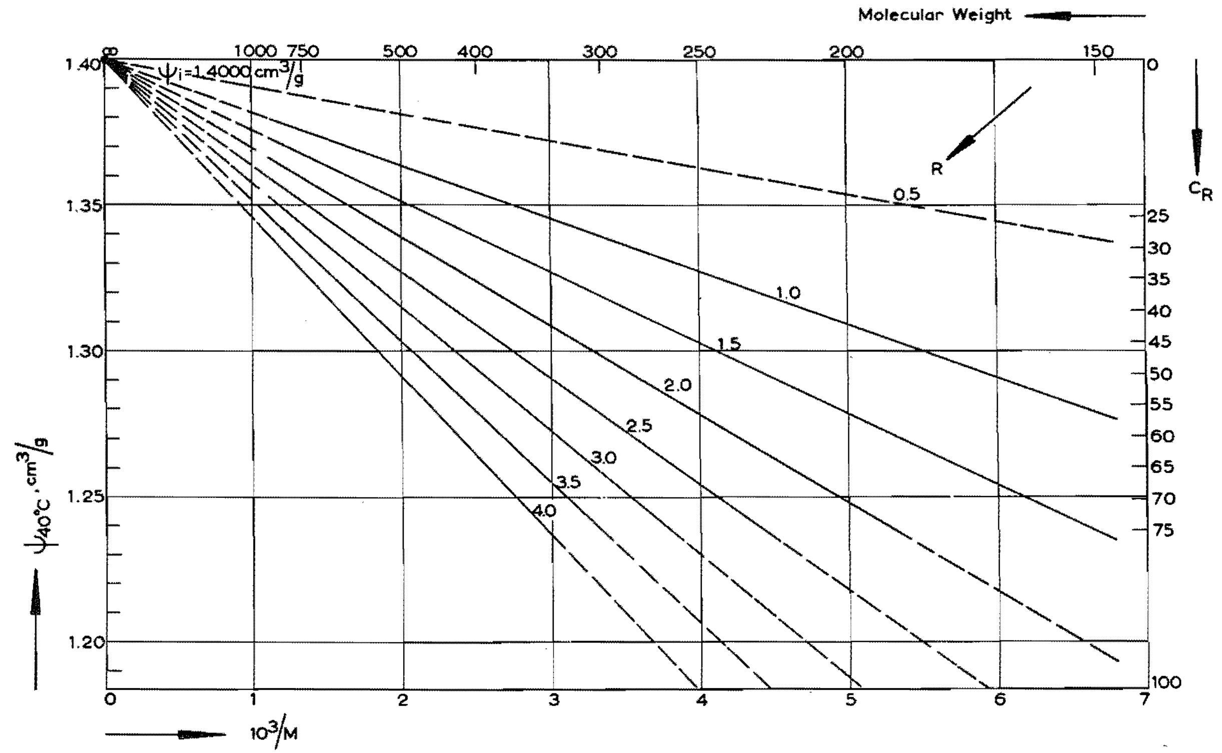

FIG. XI-7.
Correlation Between Ring Number and Specific Viscochor of Saturated Mineral Oils.

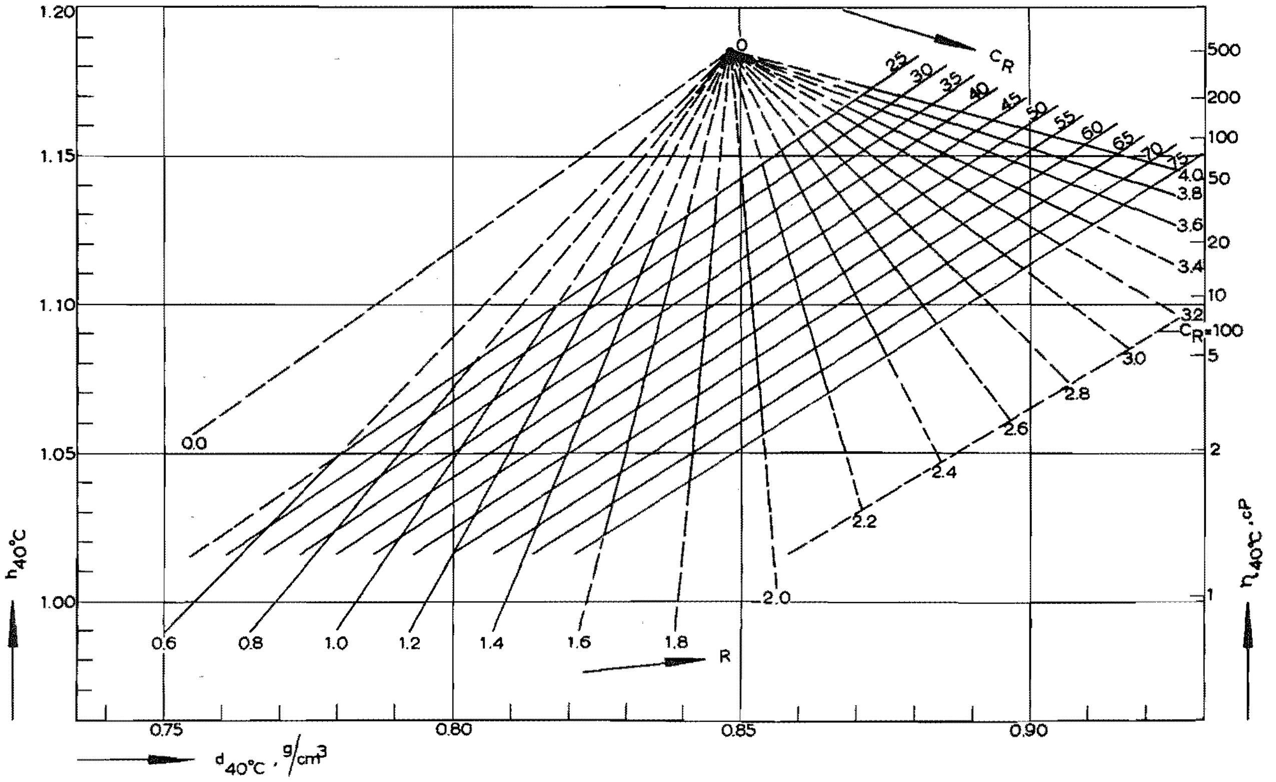

FIG. XI-8.
Chemical Constitution of Suturated Mineral Oils as a Function of Their Viscosity and Density.

of saturated mineral oils.

The author has established empirically that (still at 40°C) the specific volume, in cm^3/g, of saturated mineral oils can be represented very well by the following expression, which is analogous to Equations (XI-29a) and (XI-29b) for the specific viscochor:

$$v = 1.1800 + 16.00 \left(\frac{1.90 - R}{M}\right). \qquad \text{(XI-31)}$$

Thus, for saturated mineral oils characterized by a common ring number the specific volume is related linearly to their reciprocal molecular weight. The same feature is indicated by Equation (XI-18) for homologous series of liquids, notably pure hydrocarbons.

In a plot of v against 1/M Equation (XI-31) is represented by a family of straight lines - each line relating to a distinct R-value - converging towards the point where $1/M = 0$ and $v = v_i = 1.1800$ cm^3/g ($d_i = 0.8475$ g/cm^3)*). This limiting specific volume comes fairly close to the value 1.1875 cm^3/g found above for homologous series of pure hydrocarbons with a straight methylene chain in common.

Now, by combining Equation (XI-31) with Equations (XI-29a) and (XI-29b), respectively, such that M is eliminated the following linear relationships between h and d are obtained for series of saturated mineral oils with a common ring number [compare Equation (XI-20) for homologous series of liquids, notably pure hydrocarbons]:

$$h = \left[1.4000 + 0.4460\left(\frac{3R}{1.90 - R}\right)\right]d - 0.3780\left(\frac{3R}{1.90 - R}\right), \qquad \text{(XI-32a)}$$

for $R \leqslant 1$;

and

$$h = \left[1.4000 + 0.4460\left(\frac{2R + 1}{1.90 - R}\right)\right]d - 0.3780\left(\frac{2R + 1}{1.90 - R}\right), \qquad \text{(XI-32b)}$$

for $R \geqslant 1$.

Consequently, plotting (still at 40°C) h against d, according to the latter two equations, yields two sets of straight lines, all these lines converging towards the point where $d = d_i = 0.8475$ g/cm^3 and $h = h_i = 1.1865$. Such straight lines have been constructed in the preceding Fig. XI-8 for R-values ranging from 0.6 up to 4.0.

Although the two underlying equations, that is Equations (XI-32a) and (XI-32b), have been derived by combining two approximative formulas, Fig. XI-8 permits very satisfactory predictions of R solely from h and d. All the R-readings from this figure have again been collected in Table XI-9 under the heading "Viscochor Method". The average and standard deviations of the latter R-values from those determined by means of the n-d-M method amount to only 0.04 and

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*) Substituting the latter value for v_i and the aforementioned value $\psi_i = 1.4000$ cm^3/g into Identity (XI-9b), it follows that for saturated mineral oils $h_i = 1.1865$ or $\eta_i = 533$ cP.

0.07 rings per average molecule, respectively.

A *variant* of the procedure just described consists in predicting R from the *slopes* of the lines in Fig.XI-8 or rather their reciprocal values, that is their VDQ's defined by Equation (XI-21). The consequent relationships are easily derived from Equations (XI-32a) and (XI-32b), respectively:

$$R = 42.90 - \frac{661.3}{16.1292 - \mathrm{VDQ}}, \quad \text{for} \quad R \leqslant 1; \qquad \text{(XI-33a)}$$

and

$$R = 6.11 - \frac{8.29}{1.9685 - \mathrm{VDQ}}, \quad \text{for} \quad R \geqslant 1. \qquad \text{(XI-33b)}$$

Fig.XI-9 represents the latter two equations. Of course, the accuracy of this alternative method is identical to that of the basic procedure.

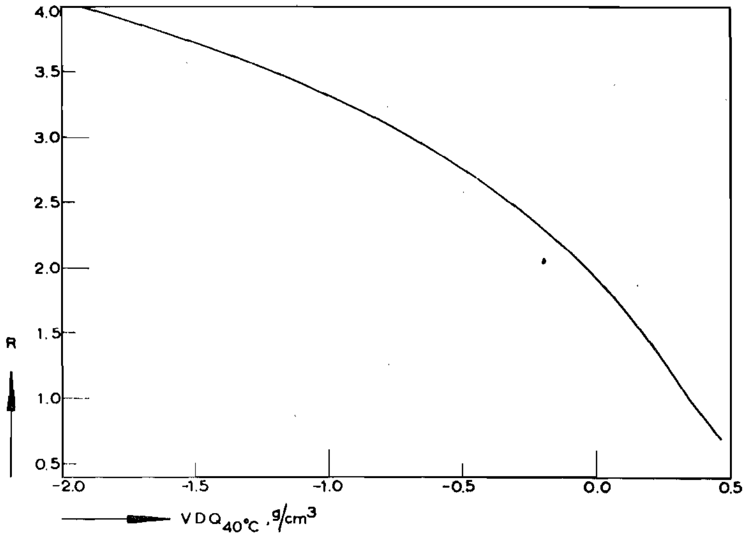

FIG.XI-9.
Correlation Between Ring Number and Viscosity-Density Quotient of Saturated Mineral Oils.

XI.4.5. *Estimating the Average Molecular Weight of Saturated Mineral Oils*

In the foregoing § XI.4.4 it has been shown that the quantities C_R and R of saturated mineral oils can be conveniently obtained from one single h-d chart. Since their average molecular weight, M, determines the relationship between C_R and R, it follows that it should be possible, at least in principle, to estimate also M from such a chart. A simple procedure which does permit such estimates will now be described.

Combination of Equation (XI-31) with Equations (XI-29a) and (XI-29b), respectively, such that R is eliminated can readily be shown to lead to two equations - one for the range corresponding to $R \leqslant 1$ and the other for $R \geqslant 1$ - which imply a linear relationship between h and d for oils of the same molecular weight. In an h-d chart the straight lines relating to constant M-values constitute *two* fans, that is one for either R-range. These lines, therefore, suffer from the basic drawback that they display irrealistic discontinuities at values of the variables h and d relating to the "transitional" ring number, R = 1. Moreover, such an h-d chart has proved to yield rather inaccurate predictions of M, particularly at high M-values.

Consequently, a slightly modified equation has been tried, starting from a plot of the appropriate data for all the fractions under consideration. At the same time it became possible to get rid of the aforementioned discontinuities at R = 1. The final equation (still at 40°C) reads:

$$h = \left(0.834 - \frac{97}{M}\right) (d - 0.6000) + 0.9800. \qquad \text{(XI-34)}$$

In a plot of h against d according to the latter equation the straight lines relating to distinct M-values constitute a fan. The point of convergence has the coordinates $d = 0.6000$ g/cm^3 and $h = 0.9800$. Fig. XI-10 represents such a plot for M-values ranging from 150 to 600. It is observed that M varies more rapidly with h, that is the viscosity grade, than with the density, d. The M-values read from such a figure have again been listed in Table XI-9 under the heading "Viscochor Method". In general, the agreement with the experimental values is very good. The relative average and standard deviations amount to 3.6 and 4.4%, respectively, whilst the experimental values may be in error by 2-5%.

XI. 4. 6. *Viscochor and Chemical Constitution of Natural Mineral Oils*

As stated in the introduction to the present section, the methods developed in the foregoing parts for the statistical constitution analysis of *saturated* mineral oils can be extended so as to include *natural* samples as well. In general, the latter oils contain aromatics - besides paraffins and naphthenes - so that the additional structural quantities R_A and C_A need to be determined.

For the latter purpose at least *three* physical constants are required$^{42)}$. By utilizing, besides the viscosity grade and the density, the readily measurable *refractive index*, n (measured for the sodium-D line, also at the standard reference temperature of 40°C) it has indeed proved possible to extend the aforementioned methods so as to include natural mineral oils as well as the saturated samples for which they were originally established.

In this context only the *principles* of the extended methods will be expounded. Their detailed description and discussion - including a comparison with various methods already available - have

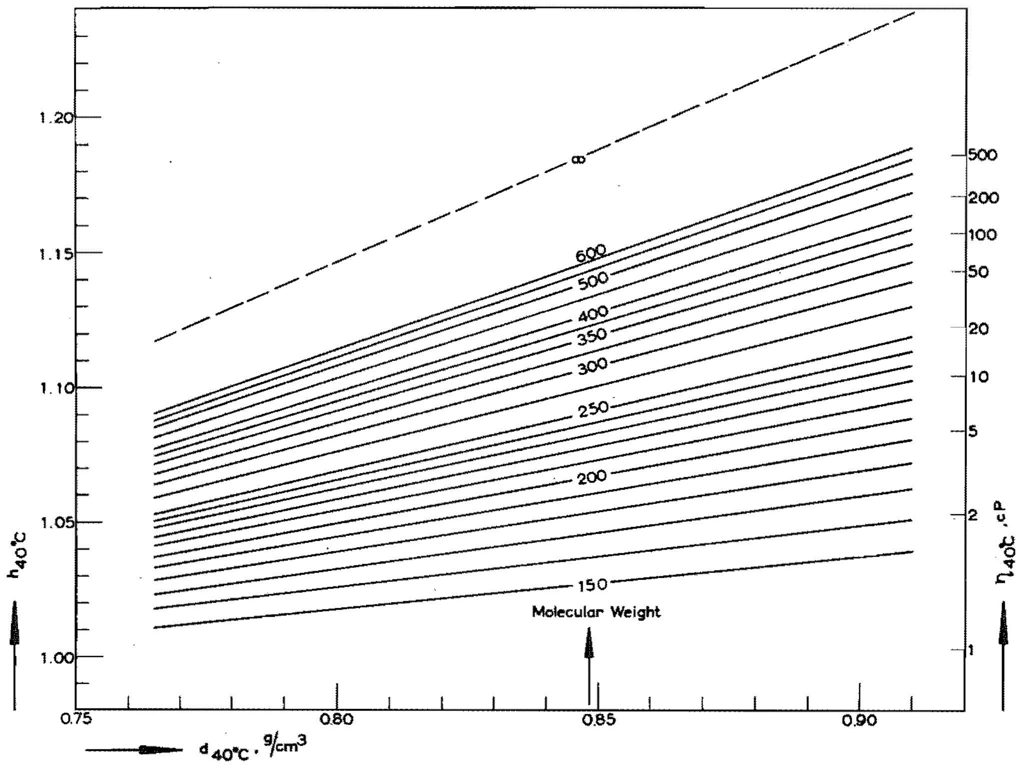

FIG. XI-10.
The Average Molecular Weight of Saturated Mineral Oils as a Function of Their Viscosity and Density.

not yet reached the reporting stage. It is intended to complete these very laborious investigations at a later time. Anyhow, the present communications will testify once more to the great importance of viscosity, and particularly the viscochor concept, to the statistical constitution analysis of mineral oils.

The *carbon-type composition* of *saturated* mineral oils can be obtained solely from the specific viscochor: according to Equation (XI-27), their percentage of carbon atoms in ring structure, C_R, is *linearly* related to their specific viscochor, ψ. It is well known that the C_R-value of saturated mineral oils can also be estimated from the refractivity intercept, r_i, introduced by Kurtz and Ward[170,50]:

$$r_i = n - \tfrac{1}{2} d, \qquad \text{(XI-35)}$$

where d must be expressed in g/cm^3. In fact, C_R is also *linearly* related to r_i (also taken at some standard reference temperature, for instance 40°C).

Thus, in a ψ-r_i chart *one single* straight line results on which, to a good approximation, the appropriate point of any saturated mineral-oil fraction should be located. Each point on this line corresponds to a distinct C_R-value, so that a linear C_R-scale can be adjusted.

When the data on *natural* mineral oils are plotted in the latter ψ-r_i chart, it is observed that their points come closer to the aforementioned straight line of the saturated samples as their percentage C_A is lower. In fact, more or less parallel to the latter straight line - which relates to $C_A = 0$ - lines of constant C_A-values can be drawn. In addition, lines of constant C_N-values can be depicted emanating from the corresponding points on the aforementioned straight line for the saturated oils (whose C_N- and C_R-values are identical). Consequently, a ψ-r_i chart results which permits very simple estimates of the carbon-type composition of a given mineral-oil fraction, either saturated or natural.

The *ring number*, R, of *saturated* mineral oils can be obtained solely from their VDQ (= $\Delta d/\Delta h$) by means of Equations (XI-33a) and (XI-33b). A function formed from the refractive index, n, and the density, d, which is quite analogous to the VDQ, has been proposed by Smittenberg[187]. This is the so-called Refractivity Quotient, RQ, defined as:

$$RQ = \frac{\Delta d}{\Delta n} = \frac{d_i - d}{n_i - n}, \qquad \text{(XI-36)}$$

where in accordance with the present notation n_i denotes the limiting value of n in the homologous series considered. Although Smittenberg has derived the RQ for homologous series of pure hydrocarbons, it can be shown to apply - like the VDQ - equally to saturated mineral oils. For saturated mineral oils the RQ (taken again at some standard reference temperature, for instance 40°C) proves to be also uniquely related to their ring number, R.

Thus, in a VDQ-RQ chart *one single* line results for all the saturated mineral oils. As long as $R_A = 0$, therefore, each point on this line corresponds to a certain R_N-value.

For *aromatic-containing* oils two sets of lines can be constructed in the VDQ-RQ chart, referring to constant R_A- and R_N-values, respectively. Consequently, a VDQ-RQ chart results - analogous to the aforementioned ψ-r_i chart for estimating their carbon-type composition - which allows a very simple prediction of the number of rings per average molecule of both saturated and natural mineral-oil fractions.

All in all, the two charts delineated are very suitable for a clear and simple characterization of the chemical constitution of both saturated and natural mineral oils. Moreover, they are of interest for easily recording - in terms of the basic physical constants - the course of chemical and physical processes mineral oils are being subjected to, for instance in industrial refining. Last but not least, they are promising for various correlational purposes.

XI. 5. CONCLUDING REMARKS

Although the present attempts to establish a reasonably additive viscosity-density function should be deemed only a first cautious step on somewhat slippery ground, the author believes that the newly developed function, the viscochor, may be claimed satisfactorily additive. The new function is thought to be at least on a par with most of the well-known additive functions devised for physical properties such as density and refractive index which have proved to lend themselves much better to such an approach.

Whatever the potentialities and limitations of the empirically established viscochor may be, it has already proved a valuable and versatile tool for systematically studying certain aspects of the viscosity of liquids, notably hydrocarbon liquids.

Further, the viscochor bears a close resemblance to various well-known additive functions devised for other physical constants. This feature may well prove advantageous when it is tried to furnish some theoretical justification of the new function.

Moreover, the basic viscosity function ($\log \eta + 1.200$) has proved highly fruitful also for evaluating with a minimum number of characteristic parameters both the temperature and the pressure dependence of the viscosity of liquids, so that it may be regarded as a kind of *universal* viscosity function (compare Section XI. 2).

Besides for *analytical* applications such as those elaborated in Section XI. 4, the viscochor concept has been found to be very suitable for a simple prediction of the *viscosity of mixtures* of interrelated liquids, notably mineral oils, solely from the viscosities and volume fractions of the components. For the latter purpose the *volume* additivity of the viscosity function h in mixtures is utilized; indeed, this particular function h, occurring in Equation (XI-9b), is seen to stand for the general volume-additive function f' of Equation (XI-4).

It is of great practical importance to have available some simple tool for predicting mixture viscosities, notably in the mineral-oil field. In fact, the author's attempts to develop a satisfactorily additive viscosity-density function have been induced to a large extent by the importance of the mixture-viscosity problem. In this problem it is, of course, not any viscosity *function* but the viscosity *itself* that is really significant. Unfortunately, viscosity, η, is very sensitive to variations in the aforementioned volume-additive function h = $= (\log \eta + 1.200)^{1/8}$. Consequently, for the numerical evaluation of the viscosities of mixtures unusually severe requirements have to be imposed on the additive behaviour of h in such mixtures.

Nevertheless, the viscosity function h has proved to pass these requirements in a satisfactory manner. The full justification of this statement will be presented in the subsequent Chapter XII.

CHAPTER XII

THE VISCOSITY GRADE AND THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP OF MINERAL-OIL MIXTURES

XII. 1. INTRODUCTION

Knowledge of the viscosity of liquid mixtures is of very great practical and theoretical importance. In the course of time a gigantic number of experimental and theoretical investigations have been performed dealing with the viscosity of mixtures prepared from *pure* compounds of very divergent constitution. It would appear that an even greater amount of work has been devoted to the viscosities of mixtures prepared from technologically important oils of not so well defined chemical constitution, notably *mineral oils*.

Hitherto any workable theory of liquid viscosity could not be advanced further than, optimistically speaking, its "*status nascendi*". Consequently, the numerous *theoretical* approaches to the viscosity of liquid mixtures still lack a good foundation. It is no wonder, therefore, that more or less convincing results would appear to have been achieved only for certain systems of the most simple liquids.

Unfortunately, the mixtures commonly encountered in practice are rather *complex*. Frequently such mixtures have been prepared from oils that are very complex already by themselves, such as mineral-oil fractions of divergent origin and chemical constitution. It would seem unrealistic to anticipate that the latter type of mixtures - whose exact composition is not even known - will ever be sufficiently accessible by any theory at all.

From the preceding remarks it is evident that normally one has to resort to essentially *empirical* findings when dealing with liquid-mixture viscosities. Accordingly, it stands to reason that convenient empirical relationships may be very valuable tools in this field.

In the present study the author will confine himself to purely *physical* mixing of two - and sometimes more - homogeneous, completely miscible liquids.

In a binary mixture two types of interaction may, at least formally, be discerned. In the first place the molecules of either component separately are subject to both intramolecular and intermolecular effects. In the second place in a binary mixture interaction effects between the different molecules of the two components are obtaining. Consequently, besides the viscosities proper of the two components, some "*interaction viscosity*" will be involved.

Since the magnitude of this interaction viscosity varies widely from one system to another, it is not possible in the general case to relate the viscosity of a mixture uniquely to the viscosities of the components. In fact, many systems have been found to exhibit a maximum or minimum in their isothermal viscosity-concentration curves. Therefore, in the general case only rough estimates of the viscosity of a mixture can be made from that of the components. For more accurate estimates at least one experimental mixture-viscosity value should be known.

A good idea of the difficulties encountered may be conceived from the schematic Figs. XII-1a and XII-1b representing the various kinds of experimentally observed viscosity-concentration*) curves[177,178b]. These two figures will now discussed.

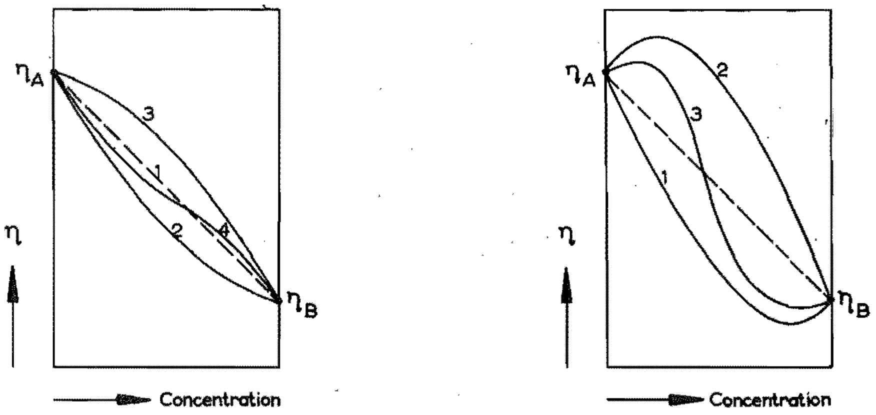

FIG. XII-1a. FIG. XII-1b.

Schematic Representation of the Various Kinds of Viscosity-Concentration Curves in Binary Liquid Mixtures.

A. The four types of curves depicted in Fig. XII-1a represent the various cases where for all possible concentrations the viscosity of the mixture remains intermediate to the viscosities of the components A and B. The existence of linear additivity of viscosity, denoted by the dashed line (No. 1), constitutes an exceptional case. In general, the deviations from this straight line increase as the ratio between the viscosities of the components increases.

Viscosity-concentration curves that are more or less convex towards the concentration axis, as indicated by curve No. 2, occur very frequently. In fact, the latter type is normally encountered in mixtures of mineral oils, of pure hydrocarbons and of many further organic liquids with more or less interrelated chemical constitution. The sagging of the relevant curves below the straight line No. 1 implies that the lower-viscosity component contributes more to the resulting viscosity of the mixture than the more viscous one; or, in other words, the lower-viscosity component shows an increased "effective" concentration[20,173].

The concave curve No. 3 and especially the curve No. 4 displaying a point of inflection represent very rarely observed types.

B. The three types of curves depicted in Fig. XII-1b represent the various cases where extremes occur in the viscosity-concentration isotherms.

A minimum in the viscosity-concentration isotherms, indicated by curve No. 1, is exhibited by many systems in which mixing is accompanied by an appreciable consumption of heat and/or by volume expansion. Examples of systems showing a minimum-viscosity point are: ethylalcohol/benzene and acetone/carbon disulfide. In the scope of the present investigation it is important to point out that such minima may also occur in certain mineral-oil as well as pure-hydrocarbon mixtures.

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*) For the purpose here intended "concentration" need not yet be specified.

A maximum as denoted by curve No. 2 occurs in many systems where mixing is accompanied by an appreciable development of heat and/or by volume contraction. A very pronounced maximum-viscosity point is observed in mixtures of several organic liquids with water, for instance the system ethylalcohol/water.

Curve No. 3, which shows both a maximum and a minimum, represents an extremely rare form of viscosity-concentration isotherms.

As indicated above, no perfect blending rule involving only the viscosities of the components can ever be established. However, confining oneself to mixtures of more or less interrelated liquids, fair estimates may be made on the basis of the approximate additivity inherent in certain viscosity functions.

Practically all the viscosity functions claimed to be at least reasonably additive have been designed primarily for *mineral oils*. This may be taken indicative of the great practical importance of a convenient method for predicting the viscosities of mineral-oil mixtures. A few of these viscosity functions permit good predictions as long as the components differ not too widely in their (average) chemical constitution. In various cases, however, the existing viscosity functions leave much to be desired.

A critical review of these functions and related prediction methods will be presented in the following Section XII. 2.

XII. 2. CRITICAL REVIEW OF EMPIRICAL MIXTURE-VISCOSITY RELATIONSHIPS

XII. 2. 1. *Introduction*

It would be beyond the scope of this study to review the various *theoretical**) approaches to the viscosity of mixtures. The author will rather confine himself to a critical review of the many *empirical* mixture-viscosity relationships which, to the best of his knowledge, are interesting from a *practical* point of view. It is no wonder, therefore, that the great majority of the latter relationships have been developed primarily for mixtures of mineral oils.

Most of the expressions for the viscosity-concentration isotherms of binary mixtures may be conceived as special cases of the general equation:

$$f(\eta_m) = (1-Q)\cdot f(\eta_1) + Q \cdot f(\eta_2), \qquad \text{(XII-1)}$$

where $f(\eta)$ stands for a particular function of the (dynamic) viscosity, η, and the viscosities η_m, η_1 and η_2 refer to the mixture, the first and second component, respectively. The symbol Q denotes the fractional concentration of the *second* component: either its molar, weight or volume fraction**).

The use of molar fractions is fully significant only with definite

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*) The reader interested in this matter may be referred especially to Bondi's publications[20, 173, 174].

**) The interrelationship between these three types of fractional concentrations has been defined in Appendix XII-1 at the end of this chapter.

chemical compounds. It has appeared that in general it does not make much difference whether the concentration is expressed in terms of weight or volume fractions. In petroleum technology it would appear to be common practice, however, to employ volume fractions rather than weight fractions.

Before reviewing various formulas which actually constitute special cases of the general Equation (XII-1), it may be useful to point out that these have shown the following serious limitation: they invariably yield mixture viscosities *intermediate* to those of the components.

XII. 2. 2. *Simplified Mixture-Viscosity Relationships*

There are a number of older expressions which constitute really simple cases of Equation (XII-1). The best-known examples of these *"simplified"* mixture-viscosity expressions will now be enumerated[177,178b,182).

As early as 1887 Arrhenius proposed an equation which involves the additivity of the logarithm of viscosity, η, in terms of the *volume* fractions of the components:

$$\log \eta_m = (1-y) \log \eta_1 + y \cdot \log \eta_2, \qquad \text{(XII-2a)}$$

where y stands for the volume fraction of the second component and where log denotes again the common or Briggsian logarithm, $\log_{10}$. This equation may also be written as:

$$\eta_m = \eta_1^{(1-y)} \cdot \eta_2^y. \qquad \text{(XII-2b)}$$

In 1905 Bingham proposed an equation based on the additivity of the reciprocal viscosity, or the *fluidity*, namely:

$$\eta_m^{-1} = (1-y)\, \eta_1^{-1} + y\, \eta_2^{-1}. \qquad \text{(XII-3)}$$

Some years later, in 1917, Kendall and Monroe made an extensive investigation concerning the applicability of various equations and concluded that for the mixtures tested the best fit was obtained with their formula:

$$\eta_m^{\frac{1}{3}} = (1-X)\, \eta_1^{\frac{1}{3}} + X\, \eta_2^{\frac{1}{3}}, \qquad \text{(XII-4)}$$

where X denotes the *molar* fraction (of the second component).

Each of the three Equations (XII-2a), (XII-3) and (XII-4) has a very limited applicability, since it may adequately describe only viscosity-concentration isotherms that are moderately convex towards the concentration axis (see Section XII. 1).

In general these equations - which are stated to have been developed primarily for *"ideal"* mixtures - yield rather rough results for mineral-oil mixtures. But the Kendall-Monroe[188) and particularly the Arrhenius equation[173,189,190) may have some value in the mineral-oil field. In fact, the well-known Arrhenius Equation (XII-2a) is still widely employed, both for mineral-oil mixtures and many other types of systems*). Indeed, the Arrhenius equation may give fair results in many cases, especially when the viscosities of the components are not too different.

XII. 2. 3. *Mixture-Viscosity Relationships Containing One Parameter*

If several experimental mixture viscosities are known, it is not very difficult to give an adequate analytical description of the viscosity-concentration isotherm considered. Since the latter question is not interesting in the present context, it may suffice here to refer to the relevant literature[182].

It may be useful, however, to consider a few of the mixture-viscosity relationships containing only *one* unknown parameter. This adjustable parameter may be regarded to account for the "interaction viscosity" indicated in Section XII. 1. At any given temperature an appropriate value for this parameter can be calculated if at least one experimental mixture viscosity is known, preferably for a mixture containing about equal amounts of either component. With such one-parameter equations very good results can be achieved.

a. Lederer (1932) has attempted to develop a theoretical expression for the viscosity of mixtures[191,192,177]. From the extensive criticism raised against the resulting expression it has become evident, however, that the theoretical considerations leading up to it are far from satisfactory[177,84,193]. Accordingly, it would appear that Lederer's equation may be upheld only as an essentially empirical one.

It can be cast into the form:

$$\log \eta_m = (1-x_1) \log \eta_1 + x_1 \cdot \log \eta_2 . \qquad \text{(XII-5)}$$

In this equation the quantity x_1 represents a "corrected" weight fraction, defined by:

$$x_1 = \frac{x}{x + q\,(1 - x)}, \qquad \text{(XII-6)}$$

where x denotes the straight *weight* fraction and the temperature-dependent parameter q is characteristic of a given mixture.

It is worthy of note that several years after Lederer the Roegiers brothers (1947) proposed a mixture-viscosity formula which in essence is identical with Lederer's[84;193-195]. According to the Roegiers brothers, their formula - in which, besides the weight fraction, the volume or molar fraction may be employed - was one of the outcomes of their "generalized viscosity theory". But their theoretical justification cannot be deemed satisfactory either[84].

Equation (XII-5) has been checked extensively, especially for mineral-oil systems. In general it gave excellent results, the order of accuracy being nearly that of the experimental determinations[194-196]. However, notwithstanding the introduction of an em-

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*) Besides volume fractions, weight and molar fractions are frequently used in Equation (XII-2a).

pirical parameter, Lederer's equation has the serious limitation that it cannot be applied to mixtures exhibiting an extreme in their viscosity-concentration curves*).

b. In addition to his undermentioned Equation (XII-16), Cragoe (1933) proposed the following extended version of it[119]:

$$\left(\log \frac{\eta_m}{\eta_c}\right)^{-1} = (1-x)\left(\log \frac{\eta_1}{\eta_c}\right)^{-1} + x\left(\log \frac{\eta_2}{\eta_c}\right)^{-1} + x\,(1-x)\,C_c\,. \qquad \text{(XII-7)}$$

In this equation the reference viscosity η_c has one common value for all liquids, namely $\eta_c = 0.0500$ cP; the parameter C_c is dependent on both the particular mixture considered and on the prevailing temperature. Instead of the weight fraction, x, the volume fraction may equally be used.

Equation (XII-7) applies very accurately to many types of mixtures, especially mineral-oil systems. Like Lederer's Equation (XII-5), Cragoe's Equation (XII-7) normally proves to be of nearly the same order of accuracy as the experimental data. In contrast to Lederer's equation, however, Equation (XII-7) can also be applied to systems exhibiting an extreme in their viscosity-concentration curve.

c. A third equation containing one parameter is due to Grunberg and Nissan (1949). These authors[197] have extended the simple Arrhenius Equation (XII-2a) as follows:

$$\log \eta_m = (1-X)\log \eta_1 + X \cdot \log \eta_2 + X\,(1-X)\,C_g\,, \qquad \text{(XII-8)}$$

where X denotes again the molar fraction and C_g is an unknown parameter whose value depends on the mixture considered and on temperature.

In fact, Equation (XII-8) is very similar to Cragoe's Equation (XII-7). It would seem that Equation (XII-8) has not widely been applied so far.

XII. 2. 4. *Mixture-Viscosity Relationships for Mineral Oils*

All the relationships now to be reviewed have been designed primarily for mineral-oil mixtures. As a matter of fact, they are entirely *empirical*.

It may be remarked that, although it is common practice in petroleum technology to express concentrations in terms of *volume* fractions, the use of *weight* fractions in the following relationships does not bring about any appreciable difference.

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*) In this connection it should be pointed out that Rahmes and Nelson's statement[196] that Lederer's equation can be made to predict viscosity minima appears to be basically incorrect.

A. HERSCHEL'S AND WILSON'S METHODS

a. Herschel (1920) undertook one of the earlier attempts to predict the *kinematic* viscosities of mineral-oil mixtures solely from those of the components[189,190].

By applying suitable correction factors to the viscosities calculated on the basis of the Arrhenius Equation (XII-2a) he succeeded in achieving reasonable predictions. Herschel provided diagrams for estimating the appropriate correction factor for a given mixture with $y = 0.50$. This factor would become more influential as the ratio between the component viscosities increases and would further vary with the source of the component oils. In order to account for the effect of the oil source mineral oils were classified as "paraffinic" or "naphthenic"; the correction factor would assume different values according as the paraffinic or the naphthenic oil shows the higher viscosity.

Herschel's method should be deemed an important contribution at the early time of its introduction. Unfortunately, his method has a rather restricted validity range and is inconvenient to employ. In later years it has remained only of historical interest.

b. Wilson's method (1929) may be conceived as an extension and refinement of Herschel's. From Wilson's systematic investigation[198] it became clear that no formula involving only the viscosities of the components is able to cover all mineral-oil systems. At least the influence of pronounced differences in the chemical constitution of the component oils should be additionally accounted for. To this end Wilson developed a set of three distinct mixture-viscosity charts, one of which would rectify the viscosity-concentration isotherms of any given mineral-oil mixture. Each chart is based on the following power-type equation relating *kinematic* viscosity, ν, in cS, to the volume fraction, y:

$$\nu^w = (1-y)\,\nu_1^w + y\,\nu_2^w. \qquad \text{(XII-9)}$$

In this equation*) the exponent w is taken dependent only on the qualitative difference in chemical nature - "paraffinic" or "naphthenic" - of the components. For oils of the same nature the exponent w would amount to - 1/6.5; for paraffinic/naphthenic mixtures the exponent w would amount to - 1/30 if the paraffinic oil has the higher viscosity and to - 1/3.1 if the naphthenic oil is the more viscous one.

In general good results are obtained with Wilson's charts. It is no wonder, therefore, that they have frequently been employed. In fact, they are still used to some extent[197].

B. METHODS USING THE ASTM, OR RELATED, VISCOSITY-TEMPERATURE CHARTS

To a very wide extent the aforementioned Wilson charts have been superseded by the ASTM viscosity-temperature chart, which

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*) As early as 1901 Lees[178b] proposed a similar equation using dynamic instead of kinematic viscosity.

was first published - as a tentative chart - in 1932 [63]. It is true that in general the Wilson charts are more reliable, notably when oils of widely different crudes are being blended. However, the single ASTM chart has the weighty advantages that it is more convenient to use and more versatile at that. Thus, the ASTM chart - or some modification of this - has become the blending chart most widely employed nowadays.

a. The suitability of the ASTM chart for predicting *kinematic* viscosities of mineral-oil mixtures from those of the components derives from the approximate additivity of the viscosity function used in this chart. This viscosity function, W, is defined as:

$$W = \log\log(\nu + 0.6), \qquad \text{(XII-10)}$$

where ν is invariably expressed in cS. In fact, the latter viscosity function represents the left-hand side of the MacCoull-Walther Equation (III-5), which constitutes the basis of the ASTM chart (see part B of § III. 1. 2)*).

In order to make this ASTM chart more adequate as a mixture-viscosity chart an *adjusted* volume-percentage scale is employed rather than a linear one.

The following equation may readily be derived for the "corrected" volume fraction, y_a, as a function of the straight volume fraction, y, of the higher-viscosity component:

$$y_a = 11.68 \cdot \log(1 + 0.218\ y), \qquad \text{(XII-11)}$$

so that for all possible y-values (between 0 and 1) the corrected volume fraction of the higher-viscosity component is greater than indicated by y. For example, for $y = 0.500$ the corrected volume fraction amounts to $y_a = 0.525$.

Accordingly, the graphical procedure of estimating mixture viscosities by means of the ASTM chart is equivalent to applying the following mathematical expression:

$$W_m = (1-y_a)W_1 + y_a W_2, \qquad \text{(XII-12)}$$

where W and y_a are defined by Equations (XII-10) and (XII-11), respectively.

Besides the ASTM viscosity-temperature chart, a few *related* charts are in use - to some reasonable extent - for estimating viscosities of mineral-oil mixtures. Amongst these related charts should be mentioned: the Walther-Ubbelohde chart [66] and the Umstätter chart [67,68]. Although their viscosity functions differ slightly from the function W of the ASTM chart, the discrepancies become more or less significant only in the range of very low viscosities (compare part B of § III. 1. 2).

The procedure of using the Walther-Ubbelohde or Umstätter chart as a blending chart is also quite similar to that outlined for the ASTM chart. Thus, in the present context there is not much sense in going further into the details of these related charts.

As regards the suitability of the ASTM chart - or some related chart - for predicting the viscosities of mineral-oil mixtures it

*) Throughout this chapter the subscript "0", relating to atmospheric pressure, has been omitted.

may be stated that in normal lubricating-oil practice it has proved to yield acceptable results. Of course, it has the same serious limitation that is inherent in any method based on the additivity of some function involving solely the viscosity of the oil: it invariably predicts mixture viscosities *intermediate* to those of the components. However, also in systems where no minima or involved and even in certain systems where the oil components are not very divergent the predicted viscosities may be rather seriously in error.

All in all, the ASTM method is insufficiently reliable for general application to mineral-oil mixtures.

b. Wright's method (1946) constitutes a very important *variant* of using the ASTM viscosity-temperature chart as a blending chart[196]. This method can be conveniently applied for estimating not merely the viscosity *grade* but rather the viscosity-*temperature* relationship of a given mineral-oil mixture solely from the rectified viscosity-temperature relationships of the component oils.

In the above-described - conventional - use of the ASTM chart "mixing" is performed by interpolating between the viscosities of the components under isothermal conditions. Wright's procedure, however, might be termed *"inverse"* in that it boils down to interpolating between the temperatures at which the components assume the same viscosity level.

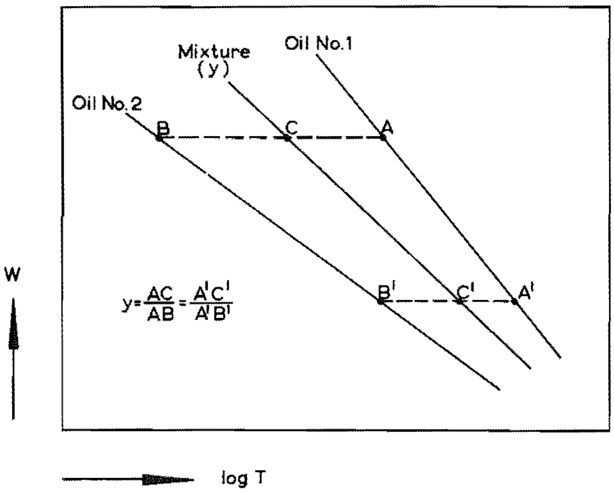

FIG. XII-2.
Schematic Representation of Wright's Method for Predicting the Viscosity-Temperature Relationship of Mineral-Oil Mixtures.

Referring to Fig. XII-2, this may be elucidated as follows. At an arbitrary (constant) viscosity level a point C is estimated by linearly interpolating between the corresponding points A and B of the component oils, that is point C is fixed such that: y=AC/AB; point C would then be located on the viscosity-temperature line of the mixture, which line is yet to be constructed. Likewise, at a second - also arbitrarily chosen - viscosity level a point C' is fixed such that: y=A'C'/A'B'=AC/AB. Then, the complete viscosity-temperature relationship of the mixture considered would be depicted by the straight line drawn through the points C and C'.

Like the aforementioned conventional method Wright's modified method was designed as a purely *graphical* one. Therefore, provided the basic viscosity-temperature chart possesses a sufficiently extensive format, Wright's method is also very convenient in that it does not require any computations.

Nevertheless, it would appear interesting and illuminating to find out which mathematical expressions constitute the basis of Wright's method. Referring to an analogous prediction method yet to be developed in Section XII.6, the present author has derived the following (isothermal) expression equivalent to Wright's graphical procedure of estimating mixture viscosities:

$$W_m = (1 - y_w)\,W_1 + y_w W_2, \qquad \text{(XII-13)}$$

where W stands again for the viscosity Function (XII-10) used in the ASTM chart and y_w denotes the "corrected" volume fraction of the second component. The latter quantity proves to be given by the formula:

$$y_w = \frac{\frac{m_1}{m_2}\,y}{1 + \left(\frac{m_1}{m_2} - 1\right)y}, \qquad \text{(XII-14)}$$

where m_1 and m_2 represent the slopes of the viscosity-temperature lines, rectified in the ASTM chart, of the first and the second component, respectively, and where, by definition, $m_1 \geqslant m_2$.

Consequently, it has been derived analytically that Wright's method boils down to introducing the corrected volume fraction y_w. However, in contrast to the corresponding volume fraction y_a of the conventional method, the volume fraction y_w proves to be not invariably the same function of the straight volume fraction, y. According to Equation (XII-14), y_w also depends on the ratio between the slopes of the components.

The basic feature of Wright's method for predicting the viscosities of mineral-oil mixtures consists in that, in addition to the indispensable viscosity grade of the components, their slope ratio is taken into consideration, the latter quantity being characteristic of a given mineral-oil mixture.

Strictly speaking, therefore, the slopes of the two components need not be known individually as long as it is desired to estimate the viscosity of the mixture only at the standard reference temperature where the viscosity grades of the components are given. But if it is desired to estimate the viscosity-temperature relationship of the mixture, a knowledge of the two individual slopes, m_1 and m_2, proves to be essentially indispensable. This may readily be inferred from the schematic Fig.XII-2; it is also apparent from the following equation relating the slope of the mixture, m_m, to the slopes of the two components:

$$\frac{1}{m_m} = \frac{1 - y}{m_1} + \frac{y}{m_2}. \qquad \text{(XII-15)}$$

For the derivation of Equation (XII-15) reference is made once again to Section XII.6. According to Equation (XII-15), the reciprocal slopes, 1/m, of mineral oils are additive in terms of straight volume fractions. Indeed, the validity of Equation (XII-15) would tally well with experimental findings. In this connection it may be useful to point out that the additivity of the slope m proper has been studied more than once. The relevant studies have led to the conclusion that in accordance with the new Equation (XII-15) the slopes m may be far from additive 199,71).

Wright's graphical prediction method has indeed been found to constitute a substantial improvement over the conventional method of using the ASTM chart as a blending chart 196). As a rule Wright's method proves to yield considerably better results than this conventional method. In addition, it may be termed *"complete"* in that it aims at predicting the complete viscosity-temperature relationship of the mixtures considered rather than the viscosity at only one representative temperature. Wright's way of using the ASTM chart is also definitely superior to using the appropriate chart of Wilson's set of three viscosity-blending charts 196).

Nevertheless, in certain cases Wright's method also leaves much to be desired. Notably this holds for mixtures whose component oils combine a fairly small difference in their viscosity grade with a relatively great difference in their viscosity-temperature dependence 196). As will be further elucidated in Section XII. 8, such systems may exhibit a pronounced *minimum* in their viscosity-concentration curve. In fact, it will there be shown that, in contrast to what has been widely assumed so far, the occurrence of a minimum in such systems would be the *rule* rather than the *exception*. Now, Wright's method is also afflicted with the basic shortcoming that it invariably yields mixture viscosities that are *intermediate* to those of the two components.

C. THREE ADDITIONAL EQUATIONS

Finally, three additional equations will be presented which prove to be particularly interesting in connection with the author's equations to be described in Sections XII. 5 through XII. 7.

a. One of the earlier equations intended primarily for application to mineral oils is due to Cragoe 119). Cragoe's formula, published in 1933, can be reduced to the following form [compare Equation (XII-7) above]:

$$\left(\log\frac{\eta_m}{\eta_c}\right)^{-1} = (1-x)\left(\log\frac{\eta_1}{\eta_c}\right)^{-1} + x\left(\log\frac{\eta_2}{\eta_c}\right)^{-1}. \qquad \text{(XII-16)}$$

In this equation the reference viscosity η_c has one common value for all oils, namely $\eta_c = 0.0500$ cP.

According to Cragoe, Equation (XII-16) is more accurate than the aforementioned equations of Arrhenius (XII-2a), Bingham (XII-3) and Kendall-Monroe (XII-4), particularly in that it fits the data on many mineral-oil mixtures much better. The claimed superiority for mineral-oil mixtures was later confirmed by Rahmes and Nelson 196); according to these investigators, Cragoe's Equation (XII-16) even proves to be nearly on a par with the conventional ASTM method.

b. The second equation is a generalized version of the one casually indicated by Nederbragt (1952) in his discussion on Blott and Verver's paper[200]. Without reporting any quantitative figures Nederbragt stated that the linear relationship between the volume fraction and the viscosity function log log ν, with kinematic viscosity ν in mS, would be useful for calculating mixture viscosities in many cases, especially when the viscosities of the components are widely different. Further, he mentioned that this viscosity function would suffer from the drawback of being dependent on the unit of measurement (mS).

The latter feature, however, is only seemingly a drawback. Indeed, by rewriting the latter viscosity function in the generalized form log log (ν/ν_s), where ν_s = 0.100 cS, the viscosity may be expressed in *any* unit, provided of course that ν_s is expressed in the same unit. Accordingly, the *generalized* version of the equation indicated by Nederbragt reads:

$$\log\log\frac{\nu_m}{\nu_s} = (1-y)\log\log\frac{\nu_1}{\nu_s} + y\cdot\log\log\frac{\nu_2}{\nu_s}. \quad \text{(XII-17a)}$$

With kinematic viscosity, ν, expressed in cS it may be rewritten as:

$$\log(\log\nu_m + 1.000) = (1-y)\log(\log\nu_1 + 1.000) + + y\cdot\log(\log\nu_2 + 1.000). \quad \text{(XII-17b)}$$

The author has found that, as regards the accuracy of viscosities predicted for mineral-oil mixtures, Equation (XII-17a) is practically equivalent to the conventional ASTM method.

c. As a third equation the author would like to introduce a mixture-viscosity relationship which is based on Souders's additive viscosity-density function, the so-called viscosity-constitutional constant, defined already by Expression (XI-6):

$$I = M\,\frac{\log\log(10\,\eta) + 2.9}{d}, \quad \text{(XI-6)}$$

where viscosity, η, is expressed in cP and where M and d denote the molecular weight and the density, respectively, of the liquid considered[179]. On the assumptions that the additivity - in terms of molar fractions - of the viscosity-constitutional constant would hold good for mixtures and that no appreciable volume changes would ensue from mixing, the following mixture-viscosity relationship should apply with reasonable accuracy:

$$\log(\log\eta_m + 1.000) = (1-y)\log(\log\eta_1 + 1.000) + + y\cdot\log(\log\eta_2 + 1.000), \quad \text{(XII-18)}$$

where viscosity, η, has again been expressed in cP.

Remarkably enough, the latter equation differs from Equation (XII-17b) only in that it employs *dynamic* instead of *kinematic* viscosity. As far as the author knows, the simple Equation (XII-18) has never been proposed in the literature. But he could already show it to give results fully on a par with those obtained by means of the conventional ASTM method.

D. CONCLUSIONS

The author's findings concerning the applicability of the aforementioned relationships for predicting the viscosities of mineral-oil mixtures may be summarized in a few conclusions. For convenience the prediction methods involving only the viscosity *grades* of the components and those using *additional* information will be considered separately, that is under points a and b, respectively.

a. The following relationships are included in the first group: Equation (XII-12), underlying the conventional ASTM method; Cragoe's Equation (XII-16); the generalized Nederbragt Equation (XII-17a) or (XII-17b); and the new equation based on Souders's viscosity-constitutional constant, that is Equation (XII-18).
   1. All these relationships would seem to yield acceptable results in normal lubricating-oil practice. But in view of the large deviations observed in certain cases, they are insufficiently reliable for *general* application to mineral-oil mixtures.
   2. These various relationships are nearly equivalent with respect to the accuracy inherent in the predicted viscosities.
   3. The conventional method of using the ASTM viscosity-temperature chart as a blending chart constitutes the most attractive procedure.
   4. From the author's investigations (compare Section XII. 5) the significant conclusion has emerged that - although, of course, the relevant question can never be settled in any rigorous manner - there is no sound reason at all to uphold the possibility of developing a method that would constitute a *substantial* improvement over the methods under discussion. Therefore, it may safely be assumed that the highest achievable degree of correlational accuracy has indeed been reached with the methods now available.

b. Herschel's, Wilson's and Wright's method have been treated as examples of the second group.
   1. Whilst Herschel's method is nowadays only of historical interest, Wilson's is still in use. The Wilson charts are definitely superior to the relationships discussed in the preceding group a. However, the use of a set of three charts is rather inconvenient.
   2. *Wright's method of using the ASTM chart doubtless constitutes the most reliable procedure available in the literature. Moreover, it is "complete" in that it aims at predicting the complete viscosity-temperature relationship of a given mineral-oil mixture rather than the viscosity at some arbitrary reference temperature.*

      However, in certain cases - which have proved to be far from exceptional - Wright's method still leaves much to be desired. Just like all other relationships and methods consid-

ered in this entire section, it has the basic limitation that it invariably yields viscosities intermediate to those of the components.

XII. 3. OUTLINE OF THE PRESENT APPROACH

A practical method for predicting the viscosity *grade* as well as the viscosity-*temperature* relationship*) of mineral-oil mixtures should involve only easily assessable properties of the component oils. Preferably it should require a knowledge solely of the viscosity-temperature relationship of the components. Moreover, such a method should be both convenient and sufficiently widely applicable, that is applicable even to mineral oils of widely different viscosity grade and/or chemical constitution.

From the foregoing critical review of available prediction methods the conclusion has been obtained that none of these is really satisfactory in general. Therefore, an *improved* method would be highly desirable.

It stands to reason that the present attempts to develop such an improved method will be founded on an essentially *empirical* basis.

In the first instance attention is concentrated on the viscosity *grade* of mixtures of *pure hydrocarbons* (of high molecular weight) in order to obtain some information of a more basic kind (Section XII. 4).

As a logical consequence of the results obtained in the preceding Chapter XI (see in particular Section XI. 5) with the newly developed additive viscosity-density function, the *"viscochor"*, its applicability to pure-hydrocarbon mixtures has been tried out.

Indeed, the viscochor has proved to be a convenient tool also for predicting the viscosities of such mixtures. Yet, this may not be taken to involve that the simple viscochor would permit satisfactory predictions throughout. In fact, as will be further eludicated in the relevant Section XII. 4, the latter feature might not fairly be expected from any additive viscosity-density function conceivable. The basic reason is that, even though pure hydrocarbons are chemically interrelated, they may still display very pronounced differences in their chemical constitution. Nevertheless, the viscochor does yield reasonable viscosity predictions, certainly so as a first approximation.

Considerably *improved* accuracy in the predicted mixture viscosities would be achievable only by properly allowing for the intermolecular viscosity effects between the components. It has appeared that this can be conveniently achieved by introducing solely the difference between the *Slope Indices* (see § III. 1. 3) of the components as an additional correlational variable.

By means of the consequent (tentative) correlation excellent viscosity predictions have been obtained for all the divergent mixtures of high-molecular-weight hydrocarbons tested.

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*) As indicated by its title, this entire chapter is confined to atmospheric viscosities.

Sections XII. 5 through XII. 8 are devoted to the main purpose of the present investigation: the development of convenient methods for predicting the (atmospheric) viscosity-temperature relationship of *mineral-oil* mixtures solely from that of the components.

For evaluating the viscosity-temperature relationship of mineral oils the convenient Equation (III-6h) has again been resorted to. According to this equation, only the viscosity grade and the Slope Index of mineral-oil mixtures need to be predicted in order to know their *complete* viscosity-temperature relationship.

It has now been derived analytically and verified by experimental data that for predicting the viscosities of mineral-oil mixtures the additivity of the simple viscosity function H occurring in the basic viscosity-temperature Equation (III-6h) is practically on a par with that of the specific viscochor. Moreover, the additivity of H has proved to hold reasonably good over a wide temperature range, which means that the Slope Indices, S, of the component oils are also approximately additive.

Consequently, the basic viscosity-temperature Equation (III-6h) is very suitable indeed for predicting the complete viscosity-temperature relationship of mineral-oil mixtures. The latter feature constitutes another weighty advantage of the latter equation over conventional equations and charts.

It goes without saying that the establishment of improved prediction methods has been attempted on the basis of the latter equation. The consequent approach will now be outlined.

1. The new method for predicting the viscosity-temperature relationship of mineral-oil mixtures from the additivity of the viscosity function H - standing for the viscosity *grade* - and the Slope Index is denoted as the *"Simplified Prediction Method"* (see Section XII. 5). The mixture viscosities thus predicted will turn out sufficiently accurate for normal lubricating-oil practice.

   These predictions can also be performed very conveniently by means of a viscosity-temperature *chart* constructed in accordance with Equation (III-6h). The use of such an H-Θ chart obviates the necessity of making any computations.
2. The latter chart may also be utilized in an alternative way, that is similarly to Wright's variant of using the ASTM chart (see part B of § XII. 2. 4). The resulting *"Graphical Prediction Method"* aims at predicting the complete viscosity-temperature relationship of a given mineral-oil mixture solely from the rectified viscosity-temperature relationships of the two components (see Section XII. 6).

   The latter method proves to constitute a substantial improvement over the aforementioned *simplified* method, which is based on the straight additivity of the viscosity function H. Nevertheless, just like Wright's method the present variant still leaves much to be desired in various systems, notably when the component oils combine a fairly small difference in their viscosity grades with a relatively great difference in their Slope Indices.
3. The ideas underlying the *"Refined Prediction Method"* (see Sec-

tion XII. 7) finally established as a really satisfactory one are quite similar to those which are basic to the described refined method for pure-hydrocarbon mixtures. The only essential difference is that the specific viscochor utilized in the latter method has been replaced - for reasons of simplicity - by the viscosity function H.

Accordingly, the refined method for predicting the viscosity *grade* of mineral-oil mixtures starts from the approximate additivity of the viscosity function H. At any given temperature the additional *"interaction viscosity"* could be conveniently accounted for by introducing solely the difference between the *Slope Indices* of the two component oils.

Likewise, it has appeared that the accuracy inherent in the simplified method for predicting the *Slope Index* of mineral-oil mixtures can be considerably improved simply by accounting for this difference between the Slope Indices of the two components.

All in all, it may be stated that the author has indeed succeeded in developing an improved, generally satisfactory method for conveniently estimating the complete viscosity-temperature relationship of binary mineral-oil mixtures solely from that of both components. The refined prediction method even embodies the unique feature that it permits predicting quantitatively the occurrence of minima in the viscosity-concentration curves of mineral-oil systems. The latter aspect will be extensively discussed in Section XII. 8.

Various additional applications of the relationships and correlations underlying the aforementioned prediction methods will be presented in the concluding Section XII. 9.

Experimental Data on Mineral-Oil Mixtures

The newly developed methods for predicting the viscosity-temperature relationship of mineral-oil mixtures have been based mainly on the extensive experimental data reported by Rahmes and Nelson[196]. These methods have further been checked for the few additional mixtures on which sufficient data could be found in the literature.

Rahmes and Nelson have presented viscosity data on 26 binary mineral-oil systems with widely varying properties. As a rule the viscosities of the various systems have been determined - with an estimated accuracy of 0.5% - at three compositions and two temperatures. These compositions correspond to volume fractions of 0.25, 0.50 and 0.75, the two temperatures being 100 and 210°F (37.8 and 98.9°C).

Viscosities*) and viscosity-temperature criteria**) of the 17 com-

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*) Rahmes and Nelson have listed only kinematic viscosities. The densities required for converting these kinematic into dynamic viscosities have been calculated from the reported API Gravity, using the accurate method proposed by Lipkin and Kurtz[51]. The molecular weights, which are involved in the latter method, have been estimated from the kinematic viscosities reported for 100 and 210°F according to Hirschler's procedure[153].

**) For the present purpose three decimal places have been retained in the Slope Indices. In practice, however, only two decimal places are normally significant, particularly if a relatively wide temperature range is covered (compare § III. 1. 3).

TABLE XII-1a

Data on Component Mineral Oils

Oil Code	Experiments' Designation	Viscosity, cP		Viscosity-Temperature Criteria		
		100°F	210°F	S	DVI	VI
B	Solvent-Refined Oil	193.2	15.14	1.260	92	97
C	ditto	25.8	4.02	1.221	104	92
D	Raw Distillate from Naphthenic Crude	19.28	3.08	1.278	87	14
E	ditto	363	14.49	1.537	-21	-5
F	"	28.8	3.80	1.327	72	7
G	"	449	17.50	1.504	-3	19
H	Solvent Extract	182.0	8.43	1.611	-66	-84
J	Solvent-Refined Oil	29.1	4.57	1.187	112	113
K	Solvent Extract	490	15.03	1.627	-77	-62
L	Acid-Treated Paraffin Base Oil	87.3	9.08	1.240	98	100
M	From Mixed Base Crude	81.7	8.07	1.288	84	88
N	Acid-Treated Naphthenic Base Oil	107.4	8.51	1.375	54	53
O	Not Known	278	16.94	1.340	67	78
P	Solvent Extract Blended to 0 VI	84.[illegible]	6.56	1.450	23	4
Q	Raw Distillate from Naphthene Base Crude	12.08	2.32	1.243	98	13
R	Technical White Oil	27.5	4.24	1.215	105	99

ponent mineral oils are specified in Table XII-1a. Apparently, these oils represent very divergent sources and chemical constitutions; even a few aromatic extracts are included.

Accordingly, the various binary systems prepared from these oils constitute a really great variety of mineral-oil mixtures. In fact, several systems represent rather *extreme* cases in that their components differ unusually widely in chemical constitution. A few systems even display the hitherto rarely observed feature of a *minimum* in their viscosity-concentration curve.

All the pertinent data on the aforementioned 26 mineral-oil systems have been compiled in Tables XII-1b and XII-1c. The volume fraction y invariably refers to the *second* component, defined as the oil with the *lower* Slope Index, S_2. The viscosity *ratio* is defined simply as the ratio of the higher to the lower viscosity grade (at the standard reference temperature involved), irrespective whether the first or the second component is the more viscous one. It may be noted that the first 13 systems display relatively large, the remaining 13 systems relatively small viscosity ratios. For both groups the differences between the Slope Indices of the component oils cover a wide range.

All in all, this variety of 26 mineral-oil systems warrants a really severe test of any method for predicting the viscosities of such systems. It should be properly realized, however, that the results obtained with the present systems may *not* be taken representative of the results to be expected in normal lubricating-oil practice. Indeed, it may be assumed that the latter results would generally turn out even appreciably *better*.

TABLE XII-1b

Data on Mineral-Oil Mixtures

System		Viscosity Ratio		$\Delta H = \lvert H_1 - H_2 \rvert$		S_1-S_2	DVI_1-DVI_2	VI_1-VI_2
No.	Components	100°F	210°F	100°F	210°F			
1	E-F	12,62	3,81	0,1505	0,1227	0,210	-93	-12
2	E-J	12,47	3,17	0,1497	0,1036	0,350	-133	-118
3	F-B	6,71	3,98	0,1176	0,1262	0,067	-20	-90
4	B-J	6,64	3,31	0,1168	0,1071	0,073	-20	-16
5	D-L	4,53	2,95	0,1016	0,1066	0,038	-11	-86
6	L-C	3,39	2,26	0,0802	0,0778	0,019	-6	8
7	N-D	5,57	2,77	0,1139	0,1010	0,097	-33	39
8	N-C	4,17	2,12	0,0925	0,0722	0,154	-50	-39
9	K-D	25,4	4,89	0,1945	0,1486	0,349	-164	-76
10	K-Q	40,6	6,47	0,2316	0,1812	0,384	-175	-75
11	O-R	10,09	4,00	0,1400	0,1236	0,125	-38	-21
12	O-C	10,79	4,22	0,1448	0,1292	0,119	-37	-14
13	Q-L	7,23	3,91	0,1387	0,1392	0,003	0	-87
14	Q-C	2,13	1,730	0,0585	0,0614	0,022	-6	-79
15	F-Q	2,38	1,636	0,0664	0,0556	0,084	-26	-6
16	D-Q	1,596	1,324	0,0371	0,0326	0,025	-11	1
17	Q-J	2,41	1,968	0,0672	0,0747	0,056	-14	-100
18	O-B	1,439	1,120	0,0193	0,0088	0,080	-25	-19
19	E-O	1,306	1,170	0,0136	0,0123	0,197	-88	-83
20	G-O	1,614	1,033	0,0241	0,0025	0,164	-70	-59
21	K-O	1,762	1,127	0,0283	0,0094	0,287	-144	-140
22	H-B	1,062	1,795	0,0032	0,0490	0,351	-158	-181
23	P-M	1,040	1,230	0,0023	0,0190	0,162	-61	-84
24	P-L	1,028	1,384	0,0016	0,0293	0,210	-75	-96
25	F-C	1,117	1,057	0,0079	0,0058	0,106	-32	-85
26	F-J	1,012	1,202	0,0008	0,0191	0,140	-40	-106

TABLE XII-1c

Experimental Viscosities and Slope Indices of Mineral-Oil Mixtures

System	Viscosity at 100°F, cP			Viscosity at 210°F, cP			Slope Index		
No.	y=0.25	y=0.50	y=0.75	y=0.25	y=0.50	y=0.75	y=0.25	y=0.50	y=0.75
1	165.2	85.9	48.0	9.82	6.98	5.07	1.468	1.411	1.367
2	149.6	75.7	45.1	10.05	7.31	5.72	1.411	1.320	1.246
3	45.4	73.0	118.8	5.35	7.46	10.79	1.300	1.289	1.266
4	113.5	69.8	44.7	11.04	8.04	6.04	1.231	1.219	1.200
5	28.1	40.9	60.3	3.95	5.28	6.79	1.282	1.255	1.266
6	63.8	46.6	34.5	7.40	5.96	4.86	1.232	1.230	1.230
7	68.6	44.3	28.8	6.49	5.00	3.90	1.359	1.336	1.307
8	71.4	48.9	34.8	6.90	5.70	4.78	1.335	1.289	1.253
9	171.8	72.8	35.6	9.25	6.05	4.26	1.524	1.436	1.348
10	142.2	54.1	23.7	8.43	5.16	3.38	1.504	1.410	1.314
11	140.6	77.8	45.2	11.46	8.02	5.73	1.299	1.271	1.246
12	139.6	75.5	43.0	11.38	7.91	5.60	1.301	1.267	1.238
13	19.59	32.2	52.8	3.26	4.58	6.40	1.237	1.239	1.244
14	14.52	17.62	21.1	2.65	3.06	3.52	1.240	1.228	1.217
15	22.8	18.36	14.79	3.35	2.97	2.62	1.302	1.279	1.259
16	17.18	15.21	13.58	2.89	2.68	2.49	1.263	1.258	1.252
17	15.07	18.79	23.5	2.75	3.33	3.94	1.230	1.198	1.187
18	254	230	209	16.33	16.00	15.60	1.326	1.298	1.276
19	322	304	290	15.14	15.52	16.22	1.464	1.426	1.382
20	384	328	301	17.30	17.30	16.94	1.452	1.391	1.371
21	399	342	307	15.38	15.67	16.33	1.537	1.466	1.402
22		168.3							
23	81.5	80.0	80.4						
24	83.4	83.2	84.3						
25	27.5	26.8	26.1						
26	28.4	28.3	28.8						

XII. 4. THE VISCOCHOR AS A TOOL FOR PREDICTING THE VISCOSITY GRADE OF PURE-HYDROCARBON MIXTURES

XII. 4. 1. *Introduction*

The correlation between the viscosities of pure hydrocarbons and their mixtures has been extensively studied. The main object of the major part of the relevant work was to obtain some *basic* information concerning the viscosity of mineral lubricating oils.

Particularly in the scope of API Research Project 42 very interesting investigations into the viscosity - and likewise other physical properties - of pure-hydrocarbon mixtures have been carried out [201-203]. As part of these investigations various empirical functions have been tested for additivity, involving either viscosity alone, viscosity plus density, or even the combination of viscosity, density and molecular weight. However, in contrast to such physical properties as density and refractive index, viscosity could not be comprised by some satisfactory additive function. Even the function - containing viscosity, density and molecular weight - finally arrived at proved far from adequate. Nevertheless, this particular function was claimed far superior to any of the functions previously proposed [203]. The latter statement may well go to illustrate the considerable difficulties connected with the prediction of the viscosities of such hydrocarbon mixtures.

As stated already in Section XII. 3, the present approach to the problem of predicting the viscosities of pure-hydrocarbon mixtures has been based on a newly developed additive viscosity-density function, the "*viscochor*". Indeed, in view of previous experiences with the viscochor (see Chapter XI) it may be expected to prove a valuable tool also for predicting the viscosities of the mixtures under consideration.

This has been investigated for various mixtures of high-molecular-weight hydrocarbons of fairly complicated and divergent chemical structure. The findings with such mixtures should be of special interest because of their bearing on the technologically important mineral-oil mixtures. Accordingly, this section may be conceived as a kind of introductory exploration of the *mineral-oil* field to be entered hereafter.

Experimental Data

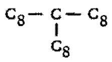
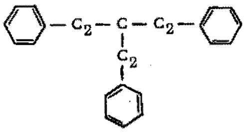
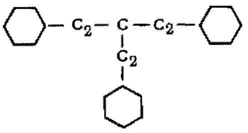
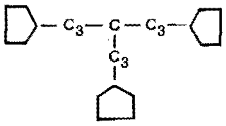
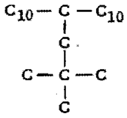
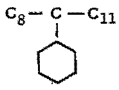
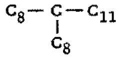
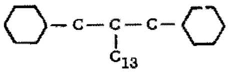
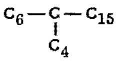
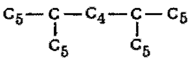
The pure hydrocarbons involved are designated in Table XII-2a, whilst various data on their mixtures are compiled in Table XII-2b.

These very interesting mixtures have been prepared and studied by Schiessler *et al.* in the scope of the above-cited API Research Project 42 [201-203;139). For proper consideration it should be noted that some of the systems are non-ideal in the sense that an appreciable volume change ensues from mixing. Notably the mixtures containing compound No. 89 are far from ideal ones.

The present systems will permit a very severe test of any mixture-viscosity equation. For most of these systems the components

TABLE XII-2a

Data on Component Hydrocarbons

Component			Viscosity, cP		Density, g/cm^3		Specific Viscochor, cm^3/g		S
PSU No.	Structural Formula	M, calc	100°F	210°F	100°F	210°F	100°F	210°F	
25	 $C_8-\underset{\underset{C_8}{\vert}}{C}-C_8$	352.7	7.04	1.86	0.7905	0.7507	1.3834	1.3973	1.099
89		328.5	25.5	3.63	0.9952	0.9537	1.1327	1.1254	1.297
90		346.6	152*)	8.58	0.8920*)	0.8526	1.3053	1.2896	1.519
113		346.6	22.5	3.87	0.8774	0.8379	1.2813	1.2834	1.174
67	 $C_{10}-\underset{\underset{\underset{\underset{C-\underset{\underset{C}{\vert}}{C}-C}{\vert}}{C}}{\vert}}{C}-C_{10}$	366.7	9.24	2.17	0.7915	0.7525	1.3914	1.4022	1.134
78		364.7	13.33	2.76	0.8254	0.7863	1.3462	1.3530	1.152
63	 $C_8-\underset{\underset{C_8}{\vert}}{C}-C_{11}$	394.7	9.55	2.34	0.7959	0.7564	1.3850	1.3985	1.085
65		390.7	34.2	4.57	0.8518	0.8135	1.3312	1.3283	1.272
3	 $C_6-\underset{\underset{C_4}{\vert}}{C}-C_{15}$	366.7	8.77	2.20	0.7926	0.7522	1.3876	1.4035	1.087
22	 $C_5-\underset{\underset{C_5}{\vert}}{C}-C_4-\underset{\underset{C_5}{\vert}}{C}-C_5$	366.7	9.36	2.06	0.7952	0.7549	1.3854	1.3951	1.190

*) Extrapolated Data

TABLE XII-2b

Data on Pure-Hydrocarbon Mixtures

System					Viscosity, cP		Density, g/cm^3		Viscosity Ratio, 100°F	S_1-S_2	$\Delta\psi$, cm^3/g	
No.	Comp.	X	x	y	100°F	210°F	100°F	210°F			100°F	210°F
1a	89-25	0.667	0.682	0.730	8.28	2,07	0.8451	0.8051	3.61	0.198	0.2507	0.2719
1b	ditto	0.333	0.349	0.403	12.00	2.54	0.9117	0.8712	"	"	"	"
2a	89-113	0.667	0.678	0.705	18.79	3.44	0.9100	0.8706	1.135	0.123	0.1486	0.1580
2b	ditto	0.333	0.345	0.375	19.32	3.36	0.9489	0.9086	"	"	"	"
3a	90-25	0.667	0.670	0.696	12.36	2.60	0.8212	0.7816	21.5	0.420	0.0781	0.1077
3b	ditto	0.333	0.337	0.364	30.0	4.16	0.8542	0.8157	"	"	"	"
4a	113-25	0.667	0.670	0.693	9.44	2.28	0.8174	0.7779	3.18	0.075	0.1021	0.1139
4b	ditto	0.333	0.337	0.361	13.65	2.90	0.8463	0.8067	"	"	"	"
5a	90-113	0.667	0.667	0.670	36.6	4.82	0.8817	0.8431	6.76	0.345	0.0240	0.0062
5b	ditto	0.333	0.333	0.337	67.9	6.30	0.8867	0.8481	"	"	"	"
6a	78-67	0.747	0.748	0.756	10.14	2.31	0.7998	0.7608	1.442	0.018	0.0452	0.0490
6b	ditto	0.498	0.500	0.510	11.07	2.44	0.8082	0.7692	"	"	"	"
6c	"	0.250	0.251	0.259	12.13	2.61	0.8168	0.7778	"	"	"	"
7a	65-63	0.746	0.748	0.760	12.02	2.68	0.8093	0.7703	3.58	0.187	0.0538	0.0702
7b	ditto	0.496	0.498	0.515	15.85	3.13	0.8230	0.7842	"	"	"	"
7c	"	0.246	0.248	0.261	22.3	3.73	0.8372	0.7988	"	"	"	"
8a	22-3	0.753	0.753	0.754	8.93	2.19	0.7933	0.7529	1.066	0.103	0.0022	0.0084
8b	ditto	0.500	0.500	0.501	9.06	2.14	0.7939	0.7535	"	"	"	"
8c	"	0.254	0.254	0.254	9.25	2.13	0.7946	0.7542	"	"	"	"

show relatively wide differences in their viscosity grades. Moreover, in systems Nos. 2a and 2b the viscosity of the mixture is smaller than that of either component at both 100 and 210°F.

XII.4.2. *A Simplified Prediction Method*

As outlined in the preceding Chapter XI, the specific viscochor, ψ, would be approximately additive (at constant temperature) in terms of the *weight* fractions of the components, that is:

$$\psi_m = (1-x)\ \psi_1 + x\ \psi_2 . \qquad \text{(XII-19)}$$

TABLE XII-3a

Experimental and Predicted Specific Viscochors of Pure-Hydrocarbon Mixtures

System No.	$\psi_{100°F}$, cm^3/g			$\psi_{210°F}$, cm^3/g		
	Exp.	Eq.(XII-19)	Eqs.(XII-20) and(XII-21a)	Exp.	Eq.(XII-19)	Eqs.(XII-20) and (XII-21b)
1a	1.2997	1.3037	1.2990	1.3084	1.3109	1.3080
1b	1.2157	1.2202	1.2153	1.2177	1.2203	1.2173
2a	1.2308	1.2334	1.2310	1.2307	1.2325	1.2310
2b	1.1810	1.1839	1.1814	1.1782	1.1798	1.1783
3a	1.3509	1.3577	1.3514	1.3584	1.3618	1.3574
3b	1.3239	1.3316	1.3252	1.3213	1.3258	1.3214
4a	1.3483	1.3498	1.3485	1.3588	1.3598	1.3590
4b	1.3138	1.3156	1.3143	1.3209	1.3217	1.3209
5a	1.2879	1.2893	1.2864	1.2837	1.2855	1.2845
5b	1.2954	1.2973	1.2944	1.2859	1.2875	1.2865
6a	1.3802	1.3800	1.3798	1.3899	1.3898	1.3897
6b	1.3698	1.3688	1.3686	1.3776	1.3776	1.3774
6c	1.3575	1.3576	1.3574	1.3651	1.3654	1.3653
7a	1.3698	1.3714	1.3694	1.3796	1.3808	1.3794
7b	1.3555	1.3580	1.3553	1.3622	1.3633	1.3615
7c	1.3427	1.3445	1.3425	1.3448	1.3457	1.3443
8a	1.3873	1.3871	1.3868	1.4017	1.4014	1.4011
8b	1.3866	1.3865	1.3861	1.3996	1.3993	1.3989
8c	1.3863	1.3860	1.3857	1.3980	1.3972	1.3969

The data collected in Table XII-3a demonstrate the good applicability of Equation (XII-19) to the variety of pure-hydrocarbon mixtures considered. Even for the systems (Nos. 2a and 2b) exhibiting a minimum in their viscosity-concentration curves the latter equation yields quite reasonable predictions. It may further be noted that the discrepancies between experimental and predicted ψ-values decrease rapidly with rising temperature, which may be ascribed to the accompanying decrease of intermolecular effects. In conclusion it may be stated that the simple Equation (XII-19) does permit valuable estimates of the specific viscochors of the various mixtures under consideration.

TABLE XII-3b

Percentage Deviations Between Experimental and Predicted Viscosities of Pure-Hydrocarbon Mixtures

System No.	$\% \delta \eta_{100^\circ F}$*)				$\% \delta \eta_{210^\circ F}$	
	Additivity of η	Additivity of log η	Eq.(XII-19)	Eqs.(XII-20) and (XII-21a)	Eq.(XII-19)	Eqs.(XII-20) and (XII-21b)
1a	45.2	20.5	13.0	-2.1	5.4	-0.9
1b	50.7	26.5	17.0	-1.4	6.4	-0.9
2a	24.4	29.7	10.2	0.9	4.7	0.9
2b	26.2	20.8	12.2	1.9	4.2	0.2
3a	314	44.9	24.2	1.6	7.9	-2.1
3b	230	65.6	34.0	5.0	12.4	0.2
4a	21.1	6.4	4.5	0.7	1.9	0.5
4b	22.8	8.2	6.2	1.6	1.9	0.0
5a	77.8	15.1	5.7	-5.8	5.2	2.3
5b	59.6	17.2	8.4	-4.1	4.7	1.9
6a	0.9	-0.2	-0.7	-1.1	-0.2	-0.5
6b	1.6	0.0	-0.5	-0.9	0.0	-0.2
6c	2.1	0.0	0.5	-0.2	0.7	0.5
7a	28.8	7.9	5.2	-1.1	2.6	-0.5
7b	35.5	11.9	7.9	-0.9	2.6	-1.6
7c	24.7	10.2	6.6	-0.5	2.3	-1.1
8a	-0.2	-0.2	-0.7	-1.4	-0.9	-1.8
8b	0.0	0.0	0.0	-1.1	-0.5	-1.4
8c	-0.5	-0.5	-0.9	-1.8	-1.6	-2.1
Average Deviation**)	50.8	15.0	8.3	1.8	3.5	1.0
Standard Deviation***)	97.4	23.2	12.4	2.4	4.7	1.3

*) $\% \delta \eta = 100 \dfrac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) Defined by $\dfrac{1}{n} \sum_{i=1}^{i=n} \left| \% \delta_i \right|$

***) Defined by $\sqrt{\dfrac{\sum_{i=1}^{i=n} (\% \delta_i)^2}{n-1}}$

The calculation of *viscosities* from the predicted ψ-values and the experimental densities, however, is seriously handicapped by the fact that viscosity proper is highly sensitive to variations in ψ. Nevertheless, as demonstrated by the data listed in Table XII-3b, reasonable values for the viscosities of the mixtures in question can thus be obtained.

For comparison the viscosities calculated on the assumption that viscosity, η, and log η, respectively, are additive in terms of *volume* fractions have also been included. The considerable deviations inherent in the latter viscosities may be taken indicative of the difficulties encountered in establishing a satisfactory mixture-viscosity formula for the present systems. In this connection reference may further be made to the aforementioned API-attempts[203,20,173].

A most remarkable feature of the new Equation (XII-19) consists in that it correctly predicts the occurrence of minima in systems Nos. 2a and 2b. Presumably the considerable viscosity decrease observed in the latter systems will at least partly be due to the appreciable volume expansion ensuing from mixing; for instance, in system No. 2a the volume expansion at 100°F amounts to no less than 0.24%.

XII.4.3. *A Refined Prediction Method*

In the foregoing § XII.4.2 the interaction effects of the component molecules have not specifically been taken into consideration. Particularly with components of strongly different structure, however, such intermolecular effects have to be properly accounted for. Consequently, the basic Equation (XII-19) should be extended and refined by introducing some *"interaction viscochor"*, ψ_{12}. For the mixtures involved the following extended equation has proved very fruitful:

$$\psi_m = (1-x)\,\psi_1 + x\,\psi_2 + x\,(1-x)\,\psi_{12}\,, \qquad \text{(XII-20)}$$

where ψ_{12} is characteristic of a given mixture.

Analysis of the - apparently small - discrepancies between the ψ-values predicted from Equation (XII-19) and the experimental data (see Table XII-3a) leads to the conclusion that these are strikingly regular. In fact, for all systems considered the deviation ($\psi_{\text{pred}} - \psi_{\text{exp}}$) is slightly positive and, moreover, roughly proportional to the *absolute* difference between the *Slope Indices* of the component hydrocarbons, that is to the quantity $\Delta S = (S_1 - S_2)$[*].

Consequently, the same complexity of structural parameters that finds expression in ΔS is largely responsible for the intermolecular effects giving rise to deviations from the additivity rule for ψ, that is from Equation (XII-19). In this connection it is interesting to quote one of the suggestions made by Schiessler *et al.*[203] with respect to the development of a suitable function for predicting the viscosities of pure-hydrocarbon mixtures: "Possibly a satisfactory viscosity function will have to contain some expression of the rate of change of viscosity with temperature".

The present finding implies that the factor ψ_{12} in Equation (XII-20)

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[*] As stated in Section XII.3, $S_1 \geqslant S_2$.

should likewise be roughly proportional to the quantity ΔS. It has further appeared that an even more refined correlation for estimating ψ_{12} can be obtained by introducing the *absolute* difference between the ψ-values of the components, denoted by $\Delta\psi$, as an additional correlational variable.

For the standard reference temperature of 100°F the following *tentative* correlation has thus been established for ψ_{12}:

$$\psi_{12,100^\circ\mathrm{F}} = -0.10 \cdot \Delta S \left[\log\left(\Delta\psi_{100^\circ\mathrm{F}} + 0.0300\right) + 1.650\right]. \quad \text{(XII-21a)}$$

Accordingly, plotting $\psi_{12,100^\circ\mathrm{F}}$ against the main variable ΔS and using $\Delta\psi_{100^\circ\mathrm{F}}$ as a parameter yields a family of straight lines emanating from the origin. Fig. XII-3 constitutes such a plot for the ranges of ΔS and $\Delta\psi_{100^\circ\mathrm{F}}$ covered by the present data.

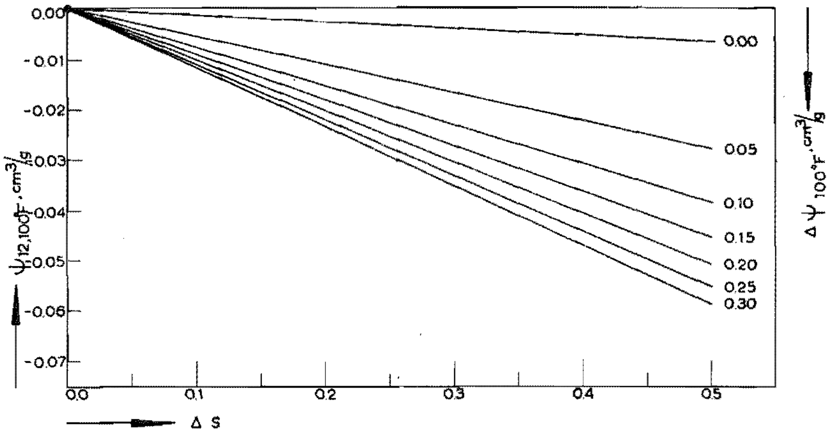

FIG. XII-3.
The Interaction Viscochor of Binary Pure-Hydrocarbon Systems According to the Tentative Correlation (XII-21a).

With increasing temperature the interaction viscochor, ψ_{12}, becomes smaller. For the standard reference temperature of 210°F the correlation has been found to read:

$$\psi_{12,210^\circ\mathrm{F}} = -0.06 \cdot \Delta S \left[\log\left(\Delta\psi_{210^\circ\mathrm{F}} + 0.0300\right) + 1.650\right]. \quad \text{(XII-21b)}$$

The "*refined* prediction method" just described permits excellent estimates of the specific viscochor and even of the viscosities of all the various mixtures under consideration. As demonstrated in Tables XII-3a and XII-3b, respectively, the predicted data come very close to the experimental values.

For the sake of clearness, it should be stated explicitly that very small errors in the employed experimental *densities* may already interfere seriously with the accuracy of the predicted mixture viscosities. For example for the mixtures considered the stated possible errors in their experimental densities of only 0.0002 g/cm^3 may introduce deviations of no less than about 2% in the predicted viscosities.

It has thus been shown that the viscosity (at some standard reference temperature) of a given pure-hydrocarbon mixture depends not only on the (isothermal) viscosities of the two components but also on their Slope Indices.

In fact, it may be concluded that, within the correlational accuracy of the refined prediction method, the complete viscosity-temperature relationship of such a mixture would be determined solely by that of the two component oils.

The potentialities and limitations of the latter method will not further be discussed here. Let it suffice to state that the present method has considerable bearing on the subsequent approach to the important problem of predicting the viscosity-temperature relationship of *mineral-oil* mixtures.

XII. 5. A SIMPLIFIED METHOD FOR PREDICTING THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP OF MINERAL-OIL MIXTURES

XII. 5. 1. *A Simplified Prediction Method*

The estimation of mixture viscosities on the basis of the additivity of the specific *viscochor*, that is by means of Equation (XII-19), is handicapped by the requirement that the *densities* of both the components and their mixtures need to be known, and very accurately at that (within about 0.0002 g/cm^3).

Fortunately, one may entirely dispense with density measurements if no volume changes ensue from mixing. The latter condition implies the additivity of the specific volumes of the components in terms of their *weight* fractions. With systems of mineral oils - and also with mixtures of pure hydrocarbons of not too strongly different structure - this condition is satisfactorily fulfilled. It readily follows from Equation (XII-19) that for such systems the viscosity function $h = (\log\eta + 1.200)^{1/8}$ (see Section XI. 2) should be additive in terms of *volume* fractions (compare Section XI. 5), that is:

$$h_m = (1-y)\, h_1 + y\, h_2 . \qquad \text{(XII-22)}$$

If Equation (XII-22) is employed for estimating mixture viscosities, it should be realized that viscosity proper is very sensitive to variations in the basic volume-additive function h. Therefore, even very small deviations from Equation (XII-22) may cause already considerable errors in the predicted viscosities. This means that for numerically evaluating the viscosities of mixtures unusually severe requirements have to be imposed on the additive behaviour of h. Nevertheless, as will be shown below, the new viscosity function h has proved to pass these requirements satisfactorily.

The suitability of Equation (XII-22) for estimating viscosities of mineral-oil mixtures has been checked for the 26 systems designated in Tables XII-1b and XII-1c. Particularly the mixtures with $y = 0.50$, considered at 100°F, will permit a very severe test of the new equation.

The deviations between predicted and experimental viscosities of these mixtures are compiled in Table XII-4. For comparison the deviations observed by calculating the viscosities on the assumption that viscosity, η, and log η, respectively, would be additive - likewise in terms of volume fractions - have also been included.

Table XII-4 confirms the approximate additivity of h in terms of volume fractions. As regards the accuracy of the viscosities predicted from this additivity, a considerable improvement over the Arrhenius Equation (XII-2a) - involving the additivity of log η - has been achieved. On the whole the viscosities predicted by means of Equation (XII-22) would be acceptable for many practical purposes. It should further be recalled that several of the 26 systems in question are rather extreme in that their components differ unusually widely in chemical constitution. Therefore, it may indeed be anticipated that in normal lubricating-oil practice Equation (XII-22) would yield sufficiently accurate results.

As derived analytically in Appendix XII-2 at the end of this chapter, the additivity of the viscosity function H (= 8·log h) is practically on a par with that of the closely related function h. Accordingly, Equation (XII-22) may be transformed into:

$$H_m = (1-y)\ H_1 + y\ H_2. \qquad \text{(XII-23)}$$

Table XII-4 illustrates the approximate equivalence of Equations (XII-22) and (XII-23) for predicting mixture viscosities. In fact, the latter equation consistently yields essentially equal or only slightly lower viscosities.

It may be stated that as regards the accuracy of the predicted mixture viscosities the simple viscosity function H is at least on a par with the most prominent functions developed so far (compare part D of § XII. 2. 4).

Equation (XII-23) is somewhat more convenient for numerical evaluation than Equation (XII-22). But its most attractive feature consists in that the employed viscosity function H is also contained in the basic viscosity-temperature Equation (III-6h).

Moreover, the additivity of H has proved to hold reasonably good over a wide temperature range. This is demonstrated by Table XII-5, which lists - in the columns headed by SPM - the deviations between the viscosities predicted from Equation (XII-23) and the experimental data for the two temperatures involved, that is 100 and 210°F, and for the three mixture compositions indicated. As expected, the agreement is considerably better at the higher temperature where the viscosity ratio is much smaller.

It can readily be shown from the basic viscosity-temperature Equation (III-6h) that the approximate additivity of H over a wide temperature range implies that the *Slope Indices*, S, of the component oils are also nearly additive:

$$S_m = (1-y)\ S_1 + y\ S_2. \qquad \text{(XII-24)}$$

TABLE XII-4

Percentage Deviations Between Experimental and Predicted Viscosities of Mineral-Oil Mixtures With $y = 0.50$

System No.	$\% \delta \eta_{100^\circ F}$ *)			
	Predicted from Volume Additivity of ...			
	η	$\log \eta$	h	H
1	128.0	19.1	8.2	6.6
2	158.8	35.8	23.6	21.9
3	52.1	2.1	-3.4	-4.3
4	59.2	7.4	1.6	0.7
5	30.3	0.2	-3.6	-4.1
6	21.6	1.9	-0.7	-1.1
7	42.9	2.8	-2.1	-2.7
8	36.5	7.6	4.0	3.5
9	250.0	33.7	14.0	11.4
10	362.4	42.2	14.8	11.2
11	96.4	12.4	3.5	2.3
12	101.4	12.2	2.8	1.4
13	54.2	0.9	-5.8	-6.9
14	7.4	0.0	-0.7	-1.1
15	11.2	1.4	0.0	-0.2
16	3.0	0.5	0.0	-0.2
17	9.6	-0.2	-1.8	-1.8
18	2.8	0.9	0.9	0.9
19	5.2	4.5	4.5	4.5
20	10.9	7.6	7.2	7.2
21	12.2	7.9	7.4	7.4
22	11.4	11.4	11.4	11.4
23	4.2	4.0	4.2	4.0
24	3.5	3.5	3.5	3.5
25	1.9	1.6	1.6	1.6
26	2.3	2.3	2.1	2.1
Average Deviation**)	56.9	8.6	5.1	4.8
Standard Deviation***)	104	14.6	7.6	6.9

*) $$\% \delta \eta = 100 \frac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$$

**) Defined by $\frac{1}{n} \sum_{i=1}^{i=n} \left| \% \delta_i \right|$

***) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} (\% \delta_i)^2}{n-1}}$

TABLE XII-5

Percentage Deviations Between Experimental and Predicted Viscosities of Mineral-Oil Mixtures

System No.	$H_{12, 100^{o}F}$ Acc. to Eq.(XII-38)	$\%\delta\eta_{100^{o}F}$*)						$\%\delta\eta_{210^{o}F}$					
		y = 0,25		y = 0,50		y = 0,75		y = 0,25		y = 0,50		y = 0,75	
		SPM**)	RPM**)	SPM	RPM	SPM	RPM	SPM	RPM	SPM	RPM	SPM	RPM
1	-0,0075	7,2	4,5	6,6	3,5	4,2	2,1	1,9	2,3	1,4	1,6	0,9	1,4
2	-0,0285	18,8	7,9	21,9	8,4	11,9	3,3	5,0	2,3	7,6	4,0	3,8	1,6
3	0,0096	-2,7	0,0	-4,3	-0,5	-3,8	-0,9	-3,2	-1,1	-3,4	0,0	-4,7	-1,8
4	0,0087	1,2	3,8	0,7	4,5	-0,2	2,1	-1,1	1,4	-0,2	3,0	-0,7	1,6
5	0,0112	-3,2	-0,2	-4,1	0,0	-4,1	-0,9	-0,5	1,9	-3,2	0,0	-0,7	2,1
6	0,0105	-1,4	1,9	-1,1	3,0	-0,9	2,1	-1,4	0,9	-0,5	2,6	-1,1	2,1
7	0,0050	-2,3	-0,9	-2,7	-0,9	-1,4	-0,2	-0,7	0,2	-0,7	3,3	-0,5	1,4
8	-0,0050	2,3	0,7	3,5	1,6	3,0	1,6	0,9	1,2	0,9	1,4	0,9	1,4
9	-0,0275	10,4	0,2	11,4	-0,5	6,9	-0,9	3,8	1,2	6,2	1,9	2,1	0,2
10	-0,0333	12,4	0,7	11,2	-2,3	8,2	-0,7	3,3	0,2	3,8	0,0	2,1	-0,5
11	0,0042	3,3	4,7	2,3	4,2	1,4	2,8	0,9	3,0	0,7	3,3	1,2	2,8
12	0,0056	1,9	4,0	1,4	3,8	0,9	2,6	-0,2	2,3	-1,1	2,1	-1,1	1,2
13	0,0218	-4,5	0,7	-6,9	0,5	-5,4	0,9	-3,6	0,0	-5,2	0,0	-3,4	0,9
14	0,0072	-0,5	1,4	-1,1	1,2	0,2	2,1	-0,2	1,2	-1,1	0,7	-1,1	0,2
15	0,0008	0,2	0,7	-0,2	0,0	0,2	0,5	-0,5	0,5	-0,7	0,0	-0,5	0,5
16	0,0033	-0,5	-0,5	-0,2	0,9	-0,5	0,2	-0,9	-1,1	-0,5	0,5	0,0	0,7
17	0,0041	-0,9	-0,2	-1,8	-0,7	-1,8	-0,7	-0,9	0,2	-3,4	-2,1	-3,2	-1,8
18	-0,0047	0,0	-1,6	0,9	-1,4	0,9	-0,7	0,7	0,5	0,0	-0,2	-0,2	-0,5
19	-0,0165	5,4	-0,9	4,5	-3,6	2,6	3,4	-0,7	-2,3	0,7	-1,4	0,5	-1,4
20	-0,0126	3,5	-1,1	7,2	0,7	4,0	-0,7	0,0	-1,1	-0,5	-2,3	0,7	-0,2
21	-0,0245	5,9	-3,4	7,4	-4,7	15,1	5,2	0,5	-2,3	1,9	-1,8	0,7	-2,1
22	-0,0315			11,4	-3,6	•							
23	-0,0143	3,3	-1,4	4,0	-2,1	2,6	-1,8						
24	-0,0187	2,6	-3,4	3,5	-4,3	2,8	-3,2						
25	-0,0080	1,6	-0,5	1,6	-1,1	1,4	-0,7						
26	-0,0125	1,6	-1,6	2,1	-2,3	0,5	-2,5						
Average Deviation***)		3,9	1,9	4,8	2,3	2,8	1,7	1,5	1,3	2,1	1,5	1,4	1,3
Standard Deviation****)		5,9	2,7	6,9	3,1	5,1	2,1	2,1	1,6	3,0	2,0	2,0	1,5

*) $\%\delta\eta = \frac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) SPM = Simplified Prediction Method
RPM = Refined Prediction Method

***) Defined by $\frac{1}{n} \cdot \sum_{i=1}^{i=n} |\%\delta_i|$.

****) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} (\%\delta_i)^2}{n-1}}$

TABLE XII-6

Deviations Between Experimental and Predicted Slope Indices of Mineral-Oil Mixtures

System No.	$\delta S = (S_{pred} - S_{exp})$						
	y = 0.25		y = 0.50			y = 0.75	
	SPM*)	RPM*)	SPM	GPM*)	RPM	SPM	RPM
1	0.016	0.002	0.021	0.014	0.003	0.013	-0.001
2	0.039	0.016	0.042	0.019	0.011	0.028	0.005
3	0.010	0.006	0.005	0.004	-0.001	0.011	0.007
4	0.011	0.006	0.005	0.003	-0.001	0.005	0.000
5	-0.014	-0.017	0.004	0.003	0.001	-0.016	-0.019
6	0.003	0.002	0.000	0.000	-0.002	-0.004	-0.005
7	-0.008	-0.014	-0.010	-0.011	-0.018	-0.005	-0.011
8	0.003	-0.007	0.009	0.005	-0.004	0.007	-0.003
9	0.016	-0.007	0.016	-0.004	-0.015	0.017	-0.006
10	0.027	0.002	0.025	-0.001	-0.009	0.025	0.000
11	0.010	0.002	0.007	0.003	-0.004	0.000	-0.008
12	0.009	0.001	0.013	0.010	0.003	0.013	0.005
13	0.005	0.005	0.003	0.003	0.003	-0.003	-0.003
14	-0.002	-0.003	0.004	0.004	0.002	0.009	0.008
15	0.004	-0.002	0.006	0.005	-0.001	0.005	-0.001
16	0.009	0.007	0.002	0.002	0.000	-0.003	-0.005
17	-0.001	-0.005	0.017	0.016	0.012	0.014	0.010
18	-0.006	-0.011	0.002	0.000	-0.005	0.004	-0.001
19	0.024	0.011	0.012	0.006	-0.005	0.007	-0.006
20	0.012	0.001	0.031	0.026	0.017	0.010	-0.001
21	0.018	-0.001	0.018	0.004	-0.007	0.010	-0.009
Average Deviation**)	0.012	0.006	0.012	0.007	0.006	0.010	0.005
Standard Deviation***)	0.015	0.008	0.016	0.010	0.008	0.012	0.007

*) SPM = Simplified Prediction Method
RPM = Refined Prediction Method
GPM = Graphical Prediction Method

**) Defined by $\frac{1}{n} \sum_{i=1}^{i=n} |\delta_i|$

***) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} \delta_i^2}{n-1}}$

From the relevant data in Table XII-6, that is in the columns headed by SPM, it may be concluded that as a rule Equation (XII-24) does apply satisfactorily, even when oils of widely different Slope Indices and/or viscosity grades ("thick" and "thin" oils) are being blended*).

Since both the viscosity function H and the Slope Index, S, have proved approximately additive, the basic viscosity-temperature Equation (III-6h) is very suitable indeed for predicting the complete viscosity-temperature relationship of mineral-oil mixtures. The latter feature, in fact, constitutes another weighty advantage of Equation (III-6h) over conventional equations and charts.

It goes without saying that the establishment of further improved prediction methods - to be described in the subsequent Sections XII.6 and XII.7 - has been attempted on the basis of this new equation.

Although the computations involved in the present "*simplified* prediction method" are very simple, yet these can be completely avoided by using a chart constructed in accordance with Equation (III-6h), that is an H-Θ chart. In the consequent *graphical* procedure mixture viscosities are obtained simply by linearly interpolating (according to volume fractions) between the (isothermal) viscosities of the components. It may be added that there would be no sense in using some *adjusted*, that is a non-linear, volume-fraction scale as employed in the conventional ASTM method.

XII. 5. 2. *Additional Applications*

A. APPLICATION TO TERNARY AND HIGHER MIXTURES

It stands to reason that the described simplified method for predicting the viscosity-temperature relationship of *binary* mineral-oil mixtures solely from that of the two components also lends itself very well for application to *multi-component* mixtures. In fact, the above procedure for binary mixtures simply has to be repeated as many times as necessary.

Turning more particularly to *ternary* mixtures, the approximate additivity of the viscosity function H may be utilized for depicting the viscosity of such mixtures as a function of their composition. This can be done in a triangular composition diagram provided with linear volume-percentage scales and with (three) viscosity scales - alongside the latter scales - proportional to the viscosity function H, the latter three scales being essentially identical to those for the three corresponding binary mixtures individually. Assuming strict additivity of the viscosity function H in all the various possible ternary mixtures, straight lines of constant viscosity can then be constructed in such a triangular diagram. The resulting diagram conveys a comprehensive picture of the possibilities for preparing ternary mixtures of the desired viscosity grade. As an illustration

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*) As regards the practical significance of the deviations inherent in the predicted Slope Indices reference may further be made to § VIII.2.2.

a numerical example of the application of such a diagram is provided by Fig. XII-4. The component oils A, B and C have viscosities -

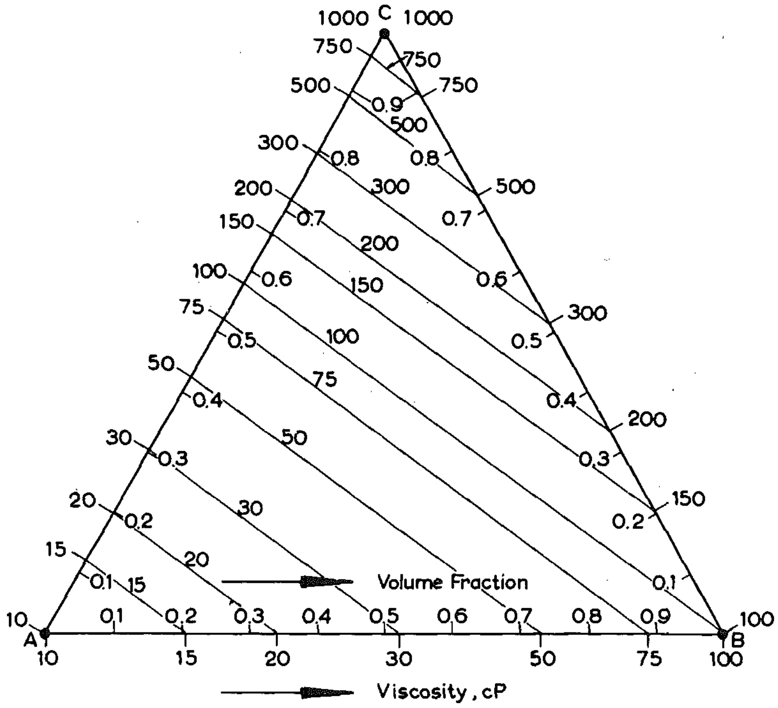

FIG. XII-4.
The Viscosities of a Particular Ternary Mineral-Oil System According to the Simplified Prediction Method.

at the same standard reference temperature - of 10, 100 and 1,000 cP, respectively. A few straight lines denoting distinct viscosities have been constructed*).

Further, a similar triangular diagram can readily be devised for the *Slope Indices* of all the various possible mixtures of the three given component oils.

B. APPLICATION TO POLYMER-BLENDED MINERAL OILS

Presumably the present method - established for natural mineral oils - may likewise be applied to *polymer-blended* samples; that is for predicting the viscosity-temperature relationship of mixtures whose component oils contain equal amounts of a given polymer.

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*) A similar diagram using viscosity scales proportional to the (kinematic) viscosity function W of the ASTM chart (see part B of § XII.2.4) was recently presented by Okon[204].

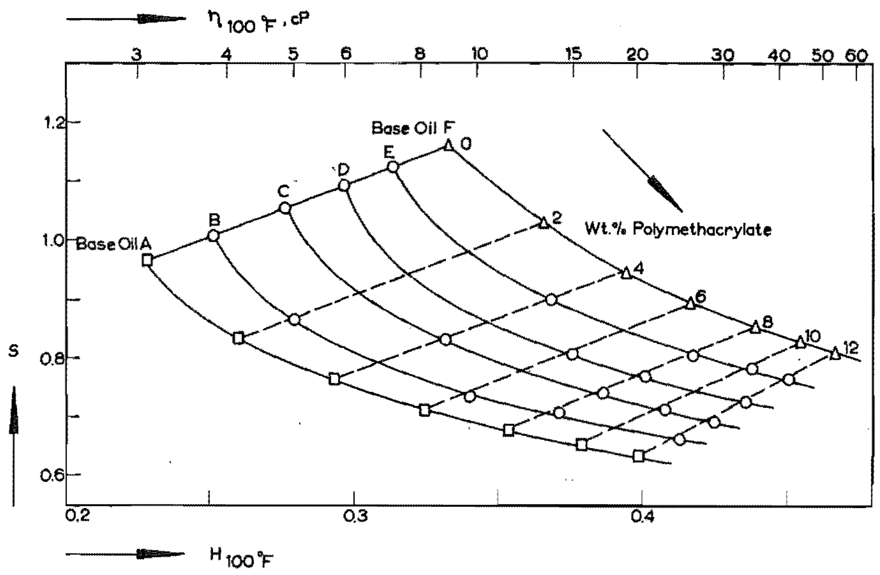

FIG. XII-5.
The Applicability of the Simplified Prediction Method to Mixtures of Polymer-Blended Mineral Oils.

This has been verified in Fig. XII-5 for two base oils (A and F) and their mixtures (B, C, D and E), using polymethacrylate as a so-called VI-improver[70,71].

Fig. XII-5 shows that, to a good approximation, the Slope Indices and corresponding viscosity grades $H_{100°F}$ *) of the various mixtures whose component oils contain equal percentages by weight of polymethacrylate are linearly interrelated. In addition, as outlined above for natural mineral oils (compare base oils A and F of Fig. XII-5), the Slope Indices and viscosity grades $H_{100°F}$ of the latter mixtures can also be obtained by linearly interpolating (according to volume fractions) between the values of the components.

All in all, a diagram such as Fig. XII-5 is very convenient in that it gives a panoramic view of the various possibilities in preparing mixtures from the component oils available.

It may further be recalled that, at least when amounts of polymer higher than about 2% (by weight) are involved, the Slope Indices and viscosity grades H_r of the various blends prepared from a given base oil can be approximated very closely by a straight-line relationship (see part C of § VIII. 4. 6).

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*) It can readily be demonstrated that for reference temperatures different from 100°F essentially the same figure would be obtained.

XII. 5. 3. *Concluding Remarks*

A. SCHEMATIC VISCOSITY-CONCENTRATION DIAGRAM

In conclusion it may be useful to present a schematic picture for illustrating the additivity of a few viscosity functions here employed for mineral-oil and pure-hydrocarbon mixtures.

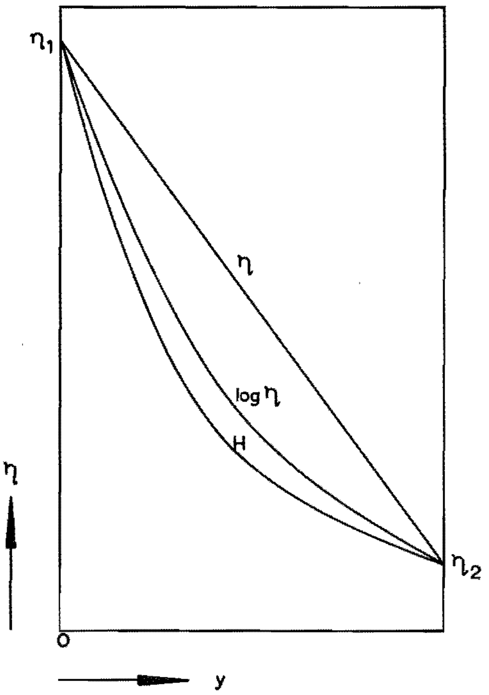


FIG. XII-6.
Schematic Illustration of the Additivity of a Few Viscosity Functions in Binary Liquid Systems.

In Fig. XII-6 the straight line labelled "η" would represent the viscosities of the various possible mixtures if viscosity itself were additive. But in all known systems the more fluid oil (η_2) has proved to contribute considerably more to the resulting viscosity of the mixture (compare Section XII. 1).

The curve marked "log η" represents the mixture viscosities for systems where the Arrhenius Equation (XII-2a) applies. In accordance with the latter remark the viscosities estimated from the Arrhenius equation have invariably been found more satisfactory than those obtained from the additivity of viscosity itself. Particularly when large viscosity ratios are involved, the improvement may become enormous. Yet, in practically all mineral-oil systems tested - and likewise in all pure-hydrocarbon mixtures considered in Section XII. 4 - the viscosities predicted from the additivity of log η are still more or less too high, the deviations being roughly proportional to the viscosity *ratio* of the particular system.

A further substantial improvement can be achieved by the new Relationship (XII-23) implying the additivity of the viscosity function H. As shown by the lower curve ("H") in Fig. XII-6, this relationship allows for an even stronger effect of the lower-viscosity component than indicated by the curve "log η".

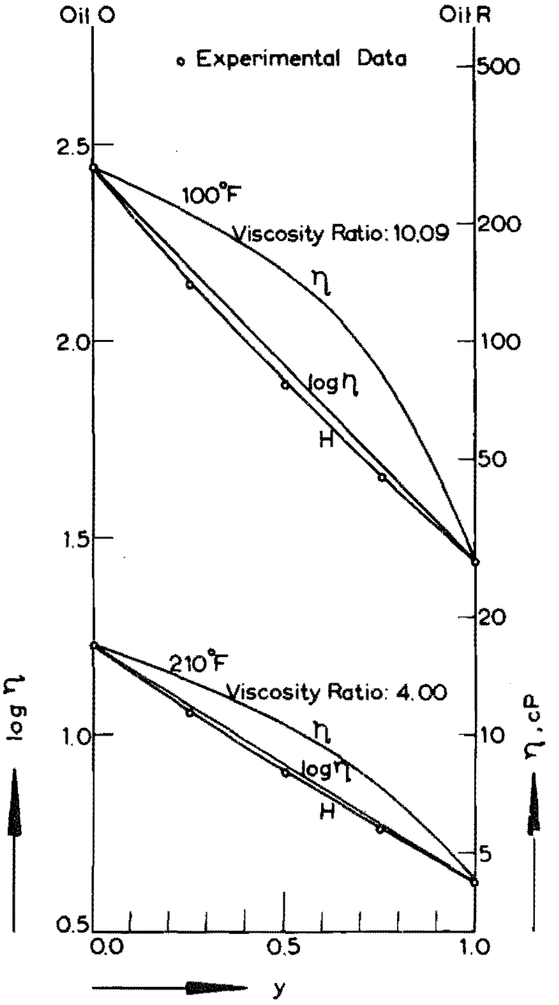


FIG. XII-7.
Comparison of Predicted Viscosity-Concentration Isotherms With Experimental Viscosity Data for a Representative Mineral-Oil System.

It stands to reason that the distances between the three lines depicted in Fig. XII-6 - and of course also the differences between the viscosities predicted from their basic equations - become smaller as the viscosity ratio decreases.

In Fig. XII-7 the latter three lines have been depicted for a representative system, namely system No. 11 of Tables XII-1b and XII-1c.

B. THE SLOPE INDEX AND THE VISCOSITY INDEX OF MINERAL-OIL MIXTURES

Owing to the very divergent nature of the oils encountered the degree of additivity that might be incorporated into *any* index for the viscosity-temperature dependence of mineral oils will anyhow leave something to be desired. But as demonstrated above, the present index, the Slope Index, S, may be considered satisfactorily additive at least for normal practical purposes.

In fact, the degree of additivity reached with S would seem even considerably higher than deemed possible at all by various previous investigators. In this connection reference may be made to the relevant statements made by, amongst others, Blott and Verver[131].

It should not be overlooked, however, that these and many similar statements have been based on the wide experience gained with the familiar ***Viscosity Index***, VI, or closely related indices. Indeed, the equation:

$$VI_m = (1-y)\ VI_1 + y\ VI_2 \qquad (XII\text{-}25)$$

has frequently been tried.

However, the VI's of mineral-oil mixtures predicted from the latter equation may be seriously in error; in general the resulting VI's are too *low*. Especially when one of the components is very fluid, the deviations may become quite considerable.

Equation (XII-25) has also been applied to the systems designated in Tables XII-1b and XII-1c, that is to the mixtures with a volume fraction $y = 0.50$. As shown by Table XII-7, the deviations between calculated and experimentally determined VI's prove to be very large in various systems. Yet, this table might give a flattering impression of the accuracy of Equation (XII-25). Indeed, the deviations encountered in practice may easily amount to over some 50 points in the VI-values, even with oil components of similar chemical constitution (see also below).

The poor applicability of Equation (XII-25) may conveniently be elucidated on the basis of Fig. XII-8, where the lines of constant VI have been replotted from Fig. VIII-10. According to the simplified prediction method, the Slope Indices and the viscosity grades H_r of the various mixtures prepared from two given oils are situated in an S-H_r diagram (such as Fig. XII-8) on the straight line connecting the points of both components. Indeed, it can then readily be seen from Fig. XII-8 that the VI's calculated from Equation (XII-25) would usually be too low, particularly so when low-viscosity oils are involved.

An illustrative example of the unrealistic trend of the VI in mineral-oil mixtures has been included in the latter figure. The depicted

TABLE XII-7

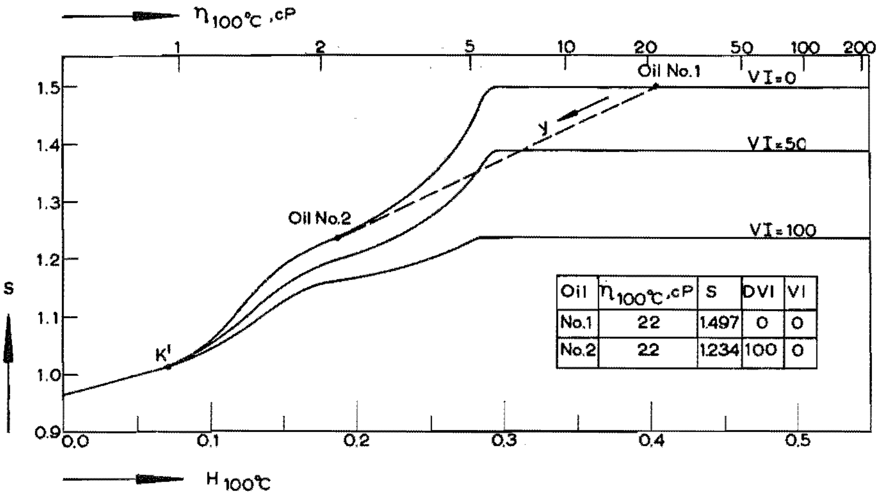
Experimental and Predicted VI's of Mineral-Oil Mixtures With y=0.50

System No.	Viscosity Index	
	Exp.	Eq.(XII-25)
1	32	1
2	74	54
3	85	52
4	108	105
5	88	57
6	101	96
7	46	34
8	77	72
9	6	-24
10	5	-24
11	93	88
12	94	85
13	89	56
14	53	52
15	10	10
16	16	14
17	83	63
18	88	88
19	47	36
20	62	48
21	31	8

oils Nos. 1 and 2 have a common Viscosity Index, namely VI = 0, but their viscosity ratio amounts to 10, the respective viscosities at 100°C being 22 and 2.2 cP. The Slope Indices of their mixtures are located, at least to a good approximation, on the straight dashed line connecting both components. Thus, these Slope Indices would vary linearly with the volume fraction y from $S_1 = 1.497$ to $S_2 = 1.234$, corresponding to a variation in their DVI's from 0 to 100. Now, Equation (XII-25) implies that all mixtures in question would have invariably the same VI of 0, although, as shown by Fig. XII-8, their *actual* VI's may reach values of about 60.

Fig. XII-8 is very suitable also for illuminating one of the basic shortcomings of the VI as a viscosity-temperature criterion: its *unrealistic* - not to say erroneous - definition in the low-viscosity range. This misleading feature may already be grasped from the highly irregular trends of the three constant-VI lines depicted in Fig. XII-8. As regards the consequences of such unrealistic VI's for the practice of mineral-oil blending, the following example may go to illustrate the kind of erratic results that may be obtained.

Returning to the various mixtures that may be prepared from the two oils depicted in Fig. XII-8, it is seen that with increasing volume fraction y the VI first rises gradually, then passes through a maximum of about VI = 60 (in the vicinity of y = 0.5) and finally falls



Oil	$\eta_{100°C}$, cP	S	DVI	VI
No.1	22	1.497	0	0
No.2	22	1.234	100	0

FIG. XII-8.

Illustration of the Unrealistic Trend of the Viscosity Index in Mineral-Oil Mixtures.

regularly towards the initial level, that is VI = 0. Consequently, since the VI has been claimed to rate the viscosity-temperature qualities of oils, the viscosity-temperature qualities of the latter mixtures would invariably be better than those of the two base stocks; moreover, with varying composition they would pass through a very pronounced maximum.

The new *rational* viscosity-temperature criterion, the Slope Index, readily removes such highly misleading impressions created by the conventional VI.

XII. 6. A GRAPHICAL METHOD FOR PREDICTING THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP OF MINERAL-OIL MIXTURES

As outlined in § XII. 5. 1, the simplified prediction method permits both numerical and *graphical* estimates of the viscosity-temperature relationship of mineral-oil mixtures. The graphical procedure amounts to linearly interpolating (according to volume fractions) between the (isothermal) viscosities of the components plotted in an H-Θ chart. Now, it has been found that this chart can be utilized even more advantageously in an alternative way, that is similarly to Wright's above-discussed variant of using the ASTM chart (see part B of § XII. 2. 4).

Just like Wright's method the "*graphical* prediction method" to be described below does not involve any computations. The present H-Θ chart, however, displays several important advantages over the conventional ASTM chart serving as a basis to Wright's method.

It will be shown that this graphical prediction method constitutes a substantial improvement over the *simplified* prediction method described in § XII. 5. 1.

Referring to the description of Wright's method and to the schematic Fig. XII-9, the present graphical prediction method may be delineated as follows.

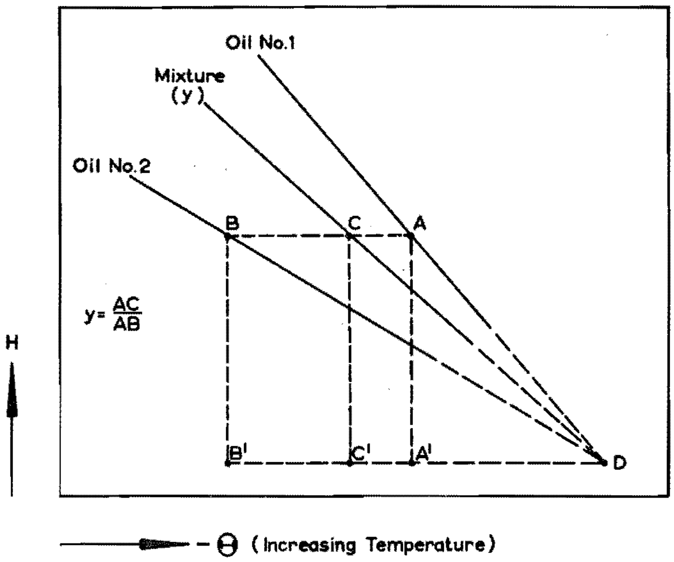


FIG. XII-9.
Schematic Representation of the Graphical Prediction Method.

At an arbitrary viscosity level a certain point - for instance point C in Fig. XII-9 - of the viscosity-temperature line of the mixture (with a given y-value) is estimated by linearly interpolating between the two rectified viscosity-temperature lines of the components. As soon as only *two* sufficiently widely spaced points of the viscosity-temperature line of the mixture have thus been estimated, its complete straight line can be drawn.

Although the above procedure is indeed intended to be executed graphically, it would appear useful yet to find out which *mathematical* expressions constitute the basis of the graphical prediction method. This may be performed as follows.

A mathematical consequence of the above concept is that the viscosity-temperature lines of the two components and their mixtures pass through one single point, so that they form a *fan*. This point, in Fig. XII-9 denoted by D, may be located in the conventional temperature range, but usually it will be located far beyond it, either at some very high or some very low temperature. For the following analytical treatment, however, the location of point D is immaterial.

From Fig. XII-9 it readily follows that:

$$\frac{S_1}{S_m} = \frac{C'D}{A'D} = 1 + \frac{AC}{A'D} \qquad \text{(XII-26a)}$$

and

$$\frac{S_1}{S_2} = \frac{B'D}{A'D} = 1 + \frac{AB}{A'D} . \qquad \text{(XII-26b)}$$

By eliminating the distance A'D from Equations (XII-26a) and (XII-26b) the following expression can be arrived at:

$$\frac{\dfrac{S_1}{S_m} - 1}{\dfrac{S_1}{S_2} - 1} = \frac{AC}{AB} . \qquad \text{(XII-27)}$$

Replacing the right-hand side of the latter expression by the volume fraction y, the following equation is readily obtained:

$$\frac{1}{S_m} = \frac{1 - y}{S_1} + \frac{y}{S_2} \qquad \text{(XII-28a)}$$

or

$$S_m = \frac{S_1}{1 + \left(\dfrac{S_1}{S_2} - 1\right) y} . \qquad \text{(XII-28b)}$$

According to Equation (XII-28a) or also (XII-28b), the present graphical method implies the additivity of the *reciprocal* Slope Indices. This means that the second component - having by definition the smaller Slope Index, S_2 - would show a somewhat greater effect on the resulting S_m-value than predicted from the straight additivity of the Slope Indices, that is from Equation (XII-24). For the considered mixtures with $y = 0.50$ Table XII-6 lists - in the column headed by GPM - the deviations between the Slope Indices predicted from Equation (XII-28a) or (XII-28b) and the experimental values. Whilst, as a rule, the simple Equation (XII-24) does yield good predictions for S_m, the S_m-values obtained from Equation (XII-28a) or (XII-28b) prove to be in *excellent* agreement with the experimental values, the deviations being almost within the experimental accuracy.

An expression for the viscosity *grade* of a given mixture can now be derived as follows. Applying the basic viscosity-temperature Equation (III-6h) to the two components and their mixture readily leads to the formula:

$$\frac{H_1 - H_m}{H_1 - H_2} = \frac{S_1 - S_m}{S_1 - S_2} . \qquad \text{(XII-29)}$$

Elimination of S_m from Equations (XII-28b) and (XII-29) yields:

$$\frac{H_1 - H_m}{H_1 - H_2} = \frac{\dfrac{S_1}{S_2}\, y}{1 + \left(\dfrac{S_1}{S_2} - 1\right) y}. \qquad \text{(XII-30a)}$$

Equation (XII-30a) can be rearranged to:

$$H_m = (1-y_g)\, H_1 + y_g H_2, \qquad \text{(XII-30b)}$$

where, by definition:

$$y_g = \frac{\dfrac{S_1}{S_2}\, y}{1 + \left(\dfrac{S_1}{S_2} - 1\right) y}. \qquad \text{(XII-31)}$$

Furthermore, this *corrected* volume fraction y_g may likewise be introduced into Equation (XII-28b), giving:

$$S_m = (1-y_g)\, S_1 + y_g S_2. \qquad \text{(XII-28c)}$$

*According to the analogous Equations (XII-30b) and (XII-28c), respectively, the graphical prediction method simply amounts to the additivity of both the viscosity function H and the Slope Index in terms of a corrected**) *volume fraction, y_g. According to Definition (XII-31), the relationship between the quantity y_g and the straight volume fraction, y, is defined for any given system by its Slope-Index ratio.*

For a constant Slope-Index ratio, that is for any given system, the quantities y_g and y prove to display a hyperbolic interrelationship, this being of such a form that the volume fraction y_g is invariably greater than y. For the sake of completeness, it may be remarked that in the limiting case where $S_1 = S_2$ - so that the viscosity-temperature lines of the two components are parallel - the corrected volume fraction y_g becomes identical with y. In that case the lines of the mixtures would be parallel to those of the components and the viscosity functions H of the latter would be additive in terms of the straight volume fraction y. It may be added that the Slope Indices S_1 and S_2 of a great many of the systems encountered in practice are not very different. For such mixtures it does not make much difference if the viscosity function H and/or the Slope Index are taken additive in terms of either y or y_g.

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*) It is interesting to note that Definition (XII-31) has a striking formal resemblance to Lederer's Definition (XII-6). In fact, as mentioned above, Lederer's mixture-viscosity Equation (XII-5) equally applies when in Definition (XII-6) the volume fraction, y, is used instead of the weight fraction, x. It can then readily be shown that the Slope-Index ratio, S_1/S_2, in the present Definition (XII-31) takes the place of the reciprocal of the a priori unknown parameter q in Lederer's Definition (XII-6).

TABLE XII-8

Application of the Graphical Prediction Method
to Mineral-Oil Mixtures With y=0.50

System		y_g Acc. to Eq.(XII-31)	$\% \delta \eta$*)	
No.	$\frac{S_1}{S_2}$		100°F	210°F
1	1,158	0,537	-2,7	-3,8
2	1.295	0,564	4.0	0.0
3	1,053	0,513	-1,8	-1.8
4	1.062	0,514	-2,1	-2,3
5	1.031	0,508	-3,0	-2,3
6	1.016	0,504	-1,6	-0,9
7	1,076	0,518	-5,6	-2,5
8	1,126	0,529	-0,5	-1,1
9	1,273	0,561	-7,7	-4,5
10	1,309	0,567	-12,5	-8,0
11	1,103	0,525	-3,2	-2,7
12	1,098	0,524	-4,1	-4,5
13	1,002	0,500	-6,7	-5,2
14	1,018	0,505	-0,9	-0,9
15	1,068	0,516	-1,4	-1,6
16	1,028	0,507	-0,7	-0,7
17	1,047	0,511	-1,1	-2,7
18	1,064	0,516	0,2	0,0
19	1,147	0,534	3,5	1.4
20	1,122	0,528	5,7	-0,5
21	1,214	0,548	4,7	2,6
22	1,278	0,562	11,9	
23	1,125	0,529	4,0	
24	1,170	0,539	3,5	
25	1,087	0,521	1,4	
26	1,118	0,528	2,1	
Average Deviation**)			3,7	2.4
Standard Deviation***)			4,9	3,1

*) $\% \delta \eta = 100 \frac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) Defined by $\frac{1}{n} \sum_{i=1}^{i=n} \left| \% \delta_i \right|$

***) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} (\% \delta_i)^2}{n-1}}$

In Table XII-8 are listed the Slope-Index ratios of the 26 mineral-oil systems under consideration, together with the above-defined y_g-values of their mixtures with $y = 0.50$. The same table contains the deviations between the viscosities predicted by means of Equation (XII-30b) and the experimental values, both for 100 and for 210°F. As compared with the results of the *simplified* prediction method (see Table XII-5) the present *graphical* prediction method proves to yield appreciably better[*] predictions at the lower reference temperature. But at the higher reference temperature the difference between the accuracies inherent in these two prediction methods has become so small that it is no longer statistically significant.

Like the simplified method the present graphical method implies that in an S-H_r chart (such as Fig. XII-8), where H_r refers to the viscosity *grade* of the oils, the quantities H_m and S_m of the various mixtures that may be prepared from two given components are located on the straight line connecting these components. The only difference consists in that the method under discussion employs an *adjusted* volume-fraction scale, namely a scale proportional to y_g. Such an S-H_r chart is very convenient for rapidly gaining an impression of the H_m- and S_m-values that would be obtainable by preparing binary blends from a variety of mineral oils available.

Summarizing, it has been shown that the "graphical prediction method" constitutes a substantial improvement over the "simplified prediction method", which is based on the straight additivity of the viscosity function H.

Nevertheless, like Wright's analogous method based on the ASTM chart the present graphical prediction method based on the new H-Θ chart leaves much to be desired in certain cases, notably when the component oils combine a fairly small viscosity ratio with a relatively great difference in their Slope Index.

Therefore, it will be attempted in the next section to develop a further improved prediction method.

XII. 7. A REFINED METHOD FOR PREDICTING THE ATMOSPHERIC VISCOSITY-TEMPERATURE RELATIONSHIP OF MINERAL-OIL MIXTURES

XII. 7. 1. *Introduction*

The ideas underlying the present "*refined* prediction method" are quite similar to those which are basic to the indicated refined method for *pure-hydrocarbon* mixtures (see § XII. 4. 3). The only essential difference consists in that the specific viscochor utilized in the latter method has been replaced - for reasons of simplicity - by the viscosity function H (compare § XII. 5. 1).

Accordingly, the refined method for predicting the viscosities of *mineral-oil* mixtures starts from the approximate additivity of the viscosity function H. At any given temperature the additional "*in-*

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[*] According to the F-test, the statistical confidence level amounts to about 95%.

teraction viscosity" could be conveniently accounted for by introducing solely the difference between the *Slope Indices* of the two component oils.

Likewise, it has appeared that the accuracy inherent in the simplified method for predicting the Slope Index of mineral-oil mixtures (see § XII. 5. 1) can be considerably improved simply by accounting for the aforementioned difference between the Slope Indices of the two components.

For convenience the improved prediction of the Slope Index of mineral-oil mixtures will be expounded first.

It is interesting to note that - as elucidated already in Chapter VI - the difference between the Slope Indices of the component oils, which is utilized as an additional parameter in the present refined prediction method, may be conceived as a viscometric yard-stick of the difference in their chemical constitution.

XII. 7. 2. *The Slope Index of Mineral-Oil Mixtures*

For the present purpose the simplified Equation (XII-24) is extended as follows:

$$S_m = (1-y)\ S_1 + yS_2 + y(1-y)\ S_{12}\ , \qquad \text{(XII-32)}$$

where the *"interaction Slope Index"* S_{12} is characteristic of a given mixture. It has been found for the great variety of mineral-oil mixtures designated in Tables XII-1b and XII-1c that the additional factor S_{12} is simply proportional to the *absolute* difference between the Slope Indices of the two components, that is to $\Delta S = (S_1 - S_2)$. The resulting correlation reads:

$$S_{12} = -0.35 \cdot \Delta S\ . \qquad \text{(XII-33)}$$

Substituting the latter expression for S_{12} into Equation (XII-32) leads to the following *refined* equation, which does not involve any unknown parameters:

$$S_m = (1-y)\ S_1 + yS_2 - 0.35\ y(1-y)\ \Delta S. \qquad \text{(XII-34a)}$$

As shown in Table XII-6, that is in the columns headed by RPM, the agreement between the Slope Indices predicted from Equation (XII-34a) and the experimental values may be deemed *excellent*. In fact, even for systems whose components exhibit widely different Slope Indices the deviations remain nearly within the experimental accuracy.

Equation (XII-34a) may further be rearranged to:

$$S_m = \Big\{1-y\big[1 + 0.35\ (1-y)\big]\Big\}\ S_1 + y\big[1 + 0.35\ (1-y)\big]\ S_2 \qquad \text{(XII-34b)}$$

or also:

$$S_m = (1-y')\ S_1 + y'S_2, \qquad \text{(XII-34c)}$$

where, by definition:

$$y' = y\left[1 + 0.35 \quad (1-y)\right]. \qquad \text{(XII-35)}$$

Consequently, it has been derived that the Slope Index is additive in terms of the *corrected* volume fraction y' rather than in terms of the straight volume fraction y. Since y' is greater than y for all possible mixture compositions, the second component has a greater effect on the resulting S_m-value than indicated by the simplified Equation (XII-24). For example, for y = 0.500 the corrected volume fraction amounts to y' = 0.588.

According to Equation (XII-35), the corrected volume fraction y' has the very attractive feature that it is invariably the same function of the straight volume fraction y. Thus, an S-y diagram can be constructed, with a volume-fraction scale proportional to y', which permits a convenient and accurate estimate of the Slope Index of any mineral-oil mixture. Fig. XII-10 represents such a diagram. As

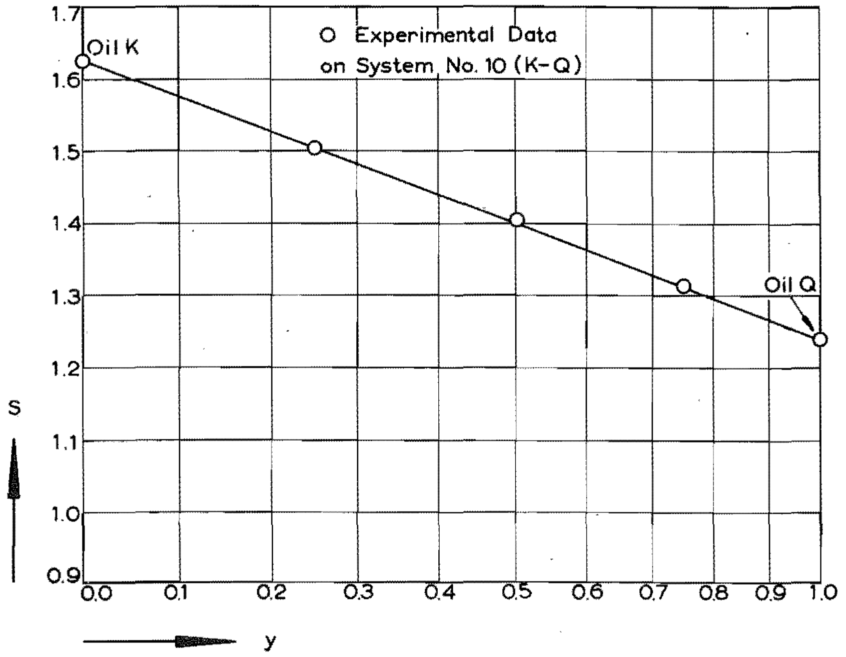

FIG. XII-10.
The Slope Indices of Mineral-Oil Mixtures According to the Refined Prediction Method.

an example the appropriate straight line has been drawn for system No. 10, whose components display an extremely wide variation in their Slope Indices, namely ΔS = 0.384 (corresponding to a difference of 175 points in their Dynamic Viscosity Indices).

XII. 7. 3. *The Viscosity Grade of Mineral-Oil Mixtures*

The accuracy inherent in the additivity of the viscosity function H can be considerably improved by introducing a factor that would allow for the *"interaction viscosity"*. This may be done as follows:

$$H_m = (1-y)\ H_1 + yH_2 + y\,(1-y)\ H_{12}\,, \qquad \text{(XII-36a)}$$

where the *"interaction viscosity function"* H_{12} is characteristic of a given mixture. If one suitable mixture-viscosity value is known - preferably for a blend containing approximately equal volumes of both components -, an appropriate value for H_{12} can readily be derived.

For the 26 systems under consideration the H_{12}-values at 100°F have thus been calculated, using the experimental viscosities of the mixtures with $y = 0.50$. Substitution of these H_{12}-values into Equation (XII-36a) yields the deviations listed in Table XII-9a for the mixtures with $y = 0.25$ and $y = 0.75$. In addition, Table XII-9b contains the deviations resulting for the various compositions of system No. 22*), which is peculiar amongst the systems considered in that it exhibits a pronounced *minimum* in its viscosity-concentration isotherm for 100°F.

Indeed, the extended Equation (XII-36a) is seen to represent the experimental data very well. This holds even for the aforementioned system No. 22 (over its entire concentration range). As a rule the agreement for all these various systems is within the experimental accuracy.

It may further be noted that besides for calculating the viscosities of mixtures with a given y-value Equation (XII-36a) is very suitable for the *inverse* procedure, that is for estimating the volume fraction, y, at which a mixture of two given components would assume the desired viscosity. For the latter purpose the volume fraction y is readily solved from the following quadratic equation, which actually constitutes a rearrangement of Equation (XII-36a):

$$H_{12}\cdot y^2 + (H_1-H_2-H_{12})\ y + (H_m-H_1) = 0. \qquad \text{(XII-36b)}$$

As indicated above, it has indeed been found that the interaction viscosity function H_{12} of binary mineral-oil mixtures can be conveniently estimated solely from the viscosity-temperature relationship of the two components. In fact, only the difference between the Slope Indices of the components, ΔS, is needed in addition to their viscosity grades. Adopting, in accordance with previous chapters, a standard reference temperature of 40°C (104°F), the following correlation has finally been established as a really satisfactory one:

$$H_{12,40^\circ C} = (0.160 - 0.4\cdot\Delta S)\ \Delta H_{40^\circ C} - 0.088\cdot\Delta S, \qquad \text{(XII-37)}$$

with the proviso: $\Delta S \leqslant 0.400$. In this equation $\Delta H_{40^\circ C}$ stands for the *absolute* difference between the viscosity function $H_{40^\circ C}$ of both components.

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*) Further particulars on this system can be found in the subsequent Section XII. 8.

TABLE XII-9a

Application of Equation (XII-36a) to Mineral-Oil Mixtures

System No.	$H_{12,100^oF}$ Exp.	$\% \delta \eta_{100^oF}$ *)	
		y = 0.25	y = 0.75
1	-0.0156	1.6	-0.2
2	-0.0480	0.9	-2.3
3	0.0104	0.2	-0.5
4	-0.0016	0.5	-0.7
5	0.0112	-0.2	-0.9
6	0.0028	-0.5	-0.2
7	0.0072	-0.2	0.5
8	-0.0088	-0.5	0.5
9	-0.0264	0.7	-0.7
10	-0.0272	2.8	0.7
11	-0.0060	1.4	-0.2
12	-0.0036	0.7	-0.2
13	0.0204	0.5	0.0
14	0.0036	0.5	1.2
15	0.0004	0.5	0.5
16	0.0008	-0.2	-0.2
17	0.0060	-0.5	-0.5
18	-0.0020	-0.7	0.2
19	-0.0088	2.1	-0.7
20	-0.0144	-1.8	-1.4
21	-0.0144	0.5	-1.1
23	-0.0096	0.0	-0.2
24	-0.0080	0.0	0.2
25	-0.0044	0.5	0.2
26	-0.0064	0.0	-1.1
Average Deviation**)		0.7	0.6
Standard Deviation***)		1.0	0.8

*) $\% \delta \eta = 100 \dfrac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) Defined by $\dfrac{1}{n} \sum_{i=1}^{i=n} | \% \delta_i |$

***) Defined by $\sqrt{\dfrac{\sum_{i=1}^{i=n} (\% \delta_i)^2}{n-1}}$

TABLE XII-9b

Application of Equation (XII-36a) to System No. 22

Volume Fraction y	$\% \delta \eta_{100^oF}$ *)
0.1	1.4
0.2	0.7
0.3	0.2
0.4	-0.5
0.5	0.0
0.6	-0.2
0.7	-0.7
0.8	-0.2
0.9	-0.7

*) $\% \delta \eta = 100 \dfrac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

According to Correlation (XII-37), $H_{12,40^\circ C}$ is linearly related to both ΔS and $\Delta H_{40^\circ C}$. A plot of $H_{12,40^\circ C}$ against the main variable ΔS, using $\Delta H_{40^\circ C}$ as a parameter, yields a family of straight lines converging towards the point where $H_{12,40^\circ C} = -0.0352$ and $\Delta S = 0.400$. This is illustrated in Fig. XII-11*).

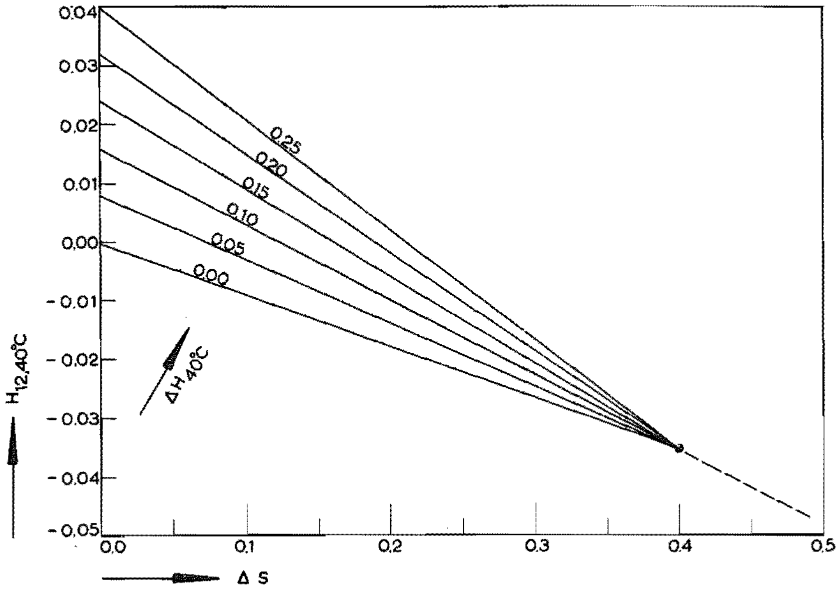

FIG. XII-11.
The Interaction Viscosity Function of Binary Mineral-Oil Systems According to Correlation (XII-37).

On the basis of the foregoing expressions in this section the following *generalized* correlation, which would hold at any arbitrary temperature Θ, has been derived in Appendix XII-3 (at the end of this chapter):

$$H_{12} = (0.160 - 0.4 \cdot \Delta S)\left|(H_1 - H_2) - \Delta S\,(0.1127 + \Theta)\right| - \Delta S\left[0.088 + 0.35\,(0.1127 + \Theta)\right]. \qquad \text{(XII-38)}$$

Notwithstanding its longish form the latter correlation permits really simple estimates of H_{12} in a wide temperature range.

XII. 7. 4. *Applicability of the Refined Prediction Method*

It should be stated explicitly that, as shown in Appendix XII-3, Equation (XII-38) implies the validity of the refined Equation (XII-34a)

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*) Since no systems were available with ΔS-values above 0.400, the line extending in the latter figure from the point of convergence towards higher ΔS-values should be regarded as tentative; actually it constitutes the produced part of the line relating to $\Delta H_{40^\circ C} = 0.10$.

for predicting the Slope Index of mineral-oil mixtures. Therefore, the following two procedures for estimating the viscosity-temperature relationship of a given mineral-oil mixture are fully equivalent:

1. Predicting its viscosity at one representative temperature by means by Equation (XII-36a) and Correlation (XII-38), and its Slope Index by means of Equation (XII-34a);
2. Predicting its viscosities at any of the desired temperatures by means of Equation (XII-36a) and Correlation (XII-38).

The excellent concurrence with experimental Slope Indices achieved by the present Equation (XII-34a) has been demonstrated already in § XII. 7. 2.

The refined prediction method has further been applied for estimating the viscosities at 100 and 210°F of all the 26 systems designated in Tables XII-1b and XII-1c. Together with the values of $H_{12,100^\circ F}$ calculated from Correlation (XII-38), the deviations between experimental and predicted viscosities have been compiled in Table XII-5, that is in the columns headed by RPM.

On the whole these deviations are seen to be really small, notwithstanding the fact that, as said before, various systems represent rather extreme cases in that their components differ unusually widely in chemical constitution. Moreover, it should not be overlooked that in several systems very great viscosity variations are involved and that the experimental viscosities employed for the component oils may contain already appreciable errors.

The agreement between experimental and predicted mixture viscosities is good even for system No. 22, which exhibits a pronounced minimum in its viscosity-concentration isotherm for 100°F. In fact, this refined prediction method is the only known method that permits predicting *quantitatively* the occurrence of such minima, solely from the viscosity-temperature relationship of the component oils. This unique feature of the present method will be elaborated in the following Section XII. 8.

The very good general agreement between experimental and predicted viscosities indicated in Table XII-5 for the great variety of systems there considered, is substantiated by the data on three additional systems designated in Tables XII-10a and XII-10b 71). System No. 29 offers an exceptionally severe test of the new prediction method in that it combines a great ΔS-value with a fantastically high viscosity ratio of nearly 7,000. Nevertheless, for this system too, the agree-

TABLE XII-10a

Data on Component Mineral Oils

Oil	$\eta_{100^\circ F}$, cP	S	Experimenters' Designation 71)
S	10.14	1.149	Pennsylvania Neutral
T	18.41	1.186	Midcontinent Neutral
U	20.0	1.289	Coastal Neutral
V	385	1.247	Pennsylvania 140 Bright Stock
W	70,100	1.408	Pennsylvania Heavy Oil

TABLE XII-10b

Data on Mineral-Oil Mixtures With y=0.50

System		Viscosity Ratio, 100°F	$\Delta H_{100°F}$	ΔS	$\eta_{100°F}$, cP	
No.	Components				Exp.	RPM*)
27	U-V	19.28	0.1801	0.042	84.1	82.4
28	V-T	20.9	0.1864	0.061	75.9	77.4
29	W-S	6,920	0.4379	0.259	293	286

*) RPM = Refined Prediction Method

ment is practically within the experimental accuracy. To emphasize the significance of the latter achievement of the refined prediction method it may be mentioned that the viscosity which would be predicted for system No. 29 from the additivity of log η (Arrhenius) exceeds the experimental value by nearly 200%; the viscosity predicted by simply averaging the viscosities of the components exceeds the experimental value by no less than a *factor* of 120.

Further evidence of the very good applicability of the refined prediction method is offered by the calculations performed for system No. 30, which is designated in Table XII-11[194]. For the latter system mixture viscosities have been determined for five compositions at each of the three temperatures 20, 50 and 100°C (68, 122 and 212°F). Besides a very great ΔS-value of 0.332, this system exhibits very high viscosity ratios at all three reference temperatures - much higher than those covered by the systems of Tables XII-1b and XII-1c. For this system too, however, experimental and predicted viscosities prove to agree very well over the entire concentration range and at each of the three temperatures involved. This is demonstrated in Fig. XII-12, where the experimental viscosities are seen to be located very close to the three predicted viscosity-concentration curves. Application of the Arrhenius Equation (XII-2a) would again lead to enormous errors, as can readily be judged from the deviations of the experimental mixture-viscosity

TABLE XII-11

Data on System No. 30[194]

<table>
<tr><td colspan="5">Components: "Western Bright Stock" (S_1 = 1.408)
"Mineral Colza" (S_2 = 1.076)</td></tr>
<tr><td colspan="5">Experimental Data</td></tr>
<tr><td rowspan="2">Temp., °C</td><td colspan="2">Viscosity, cP</td><td rowspan="2">Viscosity Ratio</td><td rowspan="2">ΔH</td></tr>
<tr><td>Comp. 1</td><td>Comp. 2</td></tr>
<tr><td>20</td><td>3142</td><td>7.68</td><td>409</td><td>0.3527</td></tr>
<tr><td>50</td><td>277</td><td>3.27</td><td>84.7</td><td>0.3273</td></tr>
<tr><td>100</td><td>25.9</td><td>1.36</td><td>19.01</td><td>0.2919</td></tr>
</table>

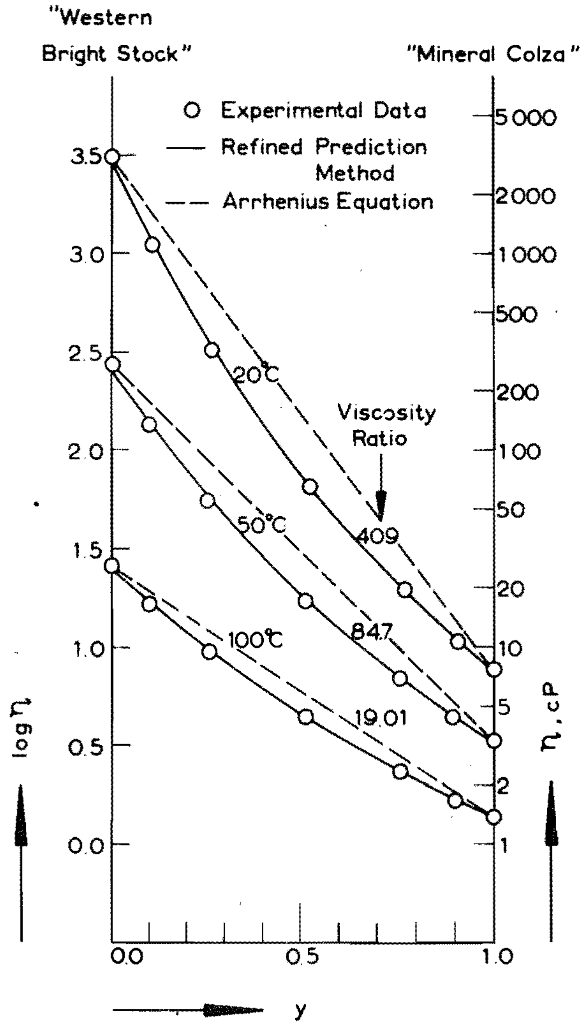

FIG. XII-12.
The Applicability of the Refined Prediction Method to a Typical Mineral-Oil System.

points from the corresponding straight lines (broken) in the latter figure.

Altogether a number of 30 representative systems have been considered. Unfortunately, not any additional mixtures could be found in the literature which are specified sufficiently for verifying the present method. For this reason, the latter method could hitherto not be checked directly beyond the temperature range from 20 to 100°C (68-212°F). Nevertheless, in view of the excellent predictions achieved for the Slope Indices of the great variety of systems tested, it may safely be assumed that the refined prediction method will yield acceptable results over almost the entire temperature range of general practical interest with mineral oils, extending, say, from 0 to 200°C (-17.8 to 392°F).

Summarizing, it is concluded that as regards its correlational accuracy the present refined method for predicting the viscosity-temperature relationships of mineral-oil mixtures solely from those of the component oils would leave hardly anything to be reasonably desired.

XII. 7. 5. *Concluding Remarks*

A. MIXTURES OF MINERAL OILS WITH A COMMON SLOPE INDEX

The refined prediction method becomes very simple indeed if confined to mixtures of mineral oils characterized by a common Slope Index. It may be recalled that, as outlined in Chapter VI, mineral oils belonging to a given naturally homologous group - excepting the more fluid members - do display substantially the same Slope Index.

According to Equation (XII-34a), the Slope Index of such oils would not appreciably be changed by mixing. Thus, in the basic H-Θ chart the viscosity-temperature relationships of the two components and their various mixtures would be depicted as a *sheaf.*

As regards the estimation of the viscosity grade of mixtures of iso-S oils, it is readily seen from Correlation (XII-38) that at any temperature involved their interaction viscosity functions H_{12} are given by $H_{12} = 0.160 \cdot \Delta H$, where ΔH is constant over the entire temperature range considered. For such oils the basic Equation (XII-36a) therefore takes the form:

$$H_m = (1 - y)\ H_1 + yH_2 + 0.160\ y\ (1 - y)\ \Delta H. \qquad \text{(XII-39a)}$$

Taking $H_1 \geqslant H_2$, the latter expression can be rewritten as:

$$H_m = \left\{1 - y\left[1 - 0.160\ (1-y)\right]\right\} H_1 + y\left[1 - 0.160\ (1-y)\right] H_2 \qquad \text{(XII-39b)}$$

or also:

$$H_m = (1-y_S)\ H_1 + y_S H_2, \qquad \text{(XII-39c)}$$

where, by definition:

$$y_S = y\ \left[1 - 0.160\ (1-y)\right]. \qquad \text{(XII-40)}$$

Consequently, for iso-S oils the viscosity function H would be additive in terms of the *corrected* volume fraction y_S rather than in terms of the straight volume fraction y. It is seen that for all possible mixture compositions y_S is smaller than y. For example for $y = 0.500$ the corrected volume fraction amounts to $y_S = 0.460$.

B. THE COMPATIBILITY OF PURE-HYDROCARBON MIXTURES WITH THE SIMPLIFIED AND REFINED METHOD FOR PREDICTING THE VISCOSITY GRADE OF MINERAL-OIL MIXTURES

Since mineral oils constitute complex mixtures of a great variety of (essentially) hydrocarbon compounds, the specific effect of any of these individual compounds on the physical properties of such mixtures will be hardly detectable. Therefore, it may be conceived that certain "averaging" effects are obtaining in mineral oils. The latter feature is of indispensable help in, for instance, the development of quantitative rules for predicting the changes in physical properties brought about by blending mineral oils.

It may be stated that in general the applicability of such blending rules becomes poorer as the differences between the (average) chemical constitution of the component oils become more pronounced. Considerable deviations from blending rules established for mineral oils may therefore be anticipated when these are applied to mixtures of individual, *pure* hydrocarbons. In this respect it is interesting to investigate the compatibility of pure-hydrocarbon mixtures with the simplified and refined method for predicting the viscosity grade of mineral-oil mixtures.

For all the various pure-hydrocarbon mixtures designated in Table XII-2b the viscosities at 100 °F have thus been estimated, the results being compiled in Table XII-12. Indeed, the deviations appear to be considerably higher than found for mineral-oil mixtures. In addition, the apparent improvement*) achieved with the refined method is not quite so considerable as in the case of mineral-oil mixtures.

Finally, an interesting example for illustrating the indicated "averaging" effect in multi-component mixtures may be derived from the quoted investigations by Schiessler *et al.* 202).

Two complex mixtures, each prepared from a great variety of pure hydrocarbons, were blended. The first mixture comprised 22 specified hydrocarbons with VI-values above 100, its viscosity at 20°C (68°F) being 21.5 cP; the second mixture consisted of 17 specified hydrocarbons with lower VI's, its viscosity at 20°C amounting to 28.9 cP. The blend (with $y = 0.428$) prepared from these two mixtures showed a viscosity $\eta_{20^\circ C} = 24.1$ cP. From the simple additivity of the viscosity function H a viscosity $\eta_{20^\circ C} = 24.4$ cP would be found for this particular blend.

Accordingly, the simplified method established for mineral-oil mixtures does apply very well to the considered multi-component mixture of pure hydrocarbons. This finding may indeed be taken indicative of the aforementioned "averaging" effect.

C. THE VISCOSITY-PRESSURE INDICES OF MINERAL-OIL MIXTURES

Little attention has been devoted so far to the effect of *pressure* on the viscosity of liquid mixtures. Whilst the viscosity-pressure dependence of several mixtures of pure liquids has been determined by Dow 112), by Kuss and Schultze 15) and by Griest *et al.* 11), not

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*) This improvement is not even fully significant, the statistical confidence level, according to the F-test, amounting to about 85%.

TABLE XII-12

The Compatibility of the Pure-Hydrocarbon Mixtures Designated in Table XII-2b With the Simplified (SPM) and Refined (RPM) Prediction Method for Mineral-Oil Mixtures

System No.	$\Delta H_{100^\circ F}$	$\%\delta\eta_{100^\circ F}$*)	
		SPM	RPM
1a	0.1051	16.4	14.3
1b	"	21.6	18.3
2a	0.0093	23.9	20.8
2b	"	25.6	22.2
3a	0.2181	23.3	11.4
3b	"	37.7	20.8
4a	0.0958	3.5	5.0
4b	"	5.0	6.6
5a	0.1223	8.4	-1.1
5b	"	10.4	-0.2
6a	0.0308	-0.5	0.0
6b	"	-0.5	0.5
6c	"	-0.2	0.5
7a	0.0984	5.2	3.3
7b	"	7.9	5.0
7c	"	6.9	4.7
8a	0.0056	-0.2	-2.1
8b	"	0.0	-2.5
8c	"	-0.5	-2.3
Average Deviation**)		10.4	7.4
Standard Deviation***)		14.2	11.0

*) $\%\delta\eta = 100\,\dfrac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) Defined by $\dfrac{1}{n}\sum_{i=1}^{i=n} |\%\delta_i|$

***) Defined by $\sqrt{\dfrac{\sum_{i=1}^{i=n} (\%\delta_i)^2}{n-1}}$

any experimental information seems to be available on the high-pressure viscosity of mineral-oil mixtures.

However, it may safely be assumed that, as regards the effect of temperature and pressure on their viscosity, mixtures of mineral oils would behave not substantially differently from so-called *natural* mineral-oil fractions. This would imply that the correlation of Fig. X-1 for predicting the Viscosity-Pressure Index of mineral oils would equally apply to their mixtures. Accordingly, once the viscosity grade and the atmospheric Slope Index of mineral-oil mixtures have been measured or estimated - preferably by means of the present refined prediction method -, their Viscosity-Pressure Indices would readily be predictable.

Further, it may be assumed that, like their atmospheric Slope Indices (see § XII. 5. 1), the Viscosity-Pressure Indices, Z, of the component mineral oils would be approximately additive. Therefore, the following interrelationship would apply, at least to a fair approximation, at any constant temperature:

$$Z_m = (1-y)\ Z_1 + yZ_2. \qquad \text{(XII-41)}$$

In fact, if the approximate additivity of the viscosity function H established for atmospheric pressure would prove to hold also at *elevated* pressures - which seems quite probable -, the validity of Correlation (XII-41) would follow at once. Moreover, starting from the additivity of the viscosity function H at atmospheric pressure and of the atmospheric Slope Index, the approximate validity of the latter correlation may be inferred from the shape of the various curves depicted in the aforementioned Fig. X-1.

XII. 8. THE OCCURRENCE OF MINIMA IN THE VISCOSITY-CONCENTRATION CURVES OF MINERAL-OIL MIXTURES

XII. 8. 1. *Introduction*

One of the most outstanding - apparently even unique - features of the present *refined* method for predicting the viscosity-temperature relationship of mineral-oil mixtures consists in that it applies equally well to systems exhibiting a *minimum* in their viscosity-concentration curves.

Amongst the 26 mineral-oil systems designated in Tables XII-1b and XII-1c the systems Nos. 22, 23, 24 and 26 display such a minimum, although at only one of the two reference temperatures involved, namely at 100°F. Whilst for the latter three systems the minimum is hardly appreciable, it is rather pronounced for system No. 22. For this system Rahmes and Nelson[196)] measured the viscosities at a few more compositions than the usual three in order to obtain a fairly complete viscosity-concentration curve. Accordingly, the viscosity data on system No. 22 are very feasible for illustrating the suitability of the new prediction method for minimum-viscosity mixtures.

Table XII-13 demonstrates that at the reference temperature where

TABLE XII-13

Application of the Refined Prediction Method (RPM) to System No. 22

Volume Fraction y	η_{100^oF}, cP		η_{210^oF}, cP		Slope Index	
	Exp.	RPM	Exp.	RPM	Exp.	RPM
0.0	182.0	182.0	8.43	8.43	1.611	1.611
0.1	173.8	173.8				
0.2	170.6	167.9	9.35	9.18	1.513	1.521
0.3	168.6	164.4				
0.4	168.6	162.2	10.45	10.14	1.435	1.442
0.5	168.3	162.2				
0.6	170.2	164.1	11.75	11.38	1.364	1.371
0.7	174.2	167.9				
0.8	178.6	174.2	13.37	13.00	1.303	1.310
0.9	186.2	182.4				
1.0	193.2	193.2	15.14	15.14	1.260	1.260

the minimum occurs, that is at 100°F, the predicted and experimental viscosities do agree very well. At the second reference temperature, 210°F, where the minimum has disappeared, the agreement is equally good.

The satisfactory agreement between predicted and experimental viscosities at the latter two, fairly widely spaced, reference temperatures implies that the *Slope Indices* of the considered system No. 22 should conform to Equation (XII-34a) of the refined prediction method. Table XII-13 also shows this to be true, and with an excellent degree of accuracy at that.

It is interesting to remark that, in contrast to the corresponding *viscosities* at 100°F, the various *Slope Indices* of system No. 22 do *not* show a minimum value. In fact, in all known mineral-oil systems the Slope Indices invariably appear to remain intermediate to those of the components.

Both the experimental and predicted viscosities listed in Table XII-12 have been plotted in Fig. XII-13 against the corresponding volume fractions of the involved system No. 22. The same figure depicts three additional viscosity-concentration isotherms estimated by the refined prediction method.

Fig. XII-13 indicates that a minimum in the viscosity-concentration isotherms of system No. 22 would occur over a fairly wide temperature range.

At the temperature where the component oils H and B are *isoviscous* - for the present system amounting to 34°C (94°F) - the minimum point would be produced by the mixture containing equal volumes of both components, that is with $y = 0.50$. With increasing temperature the minimum would not only become less marked, but it would also shift towards the side of the more fluid component (at the temperature involved). Finally, a temperature is reached where the minimum-viscosity point would coincide with the viscosity of the

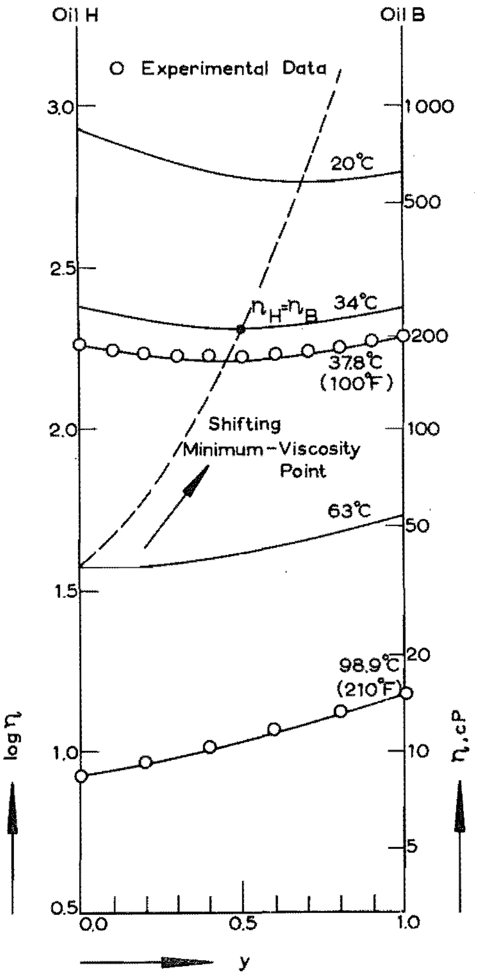

FIG. XII-13.
Viscosity-Concentration Isotherms of a Typical Minimum-Viscosity System According to the Refined Prediction Method.

more fluid component (y=0); for the present system the latter temperature would amount to 63°C (146°F). At still higher temperatures the difference between the viscosities of the two components would become so great that a minimum can no longer be realized.

A similar consideration applies to the opposite case where the temperature is decreased downwards from the temperature of isoviscosity, that is from 34°C. In this case, however, the other oil will be the more fluid component. According to the refined prediction method, a minimum does no longer occur at temperatures below -13°C (+9°F).

XII. 8. 2. *Practical Importance*

For the system depicted in Fig. XII-13 the relative viscosity decrease - as compared with the viscosity of the more fluid component - would reach its maximum value at the temperature where the component oils are isoviscous, that is in the mixture containing equal volumes of them. As will be shown below, the same would apply to any other system.

The experimental data indicate that at 100°F the maximum viscosity decrease in system No. 22 amounts to 7.5%. The latter percentage, however, may hardly be taken representative of the viscosity decreases which, according to the refined prediction method, should be observed for oils with viscosity grades and Slope Indices encountered in lubrication practice.

In order to emphasize the practical importance which such viscosity decreases may well assume in certain cases, Table XII-14 has been prepared.

TABLE XII-14

Percentage Viscosity Decreases Ensuing from Mixing Equal Volumes of Two Mineral Oils Being Isoviscous at 40°C (104°F)

$\eta_{40^\circ C}$ of Both Oils, cP	Percentage Viscosity Decrease			
	At 0°C (32°F)		At 40°C (104°F)	
	$\Delta S = 0.200$	$\Delta S = 0.400$	$\Delta S = 0.200$	$\Delta S = 0.400$
1	3.6	7.7	2.7	5.4
10	6.7	13.7	4.9	9.6
100	9.6	19.5	7.3	13.7
1,000	12.3	24.7	9.4	17.8
10,000	14.9	29.4	11.3	21.3
100,000	17.6	33.9	13.5	24.8

This table contains the percentage viscosity decreases that would ensue from mixing equal volumes of two *isoviscous* mineral oils whose Slope Indices differ by 0.200 and 0.400 units, respectively (corresponding to DVI-differences of about 100 and 200 points, respectively). The relevant calculations have been carried out for two reference temperatures, that is 0 and 40°C (32 and 104°F).

Table XII-14 may suffice to illustrate that the predicted viscosity decreases may be far from negligible. On the contrary, particularly with component oils of high viscosity grades and widely different Slope Indices such viscosity decreases may become quite appreciable.

XII. 8. 3. *Qualitative and Quantitative Aspects*

Coming to the question as to which kinds of mineral-oil systems may exhibit a minimum in their viscosity-concentration curves, it may already be conceived from Fig. XII-13 that the occurrence of such a minimum is dependent not so much on the system proper as on the particular *temperature* at which it is being considered.

This would appear to be the basic reason why only a few examples of mineral-oil systems with such a minimum have been reported in the literature[196]. In fact, the aforementioned systems Nos. 22, 23, 24 and 26, prepared and investigated by Rahmes and Nelson[196], still constitute the only actual examples known to the present author. Moreover, for the sake of clearness, it should be added that Rahmes and Nelson have purposefully attempted to obtain such mixtures.

Therefore, it may sound not so unreasonable that Rahmes and Nelson, in their discussion on minimum-viscosity systems[196], denoted these as "*unusual*" in the mineral-oil field. In the opinion of the present author, however, the latter qualification would be at least somewhat misleading, as will become clear from the considerations now to follow.

The problem as to which *conditions* have to be fulfilled in order that a minimum may occur in the viscosity-concentration isotherms of mineral-oil mixtures can be approached very well by means of the refined prediction method. This is demonstrated in Appendix XII-4 (at the end of this chapter), where the latter problem has been treated in a more general sense, that is the possibility for the occurrence of a *maximum* has likewise been investigated.

The conclusions reached in Appendix XII-4 may be summarized as follows:

> *Starting from the validity of the refined method for predicting the viscosity-temperature relationship of mineral-oil mixtures, it has been shown that in any such mixture a minimum in its viscosity-concentration isotherms would occur within a more or less restricted temperature range in the vicinity of the temperature where the component oils display the same viscosity, provided that this temperature is not higher than about 125°C (260°F).*
>
> *If the iso-viscosity temperature exceeds this level of about 125°C, the minimum may be vanishing; or it might even turn into a maximum, which, however, would be hardly detectable, let alone of practical significance.*

The indicated effect of the iso-viscosity temperature - which assumes a characteristic value for a given system - is reflected in Fig. XII-14. Any system located on the depicted curve of "*transition temperatures*" would invariably display the same viscosity as either component, so that neither a minimum nor a maximum would be encountered (see Appendix XII-4).

The new concept of the occurrence of minima in the viscosity-concentration isotherms of mineral-oil mixtures will now be further elucidated on the basis of the schematic picture of Fig. XII-15. For an elaborate treatment of the underlying equations, however, reference is made again to Appendix XII-4.

A. According to Fig. XII-15, solely the viscosity functions ΔH and H_{12} should decide on the occurrence of a minimum in a given mineral-oil system.

Denoting the temperature where the two component oils are iso-

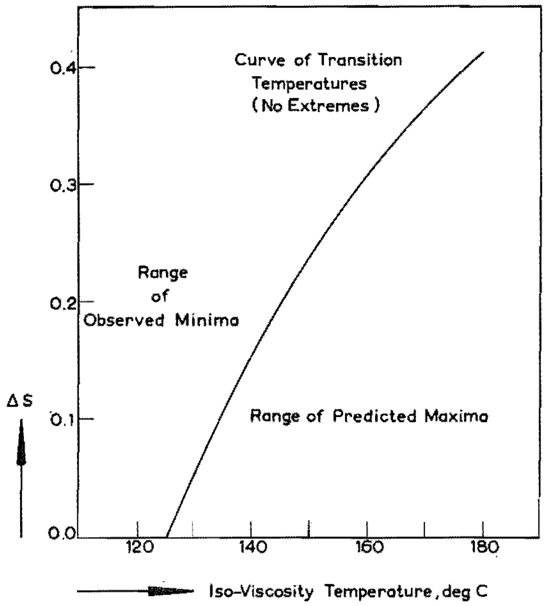

FIG. XII-14.
The Occurrence of Extremes in the Viscosity-Concentration Curves of Binary Mixtures of Isoviscous Mineral Oils According to the Refined Prediction Method.

viscous by Θ_{iv} (or t_{iv}, with t in deg C), the temperature dependence of the viscosity function ΔH can be defined as follows:

$$\Delta H = \left| H_1 - H_2 \right| = \Delta S \left| \Theta - \Theta_{iv} \right| \qquad \text{(XII-42)}$$

Substitution of the latter expression into Correlation (XII-38) yields for the temperature dependence of the viscosity function H_{12}:

$$H_{12} = (0.160 - 0.4 \cdot \Delta S) \left| -\Delta S (0.1127 + \Theta_{iv}) \right| - \Delta S \left[0.088 + 0.35\ (0.1127 + \Theta) \right]. \qquad \text{(XII-43)}$$

In Fig. XII-15 the quantities ΔH and $-H_{12}$ have been plotted against $-\Theta$. In accordance with Equation (XII-42) two straight lines for ΔH emanate from the temperature t_{iv}, where $\Delta H = 0$. For temperatures below t_{iv} the slope of the ΔH-line amounts to $-\Delta S$; for higher temperatures it has the opposite value, $+\Delta S$. It is readily seen from the underlying Equation (XII-43) that the straight line obtained on plotting $-H_{12}$ against $-\Theta$ possesses a slope of $-0.35 \cdot \Delta S$.

B. As defined by the basic Equation (XII-59b) of Appendix XII-4, a minimum viscosity should be observed over the entire temperature range where $-H_{12} \geqslant \Delta H$. This range is indicated by the shaded part of Fig. XII-15.

The *lower* temperature limit, in Fig. XII-15 denoted by t_L, can

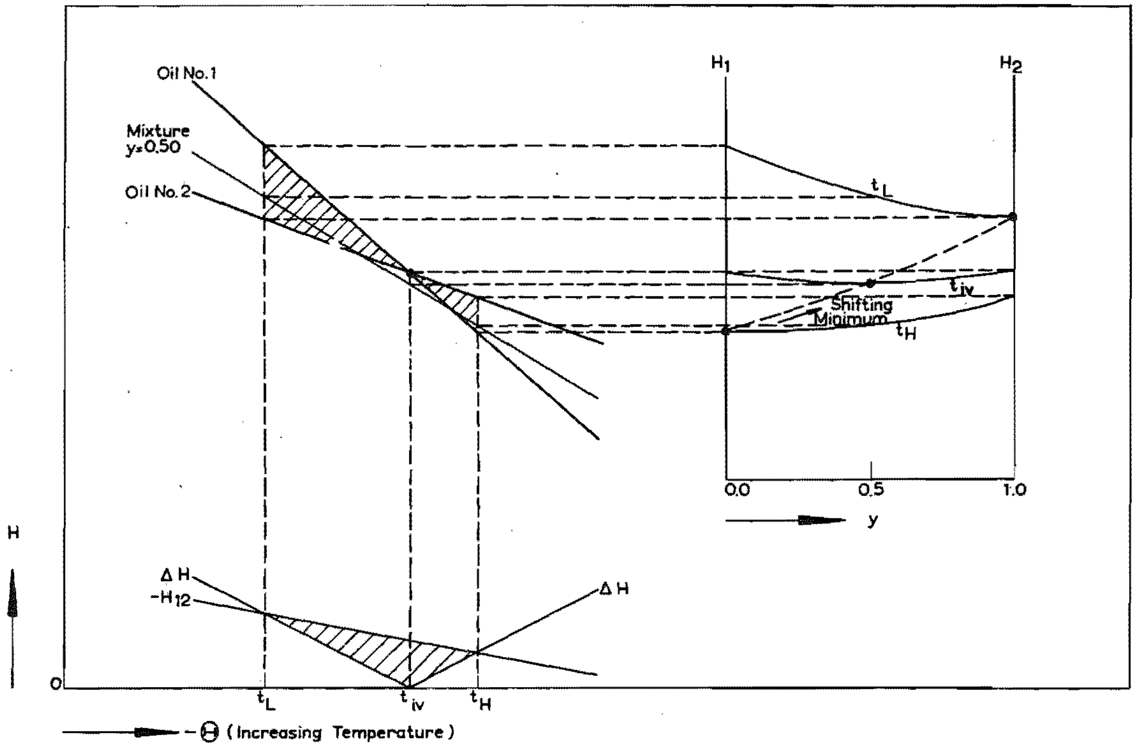

FIG. XII-15.
Schematic Illustration of the Occurrence of Minima in the Viscosity-Concentration Isotherms of a Given Mineral-Oil Mixture.

be solved after substituting the appropriate temperature expressions into the basic condition: $-H_{12} = (H_1 - H_2)$.

The *upper* temperature limit, in Fig. XII-15 denoted by t_H, can be derived after substituting the appropriate temperature expressions into the basic condition: $-H_{12} = -(H_1 - H_2)$.

These lower and upper temperature limits have thus been calculated for systems whose components are *isoviscous* at some standard reference temperature. Three standard reference temperatures have been considered, namely 0, 40 and 100°C (32, 104 and 212°F). The differences between the Slope Indices of the components have been varied from $\Delta S = 0.100$ to $\Delta S = 0.400$. The results of these calculations are compiled in Table XII-15.

TABLE XII-15

Temperature Ranges Where a Minimum May Occur in the Viscosity-Concentration Curves of Binary Mineral-Oil Mixtures

ΔS	Temperature Range of Minimum Viscosity		
	$t_{iv} = 0^oC$ (32^oF)	$t_{iv} = 40^oC$ (104^oF)	$t_{iv} = 100^oC$ (212^oF)
0.100	$-45 / 29^oC$ $(-49 / 84^oF)$	$-7 / 68^oC$ $(19 / 154^oF)$	$78 / 111^oC$ $(172 / 232^oF)$
0.200	$-46 / 30^oC$ $(-51 / 86^oF)$	ditto	$74 / 114^oC$ $(165 / 237^oF)$
0.300	$-48 / 32^oC$ $(-54 / 90^oF)$	"	$70 / 116^oC$ $(158 / 241^oF)$
0.400	$-49 / 33^oC$ $(-56 / 91^oF)$	"	$67 / 118^oC$ $(153 / 244^oF)$

It is seen from this table that for $t_{iv} = 40^\circ C$ the temperature range where a minimum viscosity may occur would be independent of the ΔS-value of the system considered. For the other two temperatures the width of this range would increase somewhat with higher ΔS-values; but, remarkably enough, the effect of ΔS on the width and the location of this range remains very small.

Table XII-15 indicates that for the standard reference temperatures of 0 and 40°C the extent of the temperature range where a minimum viscosity may occur would be fairly wide and practically the same, namely about 75 to 80°C (about 170°F). For $t_{iv} = 100^\circ C$ this extent would be much smaller; this is not so surprising, since the latter temperature comes fairly close to the "transition temperatures" depicted in Fig. XII-14.

It stands to reason that, anyhow, solidification sets a definite boundary to the lower temperature limits actually observed.

C. Another point of practical interest is to find out which *viscosity differences* the two components may display in order that a minimum viscosity would still be possible.

At the temperature t_{iv} both components have the same viscosity, so that their viscosity ratio amounts to unity. This ratio increases regularly both with increasing and with decreasing temperature. As shown by Equation (XII-42) - and also indicated in Fig. XII-15 -, the absolute difference, ΔH, between the viscosity functions H_1 and H_2 increases proportionally to $|\Theta - \Theta_{iv}|$, the quantity ΔS being the proportionality constant.

Now, a minimum would occur only at those temperatures where the difference ΔH is smaller than the function $-H_{12}$. Obviously,

ΔH becomes equal to $-H_{12}$ at the two aforementioned temperature *limits* denoted by t_L and t_H. Considering separately the temperature range from t_L to t_S and that from t_S to t_H, it is evident that in either range a maximum viscosity ratio is reached at the respective temperature limit. Further, as indicated in Fig. XII-15, the difference ΔH, and therefore also the corresponding viscosity *ratio*, will be greater at the lower than at the upper temperature limit.

In order to convey a good impression of the maximum admissible viscosity ratios in minimum-viscosity systems the viscosity ratios at the two temperature limits have been calculated for a variety of mineral-oil systems whose components are isoviscous at 40°C; various viscosity grades as well as ΔS-values have been taken into consideration. The results of these calculations are compiled in Table XII-16.

TABLE XII-16

Viscosity Ratios at Lower and Upper Temperature Limit of Minimum-Viscosity Range for Binaty Mixtures of Mineral Oils Being Isoviscous at 40°C (104°F)

$\eta_{40^\circ C}$ of Both Oils, cP	Viscosity Ratios at Lower and Upper Temperature Limit							
	Lower Temp. Limit (-7°C)				Upper Temp. Limit (68°C)			
	ΔS				ΔS			
	0.100	0.200	0.300	0.400	0.100	0.200	0.300	0.400
1	1.14	1.30	1.49	1.71	1.04	1.07	1.11	1.14
10	1.26	1.61	2.07	2.69	1.07	1.13	1.20	1.28
100	1.41	2.02	2.89	4.22	1.09	1.20	1.31	1.43
1,000	1.57	2.49	4.03	6.59	1.13	1.27	1.43	1.60
10,000	1.75	3.10	5.60	10.4	1.16	1.34	1.55	1.79
100,000	1.94	3.85	7.80	16.2	1.19	1.42	1.69	2.00

This table demonstrates that it would be far from correct to state that a minimum viscosity may occur *only* in systems whose components have nearly the same viscosity grade. Indeed, even in the rather conventional temperature range covered by Table XII-15 the viscosities of the components may differ quite considerably, particularly at higher viscosity grades and/or ΔS-values.

D. As regards the particular *composition* for which a minimum-viscosity point would be observed in a given system, it has already been indicated in Fig. XII-13 - though only for system No. 22 - that this composition varies with the prevailing temperature. As illustrated also in Fig. XII-15, the consequent shifting of the minimum-viscosity point would be invariably such that at any temperature involved the minimum is located on the side of the more fluid component. The latter finding will hardly be surprising, since a similar shifting has been observed in the vast majority, if not all, of the pure-compound mixtures mentioned in the literature[177,178b)].

Denoting the volume fraction for which a minimum would occur in a given viscosity-concentration isotherm by y_{min}, the following mathematical expression readily emerges from Equation (XII-56) in Appendix XII-4:

$$y_{min} = 0.50 - \frac{H_1 - H_2}{2H_{12}}. \qquad \text{(XII-44)}$$

By means of this simple expression the location of the minimum in a particular viscosity-concentration isotherm of a sufficiently defined system can easily be predicted. At the temperature t_{iv} (where $H_1 = H_2$) the value of y_{min} would amount to 0.50. At the aforementioned lower and upper temperature limit the minimum would be located at $y_{min} = 1$ and $y_{min} = 0$, respectively.

E. It has further been stated in § XII. 8. 2 that the relative viscosity decrease - as compared with the viscosity of the more fluid component - would invariably reach its maximum value at the iso-viscosity temperature, that is in the mixture containing equal volumes of both components ($y_{min} = 0.50$).

Without entering into the relevant mathematical details it can be conceived from the schematic Fig. XII-15 that the minimum would reach its greatest depth - as expressed in terms of the difference between the viscosity functions H of the minimum-viscosity mixture and the more fluid component - at this very iso-viscosity temperature, that is in accordance with Equation (XII-44) in the mixture with $y = 0.50$. Further, it can be shown that this greatest depth of the minimum does correspond with the maximum *relative* viscosity decrease as defined above.

XII. 8. 4. *Concluding Remarks*

A. One should not lose sight of the fact that, according to the foregoing discussion, minima in the viscosity-concentration curves of mineral-oil mixtures may occur only in a rather *restricted* temperature range where the ratio between the viscosities of the components remains fairly small.

For many systems, therefore, no minima would be encountered in the temperature range of practical interest or even in the entire range where the oils may occur in the liquid state. Thus, it would become comprehensible why very few examples of mineral-oil systems exhibiting such a minimum can be traced in the literature: the great majority of previous investigations has been confined to a small temperature range - if not to only one arbitrary temperature -, the components of many systems displaying rather great viscosity ratios at that.

In the light of the present findings, however, it will be clear why in the author's opinion the above-cited statement that minimum-viscosity systems are "*unusual*" in the mineral-oil field [196] cannot properly be upheld (compare the introductory notes to § XII. 8. 3). In fact, when two arbitrary mineral oils with comparable viscosity grades are mixed together - in various proportions -, the occurrence of a minimum-viscosity point in the resulting viscosity-concentration curve would be the *rule* rather than the *exception.*

B. Rahmes and Nelson[196] would seem the only investigators who have attempted so far to specify the *conditions* necessary for the occurrence of minima in the viscosity-concentration curves of mineral-oil mixtures. They concluded that, apart from other possibly necessary conditions, the oils should vary "considerably" in Viscosity Index and their viscosity ratio should be "relatively small".

It appears that the latter - admittedly somewhat tentative - conclusion can only partly be substantiated by the present findings.

Although the rather obvious condition that the viscosity ratio of the component oils should be "relatively small" might be upheld, some more precise statement as to its admissible order of magnitude would be desirable. According to the present results (compare Table XII-16), minima might still occur at viscosity ratios *considerably* above unity; even viscosity ratios beyond 5 or even 10 would not be impossible amongst minimum-viscosity systems.

However, the other necessary condition postulated by Rahmes and Nelson - that the component oils should vary "considerably" in Viscosity Index - is in plain conflict with the present results. According to these results, it should suffice that the component oils display - besides a fairly small viscosity ratio - simply *different* Slope Indices, the quantitative magnitude of the difference being immaterial in this respect. Consequently, it would not be necessary either that the Viscosity Indices of the component oils should vary "considerably".

C. Whilst the minima in the viscosity-concentration curves of certain mineral-oil mixtures may be very pronounced, it has been shown in Appendix XII-4 that the *maxima* predicted by the present method would assume hardly any *practical* significance. Moreover, such maxima would be encountered only at very high temperatures.

As far as the author knows, such maxima have not been reported hitherto. Presumably the proper experiments for establishing whether a maximum viscosity can actually be realized have never been performed at all. Apart from the selection of suitable systems, such experiments would be rather difficult as they should be executed with extreme accuracy, notwithstanding the very high temperatures involved.

For the time being, however, the author favours the view that it should be deemed rather bold to uphold the possibility for the occurrence of maxima in the viscosity-concentration curves of mineral-oil systems (compare also the following remarks).

D. Finally, it may be useful to point out that, admittedly, some *reservation* should be made with respect to certain results reached above for minimum-viscosity mixtures, that is in so far as these results are based on *extrapolations* beyond the range explored by proper experiments. Accordingly, at some future data it may well prove desirable, or even necessary, to introduce some refinements and/or minor revisions into the consequent views here propounded.

Above all, however, the weighty fact should be emphasized that the expounded results represent simple outcomes of the refined method for predicting the viscosity-temperature relationship of mineral-oil mixtures, which method has proved to permit really good predictions for the wide variety of mixtures tested (see Section XII. 7).

XII. 9. FURTHER APPLICATIONS OF THE NEW MIXTURE-VISCOSITY RELATIONSHIPS

XII. 9. 1. *The Applicability of the Basic Equations to Non-Hydrocarbon Mixtures*

The basic equation for the viscosity *grade* of mineral-oil mixtures reads:

$$H_m = (1-y)\ H_1 + yH_2 + y\ (1-y)\ H_{12}\ . \qquad \text{(XII-36a)}$$

This one-parameter equation has proved to possess a very wide applicability: it remains valid even for many mixtures of liquids that differ strongly in chemical type. In fact, it may be stated that, by suitable adjustment of the parameter H_{12}, Equation (XII-36a) can be made to give a reasonable description of the viscosity-concentration curves of any binary system, provided only that no *point of inflection* occurs. Systems exhibiting such a point of inflection have been very rarely encountered, however (compare Section XII. 1).
Consequently, all the various liquid systems employed in normal practice may indeed be expected to conform reasonably well to Equation (XII-36a).

The basic equation for the *Slope Index* of mineral-oil mixtures has been defined as:

$$S_m = (1-y)\ S_1 + yS_2 + y\ (1-y)S_{12}\ . \qquad \text{(XII-32)}$$

Presumably Equation (XII-32) is even more generally applicable than the basic Equation (XII-36a) for the viscosity grade of mixtures.

In addition to the many examples already provided for mixtures in the hydrocarbon field - including mixtures with a minimum in their viscosity-concentration curve - the applicability of Equation (XII-36a) will now be exemplified for two rather extreme systems of *non-hydrocarbon* compounds.
The first system, ethylalcohol/water[79b], it remarkable in that it shows a pronounced *maximum*-viscosity point. The second system, glycerol/water[205], has an extremely high viscosity ratio of about 1,000, so that it covers an extensive viscosity range; incidentally, the latter system is frequently employed in viscometry for preparing calibrating liquids of the desired viscosity level.
For both systems one experimentally determined viscosity-concentration isotherm, in the normal temperature range, has been taken into consideration. An appropriate value for the interaction viscosity function H_{12} has been evaluated from the experimental blend containing approximately equal volumes of both components. The vis-

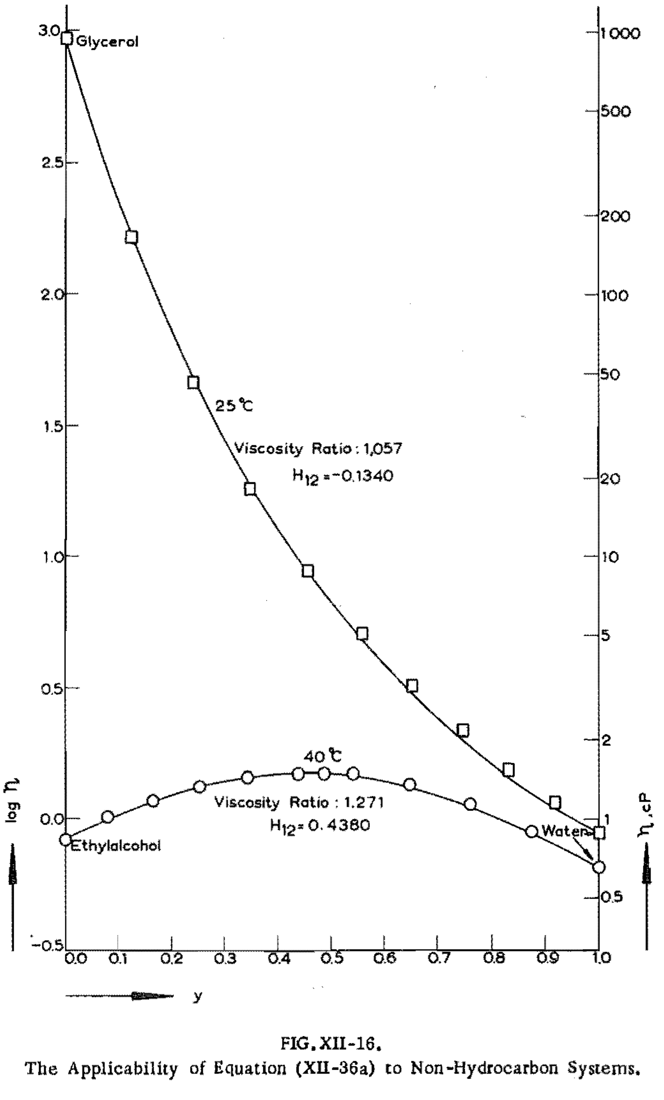

FIG. XII-16.
The Applicability of Equation (XII-36a) to Non-Hydrocarbon Systems.

cosity-concentration curves predicted from Equation (XII-36a) are depicted in Fig. XII-16, together with the various experimental viscosity data.

Predicted and experimental viscosities are in good agreement, especially in the ethylalcohol/water system. In judging the accuracy achieved for the glycerol/water system it should be well realized that this system covers an extremely wide viscosity range. It might be added that, notably in the ethylalcohol/water system, the accuracy of the predictions could be even improved by using the bestfitting H_{12} -value instead of that evaluated arbitrarily from the mixture containing about equal volumes of both components.

Finally, it is worthy of note that the basic equations under consideration can also serve as convenient tools for studying the viscosity of *polymer solutions*. It would lead too far, however, to enter into the details of this promising application.

XII. 9. 2. *A Refined Method for Predicting the Atmospheric Viscosity-Temperature Relationship of Dimethylsiloxane Mixtures*

As regards the numerical value of the interaction quantities H_{12} and S_{12} in some arbitrary system, no general statement can as yet be made. Obviously, this will remain very difficult, if not completely impossible, since a complexity of phenomena - such as association and dissociation - giving rise to pronounced changes in the physical structure of the liquids would have to be taken into consideration.

Confining oneself to mixtures of chemically interrelated liquids, however, reasonable estimates for the parameters H_{12} and S_{12} may well be achieved. In the foregoing Section XII. 7 it has indeed been demonstrated how for mineral-oil mixtures comprising a really great variety of component oils these parameters can be predicted satisfactorily, solely from the viscosity-temperature relationship of the component oils. Presumably, similar prediction methods may be set up for mixtures of different types of liquids whose basic structures are likewise interrelated.

As a corroboration of the latter presumption the results obtained for mixtures of the very interesting homologous group of the *dimethylsiloxanes* will now be described. Members of both the linear and cyclic series of dimethylsiloxanes have been included. The per-

TABLE XII-17a

Data on Component Dimethylsiloxanes

Dimethylsiloxane Compound	$\eta_{40^{\circ}C}$, cP	S
Linear Series		
M_2D_2	1.050	0.944
M_2D_3	1.439	0.899
M_2D_4	1.875	0.855
M_2D_5	2.30	0.825
M_2D_6	2.77	0.792
Cyclic Series		
D_5	2.83	0.998
D_6	4.84	0.950
D_7	7.19	0.895

TABLE XII-17b

Data on Dimethylsiloxane Mixtures

System				$\eta_{40^\circ C}$, cP	S	Viscosity Ratio, 40°C	$\Delta H_{40^\circ C}$	S_1-S_2
No.	Components	x	y					
1	M_2D_2-M_2D_3	0.553	0.546	1.244	0.931	1.371	0.0461	0.045
2	M_2D_3-M_2D_4	0.544	0.540	1.656	0.867	1.303	0.0353	0.044
3	D_5-M_2D_3	0.509	0.532	1.875	0.926	1.964	0.0849	0.099
4a	D_5-M_2D_4	0.706	0.720	2.05	0.873	1.507	0.0496	0.143
4b	ditto	0.508	0.526	2.20	0.912	"	"	"
4c	"	0.307	0.322	2.41	0.934	"	"	"
5a	D_5-M_2D_5	0.706	0.718	2.40	0.866	1.230	0.0244	0.173
5b	ditto	0.305	0.318	2.60	0.929	"	"	"
6	D_5-D_6	0.545	0.543	3.69	0.976	1.714	0.0576	0.048
7a	D_6-M_2D_5	0.706	0.720	2.68	0.842	2.11	0.0820	0.125
7b	ditto	0.305	0.320	3.56	0.894	"	"	"
8	D_6-M_2D_6	0.506	0.520	3.49	0.861	1.750	0.0601	0.158
9a	D_7-M_2D_6	0.705	0.719	3.42	0.814	2.60	0.0980	0.103
9b	ditto	0.506	0.522	4.00	0.837	"	"	"
9c	"	0.305	0.318	4.84	0.855	"	"	"

tinent data on the pure dimethylsiloxanes*) and their mixtures - derived from reliable data reported by Waterman *et al.* 146) - are compiled in Tables XII-17a and XII-17b, respectively.

Following the line of approach adopted for mineral-oil mixtures (see Section XII. 7), the *Slope Indices* of the dimethylsiloxane mixtures have been considered first. As shown in Table XII-18a, the S-values of the latter mixtures conform satisfactorily to the simplified equation:

$$S_m = (1-y)\, S_1 + yS_2. \qquad \text{(XII-24)}$$

Improved accuracy can again be achieved by applying the extended Equation (XII-32). Curiously enough, the correlation established for the S_{12}-values of dimethylsiloxane mixtures happens to be identical to that previously given for mineral-oil mixtures, that is:

$$S_{12} = -0.35 \cdot \Delta S. \qquad \text{(XII-33)}$$

By substituting the S_{12}-values predicted from Equation (XII-33) into the basic Equation (XII-32) excellent predictions are obtained. As demonstrated by Table XII-18a, the deviations between the S_m-values thus predicted and those obtained from the experimental viscosities remain practically within the experimental viscometric accuracy.

It may be noted that, in view of the validity of Equations (XII-32) and (XII-33), the S-y diagram of Fig. XII-10 constructed for *mineral-oil* mixtures would equally apply to mixtures of dimethylsiloxanes.

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*) Compare Section XI. 2.

TABLE XII-18a

Deviations Between Experimental and Predicted Slope Indices of Dimethylsiloxane Mixtures

System No.	$\delta S = (S_{pred} - S_{exp})$	
	Eq.(XII-24)	Eqs.(XII-32) and (XII-33)
1	-0.012	-0.016
2	0.008	0.004
3	0.019	0.010
4a	0.022	0.012
4b	0.011	-0.001
4c	0.018	0.007
5a	0.008	-0.004
5b	0.014	0.001
6	-0.004	-0.008
7a	0.018	0.009
7b	0.016	0.006
8	0.004	-0.005
9a	0.007	0.000
9b	0.004	-0.005
9c	0.007	-0.001
Average Deviation*)	0.012	0.006
Standard Deviation**)	0.013	0.008

*) Defined by $\frac{1}{n} \sum_{i=1}^{i=n} |\delta_i|$

**) Defined by $\sqrt{\frac{\sum_{i=1}^{i=n} \delta_i^2}{n-1}}$

It has appeared that the problem of estimating the interaction viscosity function H_{12} in the basic Equation (XII-36a) for predicting the viscosity grade of dimethylsiloxane mixtures can conveniently be solved by utilizing again the quantities ΔS and ΔH as correlational variables. The following correlation has been arrived at:

$$H_{12,40^\circ C} = -2.00 \cdot \Delta H_{40^\circ C} \cdot \Delta S . \qquad \text{(XII-45)}$$

According to Equation (XII-45), a plot of $H_{12,40^\circ C}$ against ΔS, with $\Delta H_{40^\circ C}$ as a parameter, yields a family of straight lines emanating from the origin. Fig.XII-17 represents such a plot for the ranges of the correlational variables ΔS and $\Delta H_{40^\circ C}$ covered by the basic data. In the latter ranges the quantity ΔS has by far the greater effect on the magnitude of $H_{12,40^\circ C}$.

TABLE XII-18b

Percentage Deviations Between Experimental and Predicted Viscosities of Dimethylsiloxane Mixtures

System No.	$\%\delta\eta_{40^\circ C}$*)			
	Volume Additivity of ...			Eqs.(XII-36a) and (XII-45)
	η	log η	H	
1	1.4	0.2	-0.2	-0.9
2	1.2	0.2	0.0	-0.7
3	11.4	5.2	3.5	0.2
4a	4.2	2.6	2.1	-0.2
4b	5.7	3.3	2.8	-0.2
4c	4.5	2.8	2.3	-0.5
5a	2.1	1.4	1.4	0.0
5b	2.3	1.6	1.6	0.0
6	6.2	2.6	1.9	0.5
7a	12.4	5.7	4.2	0.5
7b	13.2	6.4	5.7	1.4
8	7.6	3.8	2.8	-1.6
9a	17.2	5.9	2.8	-0.9
9b	21.9	9.2	6.4	1.4
9c	19.7	9.6	6.9	2.1
Average Deviation**)	8.7	4.0	3.0	0.7
Standard Deviation***)	11.3	5.1	3.7	1.0

*) $\%\delta\eta = 100 \dfrac{\eta_{pred} - \eta_{exp}}{\eta_{exp}}$

**) Defined by $\dfrac{1}{n} \sum_{i=1}^{i=n} |\%\delta_i|$

***) Defined by $\sqrt{\dfrac{\sum_{i=1}^{i=n} (\%\delta_i)^2}{n-1}}$

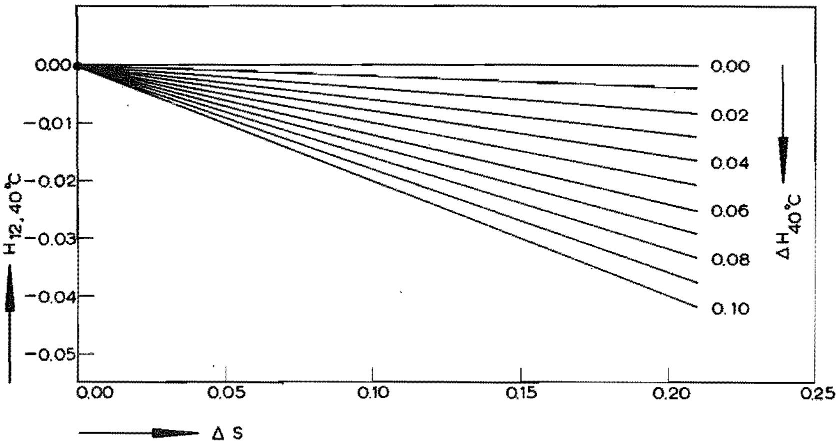

FIG. XII-17.
The Interaction Viscosity Function of Binary Dimethylsiloxane Systems According to Correlation (XII-45).

Referring to Appendix XII-3, the following expression can be derived for H_{12} at an *arbitrary* temperature denoted by Θ:

$$H_{12} = -2.00 \cdot \Delta S \left| (H_1 - H_2) - \Delta S(0.1127 + \Theta) \right| - 0.35 \cdot \Delta S (0.1127 + \Theta). \quad \text{(XII-46)}$$

In the last column of Table XII-18b are compiled, for a standard reference temperature of 40°C, the deviations between the experimental mixture viscosities and those predicted from Equations (XII-36a) and (XII-45). Indeed, the agreement may be stated to be excellent.

For comparison the deviations between the experimental viscosity values and those calculated from the straight additivity of viscosity, η, of $\log \eta$ and of H, respectively, have also been included in Table XII-18b. Since only moderate viscosity ratios are involved, the differences between the various predictions are much less pronounced than found for the mineral-oil systems tested in the preceding parts (see in particular Tables XII-4 and XII-5).

Nevertheless, the *relative* improvement achieved by the new prediction method - using Equations (XII-36a) and (XII-45) - again proves to be quite considerable.

APPENDICES

Appendix XII-1. *The Relationship Between Molar, Weight and Volume Fractions*

Since mass is strictly additive, the relationship between the molar fraction, X, and the weight fraction, x, (both fractions relating to the second component) is defined by:

$$x = \frac{XM_2}{(1-X)M_1 + XM_2}, \qquad \text{(XII-47)}$$

where M_1 and M_2 denote the molecular weight of the first and the second component, respectively.

For expressing the volume fraction y (likewise relating to the second component) in terms of the weight fraction, x, the densities of both components are required as parameters. The resulting relationship leads:

$$y = \frac{\frac{d_1}{d_2}\,x}{1 + \left(\frac{d_1}{d_2} - 1\right)x}, \qquad \text{(XII-48)}$$

where d_1 and d_2 represent the densities of the first and the second component, respectively.

Strictly speaking, the volume fraction, y, may vary somewhat with the reference temperature, since the density ratio, d_1/d_2, is not entirely independent of temperature. For the interrelated hydrocarbon liquids under investigation, however, the variations of y with temperature are fully insignificant. Consequently, there is no real objection at all against the common practice of using *volume* fractions when dealing with mineral-oil mixtures.

Appendix XII-2. *The Additivity of the Viscosity Functions h and H*

The interrelationship between the viscosity functions h and H may be written as:

$$h = 10^{\frac{H}{8}} \qquad \text{(XII-49a)}$$

or

$$h = e^{0.288\,H}. \qquad \text{(XII-49b)}$$

The right-hand side of the latter equation may be expanded into a series as follows:

$$h = 1 + \frac{0.288\,H}{1!} + \frac{(0.288\,H)^2}{2!} + \frac{(0.288\,H)^3}{3!} + \cdots\cdots \qquad \text{(XII-49c)}$$

Substituting the latter expression for the h-values into Equation (XII-22), the following formula can be obtained after some rearrangement:

$$H_m = (1-y)H_1 + yH_2 + 0.144\left[(1-y)H_1^2 + yH_2^2 - H_m^2\right] + \\ + 0.014\left[(1-y)H_1^3 + y\,H_2^3 - H_m^3\right] + \cdots\cdots\cdots\cdots \qquad \text{(XII-50a)}$$

The terms containing second and higher powers of H give only a very small contribution to the right-hand side of Equation (XII-50a). Consequently, it is admissible to substitute for the H_m-values occurring in the latter terms their *first* approximation as defined by:

$$H_m = (1-y)H_1 + yH_2 \,. \qquad \text{(XII-23)}$$

Thus, Equation (XII-50a) may be reduced to:

$$H_m = (1-y)H_1 + yH_2 + 0.144\, y(1-y)\,(H_1 - H_2)^2, \qquad \text{(XII-50b)}$$

where the terms with the viscosity function H raised to third and higher powers have been omitted, since these are fully insignificant in practical cases.

A nearer consideration of Equation (XII-50b) shows that in many cases its last term may safely be neglected. Only for mixtures where the components have a very high viscosity ratio may the latter term have some significance. Consequently, it has been shown that the additivity of H according to Equation (XII-23) is practically on a par with the additivity of h according to Equation (XII-22).

It may be added that, as shown by the extended Equation (XII-50b), the mixture-viscosity values calculated from Equation (XII-23) will be more or less below those obtained from Equation (XII-22).

Appendix XII-3. *The Temperature Dependence of the Function* H_{12}

According to the basic viscosity-temperature Equation (XII-6h), one may write for any given mixture:

$$H_m - H_{m,40^\circ C} = S_m\,(0.1127 + \Theta). \qquad \text{(XII-51)}$$

Substituting the appropriate expressions according to Equations (XII-36a) and (XII-32) for H_m and S_m, respectively, one obtains:

$$(1-y)\,(H_1 - H_{1,40^\circ C}) + y(H_2 - H_{2,40^\circ C}) + y(1-y)\,(H_{12} - H_{12,40^\circ C}) =$$
$$\left[(1-y)S_1 + yS_2 + y(1-y)S_{12}\right]\,(0.1127 + \Theta). \qquad \text{(XII-52a)}$$

This expression may be simplified into:

$$H_{12} = H_{12,40^\circ C} + S_{12}\,(0.1127 + \Theta), \qquad \text{(XII-52b)}$$

or, by combination with Correlation (XII-33):

$$H_{12} = H_{12,40^\circ C} - 0.35 \cdot \Delta S\,(0.1127 + \Theta). \qquad \text{(XII-53)}$$

By substituting Correlation (XII-37) for $H_{12,40^\circ C}$, the latter equation may be transformed into:

$$H_{12} = (0.160 - 0.4 \cdot \Delta S)\,\Delta H_{40^\circ C} - \Delta S\left[0.088 + 0.35\,(0.1127 + \Theta)\right]. \qquad \text{(XII-54)}$$

Further, the quantity $\Delta H_{40^\circ C}$ in Formula (XII-54) may be replaced by the right-hand side of the following equation, which readily follows from the basic viscosity-temperature Equation (III-6h):

$$\Delta H_{40^\circ C} = \left|(H_1 - H_2) - \Delta S\ (0.1127 + \Theta)\right| . \qquad \text{(XII-55)}$$

Thus, one ultimately arrives at the expression:

$$H_{12} = (0.160 - 0.4 \cdot \Delta S)\ \left|(H_1 - H_2) - \Delta S\ (0.1127 + \Theta)\right| - \\ - \Delta S \left[0.088 + 0.35\ (0.1127 + \Theta)\right] . \qquad \text{(XII-38)}$$

Appendix XII-4. *Extremes in the Viscosity-Concentration Curves of Mineral-Oil Mixtures*

The basic mixture-viscosity equation reads:

$$H_m = (1-y)H_1 + yH_2 + y(1-y)H_{12} , \qquad \text{(XII-36a)}$$

where the volume fraction y may assume values from 0 to 1.

To investigate the occurrence of a *maximum* or a *minimum* in the viscosity-concentration curve or, say, in the H_m-values at some distinct y-value, the first and second derivative of H_m with respect to y have to be considered. From Equation (XII-36a) the subsequent expressions are readily derived:

$$\frac{dH_m}{dy} = (1-2y)\ H_{12} - (H_1 - H_2) \qquad \text{(XII-56)}$$

and

$$\frac{d^2 H_m}{dy^2} = -2\ H_{12} . \qquad \text{(XII-57)}$$

Putting the right-hand side of Equation (XII-56) equal to zero, it follows that the first condition for the occurrence of an extreme may be reduced to:

$$|H_{12}| \geqslant \Delta H, \qquad \text{(XII-58)}$$

where, by definition $\Delta H = |H_1 - H_2|$.

According to Equation (XII-57), the sign of the interaction viscosity function H_{12} decides whether the extreme will be a maximum or a minimum*). From Equations (XII-57) and (XII-58) the following conditions are finally obtained:

$$\text{for a } \textit{maximum:} \quad H_{12} \geqslant \Delta H \qquad \text{(XII-59a)}$$

and

$$\text{for a } \textit{minimum:} \quad -H_{12} \geqslant \Delta H. \qquad \text{(XII-59b)}$$

Consequently, solely the viscosity functions H_{12} and ΔH would decide on the occurrence of a maximum or a minimum in a given mineral-oil system.

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*) Obviously, Equation (XII-36a) cannot give rise to the occurrence of a point of inflection in the viscosity-concentration curves.

Equation (XII-58) implies that an extreme may occur only within a more or less restricted temperature range around the temperature where the component oils become isoviscous. Consequently, for settling the question whether a maximum or a minimum should be anticipated it is sufficient*) to confine oneself to a consideration of the H_{12} -values that may be encountered at this very iso-viscosity temperature, denoted by Θ_{iv} (or t_{iv} with t in deg C).

Substituting the latter temperature into Correlation (XII-38) for H_{12} leads to:

$$H_{12,\Theta_{iv}} = (0.160 - 0.4\cdot\Delta S)\,\left| - \Delta S(0.1127 + \Theta_{iv})\right| - \\ - \Delta S\left[0.088 + 0.35\,(0.1127 + \Theta_{iv})\right] \qquad \text{(XII-60)}$$

For evaluating Equation (XII-60) it is necessary to distinguish between two cases: the first one relating to $\Theta_{iv} \geqslant -0.1127$, that is to $t_{iv} \leqslant 40^{\circ}C$ (104°F); and the second one relating to $\Theta_{iv} \leqslant -0.1127$, that is to $t_{iv} \geqslant 40^{\circ}C$.

1. In the case where $t_{iv} \leqslant 40^{\circ}C$, Equation (XII-60) may be rewritten as:

$$H_{12,\Theta_{iv}} = - \Delta S\left[(0.190 + 0.4\cdot\Delta S)\,(0.1127 + \Theta_{iv}) + 0.088\right]. \qquad \text{(XII-61a)}$$

In the temperature range under consideration the right-hand side of the latter equation is negative for all possible values of ΔS. Therefore, according to Equation (XII-59b), a *minimum* occurs in the viscosity-concentration curves of mineral-oil mixtures at temperatures in the vicinity of the temperature where the components become isoviscous, provided that the latter temperature does not exceed 40°C.

2. In the second case, where $t_{iv} \geqslant 40^{\circ}C$, Equation (XII-60) may be rewritten as:

$$H_{12,\Theta_{iv}} = - \Delta S\left[(0.510 - 0.4\cdot\Delta S)\,(0.1127 + \Theta_{iv}) + 0.088\right]. \qquad \text{(XII-61b)}$$

The right-hand side of Equation (XII-61b) may be either positive, or zero or negative. In fact, for any possible value of ΔS a "transition" value may be calculated for the iso-viscosity temperature where the function $H_{12,\Theta_{iv}}$, as defined by Equation (XII-61b), becomes zero. Whilst the function $H_{12,\Theta_{iv}}$ becomes negative for temperatures below the latter transition values, it assumes positive values for higher temperatures.

The relevant *"transition temperatures"*, denoted by $\Theta_{iv,tr}$ or $t_{iv,tr}$, can be obtained from Equation (XII-61b) simply by putting its right-hand side equal to zero. The resulting expression reads:

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*) When a given system does not exhibit an iso-viscosity temperature, that is when the rectified viscosity-temperature lines of its components are parallel, the function ΔH is constant over the entire temperature range and $\Delta S = 0$. It readily follows from Equation (XII-52) in the preceding Appendix XII-3 that in the latter case the function H_{12} is likewise constant over the entire temperature range, namely $H_{12} = 0.160\cdot\Delta H$. Thus, the basic Condition (XII-58) excludes the occurrence of an extreme.

In the following analysis the value $\Delta S = 0$ will therefore be consistently left out of consideration.

$$\Theta_{iv,tr} = \frac{0.088}{0.4 \cdot \Delta S - 0.510} - 0.1127 \qquad \text{(XII-62)}$$

For a few distinct values of ΔS the transition temperatures $t_{iv,tr}$ have been listed in Table XII-19.

TABLE XII-19

"Transition Temperatures" $t_{iv,tr}$ for a Few Distinct Values of ΔS

ΔS	$t_{iv,tr}$	
	deg C	deg F
0.000*)	125	260
0.100	135	275
0.200	145	295
0.300	160	320
0.400	180	350

*) The listed transition temperature represents the limiting value for ΔS approaching zero.

It is concluded that in this second case a *minimum* would invariably occur if the iso-viscosity temperature does not exceed 125°C (260°F). But for the higher temperatures specified in Table XII-19 the surprising and rather bold conclusion emerges that a *maximum* might occur on mixing isoviscous oils.

It should be well realized, however, that the indicated maxima would be encountered only at very high temperatures.

Moreover, at these very high temperatures the involved viscosities usually are very small. Accordingly, the *practical* importance of the predicted viscosity increases might off-hand be anticipated to be quite moderate. Indeed, quantitative calculations have proved to confirm this conjecture.

As examples some oils having a common Slope Index $S = 1.234$ (corresponding to a DVI of 100) and covering a wide range of viscosities have successively been taken as *second* components of binary oil mixtures. As the respective *first* components two sets of oils have been used which would display the same viscosity as the aforementioned second components at a temperature of 200°C (392°F). The oils of the one set of first components have Slope Indices 0.200 units above the aforementioned value, so that they yield mixtures with $\Delta S = 0.200$; for the other set of first components $\Delta S = 0.400$. The percentage viscosity increases which would ensue at the iso-viscosity temperature of 200°C from mixing equal volumes of the specified oils are collected in Table XII-20.

This table conveys a good picture of the quantitative significance of the predicted viscosity increases.

TABLE XII-20

Percentage Viscosity Increases Ensuing from Mixing Equal Volumes of Two Mineral Oils ($S_2 = 1.234$) Being Isoviscous at 200°C (392°F)

$\eta_{40°C}$ of Second Oil, cP	$\eta_{200°C}$ of Both Oils, cP	Percentage Viscosity Increase at 200°C	
		$\Delta S = 0.200$	$\Delta S = 0.400$
1	0.22	0.2	0.2
10	0.61	0.9	0.7
100	1.72	1.2	0.9
1,000	4.83	1.6	1.2
10,000	13.6	2.1	1.4
100,000	38.2	2.3	1.6

From these and additional calculations it is indeed concluded that - disregarding yet the unusually high temperature range involved - the predicted viscosity increases would assume hardly any *practical* significance.

CHAPTER XIII

SOME APPLICATIONS IN HYDRODYNAMIC LUBRICATION

XIII. 1. INTRODUCTION

The preceding chapters of this thesis have aimed primarily at achieving a rational and convenient *characterization* of the viscosity-temperature-pressure relationships of lubricating oils - notably mineral oils - and at *predicting* these relationships from their chemical constitution or from easily assessable physical constants.

The resulting equations and correlations may be claimed to have some most significant technological and economical implications. As an introduction to this concluding chapter it is thought useful to restate these implications as inherent in the subject of the present thesis.

From the view-point of the *oil technologist* not only are there the important aspects of conveniently rating and/or predicting the viscosity characteristics of his products but also those of preparing oils with viscometrical properties specified or desired by the lubrication engineer, either through efficient refining or conversion of naturally available oils or through purposeful synthesis. Since in lubrication engineering increasingly keener demands are made on the viscometrical properties of the oils, the latter aspect in particular may be considered to assume steadily growing importance.

The principal aspect from the view-point of the *lubrication engineer* consists in the evaluation, and ultimately the correlation and prediction of the hydrodynamic lubrication performance of oils. In fact, once satisfactory correlations have thus been established, these can be advantageously applied in the selection of suitable oils and in predicting the consequent performance characteristics of machine elements working under specified operating conditions.

Finally, as indicated in Chapter I, the *designer* of machine elements which are to act under hydrodynamic lubrication conditions should treat the oil as a real constructional material. Now, the constructional value of such an oil has been shown to be essentially determined by its viscosity-temperature-pressure relationship.

In connection with the description, in the preceding chapters, of the newly developed equations and correlations various more or less general applications of these have there been expounded. Further, it would appear fairly simple to elaborate several additional applications. All in all, these equations and correlations have proved straightforward and reliable tools for efficiently tackling a great variety of viscosity problems.

This concluding chapter intends to delineate some simple applications of the aforementioned findings more specifically in the theory and practice of *hydrodynamic lubrication.*

XIII. 2. CORRELATION BETWEEN THE HYDRODYNAMIC LUBRICATION PERFORMANCE OF OILS AND THEIR VISCOSITY-TEMPERATURE-PRESSURE RELATIONSHIP

XIII. 2. 1. *Introduction*

As elucidated in Section I. 3, the hydrodynamic lubrication performance of oils is, in general, essentially determined by their viscosity-temperature-pressure relationship. Accordingly, an important basic problem in lubrication research consists in accounting for the latter relationship by means of convenient, yet sufficiently representative, viscosity characteristics which may be feasibly correlated with the hydrodynamic lubrication performance of the oil concerned.

Some investigators have suggested that this basic problem could be solved simply by introducing the concept of a suitably chosen *"representative"* viscosity. Thus, for the correlational purpose intended such a representative viscosity might well allow sufficiently not only for the effects of the oil's viscosity grade but also for those of the viscosity variations ensuing throughout the oil film from the non-uniformity of temperature and/or pressure.

One might, for instance, conceive some viscosity value defined and determined by "averaging" over the entire oil film as such a representative one. Actually, in various problems the solution would appear even much simpler. In fact, it has proved permissible in such problems to take simply the viscosity of the oil under the conditions prevailing at the *inlet* to its film as a representative one, without accounting explicitly for the viscosity variations encountered throughout this film.

But on closer consideration it would appear that, as demonstrated by Blok[206)], the latter solution would in general be oversimplified. Indeed, it can be stated that generally it would amount to stretching imagination too far to uphold the concept of a "representative" viscosity as a really valuable one in attempts to provide some acceptable solution to the basic lubrication problem under discussion.

XIII. 2. 2. *The Conventional Procedure*

The conventional procedure for correlating the hydrodynamic lubrication performance of oils with their viscosity-temperature-pressure relationship is based on the use of three straightforward quantities for this relationship. Besides the viscosity grade, $\eta_{0,r}$, of the oil, the conventional procedure involves its viscosity-temperature coefficient $\beta_{0,r}$ (see § VI. 3. 1) and its viscosity-pressure coefficient $\alpha_{0,r}$ (see Section VII. 4), both coefficients taken at the same conditions as the viscosity grade, that is at atmospheric pressure and at the same (standard) reference temperature, t_r.

Now, the conditions prevailing at the *inlet* to the oil film are frequently adopted as suitable reference conditions for the three aforementioned viscosity characteristics. But, whilst the inlet pressure can simply be considered as atmospheric, the inlet temperature cannot so easily be assessed. Fortunately, owing to the very effective transfer of heat between the rubbing surfaces and the minute amount of oil flowing into the film, the temperature of the oil at the inlet to this film may be taken to have assumed practically the same level as that of the rubbing surfaces themselves, irrespective of the temperature at which the oil is being *supplied.*

Although it is not necessary to take the inlet temperature proper as the reference temperature, this choice has the advantage that the viscosity-temperature coefficient $\beta_{0,r}$ can be dispensed with entirely in cases where the *temperature* variations over the oil film remain quite moderate. On the other hand, by using invariably the *same* standard reference temperature - irrespective of the particular inlet temperature - one achieves that the consequent correlations can be put on a more *uniform* basis.

XIII. 2. 3. *The Present Procedure*

The newly developed procedure for correlating the hydrodynamic lubrication performance of oils with their viscosity-temperature-pressure relationship has the weighty advantage over the conventional one that it involves a more adequate and more convenient combination of three parameters for the latter relationship. In fact, the present procedure employs the two dimensionless parameters S_0 and Z_r in addition to the viscosity grade, $\eta_{0,r}$, of the oil considered; once again the index r relates to a particular reference temperature, which may be either some suitably chosen *standard* reference temperature or the *inlet* temperature concerned.

Thus, the new procedure is based on the validity of the simplified viscosity-temperature-pressure equation presented in Chapter V:

$$H = S_0\Theta + Z_r\Pi + \log G_0 \ . \qquad \text{(V-9b)}$$

It may be recalled that this equation applies better according as the parameter C in the basic Equation (V-1a) approximates closer to zero. In general, Equation (V-9b) may be regarded to give a satisfactory description of the complete viscosity-temperature-pressure relationship of oils within fairly wide ranges of temperature and pressure, that is from about 20 to 120°C (68-248°F) and up to pressures of about 2, 000 kgf/cm (28, 000 psi). But for the correlational purposes normally intended in lubrication research, the accuracy inherent in Equation (V-9b) may be taken satisfactory even in considerably wider ranges of temperature and pressure. In fact, these ranges may then be regarded as sufficiently wide to comprise the temperature and pressure variations encountered in practically all lubrication problems.

This leads up to the significant conclusion that for correlational purposes in hydrodynamic lubrication the indices S_0 *and* Z_r *in conjunction with the oil's viscosity grade,* $\eta_{0,r}$, *may as a rule be regarded as representative, to a good approximation, of its complete viscosity-temperature-pressure relationship.*

The delineated analytical background explains the definite superiority of the present procedure over the conventional one. Moreover, in contrast to the coefficients $\beta_{0,r}$ *and* $\alpha_{0,r}$ *used in the con-*

ventional procedure, the indices S_0 and Z_r display the significant feature that they are substantially constant in wide ranges of temperature and pressure, so that they permit a simpler and more adequate analytical evaluation of the complete viscosity-temperature-pressure relationship of the oil considered. Further, these indices have proved more convenient also in the viscometrical selection of lubricating oils (see Section XIII. 3).

It is true that, in contrast to the viscosity-temperature and the viscosity-pressure coefficients used in the conventional procedure, the two dimensionless indices S_0 and Z_r cannot be employed *directly* as influential quantities in correlational attempts based on *dimensional analysis*. This might seem a serious drawback of the present procedure since dimensional analysis constitutes a powerful tool in the theory of lubrication, be it fully or only partially hydrodynamic. In fact, in lubrication problems where several effects have to be considered at the same time dimensional analysis would even remain as the only really workable expedient[206,207].

On nearer consideration, however, the indicated drawback inherent in the present procedure proves to be of minor importance. This accrues from the existence of simple interrelationships between the two indices S_0 and Z_r used in this procedure and the corresponding viscosity-temperature and viscosity-pressure coefficients, respectively. Referring to Equations (VI-5) and (VII-5), the relevant interrelationships can be written as:

$$\beta_{0,r} = q_1 \; S_0(\log \eta_{0,r} + 1.200) = q_1 \; S_0 \cdot \log \frac{\eta_{0,r}}{\eta_\infty} \qquad \text{(VI-5a)}$$

and

$$\alpha_{i,r} = q_2 \; Z_r(\log \eta_{0,r} + 1.200) = q_2 \; Z_r \cdot \log \frac{\eta_{0,r}}{\eta_\infty}\,, \qquad \text{(VII-5a)}$$

where the constants q_1 and q_2 are functions only of the standard reference temperature, t_r.

Consequently, in establishing correlations through dimensional analysis the right-hand sides of the latter two expressions can be used simply instead of the coefficients $\beta_{0,r}$ and $\alpha_{0,r}$*). Moreover, a similar substitution applies to any correlation already available. This is important because the applicability range of some newly established or properly revised correlation will thus become markedly wider than that of the corresponding correlation developed on the basis of the coefficients $\beta_{0,r}$ and $\alpha_{0,r}$. In addition, with various correlations which have thus been put into a more *general* and more *convenient* form, some further simplification may well be possible.

The indicated generalization method may be elucidated for the case of a tentative correlation propounded by Blok[206].

In an attempt to correlate disk friction results obtained by Misharin, Blok devised - through the technique of dimensional analysis - a tentative correlation for the coefficient of friction which involves not only the viscosity grade of the oil but also its atmospheric viscosity-temperature and

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*) As a matter of fact, this atmospheric viscosity-pressure coefficient $\alpha_{0,r}$ should first be replaced by the more appropriate initial viscosity-pressure coefficient $\alpha_{i,r}$ (see Section VII.4).

viscosity-pressure coefficient. Representing the coefficient of friction by f and combining the remaining influential quantities into one single variable K_1, Blok's relevant Correlation (29b) can be rewritten as:

$$f = K_1\, \eta_{0,r}^{s_1} \cdot \beta_{0,r}^{s_2} \cdot \alpha_{i,r}^{s_3} \; . \qquad \text{(XIII-1a)}$$

where the exponents s_1, s_2 and s_3 denote constants. Substituting the foregoing Expressions (VI-5a) and (VII-5a), Blok's correlation*) can now be put into the generalized form:

$$f = K_2\, \eta_{0,r}^{s_1} \left(\log \frac{\eta_{0,r}}{\eta_\infty} \right)^{s_2 + s_3} S_0^{s_2} \cdot Z_r^{s_3} \; , \qquad \text{(XIII-1b)}$$

where the quantity K_2 represents the product of the variable K_1 and the constants q_1 and q_2 of Equations (VI-5a) and (VII-5a), raised to the powers s_2 and s_3, respectively. Further, since the exponent s_1 happens to be equal**) to the sum of the exponents s_2 and s_3, Equation (XIII-1b) may be reduced to:

$$f = K_2 \left(\eta_{0,r} \cdot \log \frac{\eta_{0,r}}{\eta_\infty} \right)^{s_1} S_0^{s_2} \cdot Z_r^{s_3} \qquad \text{(XIII-1c)}$$

or

$$f = K_2 \left(Z_r\, \eta_{0,r} \cdot \log \frac{\eta_{0,r}}{\eta_\infty} \right)^{s_1} \left(\frac{S_0}{Z_r} \right)^{s_2} \; . \qquad \text{(XIII-1d)}$$

XIII. 3. VISCOMETRICAL SELECTION OF LUBRICATING OILS

The viscometrical selection of lubricating oils can be conveniently performed on the basis of the new characterization method elucidated in the preceding section. Indeed, the sole use of the indices S_0 and Z_r has proved to permit a rational comparison of the atmospheric temperature and the pressure variation, respectively, of oils meeting some specified viscosity grade. Further, the relative importance of the effects of temperature and pressure variations on the viscosity of different oils can be judged simply from the *ratio* between both indices.

A. ATMOSPHERIC VISCOSITY-TEMPERATURE EFFECT

In many hydrodynamic lubrication problems some suitable oil has

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*) It may be noted that power-type functions similar to Blok's correlation have proved useful in a variety of lubrication problems.

**) This equality results from the reasonable assumption that the exponent "q" in Blok's Correlation (29b) amounts to zero.

to be selected primarily on the basis of the *temperature* variation of its atmospheric viscosity. As indicated in Section I. 3, for proper functioning of a given machine element it is generally necessary that the viscosity of the lubricating oil employed is kept within a more or less restricted range under the varying temperatures encountered. In fact, at the lowest temperature encountered the viscosity should not exceed a certain upper limit, whilst at the highest temperature involved the oil should remain sufficiently viscous.

The consequent limits to be imposed on the atmospheric viscosity-temperature relationships of suitable oils can be represented very conveniently in some *rectifying* viscosity-temperature chart, notably in the new H_0-Θ chart. Thus, the shaded rectangle - which may appropriately be termed a viscosity-temperature *"window"* - in the schematic Fig. XIII-1 comprises the range of atmospheric viscosities - varying from $(H_0)_{min}$ to $(H_0)_{max}$ - that are admissible between the minimum and maximum temperature encountered, denoted by t_{min} and t_{max}, respectively. It is seen that the depicted viscosity-temperature line with a viscosity $(H_0)_{int}$ at the arbitrarily selected standard reference temperature t_r represents the steepest atmospheric isobar permissible; its atmospheric Slope Index has accordingly been denoted by $(S_0)_{max}$. For oils with different viscosity grades $H_{0,r}$ (at the same standard reference temperature t_r) the atmospheric Slope Index, S_0, should be smaller according as their viscosity grades approximate closer to either the minimum or the maximum atmospheric viscosity prescribed. In fact, the range of atmospheric Slope Indices, S_0, admissible with each particular viscosity grade $H_{0,r}$ can be read at once from the shaded triangle of Fig. XIII-1.

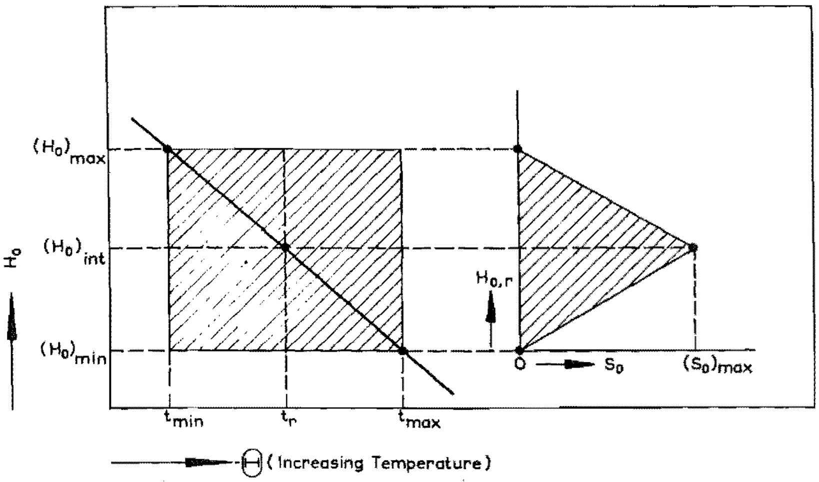

FIG. XIII-1.
Selection of Lubricating Oils According to Their Atmospheric Viscosity-Temperature Relationship by Means of the New Viscosity-Temperature Chart.

Summarizing, from the specified minimum and maximum atmospheric viscosities that are still admissible at the given highest and lowest temperature a triangular diagram as reproduced in the schematic Fig. XIII-1 can readily be constructed which permits a convenient selection of oils only on the basis of their viscosity grade $H_{0,r}$ and their atmospheric Slope Index, S_0.

It may be added that by adopting some appropriate standard reference temperature, for instance 40°C (104°F), viscosity-temperature specifications can thus also be put on a more *uniform* basis.

In the selection of oils according to their atmospheric viscosity-temperature relationship several figures included in Chapters VI and VIII may be very helpful. For a great variety of synthetic lubricating oils and miscellaneous liquids Figs. VI-3 and VI-5 represent the atmospheric Slope Indices as a function of their viscosity grades. Further, for all the various kinds of mineral oils tested so far, Chapter VIII contains several figures correlating their atmospheric Slope Index with their viscosity grade on the basis of either their chemical constitution or easily assessable physical constants.

B. VISCOSITY-PRESSURE EFFECT

In hydrodynamic lubrication problems where some suitable oil has to be selected primarily on the basis of the *pressure* variation of its viscosity this can conveniently be performed on the basis of its Viscosity-Pressure Index, Z_r.

The consequent selection applies to all those problems where a certain viscosity grade has been prescribed and pressure varies considerably throughout the oil film, notably in isothermal elasto-hydrodynamic lubrication problems (see the subsequent Section XIII. 4).

It may be recalled that the Viscosity-Pressure Indices of a great variety of synthetic lubricating oils and miscellaneous liquids have been represented in Fig. VII-2 as a function of their viscosity grades. For all the various kinds of mineral oils tested so far, Chapter IX contains several figures correlating their Viscosity-Pressure Index with their viscosity grade on the basis of either their chemical constitution or easily assessable physical constants; further, Fig. X-1 and related figures of Chapter X represent the Viscosity-Pressure Index of mineral oils as a function of their viscosity grade and their atmospheric Slope Index.

C. COMBINED EFFECTS OF TEMPERATURE AND PRESSURE

In hydrodynamic lubrication problems where both temperature and pressure vary considerably throughout the oil film simply the ratio Z_r/S_0 may be useful in the selection of oils meeting the specified viscosity grades.

Fig. X-15 represents the ratio Z_{40^oC}/S_0 of a great variety of both mineral oils, synthetic lubricating oils and miscellaneous liquids as a function of their viscosity grade, thus conveying a comparative picture of the combined effects of temperature and pressure variations on their viscosity grade. It is seen that mineral oils occupy an intermediate position with respect to their ratio Z_{40^oC}/S_0. The included polymethylsiloxanes are outstanding in that they exhibit relatively high ratios, their values of Z_{40^oC} being nearly equal to those of S_0 (see also § XIII. 5. 3).

XIII.4. THE VISCOSITY-PRESSURE EFFECT IN HYDRODYNAMIC LUBRICATION

XIII.4.1. *Introduction*

As indicated in Section I.3, the effect of the viscosity-pressure variation of oils on their hydrodynamic lubrication performance may usually be neglected when so-called *conformal* rubbing surfaces - which, by definition, fit wholly, or nearly so, on or into each other - are involved. Disregarding this viscosity-pressure effect may still be justifiable with *counterformal* surfaces, provided that at least one of them is comparatively flexible. But when both counterformal surfaces are made of rather rigid materials, such as steels, the viscosity-pressure effect does come to the fore. In fact, between such rigid counterformal surfaces pressures may well rise, even under moderate loads, to something like a few thousand kgf/cm^2.

For proper understanding, the subsequent treatment of the effect of the viscosity-pressure variation of oils on their hydrodynamic lubrication performance is to be preceded by a concise review of three *basic theories* which have proved their value in solving different kinds of hydrodynamic lubrication problems. The possibility of classifying hydrodynamic lubrication problems according to their attackability by one of these three theories has recently been introduced and elaborated by Blok$^{5,6)}$.

A. THE CLASSICAL THEORY

The *classical* theory of hydrodynamic lubrication is based on Reynolds's famous equation. This equation interrelates the *film-pressure distribution* and the *film profile* and shows the influence of the tangential velocities of the rubbing surfaces (relative to the film as a whole) and the *viscosity* - at the operating conditions - of the oil.

Notwithstanding the almost universal validity of the classical theory, its *practical* importance in solving hydrodynamic lubrication problems proves to be confined to those problems where the elastic deformations of the rubbing surfaces are relatively so small that these may reasonably be assumed to be perfectly *rigid*.

In such "*classical*" problems the film profile is thus given or prescribed, the film-pressure distribution being required. Once this film-pressure distribution has been obtained by integrating Reynolds's basic differential equation, the important criteria for rating the hydrodynamic lubrication performance of the oil film, notably its *load-carrying capacity* and the resulting *frictional losses*, can be assessed in a fairly simple manner.

Such classical problems constitute the subject of the great majority of publications on hydrodynamic lubrication.

B. THE ELASTO-HYDRODYNAMIC THEORY

Particularly in problems where the viscosity-pressure variation of the oil affects considerably its hydrodynamic lubrication performance the *elastic deformations* of the rubbing surfaces - notably when these are highly-loaded counterformal surfaces - also tend to become relatively great, that is of the same order of magnitude as the - minute - thickness of the oil film. In such problems the assumption of rigid surfaces may no longer be upheld and the so-called *elasto-hydrodynamic* theory has to be resorted to.

Thus, the elasto-hydrodynamic theory is more general than the classical theory in that it accounts - by means of the modulus of elasticity of both rubbing surfaces - for the elastic deformations caused by the pressures hydrodynamically generated throughout the oil film. It has appeared that the effect of these elastic deformations, acting in conjunction with the viscosity-pressure variation of the oil, gives rise to considerably higher load-carrying capacities than the viscosity-pressure variation would do all by itself with perfectly rigid surfaces.

It stands to reason that, in general, *"elasto-hydrodynamic"* problems will be much more difficult to attack than classical ones. In fact, in Reynolds's equation the film thickness is now affected by the elastic deformations, that is by the unknown pressure distribution, so that this equation has to be combined with that describing the elastic deformations as a function of the unknown pressure distribution.

C. THE INVERSE THEORY

In recent years a frequently convenient counterpart to the classical theory was elaborated by Blok[6]. His so-called *inverse* theory applies primarily to *flexible* rubbing surfaces, which easily yield - even under quite moderate loads - elastic deformations much greater than the thickness of the oil film interposed.

It can be shown that with such surfaces the pressure distribution in the oil film must be practically identical with the distribution of *contact* pressures that would obtain - under the given load - for no oil at all. As the latter distribution can be calculated by the sole use of the theory of elasticity, the corresponding film-pressure distribution may be considered to be known *a priori*. The film profile hydrodynamically compatible with this elastically imposed film-pressure distribution can then be determined in a simple manner from Reynolds's basic equation.

Thus, like the classical theory, Blok's theory is ultimately based on the validity of Reynolds's equation. But the latter theory may indeed be termed *"inverse"* with respect to the *"classical"* theory, that is as regards the given and required quantities. As a consequence, the inverse theory displays the important feature that the mathematics involved prove to be essentially simpler than those of the classical theory.

As indicated above, those hydrodynamic lubrication problems where the viscosity-pressure effect of the oils becomes really significant will generally belong to the category of so-called elasto-hydrodynamic problems. Blok has shown, however, that in many cases his inverse theory enables a substantially simpler attack of such complicated problems than the genuine elasto-hydrodynamic theory (see the subsequent § XIII. 4. 2).

The following treatment will be confined to *isothermal but non-isoviscous* hydrodynamic problems, that is to problems where the effect of temperature variations is negligible but where film pressures become so high that the viscosity-pressure effect comes to the fore.

For proper understanding, it should be pointed out that in hydrodynamic lubrication problems where the combined effects of temperature and pressure on the viscosity of the oil have to be taken into consideration the resulting film profile may be very different from that establishing itself, under the given load, in the corresponding isothermal problem where only the pressure variation of viscosity has to be accounted for. In fact, the high pressures created in the oil film tend to increase not only the viscosity of the oil but also the viscous-frictional heat developed in this film. If this heat cannot be transferred rapidly enough to the rubbing surfaces, the temperature in the oil film is bound to rise, especially in the film portion where the pressures are highest. In certain cases the consequent temperature rise may become so considerable as to balance, or even outbalance, the viscosity-pressure effect proper.

However, with rather rigid, *counterformal* surfaces - such as balls or rollers on their races in rolling bearings and meshing tooth faces - the transfer of viscous-frictional heat developed in the oil film normally proves to be so effective that the temperature variations throughout the oil film remain within tolerable limits*). This is generally the case when nearly pure *rolling* of the rubbing surfaces prevails - so that their sliding tendency is sufficiently suppressed - and film thickness is not too small.

Consequently, solutions achieved for strictly isothermal but non-isoviscous hydrodynamic problems have a really wide applicability range in that they constitute fair approximations also to many practical problems with non-isothermal flow.

XIII. 4. 2. *Accounting for the Viscosity-Pressure Effect in Isothermal Hydrodynamic Lubrication*

Under isothermal conditions, the influence of the viscosity-pressure variation of oils on their hydrodynamic lubrication performance is such that both the *load-carrying capacity* and the *frictional losses* are increased. However, at least as long as *full* hydrodynamic lubrication obtains, the increase in frictional losses usually proves to be of minor practical significance as compared with the gain achievable in load-carrying capacity.

The aforementioned two-fold influence of the isothermal viscosity-pressure effect of a given oil on its hydrodynamic lubrication performance can be assessed from the changes brought about in the distribution of pressures throughout the created oil film. The relevant problem was solved ingeniously by the famous Swedish investigator Weibull[208] His straightforward and convenient theory - put forward as early as 1925 - has the attractive feature that it can be

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*) It may be remarked that additional heat effects arise from the adiabatic compression and decompression of the oil in passing through the maximum in its film-pressure distribution. As a result, in certain cases the temperature at the outlet may become even lower than that at the inlet to the oil film.

applied to any given profile of the oil film and to any form of the involved viscosity-pressure relationship of the oil. Quite recently, Blok presented a lucid elaboration of Weibull's basic theory. The subsequent exposé essentially derives from Blok's extensive study.

Weibull's theory amounts to reducing *isothermal but non-isoviscous* hydrodynamic lubrication problems to the corresponding *isoviscous* ones. This is performed by introducing a new pressure variable, p_{iv}, the *"fictitiously isoviscous film pressure"* or, for shortness, the *"isoviscous pressure"*. This isoviscous pressure, p_{iv}, is related to the *actual* film pressure, p, by the integral:

$$p_{iv} = \int_0^p \frac{\eta_0}{\eta}\, dP \;, \qquad \text{(XIII-2)}$$

where η_0 represents again the viscosity of a given oil at atmospheric*) pressure and at the temperature prevailing at the inlet to the film and where η denotes its viscosity at (gauge) pressure p and at the same temperature; further, the integration variable P has the meaning of a pressure varying over the integration range, $0 \leqslant P \leqslant p$.

By working out Integral (XIII-2) for an oil whose viscosity-pressure relationship is known at the temperature concerned one can write the actual pressure, p, explicitly in terms of the isoviscous pressure, p_{iv}, and *vice versa* (see below). Consequently, on the basis of Weibull's Transform (XIII-2) the film-pressure distribution in an isothermal but non-isoviscous hydrodynamic lubrication problem can be assessed, for any particular film profile and for any particular oil, from that in the corresponding isoviscous problem, and *vice versa*.

For many isoviscous problems the distribution of isoviscous pressures, p_{iv}, is given in the literature; or, if not there given, this distribution can be assessed from the classical theory of hydrodynamic lubrication, that is from Reynolds's basic equation. Then, from the known distribution of isoviscous pressures, p_{iv}, the corresponding distribution of actual pressures, p, can be determined simply by evaluating Weibull's Transform (XIII-2) for the lubricating oil concerned, that is from its viscosity-pressure relationship at the inlet temperature.

On the other hand, as indicated by Blok, Weibull's transform is very useful also in *inverse* problems with isothermal but non-isoviscous flow. In such problems it is the distribution of actual film pressures, p, that is known - being elastically imposed upon the film - and the film *profile* that is required. Now, the film profile sought can be assessed from Reynolds's basic relationship once the corresponding distribution of isoviscous pressures, p_{iv}, has been determined by means of Weibull's Transform (XIII-2).

The integral represented by Weibull's Transform (XIII-2) can be worked out for any oil whose viscosity-pressure dependence is given at the temperature concerned, either by some analytical or some

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*) Strictly speaking, the latter viscosity relates to the pressure at the inlet to the film; usually, however, this pressure may be regarded as atmospheric.

graphical procedure. In order to show the overall trend of the relationship between the actual pressure, p, and the corresponding isoviscous pressure, p_{iv}, Weibull's transform will be worked out first of all for the usually employed exponential viscosity-pressure relationship:

$$\eta = \eta_0 \cdot e^{\alpha p} . \qquad \text{(IV-1a)}$$

This leads to the following relationships between p_{iv} and p:

$$p_{iv} = \frac{1}{\alpha} (1 - e^{-\alpha p}) \qquad \text{(XIII-3a)}$$

or

$$p = \frac{1}{\alpha} \cdot \ln (1 - \alpha\, p_{iv})^{-1} . \qquad \text{(XIII-3b)}$$

Equation (XIII-3a) implies that the isoviscous pressure, p_{iv}, approximates asymptotically to a finite upper limit, $p_{iv,as}$, when the actual pressure, p, approaches infinity (assuming the oil has not yet solidified). This limiting pressure, $p_{iv,as}$, the so-called *asymptotic* (fictitiously) isoviscous pressure, is therefore defined by:

$$p_{iv,as} = \int_0^\infty \frac{\eta_0}{\eta}\, dP . \qquad \text{(XIII-4)}$$

By substituting Equation (IV-1a) it can readily be verified that, according to Definition (XIII-4), the limiting value $p_{iv,as}$ should be identical to the reciprocal value of the viscosity-pressure coefficient α of a given oil at the temperature in question. From Barus's viscosity-pressure Equation (IV-1a) it can further be derived that for a given oil and at the temperature considered the asymptotic isoviscous pressure, $p_{iv,as}$, should be numerically equal to the real pressure that has to be applied in order to increase its relative viscosity, η/η_0, to the value of e (=2.718), the base number of the natural logarithm.

Taking $p_{iv,as} = 1/\alpha$, Equation (XIII-3a) may be rewritten in the form:

$$\frac{p_{iv}}{p_{iv,as}} = 1 - e^{-\frac{p}{p_{iv,as}}} . \qquad \text{(XIII-5)}$$

Further, combination of the latter expression with Barus's Equation (IV-1a) leads to the identity:

$$\frac{p_{iv}}{p_{iv,as}} = 1 - \frac{\eta_0}{\eta} . \qquad \text{(XIII-6)}$$

On the basis of Equations (XIII-5) and (XIII-6) both the ratio η_0/η in Weibull's Transform (XIII-2) and the ratio $p_{iv}/p_{iv,as}$ have been depicted as a function of the actual pressure, p. From the resulting

Fig. XIII-2 the important feature emerges that with increasing actual pressure, p, the corresponding isoviscous pressure, p_{iv}, approaches

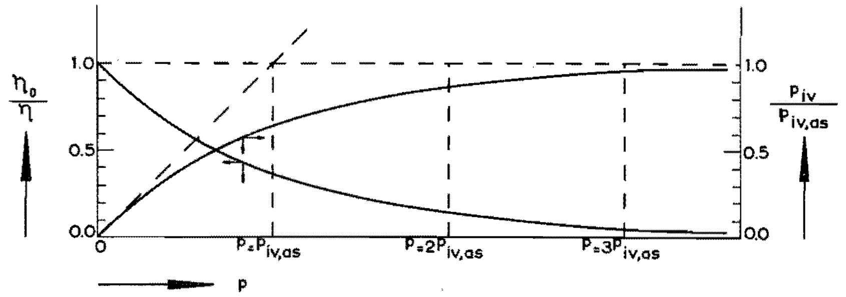

FIG. XIII-2.

The Ratios $p_{iv}/p_{iv,as}$ and η_0/η as a Function of Pressure According to Equations (XIII-5) and (XIII-6).

its asymptotic value, $p_{iv,as}$, quite rapidly. In fact, already at actual pressures above something like 3 $p_{iv,as}$ or 4 $p_{iv,as}$ the isoviscous pressure is seen to reach its limiting value within a few per cent; some of the pertinent numerical data are included in Table XIII-1.

TABLE XIII-1

The Ratios $p_{iv}/p_{iv,as}$ and η_0/η for a Few Distinct Values of the Ratio $p/p_{iv,as}$ According to Equations (XIII-5) and (XIII-6)

$p/p_{iv,as}$	η_0/η	$p_{iv}/p_{iv,as}$
0	1	0
0.5	0.606	0.394
1	0.368	0.632
2	0.135	0.865
3	0.050	0.950
4	0.018	0.982

On the other hand, Fig. XIII-2 shows that the isoviscous pressure, p_{iv}, comes close to the actual pressure, p, when the latter is considerably lower than the corresponding asymptotic isoviscous pressure, $p_{iv,as}$.

Fig. XIII-2 thus also demonstrates that the ratio $p/p_{iv,as}$ may be regarded as a simple criterion for roughly appreciating, in a particular lubrication problem and at the temperature concerned, the importance of the effect of the viscosity-pressure dependence of a given oil on its hydrodynamic lubrication performance.

Finally, it should be mentioned that, whilst Fig. XIII-2 and Table XIII-1 are based on an *exponential* variation of viscosity with pressure, a similar trend of the relationship between p and p_{iv} is observed with all other analytical viscosity-pressure equations, at least in so far as these may indeed be deemed sufficiently accurate (compare § XIII.4.4).

As regards the *magnitude* of the asymptotic isoviscous pressures, $p_{iv,as}$, of lubricating oils, it can be stated that in the conventional temperature range these pressures amount to something like 500 kgf/cm^2 (about 7,000 psi). For example, for all the various kinds of mineral oils tested so far the asymptotic isoviscous pressures at 40°C range from 150 to 1,000 kgf/cm^2 (about 2,000-14,000 psi)*).

From the preceding findings it may be concluded that for most lubricating oils and up to fairly high temperatures the actual pressure, p, at which the isoviscous pressure, p_{iv}, approaches its corresponding limiting value, $p_{iv,as}$, within a few per cent is of the order of some 1,500 to 2,000 kgf/cm^2 (21,000-28,000 psi).

Now, especially in problems where the influence of the pressure variation of viscosity on the oil's hydrodynamic lubrication performance becomes really important, the actual film pressures, p, can easily assume the latter, or even higher, values.

As elucidated by Blok, the latter result is particularly useful in applying his *inverse* theory to solving a physically significant part of the problem of the isothermal lubrication of heavily-loaded counterformal surfaces, such as gears and rolling bearings. In fact, the relevant problems become substantially simplified in that over the entire portion of the film where the prescribed pressures, p, are sufficiently high the isoviscous pressures, p_{iv}, may simply be taken equal to their asymptotic value, $p_{iv,as}$, at the film temperature concerned. In assessing the required film profile - by means of Reynolds's basic equation - it then follows that through that entire portion the film thickness must be practically constant or, say, the film profile must be nearly parallel.

In the introduction to this section it has already been pointed out that, in general, hydrodynamic problems where the viscosity-pressure effect becomes really significant may be considered to belong to the category of so-called *elasto-hydrodynamic* problems. The many solutions provided so far for such problems have usually been based on the assumption that the lubricating oil employed would obey the exponential Equation (IV-1a). Thus, in these solutions the viscosity-pressure effect has been accounted for simply by means of the viscosity-pressure coefficient, α. However, more *general* solutions would be possible through accounting for the viscosity-pressure dependence of a given oil by means of its asymptotic isoviscous pressure, $p_{iv,as}$.

In fact, Blok has arrived at the very important conclusion that all elasto-hydrodynamic results achieved hitherto for an exponential viscosity-pressure dependence can, to a fair approximation, be generalized for any given, non-exponential, dependence simply by substituting the reciprocal of the asymptotic isoviscous pressure, $1/p_{iv,as}$, *for the viscosity-pressure coefficient,* α, *occurring in these results.*

Such a generalization has been elaborated by Blok specifically for

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*) Further particulars can be found in Fig. XIII-4, which will be discussed in the subsequent Section XIII.5.

the Ertel-Grubin approximative treatment of the isothermal elasto-hydrodynamic problem of heavily-loaded counterformal surfaces which are not flexibly coated. For this important problem, which is representative of the lubrication of heavily-loaded gears and rolling bearings, Blok's generalization has been achieved mainly on the basis of his *inverse* theory.

It may be mentioned that in such generalized elasto-hydrodynamic results the ratio $\eta_0/p_{iv,as}$ frequently occurs as a single oil characteristic. In accordance with Weibull's Transform (XIII-2) this ratio may be rewritten as:

$$\frac{\eta_0}{p_{iv,as}} = \left(\int_0^\infty \frac{1}{\eta} \, dP \right)^{-1} = \left(\int_0^\infty \varphi \, dP \right)^{-1} , \qquad \text{(XIII-7)}$$

where φ denotes the reciprocal of viscosity, the so-called *fluidity.*

All in all, the asymptotic isoviscous pressure, $p_{iv,as}$, should be regarded of paramount importance in all isothermal hydrodynamic lubrication problems where the pressure variation of the viscosity of the oil becomes really significant. Although reasonable values for this quantity $p_{iv,as}$ can be derived by assuming that the oil conforms to an exponential viscosity-pressure dependence, a more accurate, yet convenient, estimating method would be desirable.

In the subsequent § XIII. 4. 3 it will be shown that this can readily be achieved on the basis of the newly developed viscosity-pressure Equation (IV-5a).

XIII. 4. 3. *Application of the New Viscosity-Pressure Equation*

According to the present viscosity-pressure Equation (IV-5a), the asymptotic isoviscous pressure, $p_{iv,as}$, of a given oil and at a given temperature can be rewritten as:

$$p_{iv,as} = \frac{\eta_0}{\eta_\infty} \int_0^\infty \left(\frac{\eta_0}{\eta_\infty} \right)^{-\left(1 + \frac{p}{2,000}\right)^Z} dP \, , \qquad \text{(XIII-8a)}$$

where the fictitious viscosity η_∞ would again amount to 0.0631 cP and be common to all liquids. By appropriate substitution the latter expression can be reduced to:

$$p_{iv,as} = 3.170 \cdot 10^{-4} \frac{\eta_0}{Z} \left(\ln \frac{\eta_0}{\eta_\infty} \right)^{-\frac{1}{Z}} \int_{\ln \frac{\eta_0}{\eta_\infty}}^{\infty} e^{-u} \, u^{\left(\frac{1}{Z} - 1\right)} \, du \, , \qquad \text{(XIII-8b)}$$

where the new integration variable u is defined by:

$$u = \left(1 + \frac{p}{2,000}\right)^{Z} \ln \frac{\eta_0}{\eta_\infty} \qquad \text{(XIII-9)}$$

and where atmospheric viscosity, η_0, has again been expressed in cP and pressure (p and $p_{iv,as}$) in kgf/cm^2.

The integral of Expression (XIII-8b) represents a so-called *incomplete gamma function*. The numerical evaluation of this function can be performed by means of Pearson's well-known tables[209]. However, in order to obviate the still rather tedious calculations involved the asymptotic isoviscous pressures, $p_{iv,as}$, have been computed for extensive ranges of the two variables, that is the atmospheric viscosity, η_0, and the Viscosity-Pressure Index, Z. In fact, the results compiled in Table XIII-2 cover nearly all oils encountered in actual lubrication practice.

For convenience, the ***logarithms*** ($\log_{10}$) of the values of $p_{iv,as}$ have been listed in the latter table for distinct values of the Viscosity-Pressure Index, Z, and of the atmospheric viscosity function H_0; in addition, the logarithms of the values of Z have been included. The reason is that in its present form this table permits accurate determinations of asymptotic isoviscous pressures also for ***intermediate*** values of the Viscosity-Pressure Index and the atmospheric viscosity. This can be performed simply by ***linearly*** interpolating, since for any constant value of the Viscosity-Pressure Index and over a fairly wide range of atmospheric viscosities the corresponding values of $\log p_{iv,as}$ and H_0 prove to be linearly interrelated, at least to a very good approximation; similarly, at any constant value of the atmospheric viscosity and over a restricted range of Viscosity-Pressure Indices the corresponding values of $\log p_{iv,as}$ and log Z are linearly interrelated, again to a very good approximation.

Table XIII-2 lists asymptotic isoviscous pressures for every 0.1 unit of the atmospheric viscosity function H_0, from $H_0 = -0.2$ up to $H_0 = 0.9$ (corresponding to atmospheric viscosities, η_0, ranging from about 0.27 to $5.5 \cdot 10^6$ cP). As regards the asymptotic isoviscous pressures obtained by linearly interpolating according to H_0, it can be stated that at any constant Z-value from about 1.50 down to 0.50 these will be accurate within about 0.5%. At Z-values from 0.50 down to about 0.20 the estimates will be accurate within about 1%. At still smaller Z-values the accuracy inherent in the estimated values of $p_{iv,as}$ will remain tolerable, that is at least as good as that inherent in the experimentally derived Z-values themselves; otherwise, at such small Z-values the accuracy of the latter estimates can be considerably improved by interpolating according to a smooth relationship between $\log p_{iv,as}$ and H_0 rather than the assumed linear one.

Table XIII-2 contains Viscosity-Pressure Indices for every 0.01 unit over the range from 0.50 to 1.10, this range covering the great majority of lubricating oils encountered. Linear interpolations according to log Z between the listed Z-values (differing by 0.05 units) from 1.10 to 1.50 will yield asymptotic isoviscous pressures accurate within about 0.2%. At Z-values (also differing by 0.05 units) from 0.50 down to 0.30 the estimates will be accurate within about 1%. At still smaller Z-values (likewise differing by 0.05 units) the accuracy inherent in the estimated values of $p_{iv,as}$ will remain good in comparison with that inherent in the experimentally derived Z-values; however, particularly with highly fluid oils the accuracy of the latter estimates can be considerably improved by interpolating according to a smooth relationship between $\log p_{iv,as}$ and log Z rather than the assumed linear one.

The existence of the aforementioned linear interrelationships between $\log p_{iv,as}$ and H_0 (at constant Z) and between $\log p_{iv,as}$ and log Z (at constant η_0) may be elucidated as follows. In Section VII.4 the initial viscosity-pressure coefficient, α_i, has been introduced and defined by

TABLE XIII-2

Asymptotic Isoviscous Pressures, $p_{iv,as}$, for Distinct Values of the Atmospheric Viscosity Function H_0 and the Viscosity-Pressure Index, Z

Viscosity-Pressure Index		Values of log $p_{iv,as}$; $p_{iv,as}$ in kgf/cm^2											
		Atmospheric Viscosity Function H_0											
Z	log Z	-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.05	0.6990-2	19.074	17.237	15.443	13.702	12.028	10.438	8.955	7.605	6.423	5.448	4.707	4.182
0.10	0.0000-1	8.870	8.033	7.239	6.497	5.822	5.225	4.719	4.305	3.972	3.706	3.487	3.300
0.15	0.1761-1	6.271	5.763	5.295	4.875	4.507	4.191	3.920	3.686	3.488	3.313	3.157	3.013
0.20	0.3010-1	5.192	4.845	4.530	4.248	3.997	3.775	3.579	3.403	3.246	3.100	2.964	2.838
0.25	0.3979-1	4.637	4.374	4.135	3.918	3.721	3.542	3.379	3.229	3.089	2.959	2.835	2.712
0.30	0.4771-1	4.300	4.087	3.888	3.711	3.541	3.388	3.242	3.105	2.978	2.854	2.734	2.621
0.35	0.5441-1	4.068	3.887	3.717	3.559	3.407	3.263	3.132	3.004	**2.884**	2.767	2.650	2.541
0.40	0.6021-1	3.901	3.739	3.585	3.440	3.301	3.169	3.044	2.923	06	**2.692**	**2.580**	**2.470**
0.45	0.6532-1	3.770	3.623	3.481	3.344	3.218	**3.091**	**2.975**	2.856	2.743	32	22	14
0.50	0.6990-1	**3.668**	**3.530**	**3.397**	**3.269**	**3.146**	26	10	**2.795**	**2.685**	**2.576**	**2.470**	**2.364**
0.51	0.7076-1	49	13	80	54	31	14	00	85	75	66	60	54
0.52	0.7160-1	31	**3.496**	65	40	19	02	**2.888**	75	65	57	50	45
0.53	0.7243-1	14	80	50	25	05	**2.991**	77	65	55	48	40	35
0.54	0.7324-1	**3.597**	65	36	14	**3.094**	80	66	55	45	39	31	27
0.55	0.7404-1	80	50	23	00	81	69	56	46	36	29	21	18
0.56	0.7482-1	65	37	10	**3.189**	70	59	46	37	27	20	12	10
0.57	0.7559-1	49	22	**3.297**	76	59	48	36	27	17	11	03	01
0.58	0.7634-1	36	09	85	65	48	38	27	18	08	02	**2.395**	**2.293**
0.59	0.7709-1	20	**3.395**	73	54	37	28	17	09	00	**2.494**	87	85
		-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

CONTINUATION OF TABLE XIII-2

Viscosity-Pressure Index		Values of log $p_{iv,as}$; $p_{iv,as}$ in kgf/cm^2											
		Atmospheric Viscosity Function H_0											
Z	log Z	-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.60	0.7782-1	**3.506**	**3.383**	**3.261**	**3.143**	**3.026**	**2.918**	**2.808**	**2.700**	**2.591**	**2.485**	**2.379**	**2.277**
0.61	0.7853-1	**3.492**	71	50	32	17	08	**2.799**	**2.692**	83	77	71	69
0.62	0.7924-1	79	59	39	22	08	**2.899**	90	83	75	69	63	61
0.63	0.7993-1	66	47	28	12	**2.998**	90	81	74	67	61	56	54
0.64	0.8062-1	54	35	17	02	89	80	72	66	59	53	48	46
0.65	0.8129-1	42	24	06	**3.092**	80	72	64	58	52	46	41	39
0.66	0.8195-1	31	13	**3.196**	83	71	63	55	50	44	38	34	32
0.67	0.8261-1	19	02	86	74	62	54	47	42	36	30	26	24
0.68	0.8325-1	07	**3.290**	75	64	54	46	39	35	29	23	19	17
0.69	0.8388-1	**3.396**	80	66	55	46	38	32	28	22	16	12	10
0.70	0.8451-1	85	70	57	46	37	30	24	20	15	09	05	03
0.71	0.8513-1	74	60	48	38	29	22	16	12	08	02	**2.298**	**2.196**
0.72	0.8573-1	64	50	39	29	21	14	09	04	00	**2.394**	92	90
0.73	0.8633-1	54	41	30	21	13	06	02	**2.597**	**2.493**	87	85	84
0.74	0.8692-1	43	32	21	13	05	**2.798**	**2.694**	90	86	80	78	77
0.75	0.8751-1	33	23	12	05	**2.897**	90	86	83	80	74	72	70
0.76	0.8808-1	23	14	03	**2.997**	89	83	79	76	73	67	65	64
0.77	0.8865-1	14	05	**3.095**	90	82	76	72	70	66	60	59	58
		-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

CONTINUATION OF TABLE XIII-2

Viscosity-Pressure Index		Values of log $p_{iv,as}$; $p_{iv,as}$ in kgf/cm^2											
		Atmospheric Viscosity Function H_0											
Z	log Z	-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.78	0.8921-1	**3.304**	**3.196**	**3.087**	**2.982**	**2.875**	**2.769**	**2.666**	**2.563**	**2.460**	**2.354**	**2.253**	**2.152**
0.79	0.8976-1	**3.295**	88	79	74	68	62	59	56	54	48	48	46
0.80	0.9031-1	86	79	71	67	61	55	52	50	47	42	42	41
0.81	0.9085-1	78	71	64	60	54	48	46	[illegible]	41	36	36	35
0.82	0.9138-1	69	63	56	52	47	42	40	37	35	30	30	29
0.83	0.9191-1	61	56	48	45	40	35	34	30	29	24	24	23
0.84	0.9243-1	53	48	41	38	33	28	27	24	23	19	19	17
0.85	0.9294-1	45	40	34	32	26	22	21	18	17	14	14	12
0.86	0.9345-1	37	32	27	25	20	16	15	13	11	08	08	06
0.87	0.9395-1	30	25	20	18	14	10	10	08	06	02	03	01
0.88	0.9445-1	22	18	14	12	07	05	04	02	00	**2.297**	**2.198**	**2.096**
0.89	0.9494-1	14	11	08	06	01	**2.699**	**2.598**	**2.496**	**2.395**	92	93	91
0.90	0.9542-1	07	04	01	00	**2.795**	93	93	91	90	87	88	86
0.91	0.9590-1	00	**3.097**	**2.994**	**2.894**	89	87	87	85	84	82	83	81
0.92	0.9638-1	**3.192**	90	88	87	83	81	81	79	79	77	78	76
0.93	0.9685-1	86	84	82	80	77	76	76	74	74	72	72	72
0.94	0.9731-1	78	77	75	74	71	70	70	68	68	67	67	67
0.95	0.9777-1	71	70	68	68	66	65	65	63	63	62	62	62
0.96	0.9823-1	64	63	62	62	60	60	60	58	58	57	57	57
		-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

CONTINUATION OF TABLE XIII-2

Viscosity-Pressure Index		Values of log $p_{iv,as}$; $p_{iv,as}$ in kgf/cm^2											
		Atmospheric Viscosity Function H_0											
Z	log Z	-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.97	0.9868-1	**3.158**	**3.057**	**2.956**	**2.856**	**2.755**	**2.654**	**2.554**	**2.453**	**2.353**	**2.252**	**2.152**	**2.052**
0.98	0.9912-1	51	51	51	50	50	49	49	48	48	48	48	48
0.99	0.9956-1	45	45	45	44	44	44	44	44	44	44	44	44
1.00	0.0000	39	39	39	39	39	39	39	39	39	39	39	39
1.01	0.0043	32	33	34	34	34	34	34	34	34	34	34	35
1.02	0.0086	26	27	28	28	29	29	29	29	29	30	30	31
1.03	0.0128	20	21	22	22	24	24	24	24	24	26	26	26
1.04	0.0170	14	15	16	17	18	19	19	19	19	21	21	22
1.05	0.0212	08	10	10	12	13	14	14	14	14	16	17	18
1.06	0.0253	02	04	05	07	08	09	09	10	10	12	13	14
1.07	0.0294	**3.096**	**2.998**	00	02	04	04	04	06	06	09	09	10
1.08	0.0334	91	93	**2.894**	**2.797**	**2.699**	00	00	01	01	04	05	06
1.09	0.0374	86	88	89	92	94	**2.596**	**2.496**	**2.396**	**2.297**	00	01	02
1.10	0.0414	80	82	84	87	89	91	91	92	93	**2.196**	**2.097**	**1.998**
1.15	0.0607	53	55	59	63	67	68	70	70	72	75	78	78
1.20	0.0792	28	32	36	40	44	46	48	50	52	55	59	60
1.25	0.0969	03	09	14	18	23	25	29	30	33	36	41	42
1.30	0.1139	**2.979**	**2.886**	**2.792**	**2.698**	03	06	10	12	15	19	24	26
		-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

CONTINUATION OF TABLE XIII-2

Viscosity-Pressure Index		Values of log $p_{iv,as}$; $p_{iv,as}$ in kgf/cm^2											
		Atmospheric Viscosity Function H_0											
Z	log Z	-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.35	0.1303	2.958	2.866	2.772	2.679	2.585	2.488	2.392	2.294	2.198	2.102	2.008	1.911
1.40	0.1461	38	46	52	60	67	70	75	77	82	2.086	1.992	1.896
1.45	0.1614	19	17	34	42	50	53	59	61	66	70	77	82
1.50	0.1761	01	09	16	25	33	36	43	46	51	55	62	68
		-0.2	-0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

Equation (VII-5). It has appeared that this quantity α_i may be claimed representative of the (isothermal) viscosity-pressure dependence of a given oil up to pressures of at least some 1,000 kgf/cm^2 (14,000 psi). As compared with the viscosity-pressure coefficient α - which normally varies appreciably with pressure - the initial viscosity-pressure coefficient may be considered to represent some averaged value of the actual α-values encountered for a particular oil throughout the indicated pressure range. Thus, in accordance with the preceding § XIII.4.3 the asymptotic isoviscous pressure may, at least to a fair approximation, be taken equal to the reciprocal of the initial viscosity-pressure coefficient, α_i. From Definition (VII-5) it then follows that:

$$\log p_{iv,as} = -\log \alpha_i = -\log Z - H_0 + 2.9388 \; . \qquad \text{(XIII-10)}$$

Indeed, the latter approximation readily explains the existence of the nearly linear interrelationships under discussion. It may be added that in accordance with Equations (XIII-8a) and (XIII-8b) the resulting value of $p_{iv,as}$ would be exactly equal to $1/\alpha_i$ for oils with Viscosity-Pressure Indices amounting to 1.00. As a consequence, these nearly linear interrelationships have proved to hold particularly good for Viscosity-Pressure Indices in the vicinity of the latter value.

XIII.4.4. *Comparison of Asymptotic Isoviscous Pressures Estimated on the Basis of Different Viscosity-Pressure Equations*

As shown in § XIII.4.2 (see in particular Fig. XIII-2 and Table XIII-1), the trend of the relationship between the actual pressure, p, and the isoviscous pressure, p_{iv}, of a given oil and at a given temperature is such that p_{iv} tends to reach its asymptotic value, $p_{iv,as}$, within a few per cent already at actual pressures of the order of 3 $p_{iv,as}$ or 4 $p_{iv,as}$.

This leads to the important conclusion - already drawn by Blok[6] *- that in applying Weibull's Transform (XIII-2) to lubricating oils it normally suffices to confine oneself to experimental data determined in the pressure range up to something like 1,500 or 2,000 kgf/cm^2 (21,000 to 28,000 psi).*

The depicted trend of the p - p_{iv} relationship of oils also implies that the accuracy inherent in their asymptotic isoviscous pressures, $p_{iv,as}$, estimated on the basis of some analytical expression for their isothermal viscosity-pressure dependence, is decisively determined by the adequacy of the particular viscosity-pressure expression in the *lower* pressure range, that is up to pressures of about 3 $p_{iv,as}$. This means that for most lubricating oils - notably the rather viscous *mineral* oils currently employed in elasto-hydrodynamic lubrication (see Fig. XIII-4) - the asymptotic isoviscous pressures can be assessed satisfactorily from any viscosity-pressure equation which is sufficiently accurate up to pressures of the order of 1,500 kgf/cm^2.

Thus, a comparison of asymptotic isoviscous pressures estimated from different viscosity-pressure equations shows that for most lubricating oils the discrepancies between the respective estimates are rather small as long as such equations apply reasonably throughout the latter pressure range. In fact, even the exponential viscosity-pressure Equation (IV-1a) usually yields fair values for the asymptotic isoviscous pressures of oils.

But the new viscosity-pressure Equation (IV-5a) has proved to permit particularly accurate estimates, which can be achieved very *conveniently at that, namely by means of Table XIII-2. Notably, the present method applies very well to all the various kinds of mineral oils encountered.*

Further, it should be recalled that the Viscosity-Pressure Index may be taken to remain practically constant in a fairly wide *temperature* range, say, from 20 to 120°C (68-248°F). Thus, as soon as only one viscosity-pressure isotherm of a given oil has been determined, its asymptotic isoviscous pressures can be estimated for that entire temperature range only from its atmospheric viscosity-temperature relationship. In addition, for *mineral* oils specifically the small temperature dependence of their Viscosity-Pressure Index can be conveniently accounted for by means of the correlations developed in Section VII. 3.

If oils with considerably higher asymptotic isoviscous pressures than the aforementioned ones are involved, say, $p_{iv,as}$ above 1,000 kgf/cm^2, the discrepancies between the estimates obtained from different viscosity-pressure expressions may become quite appreciable. In particular, the exponential viscosity-pressure Equation (IV-1a) is bound to yield rather rough estimates for such oils. But the newly developed viscosity-pressure Equation (IV-5a) will still permit acceptable estimates up to relatively high asymptotic isoviscous pressures. In fact, since the latter equation may generally be considered to hold satisfactory up to pressures of at least 3,000-5,000 kgf/cm^2 (43,000-71,000 psi), it may safely be applied for calculating asymptotic isoviscous pressures up to no less than at least some 1,500 kgf/cm^2 (21,000 psi). In this respect it should be noted that for oils with still higher asymptotic isoviscous pressures the effect of the viscosity-pressure variation on their hydrodynamic lubrication performance will seldom become considerable (compare § XIII. 4. 2).

Finally, it may be emphasized that for reliably estimating $p_{iv,as}$ of a given oil sufficient *experimental* viscosity-pressure data should be available over the pressure range up to at least something like 3 $p_{iv,as}$. This means that in applying Table XIII-2 the pertinent Viscosity-Pressure Indices should represent really representative values for this entire pressure range.

XIII. 5. CORRELATION BETWEEN THE TEMPERATURE AND PRESSURE EFFECTS ON THE VISCOSITY OF MINERAL OILS

XIII. 5. 1. *Introduction*

Mineral oils still constitute the great bulk of oils encountered in current lubrication practice. As elucidated before, both the temperature and pressure effects on the viscosity of mineral oils may vary widely from one oil to another. In contrast to their atmospheric viscosity-temperature dependence, however, their viscosity-pressure dependence is in general not determined experimentally by the oil manufacturer.

Fortunately, as could be shown in Chapter X, the viscosity-pressure variation of mineral oils is correlated quantitatively with their viscosity-temperature variation at atmospheric pressure. This has led to the important conclusion that, once the atmospheric viscosity-temperature relationship of mineral oils has been specified, nothing remains to be sensibly specified with respect to the differentiation as to their viscosity-pressure relationship, and *vice versa*.

The convenient correlation developed in Chapter X has been cast into such a form that, in addition to the indispensable viscosity grade, only *one* independent parameter enters into this correlation, namely either the atmospheric Slope Index or the Viscosity-Pressure Index at some standard reference temperature. Further, the basic analytical framework has proved very feasible indeed for predicting the *complete* viscosity-temperature-*pressure* relationship of mineral oils exclusively from their measured (or specified) atmospheric viscosity-temperature relationship.

For lubrication research the latter correlation has the significant consequence that in problems where both the temperature and the pressure variation of the viscosity of mineral oils considerably affect their hydrodynamic lubrication performance it cannot unambiguously be concluded which parts are played by the temperature and pressure variation proper. In other words, from the combined effects measured on the film profile or on the friction the influence of one variation cannot be segregated experimentally from that of the other.

This also implies that correlations - established by, for instance, the technique of dimensional analysis (compare § XIII. 2. 3) - relating to such problems cannot possibly furnish any unambiguous information concerning the justifiability of certain assumptions concerning the *separate* effects of temperature and pressure variations in the oil film on the hydrodynamic lubrication performance of the mineral oils employed. The aforementioned kind of *"inconclusiveness"* with mineral oils was pointed out already by Blok[207, 206]. However, whilst Blok's statement had to be based on the validity of the rather rough correlations between the temperature and pressure dependence of the viscosity of mineral oils achieved at that time, the present conclusion is substantially stricter in that it emerges directly from the really *quantitative* correlation developed in Chapter X.

In order to avoid the indicated kind of inconclusiveness it is imperative to include test oils with viscosity-temperature-pressure characteristics essentially different from those represented by the present correlation for mineral oils (compare Fig. X-15).

Particularly in view of their bearing on lubrication research, it yet remains to elaborate some additional aspects inherent in the overall correlation between the atmospheric viscosity-temperature relationship and the viscosity-pressure relationship of mineral oils as discussed in Chapter X. This will be done in the remaining parts of the present section.

XIII. 5. 2. *A Simplified Viscosity-Temperature-Pressure Expression for Mineral Oils*

Over fairly wide ranges of temperature and pressure, generally extending from about 20 to 120°C (68-248°F) and up to pressures of about 2,000 kgf/cm^2 (28,000 psi), the following simplified viscosity-temperature-pressure equation has been shown to apply reasonably well to any given liquid (see § V.2.3):

$$H - H_{0,r} = S_0 \, (\Theta - \Theta_r) + Z_r \, \Pi \, . \qquad \text{(V-9a)}$$

For *mineral oils* specifically, however, the latter equation can be further simplified by considering that the semi-quantitative correlation:

$$Z_{40^\circ C} = 0.55 \; S_0 \qquad \text{(X-2)}$$

will hold almost equally good at any temperature throughout the aforementioned range as at the particular standard reference temperature of 40°C. Consequently, the following reasonable approximation to the viscosity-temperature-pressure relationship of mineral oils can readily be obtained:

$$H - H_{0,r} = S_0 \left[(\Theta - \Theta_r) + 0.55 \; \Pi \right] . \qquad \text{(XIII-11)}$$

In addition to the viscosity grade $H_{0,r}$, this simplified Expression (XIII-11) contains only *one* parameter, namely the atmospheric Slope Index, S_0, of the mineral oil concerned.

Further, for *qualitative* purposes the atmospheric Slope Index of mineral oils may be estimated from some overall correlation with their viscosity grade alone. For a standard reference temperature of 40°C, for instance, the following correlation*) can be derived from Fig. VIII-2:

$$S_0 = 0.9 \; (H_{0,40^\circ C} + 1.00) \; . \qquad \text{(XIII-12a)}$$

For an arbitrary standard reference temperature Θ_r this correlation takes the form:

$$S_0 = \frac{H_{0,r} + 1.00}{\Theta_r + 1.2238} \, . \qquad \text{(XIII-12b)}$$

Combination of the latter correlation with Equation (XIII-11) leads to the expression:

$$H - H_{0,r} = \left(\frac{H_{0,r} + 1.00}{\Theta_r + 1.2238} \right) \left[(\Theta - \Theta_r) + 0.55 \; \Pi \right] , \qquad \text{(XIII-13)}$$

which may be useful for making rapid order-of-magnitude estimates of the effects of both temperature and pressure on the viscosity of a particular mineral oil.

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*) As demonstrated by Fig. VIII-14, similar linear correlations between the atmospheric Slope Index, S_0, and the viscosity grade $H_{0,r}$ have proved to hold good for any particular homologous series of liquids investigated so far.

XIII. 5. 3. *Compensating Temperature and Pressure Variations With Respect to the Viscosity of Mineral Oils*

The viscosity rise brought about in any given liquid by some pressure increase can be fully compensated by a simultaneous temperature increase. *Now, the semi-quantitative Equation (XIII-11) implies that for mineral oils specifically the compensating variations of temperature and pressure would be approximately the same, irrespective of the particular oil considered.* Indeed, by putting $H = H_{0,r}$ in the latter equation it follows that the temperatures and pressures that have to be simultaneously applied in order to maintain the viscosity, η, of mineral oils at their atmospheric level $\eta_{0,40°C}$ should be given by the *isoviscid* equation:

$$-\Theta = 0.55\,\Pi - \Theta_r \,, \qquad \text{(XIII-14a)}$$

TABLE XIII-3

Compensating Temperature and Pressure Variations With Respect to the Viscosity of Mineral Oils According to Equation (XIII-14b)

Gauge Pressure, kgf/cm^2	Temperature (t_r = 40°C)	
	deg C	deg F
0	40	104
200	49.5	121
400	58.5	137
600	67	153
800	75.5	168
1,000	84	183
1,200	92	197
1,400	99	211
1,600	107	224
1,800	114	237
2,000	121	250
2.500	138	280
3,000	155	310
3,500	170	340
4,000	185	365
4,500	200	390
5,000	215	415
6,000	240	465
7,000	265	510
8,000	290	550
9,000	310	590
10,000	335	630

or, rewritten explicitly in terms of temperature, t (in deg C), and pressure, p (in kgf/cm^2):

$$t = (t_r + 135)\left(1 + \frac{p}{2,000}\right)^{0.55} - 135 \;. \qquad \text{(XIII-14b)}$$

For a very extensive range of pressures the compensating temperatures relating to an initial temperature of 40°C have been calculated by means of Equation (XIII-14b). The results of these calculations are compiled in Table XIII-3.

From Fig.X-15 it can readily be seen that mineral oils occupy an intermediate position with respect to the relative magnitudes of their compensating temperature and pressure variations.

On the other hand, the depicted polymethylsiloxanes display an exceptionally high ratio Z_{40^oC}/S_0, which means that the temperature variation required for compensating a given pressure variation is also unusually high. It can be shown that for these liquids the compensating temperatures and pressures are approximately linearly interrelated, namely by the expression:

$$t = (t_r + 135)\,\frac{p}{2,000} + t_r \;. \qquad \text{(XIII-15)}$$

Thus, in order to compensate the effect of a pressure of 1,000 kgf/cm^2 (14,220 psi) on the viscosity of polymethylsiloxanes their temperature should be increased, at an initial temperature of 40°C (104°F), to about 125°C (257°F), whilst for mineral oils a temperature increase to only about 84°C (183°F) would suffice. As a consequence, in hydrodynamic lubrication problems where both temperature and pressure vary considerably throughout the created polymethylsiloxane film the pressure effect on the viscosity may well offset - or more than offset - the temperature effect. In any case this will occur more easily with such polymethylsiloxanes than with mineral oils.

XIII. 5. 4. *An Approximative Analytical Expression for the Graphical Correlation Developed Between the Atmospheric Viscosity-Temperature Relationship and the Viscosity-Pressure Relationship of Mineral Oils*

For certain correlational purposes it may be useful to have available an approximative *analytical* expression for the graphical correlation of Fig. X-1 between the atmospheric viscosity-temperature relationship and the viscosity-pressure relationship of mineral oils.

After various trials the following analytical formulation has been achieved:

$$\frac{Z_{40^oC}}{S_0^{\;1.5}} = -0.864\ H_{0,40^oC} + 0.885 \quad . \qquad \text{(XIII-16)}$$

In Fig. XIII-3 Correlation (XIII-16) is represented by the solid straight line; the two adjacent dashed lines comprise the ranges where the Viscosity-Pressure Indices Z_{40^oC} of mineral oils would still be predicted within 10%. This figure also depicts the experimental data on all the various kinds of no less than 113 mineral-oil fractions - including some saturated samples - designated in Table X-2.

Fig. XIII-3 clearly demonstrates that the simple analytical Correlation (XIII-16) does constitute a good approximation to the basic correlation depicted in Fig. X-1. In fact, application of Correlation (XIII-16) to all the aforementioned mineral oils has yielded *absolute* average and standard deviations in the Viscosity-Pressure Index of no more than 0.036 and 0.046 units, respectively. These correspond to *relative* average and standard deviations in both the predicted Viscosity-Pressure Indices Z_{40^oC} and the initial viscosity-pressure coefficients $\alpha_{i,40^\circ C}$ of only 4.6 and 6.1%, respectively.

In conclusion, Correlation (XIII-16) may be deemed satisfactory for most practical applications. Its practical usefulness may further be illustrated by referring to the last part of § IX.3.2, notably to Tables IX-4 and IX-5.

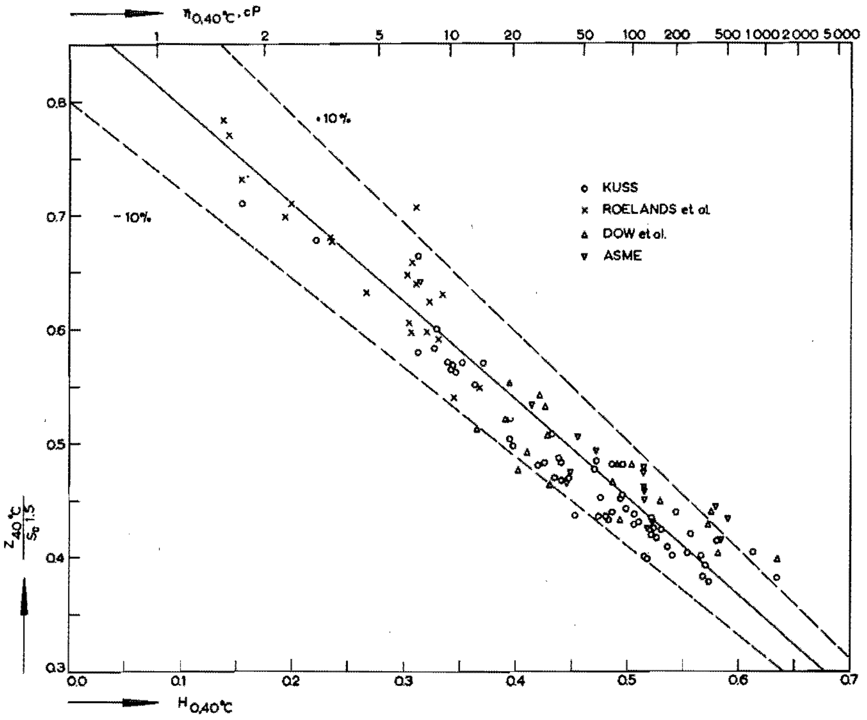

FIG. XIII-3.

The Atmospheric Viscosity-Temperature Relationship and the Viscosity-Pressure Relationship of Mineral Oils According to Correlation (XIII-16).

XIII.5.5. *Predicting the Asymptotic Isoviscous Pressures of Mineral Oils*

One of the most attractive applications of the correlation, depicted in Fig.X-1, between the atmospheric viscosity-temperature relationship and the viscosity-pressure relationship of mineral oils consists in the prediction of their *asymptotic isoviscous pressures*, $p_{iv,as}$.

As elucidated in § XIII.4.3, the asymptotic isoviscous pressure of any given liquid can be calculated accurately from its atmospheric viscosity, η_0, and its Viscosity-Pressure Index, Z, at the temperature concerned. For *mineral oils* characterized by a common atmospheric Slope Index, S_0, the correlation of Fig.X-1 defines the interrelationship, at the adopted standard reference temperature of

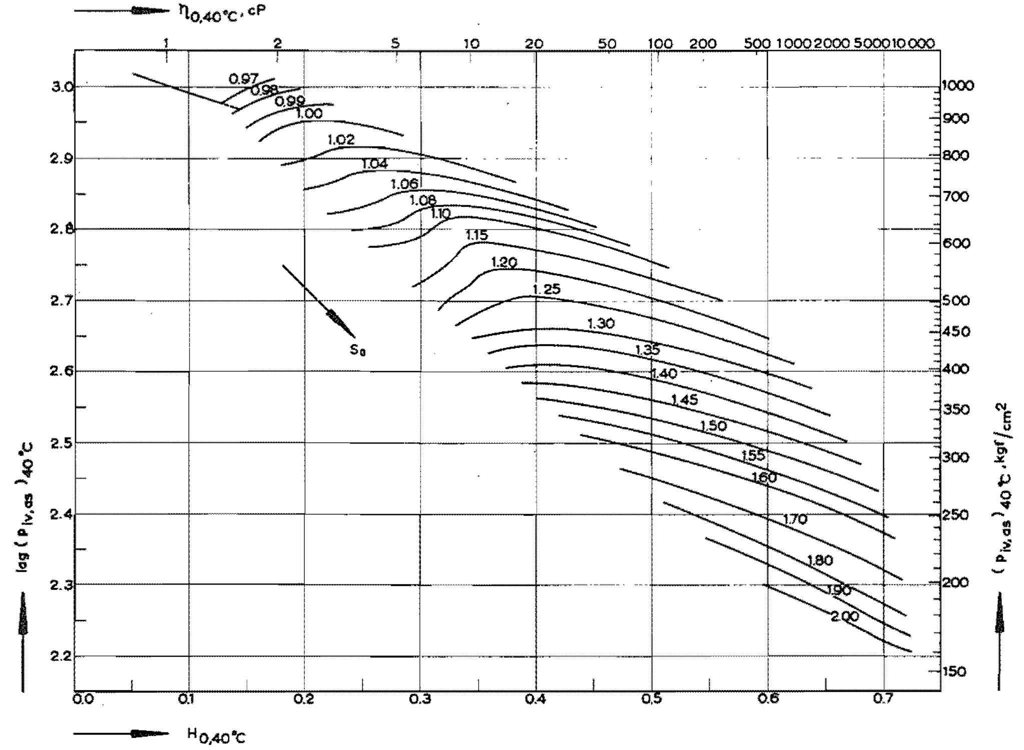

FIG. XIII-4.

Asymptotic Isoviscous Pressures of Mineral Oils as a Function of Their Atmospheric Viscosity-Temperature Relationship According to the Correlation of Fig. X-1.

40°C, between their atmospheric viscosity, η_0, and their Viscosity-Pressure Index, Z.

Consequently, the latter correlation does permit estimating their asymptotic isoviscous pressures $(p_{iv,as})_{40^\circ C}$ *simply from their viscosity grade* $\eta_{0,40^\circ C}$ *and their atmospheric Slope Index,* S_0.

For convenience the basic correlation of Fig. X-1 has been transformed into the correlation of Fig. XIII-4 which depicts the asymptotic isoviscous pressures $(p_{iv,as})_{40^\circ C}$ of mineral oils *directly* as a function of their viscosity grade $\eta_{0,40^\circ C}$, their atmospheric Slope Index being used as a parameter. It can readily be shown that the relative accuracy of the asymptotic isoviscous pressures $(p_{iv,as})_{40^\circ C}$ estimated from the correlation of Fig. XIII-4 is practically identical to that of the corresponding Viscosity-Pressure Indices $Z_{40^\circ C}$ estimated from the basic correlation of Fig. X-1. This means that the relative average and standard deviations inherent in the latter asymptotic isoviscous pressures amount to no more than 3.8 and 4.6%, respectively (see § X.2.1). In general, this accuracy will prove very satisfactory for the practical purposes aimed at.

NOMENCLATURE

Symbols

a_0, a_0', a_0''	empirical constants; see Equations (III-2), (III-3) and (III-4), respectively
A_g, A_h	empirical constants; see Equations (XI-26) and (XI-24b), respectively
A_0, A_0', A_0''	empirical constants; see Equations (III-2), (III-3) and (III-4), respectively
B_g, B_h	empirical constants; see Equations (XI-26) and (XI-24b), respectively
B_0, B_0', B_0''	empirical constants; see Equations (III-2), (III-3) and (III-4), respectively
c, c', c''	empirical constants; see Equations (IV-2), (IV-3) and (IV-4), respectively
c_1, c_2	empirical constants; see Equation (XI-22)
C	empirical constant; Definition (V-2); see also Equations (V-1a)/(V-1c)
C', C''	empirical constants; see Equations (V-15) and (V-16), respectively
C_c	empirical constant; see Equation (XII-7)
C_g	empirical constant; see Equation (XII-8)
C_v	empirical constant; see Equation (XI-18)
C_A, C_N, C_P	percentage of carbon atoms in aromatic-ring, naphthenic-ring and paraffinic-chain structures, respectively, per average molecule
C_R	$= (C_A + C_N)$, total percentage of carbon atoms in ring structure per average molecule
C_ψ	empirical constant; see Equation (XI-13b)
C_0	empirical constant; see Equation (III-1a)
d	density, g/cm^3
d_b, d_b'	liquid and vapour density, respectively, at normal boiling point
d_i	limiting density in homologous series
d_1, d_2	density of first and second component, respectively, in binary mixture
Δd	$= (d_i - d)$
D	empirical constant; Definition (V-3); see also Equations (V-1a)/(V-1c)
D', D''	empirical constants; see Equations (V-15) and (V-16), respectively
D_0, D_0'	empirical constants; see Equations (III-1a) and (III-1b), respectively
e	base number of natural logarithm ($e=2.718$)
E_{vis}	(isobaric) activation energy for viscous flow, kcal/gmole; Definition (X-11); see also Equation (III-1b)
E_{vis}^h	$= (E_{vis} - E_{vis}^j)$; Definition (X-10)
E_{vis}^j	*isochoric* activation energy for viscous flow; Definition (X-12)
f	$= (F/M)$, *specific* additive function; Definition (XI-3)
f'	$= fd$; Definition (XI-4); specific volume-additive function in Equation (XI-5)

f_j	function f of component j in mixture; see Equation (XI-3)
f'_j	function f' of component j in mixture; see Equation (XI-5)
F	*molar* additive function; Definition (XI-1)
F_j	function F of component j in mixture; see Equation (XI-2)
g	given physical constant; see Equation (XI-26)
g_l	limiting value of g in homologous series; see Equation (XI-26)
G, G^*	empirical constants; see Equations (III-10) and (III-10a), respectively
G_0, G'_0, G''_0	empirical constants; see Equations (III-6a)/(III-6h)
h	$= \psi d = (\log \eta + 1.200)^{\frac{1}{8}}$; see Equations (XI-9a) and (XI-9b)
h_l	limiting value of h in homologous series
h_m	function h of mixture
h_1, h_2	functions h of first and second component, respectively, in binary mixture
Δh	$= (h_l - h)$
I	Souders's viscosity-constitutional constant; Definition (XI-6)
k	empirical constant; see Equation (III-16)
k	number of methylene groups per molecule in Scheme (XI-10)
k_1, k_2, k_3	empirical constants; see Equation (XI-23)
K, K', K''	empirical constants; see Equations (IV-2), (IV-3) and (IV-4), respectively
K_1, K_2	empirical constants; see Equations (XIII-1a) and (XIII-1b), respectively
m	empirical constant; see Equation (III-5)
m_m	parameter m of mixture
m_0	parameter m at atmospheric pressure
m_1, m_2	parameters m of first and second component, respectively, in binary mixture
M	(average) molecular weight
M_1, M_2	molecular weights of first and second component, respectively, in binary mixture
n	refractive index (for sodium-D line)
n	shape parameter in Weibull's cumulative distribution Function (III-18a); see Appendix III-1
n_l	limiting refractive index in homologous series
n_j	number of atoms, groups or bonds per molecule in molar additive Function (XI-1)
Δn	$= (n_l - n)$
N_0	empirical constant; see Equation (III-5)
p	*gauge* pressure, kgf/cm^2 ($1 kgf/cm^2 = 14.22 psi = 0.9678 atm$)
p', p''	*gauge* pressure in psi and atm, respectively
$p(x)$	probability-density function; see Appendix III-1
p_i	*internal* pressure
p_{iv}	fictitiously *isoviscous* film pressure; Definition (XIII-2)
$p_{iv,as}$	asymptotic value of p_{iv}
p_p	pole pressure
p_0	fictitious reference pressure; see Equation (IV-8)
p_1, p_2	arbitrary reference pressures
P	integration variable; see Equation (XIII-2)
$P(x)$	probability, or statistical fraction; see Appendix III-1

q	empirical constant; see Equation (XII-6)
q_1, q_2	empirical constants; see Equations (VI-5a) and (VII-5a), respectively
Q	fractional concentration of *second* component in binary mixture
r	empirical constant; see Equation (III-16)
r_i	$= (n - \frac{1}{2}d)$, refractivity intercept; Definition (XI-35)
R	molar gas constant
R	$= (R_A + R_N)$, total number of rings per average molecule
R_A, R_N	number of aromatic and naphthenic rings, respectively, per average molecule
s_1, s_2, s_3	empirical constants; see Equation (XIII-1a)
S	Slope Index; see Equation (III-10)
S_m	Slope Index of mixture
S_0	Slope Index at atmospheric pressure; see Equations (III-6a)/(III-6h)
S_0^*	"corrected" atmospheric Slope Index; Definition (X-1)
$(S_0)_{max}$	maximum permissible atmospheric Slope Index; see Section XIII. 3, part A
S_1, S_2	Slope Indices of first and second component, respectively, in binary mixture; by definition, $S_1 \geqslant S_2$.
S_{12}	"interaction Slope Index" in binary mixture; see Equation (XII-32)
ΔS	$= (S_1 - S_2)$, where $S_1 \geqslant S_2$
t	temperature, deg C
t_a	temperature coordinate of atmospheric isobar pole; see § VIII. 2. 3, part A
t_F	temperature, deg F
t_H, t_L	upper and lower temperature limit, respectively, of minimum-viscosity range; see § XII. 8. 3, part B
t_{iv}	temperature where components of binary mixture are isoviscous
$t_{iv,tr}$	"transition" value of t_{iv}; Definition (XII-62)
t_{max}, t_{min}	maximum and minimum values of t, respectively
t_P	pole temperature
t_r	standard reference temperature
T	absolute temperature, deg K
T_0	fictitious reference temperature; see Equation (III-16)
u	integration variable; Definition (XIII-9)
v	*specific* volume, cm^3/g
v_f	specific *free* volume; see § III. 3. 2
v_f^*	minimum required specific free volume; see § III. 3. 2
v_i	limiting value of v in homologous series; see Equation (XI-18)
v_{oc}	$= (v - v_f)$, specific *"occupied"* volume; Definition (X-17)
V	*molar* volume, $cm^3/gmole$
V_{vis}	Eyring's viscosity-pressure criterion, $cm^3/gmole$; see Equation (IV-1d)
w	empirical constant; see Equation (IV-8)
w	empirical constant; see Equation (XII-9)
W	$= \log \log (\nu + 0.6)$; Definition (XII-10)
W_m	function W of mixture
W_1, W_2	functions W of first and second component, respectively, in binary mixture

x	*weight* fraction of *second* component in binary mixture
x	random variable; see Appendix III-1
$\bar{x}$	average value of random variable x
x_j	weight fraction of component j in mixture; see Equation (XI-3)
x_l	"corrected" weight fraction; Definition (XII-6)
X	*molar* fraction of *second* component in binary mixture
X_j	molar fraction of component j in given mixture; see Equation (XI-2)
y	*volume* fraction of *second* component in binary mixture
y'	"corrected" volume fraction; Definition (XII-35)
y_a	"corrected" volume fraction; Definition (XII-11)
y_g	"corrected" volume fraction; Definition (XII-31)
y_j	volume fraction of component j in mixture; see Equation (XI-5)
y_{min}	volume fraction where a minimum occurs in viscosity-concentration isotherm; see Equation (XII-44)
y_S	"corrected" volume fraction for binary mixture of iso-S oils; Definition (XII-40)
y_W	"corrected" volume fraction; Definition (XII-12)
z	"reduced" variable; Definition (III-19)
Z	Viscosity-Pressure Index; see Equations (IV-5a)/(IV-5e)
Z_{Bl}	Viscosity-Pressure Index of polymer-blended mineral oil
Z_{Bl}^{*}	hypothetical value of Z_{Bl}; see Equations (X-9a) and (X-9b)
Z_m	Viscosity-Pressure Index of mixture
Z_{Or}	Viscosity-Pressure Index of mineral base oil
Z_r	Viscosity-Pressure Index at standard reference temperature
Z_1, Z_2	Viscosity-Pressure Indices of first and second component, respectively, in binary mixture

Greek Symbols

α	(isothermal) viscosity-pressure coefficient; Definition (VII-2); see also Equation (IV-1a)
α'	$= 0.4343\ \alpha$; see Equations (IV-1b) and (IV-1c)
α_i	*initial* viscosity-pressure coefficient; Definition (VII-5)
α_0	atmospheric viscosity-pressure coefficient; Definition (VII-3)
$\alpha_{0,r}$	atmospheric viscosity-pressure coefficient at standard reference temperature
β	(isobaric) viscosity-temperature coefficient; Definition (VI-3)
β_{Par}	viscosity-temperature coefficient of n-paraffins
β_V	*isochoric* viscosity-temperature coefficient; Definition (X-15)
β_0	atmospheric viscosity-temperature coefficient
$\beta_{0,r}$	atmospheric viscosity-temperature coefficient at standard reference temperature
γ	location parameter in Weibull's cumulative distribution Function (III-18a); see Appendix III-1
Γ	gamma function
ϵ	isobaric thermal expansion coefficient; Definition (X-25)

η	(dynamic) viscosity, cP
η_a	viscosity coordinate of atmospheric isobar pole; see § VIII. 2. 3, part A
η_b	viscosity at normal boiling point
η_c	fictitious reference viscosity (η_c = 0.0500 cP); see Equation (XII-7)
η_e	fictitious reference viscosity; see Equation (III-15)
η_l	limiting viscosity in homologous series
η_K	"transitional" viscosity; see § VIII. 2. 3, part A
η_m	viscosity of mixture
η_N	viscosity of *natural* mineral oil
η_p	viscosity at gauge pressure p
η_P	pole viscosity
η_r	viscosity at standard reference temperature and pressure
η_0	atmospheric viscosity
$\eta_{0,r}$	*viscosity grade:* viscosity at atmospheric pressure and standard reference temperature
η_1, η_2	viscosity of first and second component, respectively, in binary mixture
η_∞	fictitious reference viscosity at infinite temperature (η_∞ = =0.0631 cP); see Equations (III-6c) and (III-6d)
H	= log (log η + 1.200); Definition (III-6h); see also Equation (III-10)
H_a	function H of atmospheric isobar pole; Definition (VIII-5b)
H_e	function H of elevated-pressure isobar pole; Definition (IX-13)
H_m	function H of mixture
H_N	function H of *natural* mineral oil
H_P	pole value of H
H_r	function H at standard reference temperature and pressure
H_S	function H of *saturated* mineral oil
H_0	= log (log η_0 + 1.200); Definition (III-7); see also Equation (III-6h)
H_0'	= log (-log η_0 - 1.200); Definition (III-9); see also Equation (III-6h')
$(H_0)_{int}$	intermediate value of function H_0; see Section XIII. 3, part A
$(H_0)_{max}, (H_0)_{min}$	maximum and minimum permissible values of function H_0, respectively; see Section XIII. 3, part A
$H_{0,r}$	function H at atmospheric pressure and standard reference temperature
H_1, H_2	functions H of first and second component, respectively, in binary mixture
H_{12}	"interaction viscosity function" in binary mixture; see Equation (XII-36a)
ΔH	= $\lvert H_1 - H_2 \rvert$; Definition (XII-42)
Θ	= - log $[1 + (t/135)]$; Definition (III-7); see also Equation (III-6h)
Θ_a	function Θ of atmospheric isobar pole; Definition (VIII-6b)
Θ_e	function Θ of elevated-pressure isobar pole; Definition (IX-14)
Θ_{iv}	function Θ denoting temperature where components of binary mixture are isoviscous

$\Theta_{iv,tr}$	"transition" value of Θ_{iv}; Definition (XII-62)
Θ_p	pole value of Θ
Θ_r	function Θ corresponding to standard reference temperature
Θ_1	function Θ corresponding to arbitrary reference temperature
κ	isothermal compressibility coefficient; Definition (X-26)
μ	scale parameter in Weibull's cumulative distribution Function (III-18a); see Appendix III-1
ν	$= (\eta/d)$, ***kinematic*** viscosity, cS
ν_H, ν_L, ν_U	kinematic viscosities at 100°F of reference oils of the H- and L-series of the VI-system and of an arbitrary oil, respectively; see Equation (VI-1)
ν_s	fictitious reference kinematic viscosity ($\nu_s = 0.100$ cS); see Equation (XII-17a)
ν_0	kinematic viscosity at atmospheric pressure
Π	$= \log [1+(p/2,000)]$; Definition (IV-6)
Π_p	pole value of Π
Π_r	function Π corresponding to standard reference pressure
Π_1	function Π corresponding to arbitrary reference pressure
τ	shearing stress
φ	$= (1/\eta)$, fluidity
φ_j	atomic, group or bond increment; see Equation (XI-1)
ψ	*specific* viscochor; Definition (XI-9a)
ψ_i	limiting specific viscochor in homologous series; see Equation (XI-13b)
ψ_m	specific viscochor of mixture
ψ_1, ψ_2	specific viscochors of first and second component, respectively, in binary mixture
ψ_{12}	"interaction specific viscochor" in binary mixture; see Equation (XII-20)
$\Delta\psi$	$= \lvert\psi_1 - \psi_2\rvert$
Ψ	(molar) viscochor; Definition (XI-8)
ω	molecular *free* volume; see § III. 3. 2
$\bar{\omega}$	average value of ω; see § III. 3. 2
ω^*	minimum required value of ω; see § III. 3. 2

Abbreviations

API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
atm	atmosphere
c. g. s.	centimer-gram-second
cm	centimeter
cP	centipoise
cS	centistoke
deg C (°C)	degree Centigrade
deg F (°F)	degree Fahrenheit
deg K (°K)	degree Kelvin
DVI	Dynamic Viscosity Index; Definition (VI-2)
Exp.	Experimental
Fig.	Figure

GPM	Graphical Prediction Method; see Section XII. 6
g	gram
g. mass	gram-mass
gmole	gram-molecule
in	inch
kcal	kilogram-calorie
kgf	kilogram-force
ln	natural or Napierian logarithm, $\log_e$
log	common or Briggsian logarithm, $\log_{10}$
mS	millistoke
P	Poise
Pred.	Predicted
PSU	Pennsylvania State University
psi	pound per square inch
Ref.	Reference
Rh	Rheochor; Definition (XI-7)
RPM	Refined Prediction Method; see Section XII. 7
RQ	$= (\Delta d/\Delta n)$, Refractivity Quotient; Definition (XI-36)
S	Stoke
SAE	Society of Automotive Engineers
SPM	Simplified Prediction Method; see Section XII. 5
SUS	Saybolt Universal Second
sec	second
VDQ	$= (\Delta d/\Delta h)$, Viscosity-Density Quotient; Definition (XI-21)
VI	Viscosity Index; Definition (VI-1)
wt. %	per cent by weight
μP	micropoise
μR	microreyn

Main Subscripts

a	relating to atmospheric isobar pole
b	relating to normal boiling point
calc	calculated
exp	experimental
i	denoting limiting value in homologous series (unless stated otherwise)
iv	fictitiously isoviscous, or isoviscous
j	relating to atom, group or bond j in molecule, or to component j in mixture
m	relating to mixture
max	maximum
min	minimum
P	relating to viscosity-temperature-pressure pole
pred	predicted
r	relating to standard reference conditions of temperature and/or pressure
0	relating to atmospheric pressure ($p=0$)
1, 2	relating to first and second component in mixture, respectively (unless stated otherwise)
12	denoting interaction quantity in binary mixture
∞	infinite

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SUMMARY

An oil utilized for achieving *hydrodynamic lubrication* should be regarded and treated as a real *constructional material*. The consequent constructional value of such a material is governed essentially by its *viscosity* characteristics. In fact, the primary requirement for any lubricating oil consists in that it displays the desired viscosity under the usually varying conditions of temperature and/or pressure prevailing in the hydrodynamically created oil film.

Since many modern, hydrodynamically lubricated, machine elements operate over ranges of temperature and/or pressure so extensive that the resulting variations of the oil's viscosity may become very pronounced and, in turn, may seriously affect its lubrication *performance*, sufficient knowledge of the viscosity-temperature-pressure relationship of lubricating oils is of paramount importance, not only to the lubrication engineer and the oil technologist but also to the designer of lubricated machine elements.

Although very interesting results have already been obtained, it is only fair to state that our present knowledge of the viscosity-temperature-pressure relationship of lubricating oils still leaves much to be desired. In fact, it appears that the applicability of many previous results obtained in this field is quite limited.

The object of the present investigation consists in improving, at least to some extent, the indicated unsatisfactory situation, whilst trying to cast the results into a form that will prove convenient also in the theory and practice of hydrodynamic lubrication.

The basic *experimental data* employed in the present investigation are reviewed in Chapter II.

Chapters III through V aim at describing the effects of temperature and pressure on the viscosity of liquids, notably those currently employed as lubricating oils, by means of convenient, yet sufficiently accurate, analytical *equations*. Chapters III and IV are devoted, respectively, to the isobaric viscosity-temperature relationship and the isothermal viscosity-pressure relationship of a given liquid. By combining the resulting isobar and isotherm equations an expression for the complete viscosity-temperature-pressure relationship is derived in Chapter V.

The resulting equations require a *minimum* number of parameters for fully characterizing, in very wide ranges, the effects of temperature and/or pressure on the viscosity of a given liquid. They are shown to combine an almost unsurpassable simplicity with an almost universal applicability. Thus, a minimum amout of experimental information is required for making the desired calculations and estimates. Though designed primarily for mineral oils - not only natural, but also hydrogenated and polymer-blended ones - and various types of synthetic oils encountered in modern lubrication practice, these new equations have proved to apply equally to all the other divergent kinds of liquids investigated so far.

Chapter VI introduces a rational and very convenient method for *classifying*, according to their atmospheric viscosity-temperature relationship, all the various kinds of oils encountered in current lubrication practice. In fact, the proposed method constitutes a simple solution to the vexing "Viscosity-Index problem". In Chapter VII a similar method is presented for classifying lubricating oils according to their viscosity-pressure relationship. Both classification methods are based directly on the newly developed equations for the latter relationships.

Further, the present equations have proved excellently suitable as an analytical framework for *correlations* aiming at the prediction of the effects of temperature and pressure on the viscosity of liquids, either from their chemical constitution or from easily assessable physical constants. The relevant correlational attempts have been concentrated upon *mineral oils*, which, notwithstanding their great variety and complexity, are interrelated in being essentially built up from hydrocarbon compounds. After all, even though different types of synthetic oils have increasingly been introduced, mineral oils still constitute the great bulk of oils used in lubrication; and this situation may be expected to continue to exist for at least several decades.

Chapter VIII presents convenient correlations for predicting, to a good approximation, the complete atmospheric viscosity-temperature relationship of mineral oils, either from their chemical constitution - characterized by their carbon-type composition according to the "Waterman analysis" in the form of the so-called n-d-M method - or from physical constants that are easily assessable at atmospheric pressure. In addition to the indispensable viscosity grade of the oils - defined as the viscosity at atmospheric pressure and at some standard reference temperature - the resulting correlations only require either their total percentage of carbon atoms in ring structure or one of the following atmospheric physical constants: density, refractive index or molecular weight.

Chapter IX provides similar correlations for predicting, at any conventional reference temperature, the complete viscosity-pressure relationship of mineral oils. The correlations established employ, apart from the indispensable viscosity grade of the oils, either their total percentage of carbon atoms in ring structure or their atmospheric density and/or refractive index.

Finally, Chapter X discusses the direct correlation between the viscosity-pressure relationship of mineral oils and their atmospheric viscosity-temperature relationship. The significant conclusion has emerged that the complete family of viscosity-pressure isotherms of all the various kinds of mineral oils considered can indeed be predicted, to a good approximation, solely from their atmospheric viscosity-temperature isobars. The relevant correlation is unique in that it does not involve, in contradistinction to the aforementioned correlations, any additional physical or chemical data.

It should be added that the correlations developed for mineral oils become substantially simplified when adapted to any particular homologous group of synthetic lubricating oils or pure compounds because of the well-known regularities observed within each such group. This has been exemplified for various interesting homologous groups of synthetic lubricating oils.

Chapter XI touches upon certain basic problems in the field of oil viscosities in being devoted to the correlation of the above-defined *viscosity grade* of mineral oils and pure hydrocarbons both with their chemical constitution and with various easily assessable physical constants. Starting from a newly developed additive viscosity-density function, various significant correlations could be achieved. More particularly, these correlations have proved to permit a reliable statistical constitution analysis of the very complex mixtures represented by mineral oils.

Chapter XII introduces convenient methods - based on the viscosity-temperature equation developed in Chapter III - for predicting the viscosity grade as well as the complete atmospheric viscosity-temperature relationship of *mixtures* of mineral oils solely from those of the components.

The concluding Chapter XIII elaborates several *applications* of the present findings in hydrodynamic lubrication, special attention being devoted to the isothermal viscosity-pressure effect.

SAMENVATTING

Wanneer een olie wordt gebruikt ter realisering van *hydrodynamische smering*, kan hij doelmatig worden beschouwd en behandeld als een werkelijk *constructiemateriaal*. De constructieve waarde van zo'n olie wordt wezenlijk bepaald door zijn *viscositeit*. Immers, de allereerste eis welke aan een smeerolie wordt gesteld, bestaat hierin, dat deze de gewenste viscositeit zal vertonen bij de gewoonlijk variërende temperaturen en drukken in de hydrodynamisch gecreëerde oliefilm.

Nu worden vele moderne, hydrodynamisch gesmeerde werktuigonderdelen over dermate uitgebreide temperatuur- en drukgebieden toegepast, dat de in de viscositeit van de olie teweeggebrachte veranderingen zeer aanzienlijk kunnen zijn en deze, op hun beurt, de *smerende werking* van de olie sterk kunnen beïnvloeden. Bovenstaande overwegingen leiden tot de conclusie dat voldoende kennis van het viscositeit-temperatuur-drukverband van smeeroliën van zeer groot belang is, niet alleen voor de smeringstechnicus en de olietechnoloog maar ook voor de constructeur van zulke werktuigonderdelen.

Ofschoon op dit gebied reeds zeer interessante resultaten zijn bereikt, dient toch te worden geconstateerd, dat onze huidige kennis van het viscositeit-temperatuur-drukverband van smeeroliën nog steeds veel te wensen overlaat. Zo blijkt bij nadere beschouwing de toepasbaarheid van vroegere resultaten veelal zeer beperkt te zijn.

Het hier beschreven onderzoek heeft nu ten doel althans enige verbetering te brengen in deze onbevredigende situatie. Hierbij zal tevens worden getracht de resultaten in een vorm te gieten welke ook bij toepassing in de theorie en de praktijk van de hydrodynamische smering aantrekkelijk zal blijken te zijn.

De *experimentele gegevens* waarop dit onderzoek is gebaseerd, worden besproken in hoofdstuk II.

In de hoofdstukken III, IV en V is gepoogd de effecten van temperatuur en druk op de viscositeit van vloeistoffen - in het bizonder de thans als smeeroliën toegepaste typen - vast te leggen met behulp van eenvoudige, maar niettemin voldoende nauwkeurige analytische *vergelijkingen*. De hoofdstukken III en IV zijn achtereenvolgens gewijd aan het isobare viscositeit-temperatuurverband en het isotherme viscositeit-drukverband van een gegeven vloeistof. Door combinatie van de verkregen temperatuur- en drukvergelijkingen is in hoofdstuk V een uitdrukking voor het volledige viscositeit-temperatuur-drukverband afgeleid.

De opgestelde vergelijkingen zijn opmerkelijk, doordat zij met behulp van een *minimum* aantal parameters de effecten van temperatuur en/of druk, in een zeer groot gebied, op de viscositeit van een gegeven vloeistof op bevredigende wijze karakteriseren. Deze vergelijkingen blijken in feite een nauwelijks te overtreffen eenvoud te paren aan een vrijwel universele toepasbaarheid. Bijgevolg kan men ook met een minimum aan experimentele gegevens volstaan, wanneer deze vergelijkingen worden benut voor het uitvoeren van de gewenste berekeningen en het doen van bepaalde voorspellingen. De nieuwe vergelijkingen zijn in de eerste plaats opgesteld voor minerale oliën - niet alleen natuurlijke, maar ook gehydrogeneerde en met polymeer gemengde - en diverse typen synthetische oliën welke in de moderne smering worden toegepast; niettemin blijken zij evenzeer te gelden voor alle andere - zeer uiteenlopende - soorten vloeistoffen welke tot dusverre in beschouwing zijn genomen.

In hoofdstuk VI wordt een rationele en zeer aantrekkelijke methode geïntroduceerd ter *classificatie* van smeeroliën naar hun atmosferische viscositeit-temperatuurverband. De voorgestelde methode biedt in feite een eenvoudige oplossing voor het beruchte probleem van de "Viscosity Index". In hoofdstuk VII is een analoge methode uitgewerkt ter classificatie van smeeroliën naar hun isotherme viscositeit-drukverband. Deze beide classificatiemethoden zijn rechtstreeks gebaseerd op bovengenoemde vergelijkingen voor het viscositeit-temperatuurverband en het viscositeit-drukverband; zij zijn evenzo van toepassing op alle tot dusverre onderzochte - zeer uiteenlopende - vloeistoffen.

Bovendien zijn de thans opgestelde vergelijkingen uitstekend bruikbaar gebleken als een analytische basis voor *correlaties* ter voorspelling van de effecten van temperatuur en druk op de viscositeit van vloeistoffen, hetzij op grond van hun chemische constitutie, hetzij met behulp van gemakkelijk te bepalen fysische constanten. De resulterende correlaties zijn in eerste instantie ontwikkeld voor *minerale oliën*, welke - niettegenstaande hun grote verscheidenheid en gecompliceerdheid - een natuurlijke groep vormen doordat zij steeds zijn opgebouwd uit koolwaterstofverbindingen. Tenslotte bestaat het overgrote deel van alle thans toegepaste smeeroliën nog altijd uit minerale oliën, terwijl men zeker in de eerste decennia geen belangrijke wijzigingen in de huidige situatie mag verwachten.

In hoofdstuk VIII zijn eenvoudige correlaties ontwikkeld voor het in goede benadering voorspellen van het gehele atmosferische viscositeit-temperatuurverband van minerale oliën. Naast het onontbeerlijke viscositeitsniveau van de oliën - gedefinieerd als de viscositeit bij atmosferische druk en bij een bepaalde standaardtemperatuur - komt in de opgestelde correlaties slechts één variabele voor: ofwel hun totale percentage koolstofatomen in ringstructuur - als een blijkbaar voldoende nauwkeurige maat voor hun chemische constitutie -, ofwel een gemakkelijk bij atmosferische druk te bepalen fysische constante, met name hun dichtheid, brekingsindex of moleculairgewicht.

In hoofdstuk IX zijn soortgelijke correlaties uitgewerkt ter voorspelling, in een groot temperatuurgebied, van het volledige viscositeit-drukverband van minerale olien. De ontwikkelde correlaties bevatten, afgezien van het onmisbare viscositeitsniveau van de oliën, ofwel enkel hun totale percentage koolstofatomen in ringstructuur, ofwel alleen hun atmosferische dichtheid en/of brekingsindex.

Verder is in hoofdstuk X de directe samenhang tussen het viscositeit-drukverband van minerale oliën en hun atmosferische viscositeit-temperatuurverband uitvoerig bestudeerd. Deze studie heeft tot de belangwekkende conclusie geleid, dat uitsluitend het atmosferische viscositeit-temperatuurverband van een willekeurige minerale olie

inderdaad volstaat om zijn gehele verzameling viscositeit-drukisothermen in goede benadering vast te leggen. De desbetreffende correlatie heeft het unieke kenmerk dat zij, in tegenstelling tot bovengenoemde correlaties, alleen viscositeitsparameters bevat.
Hoewel de in de hoofdstukken VIII, IX en X beschreven correlaties zijn ontwikkeld voor minerale oliën, kunnen zij gemakkelijk worden aangepast aan een bepaalde homologe groep synthetische oliën of enkelvoudige verbindingen. Een dergelijke aanpassing blijkt steeds neer te komen op een essentiële vereenvoudiging van de oorspronkelijke correlatie, als gevolg van de sterke samenhang tussen de eigenschappen van de verschillende leden van zo'n homologe groep.

Hoofdstuk XI is gewijd aan het verband tussen, enerzijds, het *viscositeitsniveau* van minerale oliën en zuivere koolwaterstoffen en, anderzijds, zowel hun chemische constitutie als diverse, eenvoudig te meten fysische constanten. Dit hoofdstuk staat daarom in nauwe betrekking tot bepaalde meer fundamentele problemen op het gebied van de viscositeit van oliën. Op basis van een nieuwe additieve viscositeit-dichtheidsfunctie konden verschillende interessante correlaties worden opgesteld. Met behulp van deze correlaties is onder meer een aantrekkelijke methode uitgewerkt ter bepaling van de gemiddelde constitutie van de zeer gecompliceerde minerale oliën.

In hoofdstuk XII zijn enige eenvoudige methoden ontwikkeld ter voorspelling niet alleen van het viscositeitsniveau maar zelfs van het gehele atmosferische viscositeit-temperatuurverband van *mengsels* van minerale oliën. Deze methoden maken alleen gebruik van het atmosferische viscositeit-temperatuurverband van de componenten.

Verschillende *toepassingen* van de in voorafgaande hoofdstukken bereikte resultaten in de hydrodynamische smering zijn tenslotte nader uitgewerkt in hoofdstuk XIII, waarbij speciale aandacht is besteed aan het isotherme viscositeit-drukverband.

STELLINGEN

I

De bekende vergelijking van MacCoull en Walther, welke ten grondslag ligt aan het genormaliseerde viscositeit-temperatuurdiagram van de ASTM, is in fysisch-mathematische zin incompleet. Dit fundamentele bezwaar kan worden weggenomen door de naar oneindig hoge temperatuur geëxtrapoleerde viscositeit als een universele constante in te voeren.

N. MacCoull, Lubrication, June, 1921.
C. Walther, Erdöl und Teer 7 (1931) 382-384.
"Standard Viscosity-Temperature Charts for Liquid Petroleum Products", ASTM Designation: D 341-43.

II

De door Horváth en Hackl gesignaleerde overeenstemming tussen berekende en experimenteel bepaalde potentiaal/pH-diagrammen van enig metaal-zwavel-watersystemen is discutabel.

J. Horváth en L. Hackl, Corrosion Science 5 (1965) 528-538.

III

Bij het opstellen van correlaties - in het bizonder met behulp van statistische methoden - voor gecompliceerde fysische systemen met vele invloedsgrootheden dient meer gebruik te worden gemaakt van dimensieanalyse.

IV

De door Rahmes en Nelson uitgesproken mening als zou het optreden van een minimum in de viscositeit-concentratiecurven van binaire mengsels van minerale oliën *„ongewoon"* (*"unusual"*) zijn, is in zijn algemeenheid niet houdbaar.

M. H. Rahmes en W. L. Nelson, Analytical Chemistry 20 (1948) 912-915.
Dit proefschrift, p. 422.

V

Het gebruik van de uitdrukking *„viskeuze"* vloeistoffen ter aanduiding van vloeistoffen met zeer hoge viscositeit is taalkundig aanvechtbaar.

VI

De door Mikolajewski, Swallow en Webb beschreven experimenten geven onvoldoende steun aan hun opvatting dat het in warm water opgeloste gedeelte van gedegradeerd nylon-6.6 vrijwel niet verder zou worden afgebroken door zuurstof.

E. Mikolajewski, J. E. Swallow en M. W. Webb, Journal of Applied Polymer Science 8 (1964) 2067-2093.

VII

Ten onrechte heeft Dow de restrictie gemaakt, dat Blok's correlatie ter voorspelling van het viscositeit-drukeffect van minerale oliën welke een „homologe" groep vormen, van weinig praktische betekenis zou zijn voor oliën met een niet uitgesproken paraffinisch karakter.

R.B.Dow, "Some Rheological Properties Under High Pressure", Chap.8 in "Rheology; Theory and Applications", edited by F.R.Eirich; Vol.1, Academic Press Inc., New York, N.Y., 1956.
H.Blok, "Viscosity-Temperature-Pressure Relationships, Their Correlation and Significance for Lubrication", Proceedings of the Third World Petroleum Congress, The Hague, 1951, Section VII, pp.304-319.

VIII

De door Rao voorgestelde additieve functie van geluidssnelheid en dichtheid wordt in de literatuur ten onrechte vaak aangeduid als *„moleculaire geluidssnelheid"*. Een passende benaming voor deze functie luidt: *„sonochoor"*

M.R.Rao, Indian Journal of Physics 14 (1940) 109-116;
Journal of Chemical Physics 9 (1941) 682-685.

IX

Het is in de regel onbevredigend en zelfs irreëel om precies dezelfde recordtijd die over een afstand van een rond aantal yards - gewoonlijk 110 yards (= 100,584 meter) of een veelvoud hiervan - is gerealiseerd, tevens te erkennen als recordtijd op een vrijwel gelijke, echter iets kortere, afstand van 100 meter of een veelvoud hiervan. Hieraan is in het algemeen op een reële en eenvoudige wijze te ontkomen door de geregistreerde tijd te corrigeren op basis van de gemiddelde snelheid.

X

Aan Wright en Crouse's *„algemene"* correlatie ter voorspelling van de viscositeit van met polymeer gemengde minerale oliën mag slechts een beperkte geldigheid worden toegekend.

W.A.Wright en W.W.Crouse, Industrial and Engineering Chemistry, Product Research and Development, 3 (1964) 153-158.

XI

Chu en Cameron's beschouwingen over de compressibiliteit en de thermische expansie van in hoofdzaak minerale oliën zijn aan zeer ernstige bedenkingen onderhevig.

P.S.Y.Chu en A.Cameron, Journal of the Institute of Petroleum 49 (1963) 140-145.

XII

Door te stellen, dat de viscositeit van vloeistoffen minder met de temperatuur zal veranderen naarmate zij, bij een bepaalde temperatuur, minder viskeus zijn, maakt Sanderson zich schuldig aan een onverantwoorde generalisatie.

R.T.Sanderson, Industrial and Engineering Chemistry 41 (1949) 368-374.

XIII

In verband met de toenemende differentiatie en specialisatie van research aan onze universiteiten en hogescholen verdient het aanbeveling, proefschriften te onderwerpen aan het oordeel van landelijke commissies van op de desbetreffende gebieden deskundige hoogleraren en lectoren.

XIV

Davidse heeft geponeerd, dat het door Wada en Yamamoto bij kamertemperatuur gevonden lineaire verband tussen de dichtheid en de geluidssnelheid van verschillende typen polymeren in tegenspraak zou zijn met het - eveneens door deze auteurs geconstateerde - uiteenlopen van de verhouding tussen de temperatuurcoëfficiënt van hun geluidssnelheid en hun kubieke uitzettingscoëfficiënt. Deze door Davidse vermeende tegenspraak is echter niet houdbaar.

P.D.Davidse, Proefschrift Delft, 1959, Stelling 7.
Y.Wada en K.Yamamoto, Journal of the Physical Society of Japan 11 (1956) 887-892.

XV

Bij het comprimeren van artikelen dienen redacties van wetenschappelijke tijdschriften steeds te voorkomen, dat werkelijk waardevolle resultaten - al te snel - verloren zouden gaan.

Het verdient daarom aanbeveling, dat zij in gevallen waarin dergelijke resultaten niet in hun tijdschriften kunnen worden opgenomen, er zorg voor dragen, dat deze althans voldoend lange tijd voor geïnteresseerde onderzoekers toegankelijk blijven. Aan de andere kant zouden deze redacties eventueel aandrang dienen uit te oefenen op auteurs om de in hun artikelen verwerkte numerieke meetgegevens volledig ter beschikking te stellen.

C. J. A. Roelands,
Proefschrift Delft, 1966.