KINETIC ASPECTS OF THE VISCOSE RAYON SPINNING PROCESS

PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE TECHNISCHE WETENSCHAP
AAN DE TECHNISCHE HOGESCHOOL TE
DELFT OP GEZAG VAN DE RECTOR MAGNIFICUS Ir. H. J. DE WIJS, HOOGLERAAR IN DE
AFDELING DER MIJNBOUWKUNDE, VOOR
EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 13 FEBRUARI 1963
DES NAMIDDAGS TE 2 UUR

DOOR

ROBBERT ALDERT VROOM

geboren te Amsterdam

UITGEVERIJ WALTMAN — DELFT

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
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DANKBETUIGING

Aan de directie van de Algemene Kunstzijde Unie N.V. en aan de directie van het Centrale Research Instituut van de Algemene Kunstzijde Unie N.V. en daarmede verbonden ondernemingen te Arnhem, betuig ik mijn dank voor de toestemming tot publikatie van dit onderzoek.

Veel dank ben ik verschuldigd aan de heren A. Buurman, D. Vermaas en P. C. Limburg voor hun grote aandeel in de discussies over het in dit proefschrift beschreven onderwerp.

Mej. R. Zwarts en de heren J. Kramer, J. van Broekhoven en A. H. J. Brouwer ben ik erkentelijk voor hun toewijding bij de uitvoering van het experimentele gedeelte.

Zonder deze bijdragen en steun had dit proefschrift niet tot stand kunnen komen.

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CHAPTER I

INTRODUCTION

The viscose rayon spinning process

In the manufacture of viscose rayon an alkaline aqueous solution of cellulose xanthate, the viscose, (which solution also contains a number of salts such as sodium carbonate, sodium trithiocarbonate, sodium sulfide, the so-called viscose salts or viscose by-products) is continuously fed by a pump through a nozzle into a spinning bath.

At present this bath is usually made up of an aqueous solution of sulfuric acid and one or more sulfates, such as sodium sulfate, ammonium sulfate, magnesium sulfate, zinc sulfate.

A gel is formed, which, because it is continuously drawn off with the aid of a roller, is obtained as a filament. By a second roller, which has a higher circumferential speed, the filament is stretched while it is in the air or passes through a hot regenerating acidic aqueous second bath.

These stages in the production process together form the spinning. General experience has shown that many of the properties of the final yarn are predestined in the spinning process and can be affected by the variables of viscose and spinning bath composition and by the parameters of the spinning scheme.

The main unit-processes

In terms of the macroscopic properties of the viscose and of the freshly formed gel, the primary gel, the following effects are obtained in the spinning process:

Viscose	Primary gel	Process
liquid	solid	coagulation
alkaline	acidic	neutralization and acidification
low cell. content	high cell. content	dehydration or deswelling
cell. xanthate	cellulose	decomposition or regeneration
isotropic, homogeneous	anisotropic, inhomogeneous	orientation, formation of structure and texture
presence of viscose salts	presence of spinning bath salts + reaction products	ion-exchange

The processes and macroscopic phenomena encountered differ clearly in complexity, *e.g.*:

a. the neutralization, except for the medium effect of other factors, is only dependent on the acidic and alkaline compounds in the viscose and spinning bath;

b. the decomposition is already somewhat more dependent on other processes, too; it is initiated by the acidification and then takes the course: cell. xanthate → cell. xanthic acid → cellulose (CRANENDONK, [1]);

c. the deswelling is coupled with nearly all the other processes; starting with osmotic forces at the nozzle, it is much later still influenced by the decomposition (which is one of the slowest kinetic processes involved).

Judged from the structural properties of the final product, the balance of factors involved may vary greatly with the technological process conditions used. We consider this to be mainly caused by the balance of the kinetic factors. This consideration results partly from the observation that in general the products spun under different spinning conditions can have quite different properties, though the final product, rayon, is always cellulose and even may be cellulose of the same degree of polymerization, DP, and distribution of DP. This observation also refers to products in the same state of orientation, or even to isotropic products.

This means that thermodynamically they represent states with different free energies; possibly with the exception of one product they represent metastable states, which can only happen for kinetic reasons, one or more of the kinetic processes involved having been frozen-in somewhere.

Some characteristic process conditions and process elements

Present-day industrial process conditions reflect the efforts put into the process for many different objectives: yarn properties, the economy of the process, the amount of manual labour required, the size of the investments and of the out-of-pocket expenses, the quality requirements of the market; these and other criteria have in one way or another affected the historical development.

One of the tools which the viscose chemist could and still can apply in obtaining optimum process conditions with respect to these criteria is given by the large number of process parameters. (TABLE I summarizes the main parameters of the spinning process and indicates the range in which they usually are to be found. To indicate the composition of the viscose and of the spinning bath a number of abbreviations have come into use. This is illustrated by an example given after TABLE I.) The inherent variability of the chemical and physical conditions of the spinning of viscose represents, we believe, one of the natural values of the rayon spinning process and has resulted in a corresponding variety of product properties.

TABLE I The main parameters of the spinning process

Parameters of the spinning process	Technologically usual range
1. the cellulose concentration in the viscose	4–10% (by weight)
2. the alkali content of the viscose	3– 8%
3. the amount of CS_2 used in xanthating the alkali cellulose	30–60%, calculated on the cellulose
4. the degree of substitution with xanthate groups pro glucose monomer unit at the moment of spinning: the xanthate ratio, XR	0.25–0.80
5. the presence and amount of spinning aids, generally surface-active agents (Prestabit oil, ethomeen, lauryl pyridiniumchloride, *etc.*), in the viscose and/or spinning bath	
6. the presence and amount of modifiers or dopes in the viscose and/or spinning bath	
7. the H_2SO_4-content of the spinning bath	3–15%
8. the Na_2SO_4-content of the spinning bath	5–20%
9. the $ZnSO_4$-content of the spinning bath	0–10%
10. the temperature of the spinning bath	20–70 °C
11. the design of nozzle and nozzle holes	
12. the bath length	10–100 cm
13. the bath flow around nozzle and spinning filament	
14. the amount of stretch applied	0–150%
15. the composition and temperature of the stretching bath	
16. the thickness of the filament (the denier)	
17. the spinning speed	20–150 m/min

Technologically used abbreviations

Viscose composition

The composition of a viscose is abbreviated as, *e.g.*,

7.7/7.1/35+5% XR = 0.39

This indicates that

1. the cellulose content is 7.7% (percentages by weight are used),
2. the total-alkali content is 7.1%,
3. in preparing the cellulose xanthate 35% CS_2 (calculated on the cellulose) was used in xanthating the alkali cellulose and 5% CS_2 (calculated on the cellulose) was added during dissolving,
4. at the moment of spinning the degree of substitution with xanthate groups pro glucose monomer unit, the xanthate ratio or XR, is 0.39.

Spinning bath composition

The composition of a spinning bath is abbreviated as, *e.g.*,

7.5/17.5 M/Z 4.2/3.5 $T = 50$ °C

This indicates a spinning bath with

1. a H_2SO_4-content of 7.5%
2. a Na_2SO_4-content of 17.5%
3. a $MgSO_4$-content of 4.2%
4. a $ZnSO_4$-content of 3.5%
5. a temperature of 50 °C

On the basis of existing knowledge of process phenomena and product properties it seems possible nevertheless to distinguish a number of characteristic sets of process conditions and to recognize some characteristic process elements. A selection of some relevant patent publications, historically arranged, is given in APPENDIX I.

The original viscose spinning process

In the original procedure as given by CROSS, BEVAN, BEADLE and STEARN viscose is spun into a coagulating, more or less neutral, salt solution. The xanthate hardly decomposes in this way and the regeneration has to be carried out afterwards. The spinning gel, *i.e.* the product as it leaves the spinning bath, is still highly swollen.

Spinning in so-called Müller baths

On addition of sulfuric acid to these spinning baths (MÜLLER), the regeneration starts, in contrast with the above, already during the formation of the filament. The swelling properties of the primary gel are dependent on the bath length: several minutes are required as times of interaction between spinning bath and spinning filament in order to obtain a constant value for the degree of swelling.

Stretching the spinning filament

A process element which in general can be applied additionally is stretching (introduced in viscose spinning in 1902 by THIELE and ERNST).

Its effect, however, is dependent on other aspects of the viscose spinning bath interaction: if the stretching is applied to the filament at sufficiently large distances from the nozzle, or even in a second bath (which then very often has a high regenerative power), all the presently known anisotropy effects appear in the final product (X-ray diffraction pattern, optical and mechanical anisotropy properties); if, however, the stretching is applied close to the nozzle, this has hardly any effect on the yarn properties: the yarn remains more or less isotropic (BREDEE, [2]).

Spinning in Müller-type baths containing zinc sulfate

Ostensibly rather classical is the use of Müller-type spinning baths containing zinc sulfate (NAPPER, VAN BERGEN, DREAPER). Technologically, however, they are of paramount interest and provide both the clearest and the most subtle examples of the qualitative effects of quantitative differences in spinning conditions.

On using these baths, a wide variety of products with different properties can be obtained by proper quantitative adjustment of the spinning process.

They constitute the bulk of present-day viscose products:

regular textile yarns and staple fibres for straight-forward textile knitting and weaving purposes;
tyre yarns which have come to dominate the tyre-fabric market on account of their high strength and fatigue properties;
crimped products to be used by converters of wool;
low-swelling products for the cotton market;
high-modulus products again for certain parts of the cotton market.

This variety of product properties is at least partly related with the formation of so-called *skin cellulose.*

On examining cross-sections of a regular textile rayon, PRESTON [3] was able to identify two regions: an outer layer, the "*skin*", surrounding the central part, the "*core*".

These areas are distinguished by, *e.g.*, selective dyeing tests and were found to have different properties.

Later on the names skin cellulose and core cellulose came into use as structure definitions, skin cellulose having the properties of the skin and core cellulose having the properties of the core of the classical textile product.

The formation of skin cellulose is generally understood (MOREHEAD and SISSON [4] and VERMAAS [5]) as being connected with the presence of the zinc sulfate in the spinning bath; without zinc (or other heavy metal-ions with a comparable effect) in the spinning bath all-core yarns are obtained.

In view of the desirable properties of skin cellulose (high strength at break, low swelling value, good fatigue properties) much effort was directed to a study of the conditions of skin cellulose formation.

Even a laboratory procedure for preparing an all skin yarn (using a specially prepared cellulose xanthate solution containing sodium zincate and spinning in baths containing acetic acid) was developed by VERMAAS [5].

As regards the large number of parameters involved, empiry has shown that, besides the required presence of zinc sulfate in the spinning bath, one of the most important factors determining the formation of skin cellulose (and ergo determining the properties of the final product) is the balance between the alkali content of the viscose and the sulfuric acid content of the spinning bath; names such as "high-acid" yarn and "low-acid" spinning process came to be used.

Now it appears that for a certain viscose the (maximum) formation of skin cellulose is limited to a certain range of sulfuric acid concentrations; *i.e.* both lower and higher concentrations lead to the formation of products with less skin or even to all-core products.

In fact, on spinning almost any regular viscose the following products can successively be obtained in a suitable series of spinning baths of increasing sulfuric acid content:

a. products which possess no skin cellulose as described above,

b. products which are skin-core differentiated, with an unsymmetrical distribution of skin cellulose around the core,
c. products which possess a high percentage of skin cellulose or which even can have an all-skin character and are then moreover characterized by a low swelling value,
d. products which are skin-core differentiated, with skin-cellulose evenly present around the core,
e. products which again have all-core character.

N.B. The foregoing may serve to illustrate the importance of adjusted parameters for obtaining certain product properties.

This does not mean that as compared with the alkali-acid balance the other parameters of the spinning process are without effect on the formation of skin cellulose or that their effect is small. In fact the presence of the viscose salts is known to play an important role in the formation of skin cellulose under the usual technological spinning conditions (Cox).

Nor does it mean that by describing the yarn as composed of skin cellulose and core cellulose, its total structure and all its structural properties are defined; for instance, the strength properties of all-skin yarns are known to be very much dependent on many parameters of the spinning process, which are without apparent effect on the formation of skin cellulose.

Confining the attention to the spinning conditions under which a high percentage of skin-cellulose can be obtained, it appears that the addition of zinc sulfate to the Müller bath results in a retarded regeneration of the spinning filament, a higher stretchability, and, in cooperation with a sufficiently high osmotic pressure difference between viscose and spinning bath, in the formation of a rather deswollen primary gel.

Spinning in the presence of surfactants

On spinning in zinc-containing Müller baths, the addition of surfactants (POLAK, WEELDENBURG, MAC LAURIN, ISRAEL) either to the viscose or to the spinning bath generally exerts a favourable effect on the gel formation. As regards the structural properties of the final product, it is known that surfactants decrease or prevent the appearance of "milkiness" (= opacity, caused by rather small holes) in the final product and that besides, under properly adjusted process conditions, they can have a favourable effect on the strength properties.

Spinning in Müller-type baths containing formaldehyde

On addition of formaldehyde to a Müller-type spinning bath (KAYSER) the regeneration is again very much retarded. Besides the primary gel has a higher stretchability, with the aid of which higher strength properties can generally be obtained.

Doped spinning

The efforts to prepare an all-skin yarn led to the discovery by Cox that certain compounds, added to viscose and/or (zinc sulfate-containing Müller-type) spinning bath, render the industrial manufacture of all-skin yarns possible.

These compounds became known as *modifiers* or *additives* or *dopes* and comprise many different classes of organic compounds:

a. neutral compounds, *e.g.* prim., sec. and tert. amines, polyethylene oxides,
b. negatively charged compounds (such as viscose additives), *e.g.* dithiocarbamates,
c. positively charged compounds, *e.g.* quaternary N^{IV} compounds.

The effect of these various classes of compounds is (in general) only quantitatively different. The same applies within a class of compounds, *e.g.*, the lower homologues are often less active than the higher ones.
The action of the dopes is connected with:

a. the presence of zinc sulfate in the spinning bath ($> \sim 3\%$ $ZnSO_4$),
b. a certain alkali (in the viscose) – sulfuric acid (in the spinning bath) balance,
c. not too low a XR (generally > 0.40).

Phenomenologically, most of the effects observed in the doped spinning process are the same as those observed in spinning in zinc sulfate-containing Müller baths, but much more pronounced. A new phenomenon is the sensitivity of the spinning filament to mechanical disturbance: apparently the coagulation is very much retarded and rather long bath lengths are required. It is furthermore found that the dopes increase the distance from the nozzle at which in the spinning filament the colour change of pH-indicators (added to the viscose) takes place (Cox).

The Lilienfeld spinning process

A characteristic set of process parameters has first been described by LILIENFELD, who used a rather concentrated sulfuric acid solution ($> 50\%$) as spinning bath. Phenomenologically the use of this bath again does not cause much decomposition. The strength properties obtainable in the Lilienfeld process were for a long time the highest known for regenerated cellulose products.

The Toramomen spinning process

Also rather characteristic are the process conditions introduced by TACHIKAWA: in the so-called Toramomen process a viscose with a rather low cellulose content, a high DP and a very high xanthate ratio (which as such results in a low coagulability) is spun into a cold, nearly salt-free, rather diluted sulfuric acid solution. Here the coagulation is brought about in an entirely unclassical way; an osmotic deswelling is hardly possible; it even seems that decomposition is not necessary during the formation of the filament. The final product is described as having "cotton-like" properties because of its high mechanical modulus, its hand and, for viscose yarns, its relatively high wet strength and low swelling value.

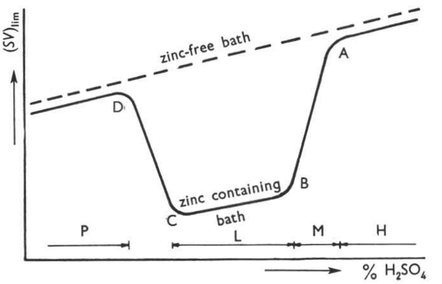
Classification of Müller-type spinning processes by means of the ultimate swelling value

The effect on yarn properties of variations in the composition of the Müller-type spinning bath can be illustrated by the effect of these variations on the so-called *ultimate swelling value* $(SV)_{lim}$.

The $(SV)_{lim}$ is the swelling value in water of a yarn sample obtained by causing the filament to return after the first godet to the spinning bath, keeping it there in principle for an infinitely long time (in practice 10 minutes generally *) suffices) and washing it till acid-free.

The sample obtained in this way has so not been exposed to any effects of the stretching or of the second bath or of the aftertreatment processes.

The determination of the swelling value then follows the regular procedure: centrifuging, weighing, drying and weighing again.



In a way the $(SV)_{lim}$ *is the swelling value in water of an unstretched, never dried yarn spun with the aid of an infinitely long bath.*

The $(SV)_{lim}$ as a function of the H_2SO_4-content of the spinning bath shows, for a certain viscose, a course as represented schematically in the figure.

We found the $(SV)_{lim}$ to be a valuable over-all parameter for characterizing the viscose spinning bath combination. It is dependent on many of the variables and therefore allows an empirical classification of viscose spinning bath combinations.

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*) Particularly on spinning in formaldehyde-containing spinning baths, the regeneration of the xanthate is so much retarded that the times of interaction between yarn and spinning bath have to be much longer; hours may be required to complete the interaction and to obtain a constant swelling value.

If the viscose spinning bath parameters are varied, but the yarn is processed under constant conditions, the $(SV)_{lim}$ correlates very well with the *swelling value* $(SV)_{sec}$ of the regularly aftertreated and dried yarn.

To a certain extent the $(SV)_{lim}$ is also correlated with the percentage of skin cellulose in the cross-section; an all-skin yarn can be obtained under spinning conditions characterized by $(SV)_{lim} < \sim 90\%$.

The breaks in the $(SV)_{lim}$-H_2SO_4 graph mark well-defined spinning regions.

At acid-concentrations below D, to be called the acid-poor P-region, the spinning conditions can result in an all-core high-modulus yarn.

At acid-concentrations between D and C skin-core differentiated crimped products can be obtained.

In the low-acid L-region between C and B yarns especially suitable for tyre-cord materials can be obtained.

The effect of the dope is found specifically in this low acid L-region; the $(SV)_{lim}$-values are still lower on spinning in the presence of a dope. The products obtained can have an all-skin character.

The H_2SO_4-contents of regular textile yarn spinning processes are found between B and A.

The H_2SO_4-concentration above A, to be called the high acid H-region, correspond to those used in the casting of cellophane (in which case, however, generally no zinc sulfate is present in the spinning bath).

Purpose of our investigations

Our investigations were related to some of the aspects mentioned; their aim was in particular to study some of the kinetic factors involved. Observations were made on the spinning filament and, in addition, in vitro model experiments were carried out.

Out of this grew the recognition of the importance of diffusion processes and chemical reactions in spinning.

In the first part of this thesis an approach to spinning on the basis of a cylindrical diffusion theory will be given together with an experimental study of the neutralization process of the spinning filament (which was carried out on a monofil spinning machine). The changes of medium brought about by the diffusion trigger a number of chemical and physical processes which affect the state and behaviour of the spinning filament.

The decomposition of the xanthate group in acidic media in the presence of a complexing metal ion, *c.q.* zinc, was studied in model experiments and forms the contents of the next part. These investigations indicate some of the conditions under which the behaviour of the spinning filament may be expected to vary.

This is followed by a study of the stretch-optical and the stretch-tension behaviour of the spinning filament (again carried out on the monofil spinning machine), starting from the idea that different "states" (sol state, gel state and possibly even different gel states) will have a different stretch-optical or stretch-tension behaviour.

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CHAPTER II

SPINNING CONSIDERED AS A CYLINDRICAL DIFFUSION PROCESS

The cylindrical diffusion process

For an infinitely long cylindrical medium (with radius r_0 and initial concentration c_b), into which matter diffuses out of an infinitely large solution (concentration c_a), the transport can theoretically be described and calculated from Fick's diffusion equation [1].

$$\frac{\partial C}{\partial t} = D\Delta C \quad \ldots\ldots\ldots\ldots \quad \text{(II-1)}$$

where D = the diffusion coefficient, considered to be concentration independent,
Δ = the Laplace operator.

The solution of (II-1) in the above case, in which the border conditions are

$$c = c_a \text{ at } r > r_0 \text{ at all } t$$

$$c = c_b \text{ at } r \leqslant r_0 \text{ at } t = 0,$$

reads [1]

$$\frac{c\ (r,\ t) - c_a}{-c_b + c_a} = 2\sum_1^\infty \frac{1}{l_n}\,\frac{J_0\left(l_n \dfrac{r}{r_0}\right)}{J_0'(l_n)}\, e^{-l_n^2 \frac{Dt}{r_0^2}} \quad \ldots\ldots \quad \text{(II-2)}$$

where $J_0(x)$ is a Bessel function of the first kind and of zero order, and $J_0'(x)$ its derivative, l_n being the n^{th} root of the equation $J_0(l_n) = 0$.

$$l_1 = 2.405 \qquad l_2 = 5.520 \qquad l_3 = 8.654$$

In (II-2) the concentration difference at a certain locus and time which is still to be overcome, divided by the total concentration difference to be annulled is expressed in terms of a distribution function $f\left(\frac{r}{r_0}\right)$ and of a function of time and dimension $f\left(\frac{t}{r_0^2}\right)$.

Hermans [2] has treated the cylindrical diffusion of a substance A into a cylindrical medium, in which it encounters a subtance B, with which it reacts.

As to the general case he states that "it is doubtful whether a simple solution of the problem can be given". In one particular case, however, considerations of symmetry lead to a straightforward answer, *viz.* when the two substances have the same diffusion coefficient $D = D_a = D_b$ and react with each other instantaneously and irreversibly. Species B then acts as a diffusable hole for species A. Mathematically, the presence of species B can therefore be regarded as a negative concentration of species A; the solution becomes:

$$\frac{c(r,t)-c_a}{c_b+c_a} = 2\sum_{1}^{\infty} \frac{1}{l_n} \mathrm{f}\left(\frac{r}{r_0}\right) e^{-l_n^2 \frac{Dt}{r_0^2}} \quad \ldots\ldots\ldots\ldots \quad (\text{II-3})$$

The total concentration difference to be annulled becomes c_b+c_a; negative values of $c(r, t)$ represent the holes, *i.e.* species B.

A useful approximation of (II-2) or (II-3) is obtained for not too small values of $\frac{Dt}{r_0^2}$, say $\frac{Dt}{r_0^2} > 0.15$. Then only the first term of the series needs to be retained, all the other ones becoming negligibly small;

$$\frac{c(r,t)-c_a}{c_b+c_a} = p\cdot\mathrm{f}\left(\frac{r}{r_0}\right) e^{-qD\frac{t}{r_0^2}} \quad \ldots\ldots\ldots\ldots\ldots \quad (\text{II-4})$$

In practical experiments it is very often not the local concentration which is determined, but the total amount of subtance given off or taken up by the cylindrical medium, *i.e.* the average concentration $\bar{c}$.

(II-3) then changes into:

$$\frac{\bar{c}(t)-c_a}{c_b+c_a} = -4\sum_{1}^{\infty} \frac{1}{l_n^2} e^{-l_n^2 \frac{Dt}{r_0^2}} \quad \ldots\ldots\ldots\ldots\ldots \quad (\text{II-5})$$

Here again, at $\frac{Dt}{r_0^2} > 0.15$, only the first term needs to be retained.

Diffusion relations

For the cylindrical diffusion process a number of conclusions follow from equations (II-2) and (II-3).

Abbreviating

$\frac{c(r,t)-c_a}{c_b+c_a} = P$, the concentration term,

$e^{-qD\frac{t}{r_0^2}} = Q$, the term including time and radius squared,

$p\cdot\mathrm{f}\left(\frac{r}{r_0}\right) = R$, the distribution function,

so that $P = RQ$, one gets the following diffusion relations:

Diffusion relation I

When P and R are kept constant: it follows both from (II-2) and from (II-3) that $Q =$ constant, *i.e.* $\frac{t}{r_0^2} =$ constant.

If a diffusion process in a cylindrical medium of radius r_{01} requires a time t_1 to progress into a certain concentration distribution, the corresponding time t_2 in a cylinder of radius r_{02} is given by:

$$\boxed{t_2 = \frac{r_{02}^2}{r_{01}^2}\, t_1}$$

Diffusion relation II

When R is kept constant, it follows from (II-4) that $\ln\{c(r,t) - c_a\} + qD\frac{t}{r_0^2} =$ $=$ constant, *i.e.* for not too small values of the time $\left(\frac{Dt}{r_0^2} > 0.15\right)$ the logarithm of the concentration-difference still to be overcome at a certain locus is a linear function of the time.

For $c_a = 0$ (= component outside the cylinder absent) this reduces to *diffusion relation II'*: $\ln c(r,t) + qD\frac{t}{r_0^2} =$ constant, *i.e.* the logarithm of the concentration at a certain locus is a linear function of the time.

Diffusion relation III

When Q and R are kept constant, it follows both from (II-2) and (II-3) that $\frac{c(r,t) - c_a}{c_b + c_a} =$ constant. From this it follows that the initial concentration values of the respective components outside and inside the cylinder, c_a and c_b, with which at a certain locus and time a certain concentration $c(r,t)$ is obtained, are linearly related.

Diffusion relation IV

When P is kept constant, and the values of c_a and c_b are given, it follows from (II-2) and (II-3) that

$$\sum_1^\infty \frac{1}{l_n} \frac{J_0\left(l_n \frac{r}{r_0}\right)}{J_0'(l_n)} e^{-l_n^2 \frac{Dt}{r_0^2}} = \text{constant}$$

i.e. the set of points for which

$$\frac{c(r,t)-c_a}{c_b+c_a}$$

has a certain value, *i.e.* the equi-concentration points in the cylinder in dependence on the time, is a bell-shaped surface of rings having their centres in the centre-line of the cylinder; the ring at $t = 0$ has a radius $= r_0$. (FIG. 1).

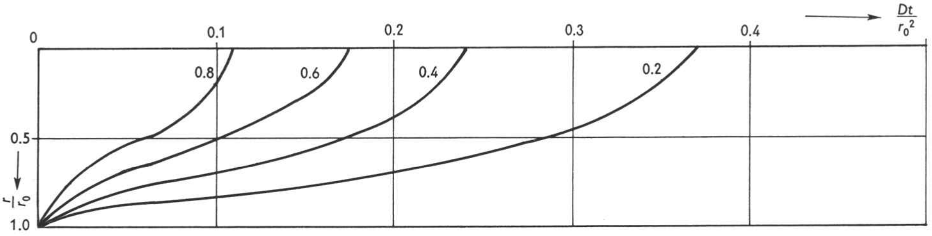


FIG. II-1 Equi-concentration lines in an infinite cylinder of radius r_0 with initial concentration c_b and final concentration c_a (= time-independent concentration outside the cylinder). The numbers at the curves are the values of $\frac{c-c_a}{c_b+c_a}$.

The higher the required value of $c(r,t)$ the more elongated the bell; the circular base $r = r_0$, however, is the same for all the values of $c(r,t)$.

The interaction between viscose and spinning bath regarded as a cylindrical diffusion process

A number of diffusing+reacting components in the viscose spinning bath interactions are:

Spinning bath	Viscose	Reaction product
H^+	OH^-	H_2O
H^+	$R{-}O{-}C\langle^{S^-}_{S}$	$R{-}O{-}C\langle^{S}_{SH} \rightarrow ROH+CS_2$
H^+	S^{--}	SH^-, H_2S
H^+	CS_3^{--}	HCS_3^-, $H_2CS_3 \rightarrow H_2S+CS_2$ (analogously for CO_3^{--})
Zn^{++}	OH^-	$Zn(OH)_2$
Zn^{++}	$R{-}O{-}C\langle^{S^-}_{S}$	$\left(R{-}O{-}C\langle^{S}_{S}\right)_2Zn$
Zn^{++}	S^{--}	ZnS (analogously for CS_3^{--}, CO_3^{--})

In the general case complications may arise:

1. the diffusion coefficients of the partners may be different,
2. one of the reaction partners or the reaction product may be immobile,
3. the reactions occurring may be reversible under the prevailing conditions of spinning,
4. the reactions occurring may be time-consuming in different orders of magnitude, varying from very fast to very slow as compared with the rate of concentration change brought about by diffusion.

As such the mathematical treatment of the cylindrical diffusion process is only a first approximation to the viscose-spinning bath interaction, even apart from the mathematical assumption of a concentration-independent diffusion-coefficient.

Spinning Relations

For the case that the above mentioned cylindrical diffusion equations may be applied, *i.e.* for the unhampered diffusion of a single substance or for an instantaneous and irreversible reaction $A+B \rightarrow AB$ with numerically equal diffusion coefficients of the two partners, $D_a = D_b$, the diffusion relations, translated into terms of the parameters of the spinning process, point to a number of phenomena which may possibly be met in the viscose-spinning bath interaction.

Viscose delivery and drawing-off speed together determine the radius of the spinning filament:

$$\pi r_0^2 = \frac{\text{viscose delivery}}{\text{drawing-off speed}}$$

The drawing-off speed determines the time it takes the spinning filament to travel a certain distance from the nozzle:

$$t = \frac{\text{distance from the nozzle}}{\text{drawing-off speed}}$$

So, under constant spinning conditions the dynamic diffusion process can be investigated by stationary observations at varying distances from the nozzle.

In terms of the parameters of the spinning process the diffusion relation I, $\frac{t}{r_0^2} = \text{constant}$ (relating to an equivalence of diffusion states), then reads: At a certain viscose composition and spinning bath composition (*i.e.* c_a and c_b are constants) a certain progress of the diffusion (*i.e.* $c(r,t) = \text{constant}$) at a certain place in the spinning filament (*i.e.* the distribution-function $f\left(\frac{r}{r_0}\right) =$ $=$ constant) will be found under the conditions at which $\frac{t}{r_0^2} =$ constant.

$$\frac{t}{r_0^2} = \text{constant} \sim \frac{\text{distance from the nozzle/drawing-off speed}}{\text{viscose delivery}\qquad\text{/drawing-off speed}}$$

$$\sim \frac{\text{distance from the nozzle}}{\text{viscose delivery}}$$

Spinning relation Ia

The distance from the nozzle at which a certain quasi-stationary state will be found is lineary dependent on the viscose delivery.

Spinning relation Ib

At constant viscose delivery, the distance from the nozzle at which a certain quasi-stationary state will be found is independent of the drawing-off speed.

In terms of distances from the nozzle, spinning relation I therefore predicts that *only the amount of viscose entering the bath pro unit time plays a role*, irrespective of how the drawing-off speed co-determines the "thickness" of the spinning filament in the bath.

As a consequence: at a viscose delivery $= 0$, any quasi-stationary state should be found at a distance from the nozzle $= 0$. This makes a calibration of measurements possible.

The other diffusion relations can analogously be translated into terms of the parameters of the spinning process.

Applied *e.g.* to the centre of the spinning filament the diffusion relation II becomes:

Spinning relation II'

For a species freely diffusing out of the spinning filament $\log c(r = 0, t)$ *is a linear function of the distance from the nozzle.*

The diffusion relation III can analogously be translated into:

Spinning relation III

A linear relation exists between the initial concentration values outside and inside the spinning filament, for a pair of diffusing+reacting components A and B obeying the *pertinent mathematical assumptions, with which at a certain distance from the nozzle a certain concentration is obtained at a certain locus.*

Spinning relation IV

This relates the distribution function with the distance from the nozzle. In the graph of diffusion relation IV, $\frac{Dt}{r_0^2}$ should be replaced by the distance from the nozzle:

the equi concentration points in the spinning filament lie on a bell-shaped surface with the nozzle hole at the base.

Literature

1. H. S. CARSLAW and J. C. JAEGER, Conduction of heat in solids, Oxford, 1957.
   R. M. BARRER, Diffusion in and through solids, Cambridge, 1941.
   J. CRANK, Mathematics of diffusion, Oxford, 1956.
2. J. J. Hermans, J. Coll. Sc. **2** – 387 (1947).

CHAPTER III

THE NEUTRALIZATION PROCESS IN THE SPINNING FILAMENT

Principle of the measurement

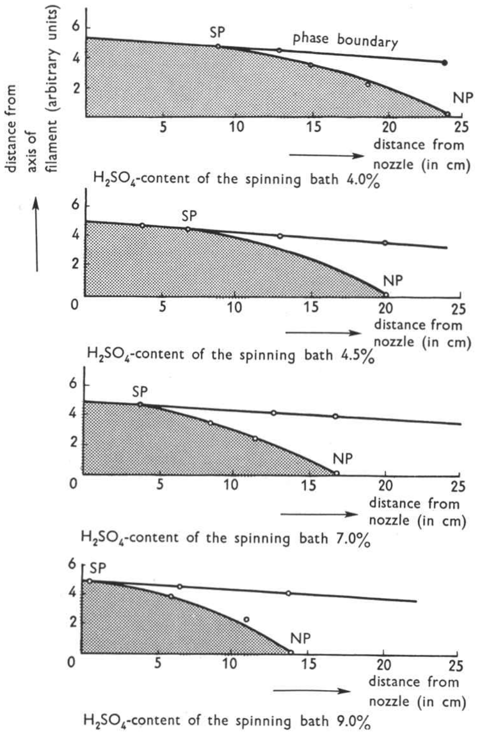
For investigating the neutralization phenomena in the spinning filament, the method of measurement consists of spinning a monofilament from a viscose to which an indicator has been added, while the monofilament is observed through a microscope.

The boundary of the colour change of the indicator is observed and measured, using as parameters

a. the distance from the nozzle,
b. the distance within the filament from the surface of the filament.

Fig. III-1 illustrates the course of the boundary for some different spinning baths, as observed with thymolphthalein as indicator. This boundary is in principle an equi-pH-line. The figure relates to half an axial section of the spinning filament (the nozzle is to the left).

This method of measurement is not new, but has been in use for fundamental studies since around 1930. Literature publications, however, have appeared only recently [1].



H_2SO_4-content of the spinning bath 4.0%

H_2SO_4-content of the spinning bath 4.5%

H_2SO_4-content of the spinning bath 7.0%

H_2SO_4-content of the spinning bath 9.0%

viscose : 8.3/4.65/33 XR = 0.48
spinning bath : x/18.0 Z = 4.0 T = 45 °C
nozzle : 200 μ
viscose delivery : 0.267 ml/min
drawing off speed: 5–10 m/min

Fig. III-1 Colour-change of thymolphthalein in the spinning filament.
Results obtained on varying the H_2SO_4-content of the spinning bath.

In the course of our investigation only the distances of two points from the nozzle were measured:

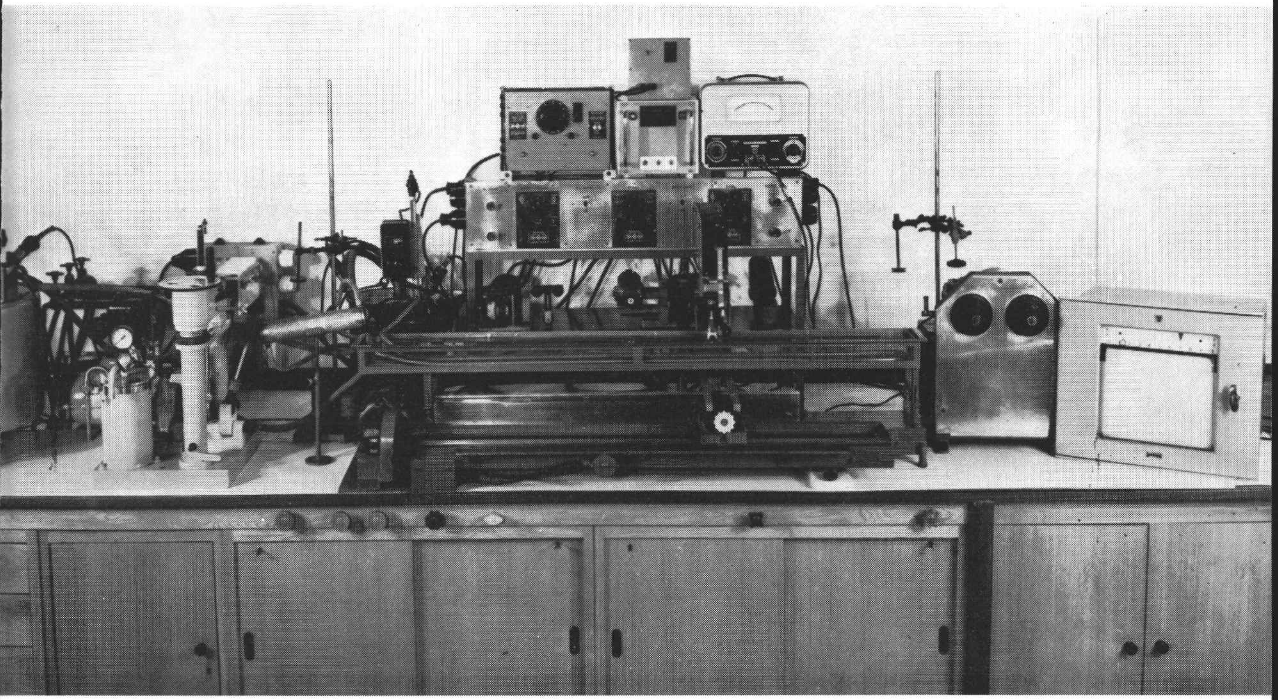
a. the point where the colour change throughout the filament has been completed: neutralization point: NP,
b. the point on the surface of the filament where the equi-pH-line (as measured by the colour change) gets free from the surface. This point has been called (more or less incorrectly, since it represents a circle) the starting point: SP.

By using different indicators an insight may be gained into the pH-distribution in the spinning filament, provided that the medium under consideration has no other effects on the colour change and on the pH at which the colour change of the indicator occurs.

The pH at colour change of the indicator is added as an index, *e.g.* NP_{10}, SP_6.

In respect of the stability of the indicators in the viscose medium and the contrast of high-pH and low-pH colours an excellent indicator is thymolphthalein (pH at colour change 9.3–10.5). Bromocresol-purple (5.2–6.8) and

Monofil spinning machine



bromophenol-blue (2.8–4.6) were the next best ones; both, however, are stable in the viscose for only a few hours.

Apparatus and procedure

The viscose is forced through a one-hole nozzle by a pump giving a viscose stream which is as free as possible from periodical fluctuations. The pump drive is continuously adjustable, which facilitates the choice of viscose delivery. The delivery can be changed from 0.05–1.00 ml/min.

The filament is observed through a microscope (magnification 100 times), the objective of which is protected against the spinning bath by a metal shell with a bottom of plane-parallel optical glass. The spinning trough is provided with a transparent bottom of either glass or perspex.

The microscope is mounted on a hand-driven screw for moving the microscope, horizontally, perpendicular to the spinning trough. The whole can be transported by a motor-driven screw along the trough.

The filament is pulled off by a simple roller device. Between nozzle and drawing-off roller no guides are used.

Some errors of the measurement

Before going into the details of the results obtained, it seems appropriate to point out some of the difficulties encountered.

The magnification used should not be too large; the boundary observed is not a very sharp one ,which is partly due to the more or less undefined transition colours between the high-pH and low-pH colours. If the magnification applied is too large, a rather blurred picture results.

Inhomogeneities present in the spinning filament are other causes of faults. They may result from the viscose per se, or may be brought about by the evolution of gas formed in reactions between the components of spinning bath and viscose.

For the above-mentioned reasons the measurements show an inaccuracy which is estimated to be between the limits -3 and $+1$ cm for the neutralization point, and -1 and $+1$ cm for the starting point at total distances of about 30 and 10 cm, respectively.

Experimental results

Some of the experimental data are represented graphically in Figs. III-2–14.

Table I summarizes the observed effects of variations in the spinning scheme, viscose composition and spinning bath composition (in dopefree spinning) on SP_{10} and NP_{10} as measured with thymolphthalein.

TABLE I Summary of some variables investigated in dope-free spinning and their effects as measured with thymolphthalein as indicator

Variations in	Effect on SP_{10}	Effect on NP_{10}
Spinning scheme		
squirting velocity	no effect	no effect
viscose delivery	positive linear relation	positive linear relation
drawing-off speed	no effect	no effect
Viscose composition		
cellulose content	no effect	no effect
total alkali content	positive relation	positive relation
xanthate ratio	no effect *)	no effect *)
Spinning bath composition		
sulfuric acid content	negative relation	negative relation
sodium sulfate content	no effect	no effect
zinc sulfate content	positive relation	no effect
magnesium sulfate content	no effect	no effect
temperature	negative relation	negative relation

*) Except at very low H_2SO_4-contents of the spinning bath ($<2\%$).

By positive/negative relation is meant an increase/decrease of the SP_{10} or NP_{10} distance from the nozzle, in dependence on an increase of the variable.

The following comments may be made on some of the variables investigated:

Sulfuric acid (FIG. III-2, 3)

Nearly always an experiment consisted of a series of measurements at varied sulfuric acid contents of the spinning bath, other parameters being kept constant.

Drawing-off speed (FIG. III-4, 5)

A way of eliminating individual errors in a single measurement consists in observing the phenomena while varying the drawing-off speed: both SP and NP (in the undoped process) are independent of the drawing-off speed at constant viscose delivery. This has been verified for drawing-off speeds up to 50 m/min.

Viscose delivery (FIG. III-6)

The neutralization phenomena show a linear dependence on the viscose delivery.

Squirting velocity; size of the nozzle hole

No influence was found.

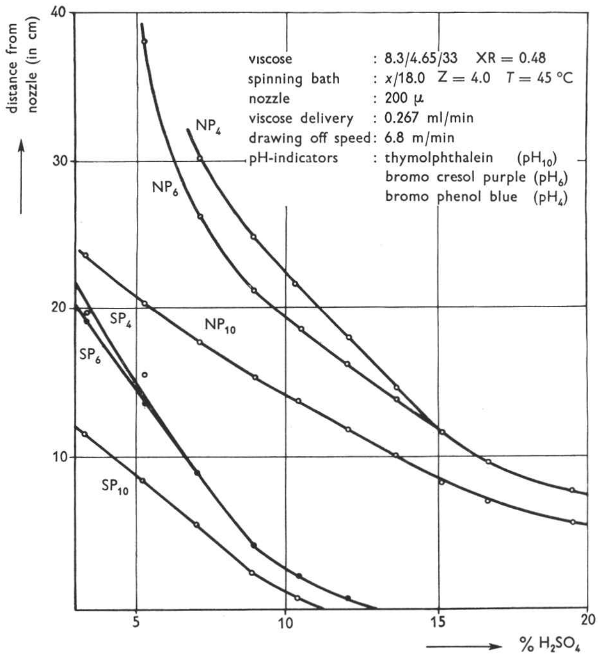


Fig. III-2 NP and SP as functions of the H_2SO_4 content of the spinning bath. Measurements carried out with different indicators.

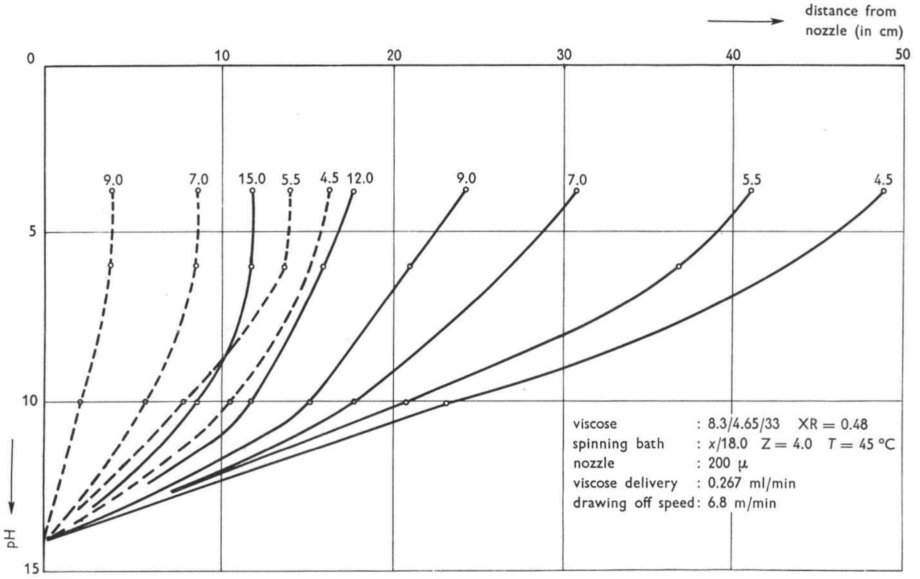
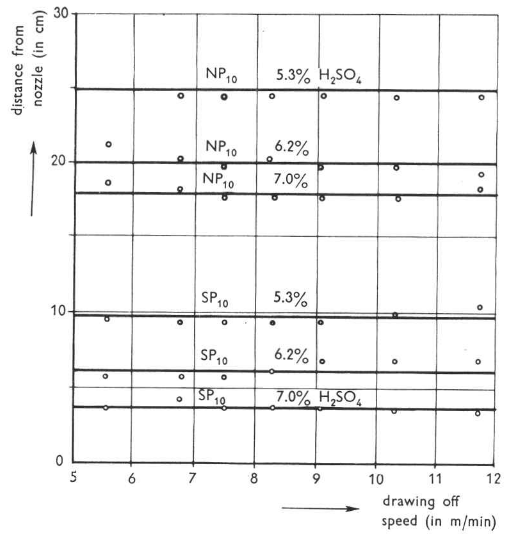
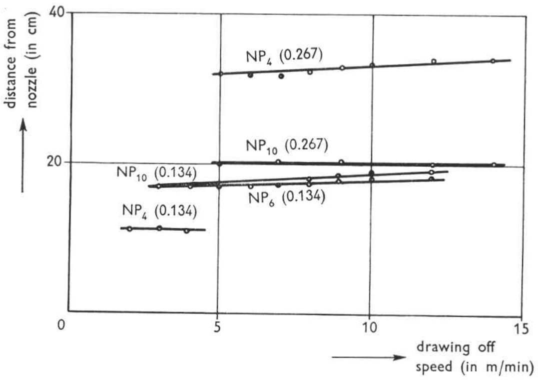


Fig. III-3 pH-distribution in the core — and on the surface - - - of the spinning filament. Results obtained on varying the H_2SO_4-content of the spinning bath.



viscose : 8.3/4.65/33 XR = 0.48
spinning bath : x/19.0 $Z = 4.5$ $T = 45$ °C
nozzle : 200 μ
viscose delivery: 0.267 ml/min

FIG. III-4 NP_{10} and SP_{10} as functions of the drawing off speed.
Results obtained on varying the H_2SO_4-content of the spinning bath.



viscose : 8.3/4.65/33 XR = 0.48
spinning bath : 5.0/18.0 $Z = 4.0$ $T = 45$ °C
nozzle : 200 μ
viscose delivery: 0.267 m/min resp. 0.134 ml/min

FIG. III-5 NP_{10}, NP_6 and NP_4 as functions of the drawing off speed.

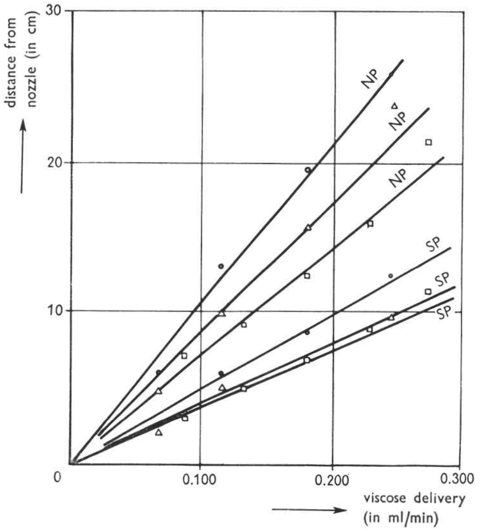


FIG. III-6 NP_{10} and SP_{10} as functions of the viscose delivery.
Results obtained with different viscose spinning bath combinations.

Alkali content (FIGS. III-7, 8)

The alkali content of the viscose is as much a determining factor as regards the SP- and NP-distances as the sulfuric acid content. The experimental results show these factors to be clearly interdependent.

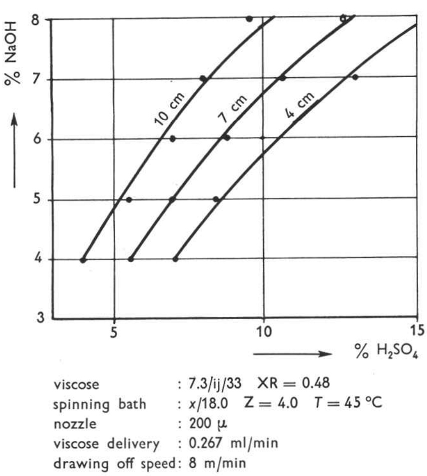


FIG. III-7 NP_{10} as a function of the H_2SO_4-content of the spinning bath and the NaOH-content of the viscose.

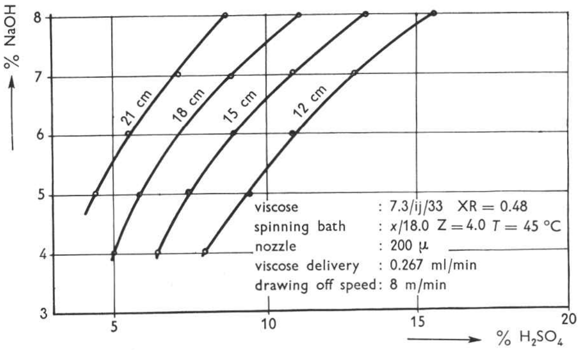


FIG. III-8 SP_{10} as a function of the H_2SO_4-content of the spinning bath and the NaOH-content of the viscose.

Xanthate ratio

Practically no effect on the SP- and NP-distance was established. A small positive effect is found at very low H_2SO_4-contents of the spinning bath ($< 2\%$ H_2SO_4).

Cellulose content and viscosity

Practically no influence on SP_{10} and NP_{10} was found.

Bath temperature

It has a pronounced effect, of the order of 2%/degree centigrade. This necessitates the use of a thermostat to maintain the bath temperature constant.

Sodium sulfate and magnesium sulfate

Practically no influence on NP_{10} was found. Na_2SO_4 has a small positive effect on NP_4.

Zinc sulfate (FIG. III-9, 10)

In the above experiments the zinc content has been kept constant at 4%. However, the presence and the amount of $ZnSO_4$ in the bath have a peculiar effect.

In the undoped process it has no influence on the NP (as such it is comparable with the other sulfates); it has, however, a marked effect on the SP. The SP-distance increases with increasing amounts of $ZnSO_4$, an effect which levels off at higher $ZnSO_4$-concentrations.

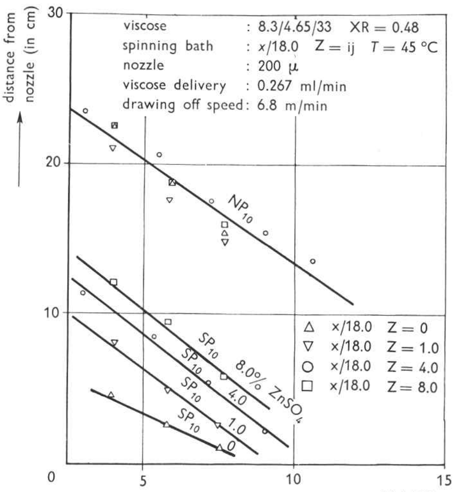
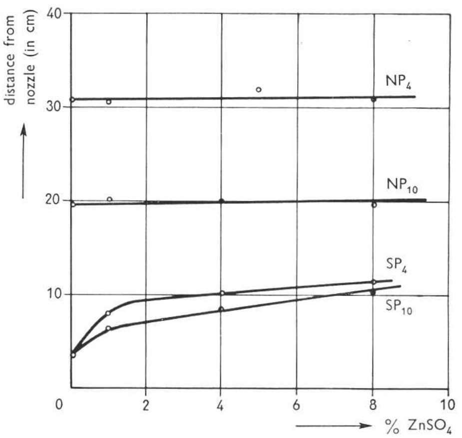


FIG. III-9 NP_{10} and SP_{10} as functions of the H_2SO_4-content of the spinning bath. Results obtained on varying the $ZnSO_4$-content of the spinning bath.



viscose : 8.3/4.65/33 XR = 0.48
spinning bath : 5.0/18.0 Z = x T = 45 °C
nozzle : 200 μ
viscose delivery : 0.267 ml/min
drawing off speed: 6.8 m/min
pH-indicators : thymolphthalein (pH_{10})
bromophenol blue (pH_4)

FIG. III-10 NP and SP as functions of the $ZnSO_4$-content of the spinning bath. Measurements carried out with different-indicators.

Doped spinning conditions (FIGS. III-11–14)

When no zinc sulfate is present in the bath (and no other metal-ion is present which can cause skin-cellulose formation) no effect of a dope is found.

When dope and zinc sulfate are present in the bath and when the acid-alkali balance and XR are such as required for the spinning of an all-skin yarn, the NP is displaced away from the nozzle.

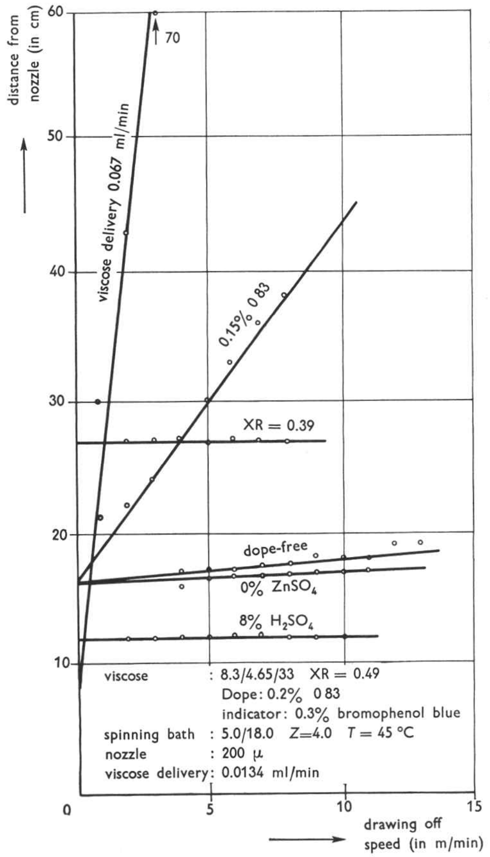


FIG. III-11 Colour change of bromophenol blue in the core of the spinning filament as a function of the drawing-off speed.
Results obtained on varying some parameters of the doped spinning conditions.
Departures from the standard spinning conditions are given in the figure.

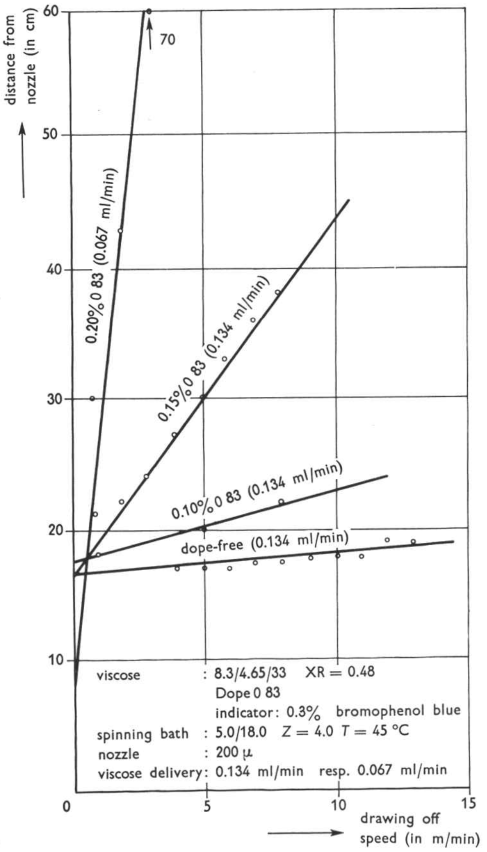


FIG. III-12 Colour change of bromophenol blue in the core of the spinning filament as a function of the drawing-off speed. Results obtained on varying the amount of dope in the viscose.

Under these spinning conditions the NP is linearly dependent on the drawing-off speed. Extrapolating the measurements to drawing-off speed equal to zero, the same distance is found as for the NP in the undoped spinning process (FIG. III-13).

The slope of the curve indicating the relationship between the distance from the nozzle and the drawing-off speed is dependent on the balance of all the factors required for obtaining an all-skin yarn (FIG. III-11).

Maladjustment of any factor in this balance, *e.g.* too low or too high an acid content of the spinning bath, generally results in skin-core differentiated

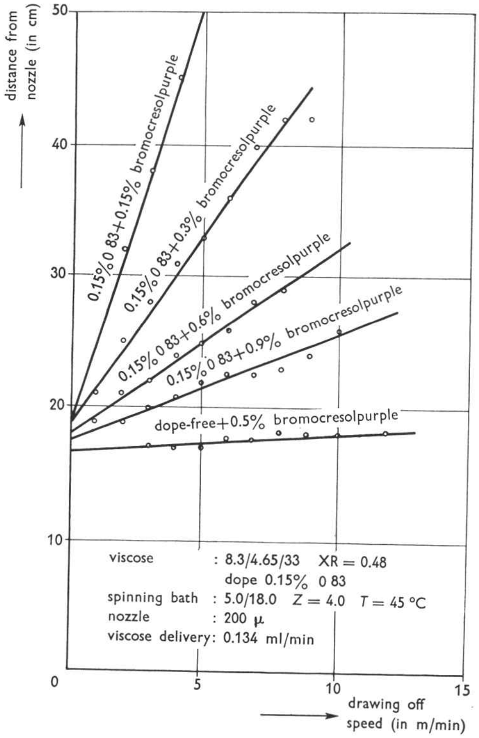


FIG. III-13 Colour change of bromocresol purple in the core of the spinning filament as a function of the drawing off speed.
Results obtained on varying the amount of indicator.

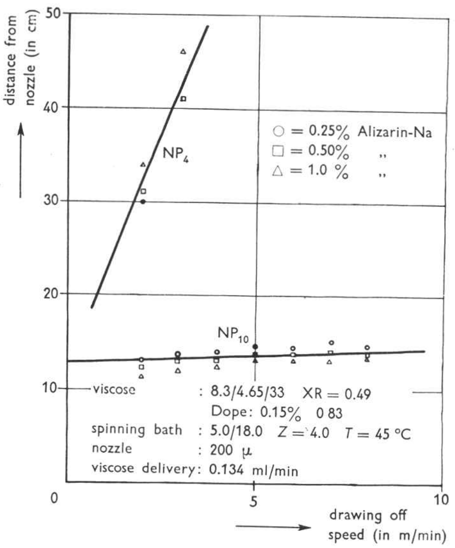


FIG. III-14 Colour change of Alizarin-Na in the core of the spinning filament as a function of the drawing off speed.
Results obtained on varying the amount of indicator.

products and decreases or eliminates this slope; this includes the variations connected with the type and amount of dope (FIG. III-12, in which the slope observed probably reflects the effectiveness of the dope in co-producing the all-skin yarn).

The slope furthermore appears to be dependent on the type and, notably with the indicator bromocresolpurple, on the amount of indicator used:
in the doped spinning process the distance of colour change on using unspecified amounts of bromocresolpurple (pH at colour change in vitro ~ 6) can *e.g.* be

further away from the nozzle than the distance of colour change on using bromophenol-blue (pH of colour change in vitro ~ 4), the amount of which does not play a role (FIG. III-13).

With Alizarine-Na two NP-distances could be determined: NP_{10}, which is independent of the drawing-off speed, and NP_4, which is linearly dependent on it (FIG. III-14). However, NP_4, as determined with this indicator, is found at much larger distances from the nozzle than NP_4 as determined with bromophenolblue.

Discussion

The experimental results can be checked against the predictions based on the diffusion theory.

For this purpose the following assumptions and restrictions are made:

1. The observed colour change of the indicators is dependent only on the $H^+ + OH^- \rightarrow H_2O$ neutralization reaction, the rate of which is only determined by the diffusion.
2. Though the neutralization process involves a many-component system, it can presumably be described by a single concentration-independent diffusion coefficient $D_{H^+} = D_{OH^-} = D$.
   Mathematically the OH-ion concentration in the spinning filament (c_b at $t = 0$) is considered to be equivalent to a negative H^+-concentration.
3. The spinning bath is considered to have a time-independent H^+-concentration $= c_a$ and to be perfectly mixed right up to the surface of the spinning filament.
4. The analytical concentrations of the components are assumed to be those for which the diffusion equation still holds.
5. If not the total series but only the first term of the solution of the diffusion equation is retained, this means that regard should only be paid to not too small distances from the nozzle.

The first assumption formulates the model on which our approach to the neutralization process is based. The other assumptions are less fundamental, but are mathematically required in order that the simple solution of the diffusion equation (as given in CHAPTER II) may be applied. As such they are equivalent to the mathematical restrictions for which this solution holds.

The spinning relations can now be found back clearly in the experimental NP-determinations in the undoped-spinning process. The NP is observed on the centreline of the spinning filament (*i.e.* at $r = 0$) and is, for a certain indicator, connected with a certain pH (*i.e.* with a certain value of c). So, the

NP-determinations measure c $(r = 0, t)$, which, for a certain indicator, is a constant.

On varying the parameters of the spinning process it was found that:

a. with a given indicator the NP-distances are linearly dependent on the viscose delivery (in agreement with spinning relation Ia);
b. with a given indicator the NP-distances are independent of the drawing-off speed (in agreement with spinning relation Ib);
c. for a H_2SO_4-content of the spinning bath $= 0$, the NP-measurements suggest that the pH on the centreline of the filament varies linearly with the distance from the nozzle (in agreement with spinning relation II);
d. the relation between viscose alkali and spinning bath acid combinations, which result in the same NP-distance, is reasonably in agreement with the linear relation predicted by spinning relation III;
e. the effect of the temperature is of the order of magnitude (2–3%/°C) which may be expected for the temperature dependence of the diffusion coefficient.

Combining these phenomena, it follows that:

$$\mathrm{NP} = \mathrm{f}\left\{D(T);\ \frac{t}{r_0^2};\ c_{\mathrm{acid}};\ c_{\mathrm{alkali}}\right\}$$

It is concluded that the agreement between the relevant experimental results and the theoretical diffusion spinning relations justifies the postulated mechanism for the neutralization process: a diffusion-triggered, spontaneous neutralization reaction.

In our opinion, the conclusion may probably not be drawn so far as to include the justification of the total frame-work of assumptions and restrictions. Though our experimental data do not show the contrary, it seems hard to believe that this many-component system (including the viscose buffer salts) can be described by a single constant diffusion coefficient. Also the buffering action of the viscose salts has entirely been left out of account, though it may be added that this buffering action actually was not found back in the experimentally determined course of the pH-distance from the nozzle.

A further complication is that the protons are also consumed by the immobile cellulose xanthate ions. However, since this is only important at low pH-values (pK_{diss} (xanthic acid) $\simeq 1.7$), this can only restrict but not invalidate the conclusion.

There is, however, a rather serious discrepancy between theory and experiment in the observation that zinc affects the starting point: the theoretical equi-pH-line should start right at the nozzle, except for a diffusion-controlling laminar layer. It is hard to understand, however, that zinc-sulfate in the bath would affect this laminar layer at all, and it would then be even more difficult to digest the observation that the NP is left undisturbed, which would mean that the overall diffusion process is not hampered.

Since the effect of zinc on the starting point and the effect of both zinc+dope on the neutralization point run parallel to the formation of skin cellulose on the outside of the filament or throughout the cross-section, the conclusion seems to be that the *colour change of the indicators in skin-forming processes is not only dependent on the pure* H^+*–*OH^-*-diffusion i.e. pH , but also on some more factors pertaining to the skin-cellulose formation.*

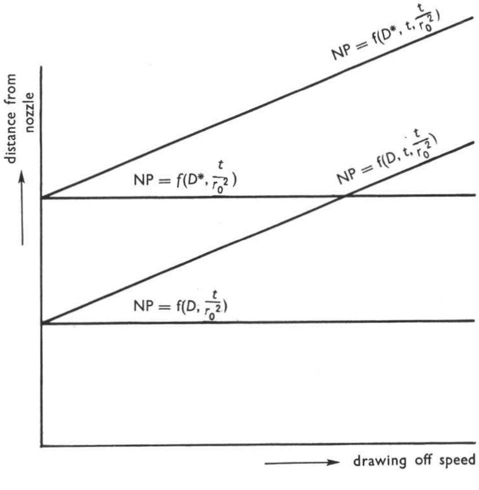
The linear dependence of the NP in the doped-spinning process on the drawing-off speed suggests that some other time-consuming process is involved under these conditions.

$$\mathrm{NP} = \mathrm{f}\left(D, \frac{t}{r_0^2}\right) \text{ for the classical process}$$

$$\mathrm{NP} = \mathrm{f}\left(D, t, \frac{t}{r_0^2}\right) \text{ for the doped-spinning process.}$$

Furthermore the extrapolation to a drawing-off speed equal to zero suggests the absence of any hampering effects on the diffusion. These effects would require

$$\mathrm{NP} = \mathrm{f}\left(D^*, t, \frac{t}{r_0^2}\right) \text{ in which } D^* \text{ means a numerically altered diffusion coefficient.}$$



The effects found in varying the type and amount of indicator suggest an interaction between the indicator and the structure of the gel formed in or during skin-cellulose formation, by which interaction the colour of the negative indicator ion is retained.

Some related phenomena

Empirically it is known that the alkali (in the viscose) – acid (in the spinning bath) balance is an important factor in determining the properties of the yarn obtained.

This can be illustrated by the dependence of the so-called ultimate swelling value, $(SV)_{\mathrm{lim}}$, on this balance.

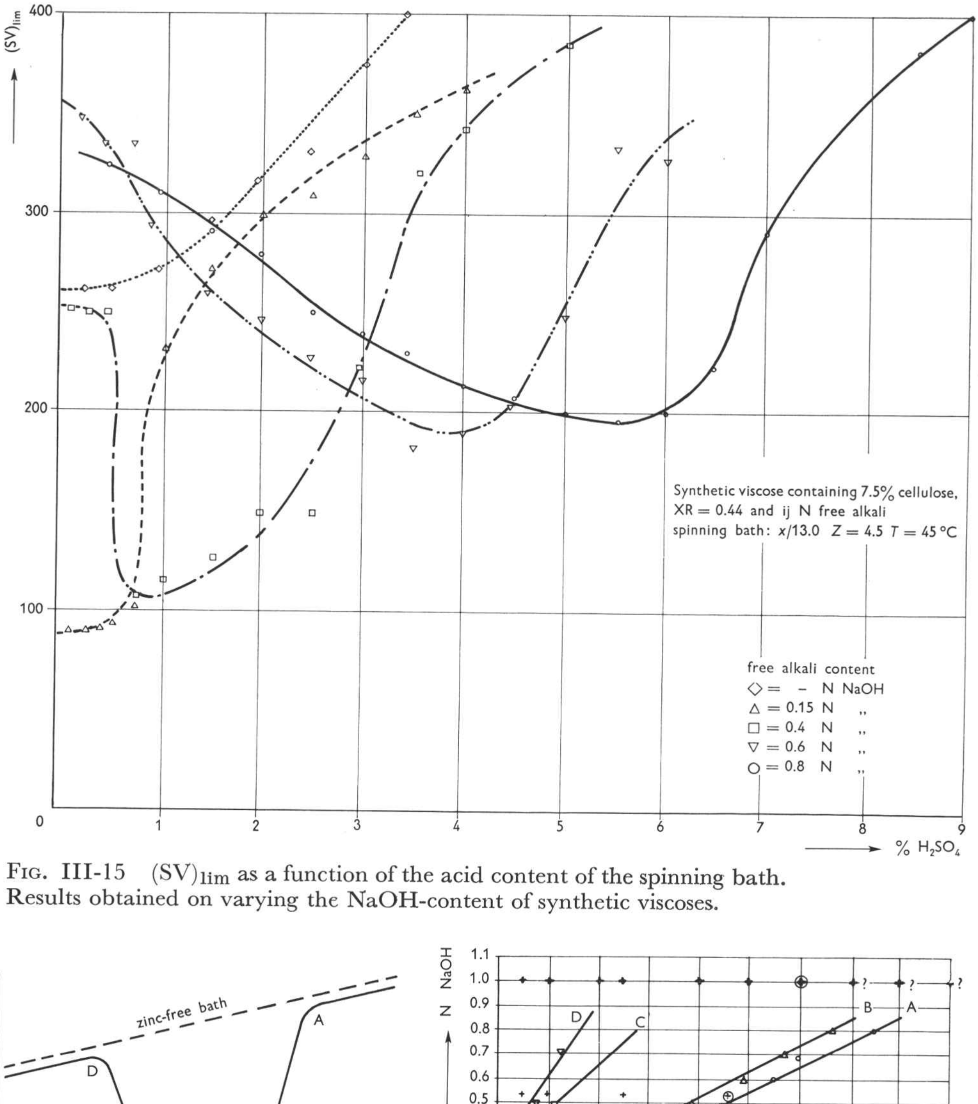


FIG. III-15 $(SV)_{lim}$ as a function of the acid content of the spinning bath. Results obtained on varying the NaOH-content of synthetic viscoses.

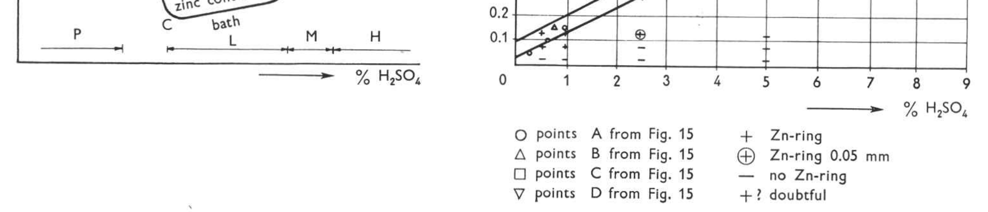


FIG. III-16 Correlation diagram (see text pag. 40).

On varying the alkali content of the viscose, the $(SV)_{lim}$-H_2SO_4 graphs are essentially comparable, but are displaced along the acid-axis. This is shown in FIG. III-15 giving the results obtained with synthetic viscoses (prepared by dissolving chemically pure Na-cellulose xanthate in aqueous NaOH-solutions).

It appears now (FIG. III-16) that the alkali-acid concentrations corresponding to the breaks A, B, C and D meet reasonably well the requirements of spinning-relation III (*viz.* the straightline relationship).

This leads to the conclusion that the difference in yarn properties obtained in the different spinning regions is connected with the H^+—OH^- diffusion conditions.

The transport of zinc ions into the spinning filament will be partly dependent on the H^+—OH^- diffusion. In the system $H^+ + Zn^{++}$—OH^-, the transport of zinc-ions will, under appropriate conditions of concentrations, be disturbed by the formation of the immobile $Zn(OH)_2$ precipitate.

The coexistence of the ions is as given by the solubility-product

$$L_{sol} = [Zn^{++}]\,[OH^-]^2 = 10^{-16}$$

e.g.

pOH =	pH =	pZn =
6	8	4
$6^1/_2$	$7^1/_2$	3
7	7	2
$7^1/_2$	$6^1/_2$	1

Between pH $\sim$ 6 and pH $\sim$ 8 a sharp decrease of activity of the zinc ions will be found.

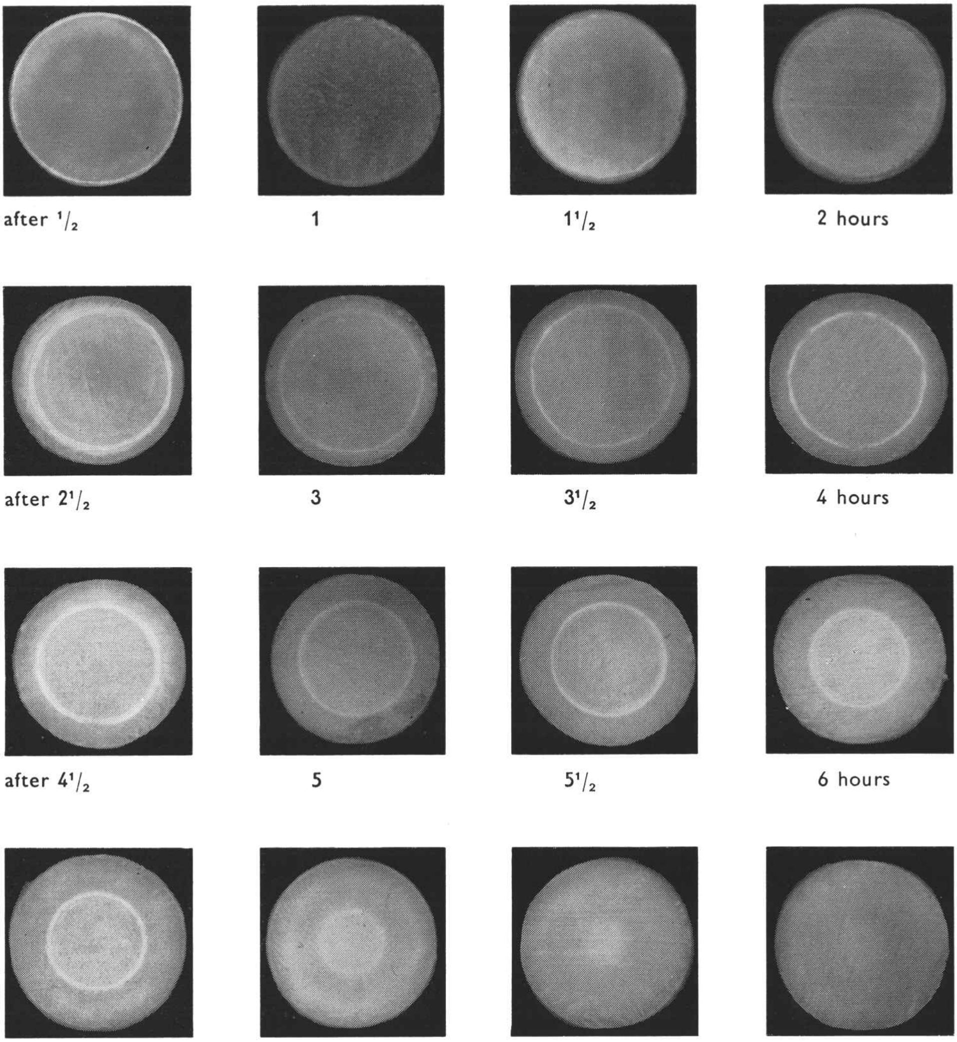
Unfortunately, we were not able to measure the zinc concentrations in the spinning filament itself.

A model experiment was therefore set up, using thick cylindrical cellulose gels (thickness $\sim$ 2 cm, cellulose content $\sim$ 10%) soaked in NaOH-solutions.

The gels were obtained by heat-coagulating viscose in glass tubes, followed by thorough washing. These gels were submerged in baths of various compositions. To study the cylindrical diffusion process, thin slices were cut out of the cylinder at such distances from the end faces that linear diffusion through the end faces could not be a disturbing factor.

FIG. III-17 shows a contact print of these slices on photographic paper: $Zn(OH)_2$ is visible as a white ring. With increasing time of diffusion these rings decrease in diameter, increase in thickness and get more diffuse, till they disappear at some distance from the centre. The pH in front of the rings appeared to be $> \sim 8$, behind the rings $< \sim 6$.

The displacement of the $Zn(OH)_2$-rings with time and the effect of varying


after $^1/_2$ 1 $1^1/_2$ 2 hours

after $2^1/_2$ 3 $3^1/_2$ 4 hours

after $4^1/_2$ 5 $5^1/_2$ 6 hours

after $6^1/_2$ 7 $7^1/_2$ 8 hours

FIG. III-17 The diffusion of zinc into NaOH containing cylindrical media.
Legenda: Soaking bath: 1N NaOH
Diffusion bath: 1.0/14.0 $Z = 4.5$ $T = 45$ °C

the alkali (in the cylindrical gel) – acid (in the bath) combination corresponded well with the mathematical description of the H^+—OH^- cylindrical diffusion process.

So one might say that the $Zn(OH)_2$ rings function as pH-indicator

Apparently the Zn^{++}-ions move in front of the H^+-ions:

$Zn(OH)_2$ is precipitated, in consequence of which the zinc diffusion is effectively blocked; the protons on the low pH-side of the ring then dissolve the $Zn(OH)_2$ again. Protons and zinc ions move essentially synchronously, the rate being determined by the diffusion of the protons.

In these studies a more important factor turned up, however. FIG. III-16 summarizes the results obtained at various alkali-acid combinations:

the alkali (in the cylinder) – acid (in the bath) balance determines whether $Zn(OH)_2$ is formed or not. With high acid – low alkali combinations the protons apparently move much faster into the cylinder than the zinc-ions and no $Zn(OH)_2$ is formed.

The border-line between the region of acid-alkali combinations where $Zn(OH)_2$ is formed and the region where it is not formed, suggests again a straight-line relationship (*cf.* Relation III).

Confronting these observations with those represented in the $(SV)_{\mathrm{lim}}$— H_2SO_4 graphs (see FIG. III-15 and the introduction p. 16), it seems sensible to assume that, at H_2SO_4-contents $<$ B, the zinc-ions are present in the spinning filament before the pH is rather low:
this holds for the acid-poor and the low-acid regions.

However, under the high-acid spinning conditions (H_2SO_4-contents above A), the effect of the respective concentrations on the diffusion is such that the protons have appreciably acidified a certain volume element before the zinc ions arrive.

Literature

1. H. KLARE and A. GROBE, Faserforschung **10** – 155 (1959).
A. GROBE, H. KLARE and R. MARON, Faserforschung **10** – 455 (1959).

HOOFDSTUK IV

THE SEQUENCE OF REACTIONS ON SPINNING VISCOSE IN ZINC CONTAINING BATHS

A number of phenomena in the viscose spinning process suggests a possibly specific role of the zinc ions present in the spinning bath. In the first place they are responsible, though in an as yet unexplained way, for the formation of the so-called skin cellulose. Empirically it has furthermore been established that zinc salts in the spinning bath have a retarding effect on the rate of regeneration of the spinning filament, which is much larger than the effect of salts such as Na_2SO_4, $(NH_4)_2SO_4$ or $MgSO_4$.

In an attempt to attack these questions we started with a speculation that zinc reacts with xanthate ions, resulting in the formation of a complex. Preliminary experiments, in which K-ethylxanthate was used as a model compound, confirmed this hypothesis. The investigation was then directed to a study of the decomposition kinetics in systems made up of K-ethylxanthate, H^+-ions and Zn^{++}-ions.

Working hypothesis regarding the reaction mechanism

The decomposition of K-ethylxanthate (KX) in zinc-free, acidic aqueous systems has been investigated by Cranendonk and Iwasaki and Cooke which authors also review older measurements [1].

Their results show that the first-order decompostion kinetics in these media can consistently be described by the reaction steps:

$$HX \rightarrow ROH + CS_2 \quad \text{(IV-1)}$$

$$H^+ + X^- \rightleftarrows HX \quad \text{(IV-2)}$$

Reaction (IV-1), which, in these media, is kinetically a first order reaction, describes the rate character of the decomposition.

The equilibrium (IV-2) is instantaneous and describes the pH-dependence of the system.

Our working hypothesis is that, in the presence of zinc ions, additionally one or more zinc-xanthate complex-equilibria appear:

$$\begin{array}{l} Zn^{++} + X^- \rightleftarrows ZnX^+ \\ ZnX^+ + X^- \rightleftarrows ZnX_2 \\ - - - - - - - - \\ \hline Zn^{++} + nX^- \rightleftarrows ZnX_n^{(n-2)-} \end{array}$$

Preliminary experiments

On mixing a solution of K-ethylxanthate with a solution containing zinc ions, a white precipitate can be obtained. Analytically it is the compound ZnX_2; it is sparingly soluble in water; the solubility product in water was determined as

$$L_{sol} = [Zn^{++}]\,[X^-]^2 \simeq 10^{-8}$$

However, it dissolves appreciably in a number of organic solvents, such as benzene, CS_2, CCl_4 (on gentle heating), which suggests a non-ionic, complex or chelate character of this compound.

It also dissolves readily in excess K-ethylxanthate solution, whereas in the same amount of water no dissolution occurs. This suggests the formation of ZnX_3^- and /or higher complexes.

Polarographic determinations *) revealed the equilibrium

$$Zn^{++} + 3X^- \rightleftarrows ZnX_3^-$$

$$K_{comp} = \frac{[Zn^{++}]\,[X^-]^3}{[ZnX_3^-]} \simeq 10^{-4.7}$$

These complex-equilibria suggest the presence of yet another species, *viz.* ZnX^+, in solutions containing excess Zn^{++}-ions.

It was then tried to obtain further information from a kinetic study of the decomposition in acidic, zinc-containing media.

Equilibria and salt effects

One of the difficulties met in determining equilibrium constants from kinetic measurements is the incongruence between activities and concentrations.

This appears to be especially difficult in studying systems containing zinc ions, since also the zinc salts of many mineral acids ($ZnCl_2$, $ZnSO_4$) are incompletely ionized.

The attention was therefore directed to the system $(ZnNO_3)_2 + HNO_3$, since the activity coefficients reported for pure $Zn(NO_3)_2$-solutions lead to the expectation that here complete ionization is present [2].

Even then, however, there exists the difficulty of a general effect of salt on the equilibria to be studied:

acting on an equilibrium involving ionic species, *e.g.* $H^+ + X^- \rightleftarrows HX$, the undissociated form will in general be disfavoured.

How the salt effect influences the overall rate of the decomposition will

---

*) The determinations were made with a Tinsley recording polarograph, type V 722.15, Zn^{++}-concentration 0.001 N $ZnSO_4$, supporting electrolyte 0.1 N KCl, temperature $T = 20\,°C$, maximum suppressor Tergitol N P X, $E_{1/2}$ in the absence of K-ethylxanthate = 1.02 V, K-ethylxanthate concentrations varied in the concentration range 0.01—1 N.

moreover depend on the course of the reaction mechanism: *e.g.* whether as transition state a charged or uncharged activated complex is involved.

We therefore attempted to isolate the specific effect of the postulated complex-equilibrium $X^- + Zn^{++} \rightleftarrows ZnX^+$ on the rate of decomposition by comparing the effect of zinc ions with the effect of magnesium ions, assuming that magnesium ions do not result in complex-formation with xanthate ions.

On using $Zn(NO_3)_2$ and $Mg(NO_3)_2$, the salt effect of both compounds is presumably comparable, since, in pure solutions, the activity coefficients of $Zn(NO_3)_2$ and $Mg(NO_3)_2$ are known to be comparable [3].

Mathematical treatment of the model

In the homogeneous system (under such conditions of pH and Zn^{++}-concentration that the species X^-, HX and ZnX^+ are present in finite amounts) the decomposition, if described by the reactions:

$$HX \rightarrow ROH + CS_2 \quad \ldots \quad (IV\text{-}1)$$

$$X^- + H^+ \rightleftarrows HX \quad \ldots \quad (IV\text{-}2)$$

$$X^- + Zn^{++} \rightleftarrows ZnX^+ \quad \ldots \quad (IV\text{-}3)$$

$$K_{diss} = \frac{[H^+]\,[X^-]}{[HX]} \qquad K_{I_{compl}} = \frac{[Zn^{++}]\,[X^-]}{[ZnX^+]}$$

is expressed by

$$\frac{d[HX]}{dt} = -k[HX] - \frac{d[X^-]}{dt} - \frac{d[ZnX^+]}{dt} \quad \ldots \quad (IV\text{-}4)$$

(A change in [HX] in the system will also bring about a change in $[X^-]$ and $[ZnX^+]$.)

In terms of $[X_{total}]$ (IV-4) gives:

$$\frac{d\{[HX]+[X^-]+[ZnX^+]\}}{dt} = \frac{d[X_{total}]}{dt} = -k[HX]$$

which, on substituting (IV-2) and (IV-3), results in:

$$\frac{d[X_{total}]}{[X_{tot}]} = d\ln[X_{total}] = -k\,\frac{1}{1 + \frac{K_{diss}}{[H^+]}\left(1 + \frac{[Zn^{++}]}{K_{compl}}\right)}\,dt$$

By using the concept of a half-lifetime $t_{1/2}$, *i.e.* the time interval $t_2 - t_1$ for which *e.g.* $[X_{total}]_{t_2} = {}^1/_2[X_{total}]_{t_1}$, this results in:

$$\boxed{t_{1/2} = \frac{\ln 2}{k}\left\{1 + \frac{K_{diss}}{[H^+]}\left(1 + \frac{[Zn^{++}]}{K_{compl}}\right)\right\}}$$

Consequently, from determinations of $t_{1/2}$ at varying $[H^+]$ and $[Zn^{++}]$ the constants k, K_{diss} and $K_{I_{compl}}$ can be evaluated.
N.B. Equivalent results are obtained on solving the equations in terms of HX or X^- or ZnX^+ instead of X_{total}.

Physically a separation of variables can be obtained under the following conditions:

I. At a sufficiently high proton concentration (= sufficiently low pH) and sufficiently low zinc concentration:

$$t_{1/2} \simeq \frac{\ln 2}{k}, \text{ for } K_{diss}\left(1 + \frac{Zn^{++}}{K_{compl}}\right) \ll [H^+],$$

because then $\left\{1 + \frac{K_{diss}}{[H^+]}\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right)\right\} \simeq 1;$

i.e. at sufficiently low pH-values, a pH-independent constant value is obtained for $t_{1/2}$, from which k can be evaluated.

N.B. At a constant $[Zn^{++}]$ it is possible to define an apparent dissociation constant.

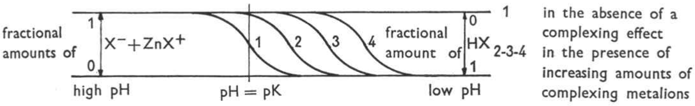
$$K_{app} = K_{diss}\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right)$$

Analogously to $pK_{diss}(= -\log K_{diss})$, which is numerically equal to the pH at which the ionization of a weak acid is half-complete (*i.e.* 50% non-ionized acid is present) it follows from

$$\frac{[HX]}{[X^-]+[ZnX^+]} = \frac{[H^+]}{K_{diss}\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right)} = \frac{[H^+]}{K_{app}}$$

that $pK_{app}(= -\log K_{app})$ gives numerically the pH-value at which 50% undissociated acid is present in the case of complex-formation: *in the presence of complexing metal ions, the acid "behaves" like a stronger one.*

Schematically this appears on plotting the fractional amounts of the xanthate and xanthic acid in dependence on the pH:



II. At a sufficiently low proton concentration (=sufficiently high pH) and sufficiently low zinc concentration:

$$t_{1/2} \simeq \frac{\ln 2}{k}\cdot\frac{K_{diss}}{[H^+]}, \text{ for } K_{diss} \gg [H^+] \quad \text{and} \quad [Zn^{++}] \ll K_{I_{compl}},$$

because then $\left\{1 + \frac{K_{diss}}{[H^+]}\left(1 + \frac{Zn^{++}}{K_{I_{compl}}}\right)\right\} \simeq \frac{K_{diss}}{H^+};$

i.e. at sufficiently high pH-values a plot of $t_{1/2}$ *against* $\frac{1}{[H^+]}$ *is a straight line with a slope of* $\frac{\ln 2}{k}\cdot K_{diss}$; or, alternately, *a plot of log* $t_{1/2}$ *against* $-\log[H^+] = pH$ *is a straight line with unit slope and an intercept* $= \log K_{diss}\cdot\frac{\ln 2}{k}$.

III. At a given constant $[H^+]$:

$$t_{1/2} = \frac{\ln 2}{k}\cdot\frac{K_{diss}}{[H^+]}\cdot\frac{[Zn^{++}]}{K_{I_{compl}}} + \frac{\ln 2}{k}\left(1 + \frac{K_{diss}}{[H^+]}\right)$$

results in a straight-line relationship between $t_{1/2}$ and $[Zn^{++}]$ with a slope of $\frac{\ln 2}{k}\cdot\frac{K_{diss}}{[H^+]}\cdot\frac{1}{K_{I_{compl}}}$.

Comparing half-lifetimes (at constant $[H^+]$) determined in the absence of zinc, $t_{1/2}{}^{\circ *}$, with those determined in the presence of $[Zn^{++}]$, $t_{1/2}$, one obtains:

$$t_{1/2} - t_{1/2}{}^{\circ *} = \frac{\ln 2}{k}\cdot\frac{K_{diss}}{[H^+]}\cdot\frac{[Zn^{++}]}{K_{I_{compl}}}$$

$$\boxed{\frac{t_{1/2} - t_{1/2}{}^{\circ *}}{t_{1/2}{}^{\circ *} - \frac{\ln 2}{k}} = \frac{[Zn^{++}]}{K_{I_{compl}}}}$$

Experimental systems

The following experimental systems were investigated:

1. Extending the investigations of CRANENDONK, decomposition measurements were carried out at different temperatures in systems containing mineral acid of various concentrations. These measurements were then evaluated on the basis of the reaction steps:

   $H^+ + X^- \rightleftarrows HX$

   $HX \rightarrow ROH + CS_2$

   Activity coefficients in this part of the investigations were neglected except for their effect on the pH. The knowledge of $[H^+]$ in these media was obtained either directly by pH-measurements or, in the higher concentration range of mineral acid, by calculation with the aid of activity coefficients of the mineral acid obtained from the literature [4].

   Since activity coefficients of the various mineral acids are best known for aqueous HCl-solutions, HCl was used in these systems.

2. To study the order of magnitude of general salt effects on the overall rate of decomposition, the decomposition rates were determined in systems composed of $HCl+NaCl$.
   This pair of components was chosen again on the basis of available literature data on the activity coefficients in aqueous $HCl+NaCl$ solutions.
   Quite probably the effect of alkali salts can only be a general salt effect, since the alkali xanthates are strong electrolytes: in the concentration range 0.003–0.05 N K-ethylxanthate has a constant equivalent conductivity.
3. Parallel runs of measurements were carried out in homogeneous media composed of either $HNO_3+Zn(NO_3)_2$ (in excess) or $HNO_3+Mg(NO_3)_2$. The evaluation of these measurements was carried out on the basis of the reaction steps:

$$H^+ + X^- \rightleftarrows HX$$

$$Zn^{++} + X^- \rightleftarrows ZnX^+$$

$$HX \rightarrow ROH + CS_2$$

   It was assumed in this evaluation that general salt-effects could be elimated by comparing the two systems.

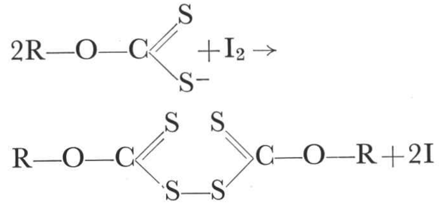
Experimental part

Standard procedures

Method A. Measurements involving the determination of $[X_{total}]$ in pH-buffered systems. This method has been described in detail by CRANENDONK (l.c.).

A solution of about 50 mg K-ethylxanthate in 25 cm³ water of the desired temperature is added as fast as possible with the aid of a pipette with a large discharge opening to an ample excess (about 600 cm³) of an aqueous solution of the required mineral acid and salt concentration and temperature.

At the required time the decomposition reaction is stopped by rapidly adding a NaOH-solution in the smallest excess required. The solution is buffered to pH ~ 7.0 with CO_2 and titrated with I_2.



The results are plotted as log $[X_{total}]$ against t, from which linear plot the half lifetime $t_{1/2}$ is obtained.

Method B. Measurements involving the determination of $\frac{\mathrm{d}[\mathrm{X}^-]}{\mathrm{d}t}$ in an unbuffered system having a constant pH.

To a solution of about 0.130 g K-ethylxanthate in 50 cm³ water of the desired temperature mineral acid is added as fast as possible, whilst stirring, till the desired pH has been reached. The amount of mineral acid required to keep this pH-value constant is determined in dependence on the time:

$$A = \frac{\mathrm{d}(\text{mineral acid})}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{X}^-]}{\mathrm{d}t}$$

The results are plotted as log A against t, from which plot the half lifetime $t_{1/2}$ is obtained.

Experimental results

Systems composed of mineral acid

The $t_{1/2}$-values obtained with systems made up of only K-ethylxanthate and mineral acid (HCl) are plotted in FIG. IV-1 as log $t_{1/2}$ against pH.

The graphs show that at the higher acid concentrations and in the absence of salts a constant value for $t_{1/2}$ is obtained, indicating that under these conditions the xanthate is (almost) entirely present as undissociated xanthic acid.

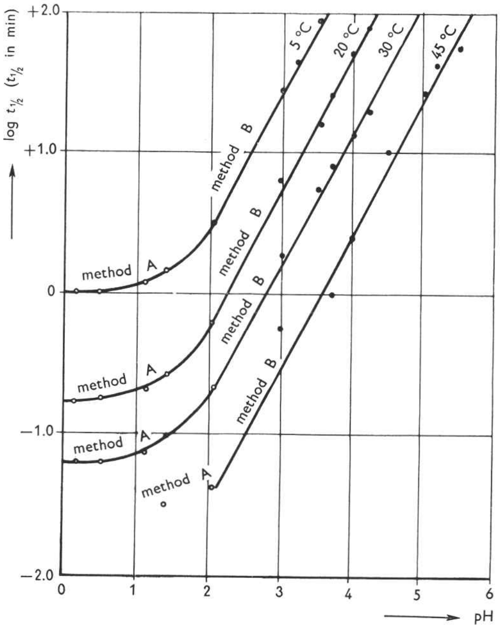


FIG. IV-1 Graphs of log $t_{1/2}$—pH for the decomposition of ethylxanthate.

Evaluation of the experimental data (compare the sections on the mathematical treatment of data) shows that they can be described by the sequence of reactions (compare **Cranendonk** l.c.):

$$H^+ + X^- \rightleftarrows HX \qquad K = \frac{[H^+]\,[X^-]}{HX}$$

$$HX \rightarrow ROH + CS_2 \qquad \frac{d[HX]}{dt} = -k[HX]$$

Inclusive of the results found by **Cranendonk** at 0 °C and by **Iwasaki** & **Cooke** at 23,5 °C the following values were obtained (Table 1):

Table 1

	0 °C	5 °C	20 °C	23.5 °C	30 °C	45 °C
$t_{1/2}$(at low pH)	–	62″=1.03′	11′=0.18′	–	4″=0.062′	
log $t_{1/2}$(at low pH)	–	0.01	−0.74	–	−1.21	
k	0.39 min^{-1}	0.67 min^{-1}	3.8 min^{-1}	4.3 min^{-1}	10.5 min^{-1}	
K/k		0.039	0.0071		0.0018	0.00039
K	0.023	0.026	0.027	0.020	0.020	
pK= −log K	1.64	1.59	1.57	1.70	1.70	

From the rate-constants at different temperatures an activation energy of 19 k cal/mol can be calculated.

The constant value obtained for $t_{1/2}$ in a wide range of HCl-concentrations (*e.g.* $t_{1/2}$ (5 °C) = 1.03′ for 0.2–1 N HCl) suggests the absence of large electrolyte effects on the mechanism of the overall-reaction:

$$HX \rightarrow ROH + CS_2$$

So, the effect of electrolytes on the reacting system:

$$H^+ + X^- \rightleftarrows HX$$

$$HX \rightarrow ROH + CS_2$$

is quite probably only an effect on the dissociation equilibrium.

Systems composed of mineral acid and indifferent electrolyte

The magnitude of the salt effect was studied only at 5 °C and appears from a series of measurements in media containing mineral acid+salts (Table IV-2); the dissociation contant K_c evaluated from these measurements was obtained from the equation:

$$t_{1/2} = \frac{\ln 2}{k}\left(1 + \frac{K}{[H^+]}\right)$$

by totally neglecting activity coefficients: $[H^+] = C_{H^+}$.

For the systems made up from 0.01 N HCl + x N NaCl, literature values of $f_{\pm(\mathrm{HCl})}$ are known (HARNED & OWEN l.c.).

For these cases the approximation $[\mathrm{H}^+] = f_{\pm}\,C_{\mathrm{H}^+}$ was tried: $K = K_c \cdot f_{\pm}$.

TABLE 2 Method A; 5 °C

Medium	$f_{\pm(\mathrm{HCl})}$	$t_{1/2}$	K_c	K
$\frac{700}{725}$ × {0.01 N HCl + }	0.906	3.60	0.025	0.022
,, ,, + 0.01 N NaCl	0.876	3.90	0.027	0.024
,, ,, + 0.05 ,,	0.821	4.15	0.030	0.025
,, ,, + 0.10 ,,	0.789	4.33	0.032	0.025
,, ,, + 0.50 ,,	0.737	5.05	0.039	0.028
,, ,, + 1.00 ,,	0.764	5.17	0.040	0.030

Medium	$t_{1/2}$	K_c
$\frac{700}{725}$ × {0.04 N HCl + }	1.62	0.022
,, ,, + 0.01 N NaCl	–	–
,, ,, + 0.05 ,,	1.70	0.025
,, ,, + 0.10 ,,	1.78	0.028
,, ,, + 0.50 ,,	1.97	0.035
,, ,, + 1.00 ,,	1.97	0.035
$\frac{700}{725}$ × {0.1 N HCl + }	1.20	0.016
,, ,, + 0.01 N NaCl	1.22	0.018
,, ,, + 0.05 ,,	1.23	0.019
,, ,, + 0.10 ,,	1.23	0.020
,, ,, + 0.50 ,,	1.42	0.038

It is found that K_c may easily vary by a factor 2; so, a corresponding variation in experimentally determined half-lifetimes can quite probably be ascribed to a general salt effect.

Systems containing zinc ions

On comparing the retarding influence of a number of salts containing kations which are of interest in viscose-spinning, it was found that electrolytes containing kations such as K^+, NH_4^+, Mg^{++} show an effect of an order of magnitude that can be ascribed to a general salt effect.

The retarding action of zinc ions, however, is many times larger (TABLE 3).

TABLE 3 Method A; 5 °C

Medium	$t_{1/2}(Mg)$	$t_{1/2}(Zn)$	$K_{I_{compl}}$ (see text below)
$\frac{700}{725} \times \{0.01\ N\ HNO_3 + \quad \}$	3.73	3.73	–
,, ,, $+ 0.01\ N\ Me(NO_3)_2$	3.84	4.12	0.10
,, ,, $+ 0.05$,,	4.30	5.75	0.11
,, ,, $+ 0.10$,,	4.55	7.20	0.13
,, ,, $+ 0.50$,,	5.62	24.67	0.12
$\frac{700}{725} \times \{0.04\ N\ HNO_3 + \quad \}$	1.75	1.75	–
,, ,, $+ 0.01\ N\ Me(NO_3)_2$	1.75	1.93	0.035
,, ,, $+ 0.05$,,	1.78	2.15	0.10
,, ,, $+ 0.10$,,	1.88	2.48	0.14
,, ,, $+ 0.50$,,	2.13	6.39	0.13
$\frac{700}{725} \times \{0.1\ N\ HNO_3 + \quad \}$	1.18	1.18	–
,, ,, $+ 0.01\ N\ Me(NO_3)_2$	1.23	1.23	–
,, ,, $+ 0.05$,,	1.26	1.32	0.20
,, ,, $+ 0.10$,,	1.28	1.52	0.10
,, ,, $+ 0.50$,,	1.34	3.11	0.09

When we assume that besides the reactions:

$$HX \rightarrow ROH + CS_2 \text{ and } H^+ + X^- \rightleftarrows HX$$

the equilibrium:

$$Zn^{++} + X^- \rightleftarrows ZnX^+$$

plays a role in these homogeneous media, these measurements can be used to determine the value of $K_{I_{compl}} = \frac{[Zn^{++}]\,[X^-]}{[ZnX^+]}$

$$K_{I_{compl}} = [Zn^{++}] \Bigg/ \frac{t_{1/2}(Zn) - t_{1/2}(Mg)}{t_{1/2}(Mg) - \frac{\ln 2}{k}}$$

$$= f_{\pm} C_{Zn^{++}} \Bigg/ \frac{t_{1/2}(Zn) - t_{1/2}(Mg)}{t_{1/2}(Mg) - \frac{\ln 2}{k}}$$

On neglecting the activity coefficient, a value $K_{I_{compl}} \simeq 0.1$ is obtained for the complex-equilibrium constant; $f_{\pm}$ presumably being in the range 0.5–0.7, it seems safe to conclude that $K_{I_{compl}} \simeq 0.05$ and $pK_{I_{compl}} \simeq 1.3$.

Discussion

Though the numerical values of the rate and equilibrium constants as determined for K-ethylxanthate will quite possibly differ from those for cellulose xanthate, the proved complex character of the zinc ethylxanthates is regarded as an indication of the analogous character of zinc cellulose xanthate.

This is confirmed by technological experience: zinc sulfate in the spinning bath exerts a larger retarding effect on the rate of regeneration of the spinning filament than salts such as Na_2SO_4 or $MgSO_4$.

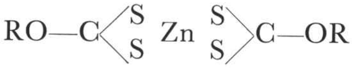
In a still somewhat looser connection one may even say that the technological experience is in harmony with the reaction kinetics dealt with in the preceding part. In spinning processes, where a fast regeneration is required, this is usually carried out with a second bath,

a. containing a sufficiently high concentration of acid,
b. having a sufficiently low zinc content (instances are even known in which chelating agents are used to decrease the activity of zinc),
c. having a sufficiently low Na_2SO_4-content,
d. of a temperature as high as technologically and economically feasible.

The complex character suggests a number of points of interest:

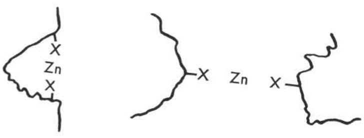
1. The (partly) non-ionic character of the chelate bonds is probably connected with a certain geometrical arrangement of the xanthate groups around the zinc,

   e.g. something like



$$RO{-}C\begin{smallmatrix}S\\S\end{smallmatrix}Zn\begin{smallmatrix}S\\S\end{smallmatrix}C{-}OR$$

   A question of interest is whether the ZnX_2-state, if formed in the case of cellulose xanthate, has an inter- or intra-molecular structure.



   Sterically, the ZnX_3^--state seems improbable in the case of cellulose xanthate.

2. Already in vitro the zinc-xanthates have a limited pH-stability region, defined by the competing equilibria:

$$X^- + H^+ \rightleftarrows HX$$

$$Zn^{++} + nX^- \rightleftarrows ZnX_n^{(n-2)-}$$

$$Zn^{++} + pOH^- \rightleftarrows Zn(OH)_p^{(p-2)-}$$

At high $[H^+]$, *i.e.* low pH, the activity of the xanthate ion becomes too low to result in appreciable zinc xanthate formation. At high $[OH]^-$, *i.e.* high pH, the activity of the zinc ion becomes too small owing to the competing complex formation with OH-ions.

In the spinning filament, however, before the formation of zinc xanthate can take place at all, the diffusion process has to bring the zinc in loco before the pH becomes too low; so, the formation of the insoluble, and therefore immobile, $Zn(OH)_2$ prevents the presence of zinc in places with $pH > \sim 8$.

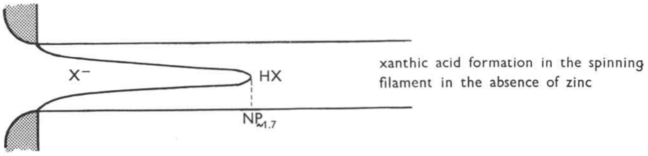
Consequently the possible formation of zinc xanthate in the spinning filament is limited to the region (formulated for the ZnX^+-state):

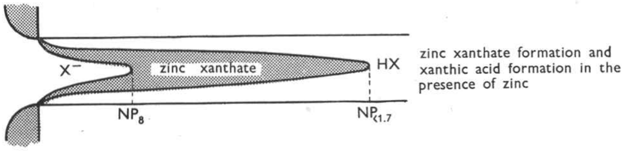
$$\sim 8 > pH > \sim pK_{app} = -\log K_{diss}\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right), \qquad \text{or}$$

$$\sim 8 > pH > \sim pK_{diss} - \log\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right)$$

in which $-\log\left(1 + \frac{[Zn^{++}]}{K_{I_{compl}}}\right)$ reflects the effect of the zinc ions on the pH at which xanthic acid formation begins to play a role.

Schematically pictured for the spinning filament:





Just as in the case of the $Zn(OH)_2$-rings, one expects the phenomenon that (provided there is a sufficient zinc activity for zinc xanthate formation) the zinc xanthate state is nowhere present throughout an *entire* cross-section: the amount present starts with zero at the nozzle, goes through a maximum at a distance from the nozzle corresponding with $NP_{\sim 8}$ and then decreases steadily; between nozzle and $NP_{\sim 8}$ the zinc xanthate state is present as a ring, beyond $NP_{\sim 8}$ as a full circle with decreasing diameter. (Compare APPENDIX II).

Conclusion

On spinning viscose in zinc containing baths it seems justified to assume that besides the neutralisation and decomposition reactions involving the xanthate-group one or more complex-forming reactions of the type

$$Zn^{++} + nX^{-} \rightleftarrows ZnX_n^{(n-2)-} \quad \text{with } n \geqslant 1$$

play a role.

In the diffusion-controlled spinning process this affects the dissociation of the xanthate ion and results in a retarding effect on the formation of xanthic acid.

However, this then requires the presence of zinc in a certain pH-region; *viz.* between pH ~ 8 (precipitation of $Zn(OH)_2$ at higher pH-values) and pH $\sim$ 1–2 (complete suppression of the xanthate-ion equilibria by formation of HX).

$$H^{+} + OH^{-} \rightleftarrows H_2O$$

$$Zn^{++} + 2OH^{-} \rightleftarrows Zn(OH)_2$$

$$H^{+} + X^{-} \rightleftarrows HX$$

$$Zn^{++} + nX^{-} \rightleftarrows ZnX_n^{(n-2)-} \quad \text{with } n \geqslant 1$$

$$HX \rightarrow ROH + CS_2$$

Literature

1. A. Cranendonk, Rec. Trav. Chim. **70** – 431 (1951).
   I. Iwasaki and S. R. B. Cooke, J. Am. Chem. Soc. **80** – 285 (1958).
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4. B. E. Conway Electrochemical Data, Elsevier 1952.
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HOOFDSTUK V

THE COAGULATION PROCESS IN THE SPINNING FILAMENT

Principle of the measurement

By spinning a monofilament, whilst applying stretch deformation at varying distances from the nozzle and measuring the response of the spinning filament towards this deformation, we hoped to obtain information about the course of the coagulation process.

Two methods have been used for studying the deformation effects:

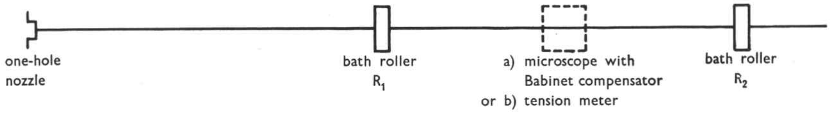
a. measurement of the birefringence (actually: the optical retardation $R = n \times d$) in the spinning filament with the aid of a microscope and a Babinet compensator.
This type of compensator makes it possible to measure differentially over the cross section; the measurements are however limited to circular cross-sections; it follows that *e.g.* filaments spun in zinc-containing spinning baths cannot be investigated by this method.

b. measurement of the deformation tension in the spinning filament with an appropriate method. This method measures integrally over the cross-section, however with no other restrictions.

With both methods the effect of the applied, known stretch deformation can be observed and quantitatively determined.

For applying the stretch deformation, the spinning filament is given one wrap around each of two bath rollers R_1 and R_2 rotating at set, known, different speeds (S_1 and S_2).

Schematically the set-up is as follows:



The bath rollers R_1 and R_2, together with the measuring system, can be moved along the spinning filament by a motor-driven screw.

Apparatus

The set-up for spinning a monofilament has been described in the chapter on the neutralization process in the spinning filament.

A detailed view of the microscopic method of investigation is given in Fig. V-1. The supports for the rollers and microscope can be moved synchronously along the spinning bath by a motor-driven screw.

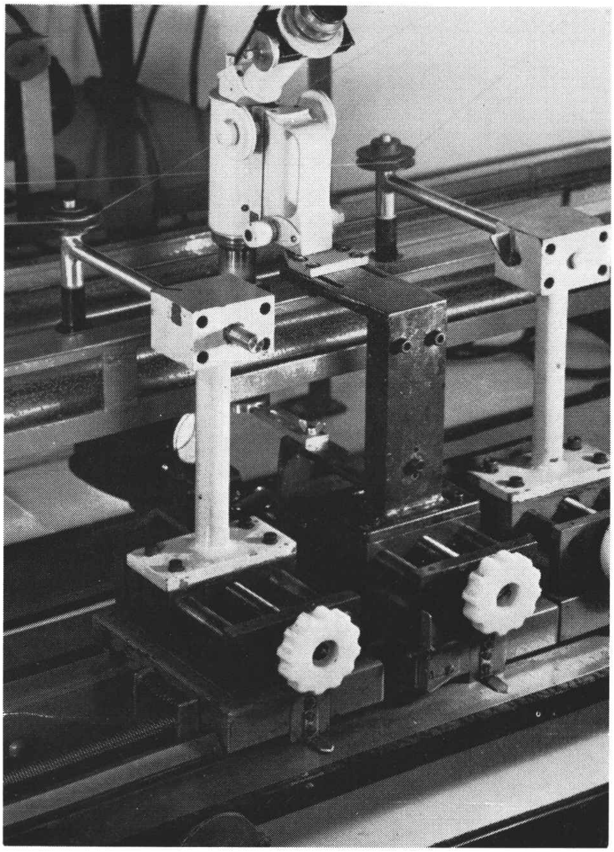


Fig. V-1.

For determining the stretch tensions two instruments are in use, both measuring the tensions against a spring, the displacement of which is measured inductively (Philips – PR 9310). The signal obtained is fed into a bridge (Philips – PR 9300) and recorded (Philips – PR 2200 A 21).

Fig. V-2 shows the use of a torsion balance. This instrument allows the measurements to be carried out while the spinning filament is below the bath surface.

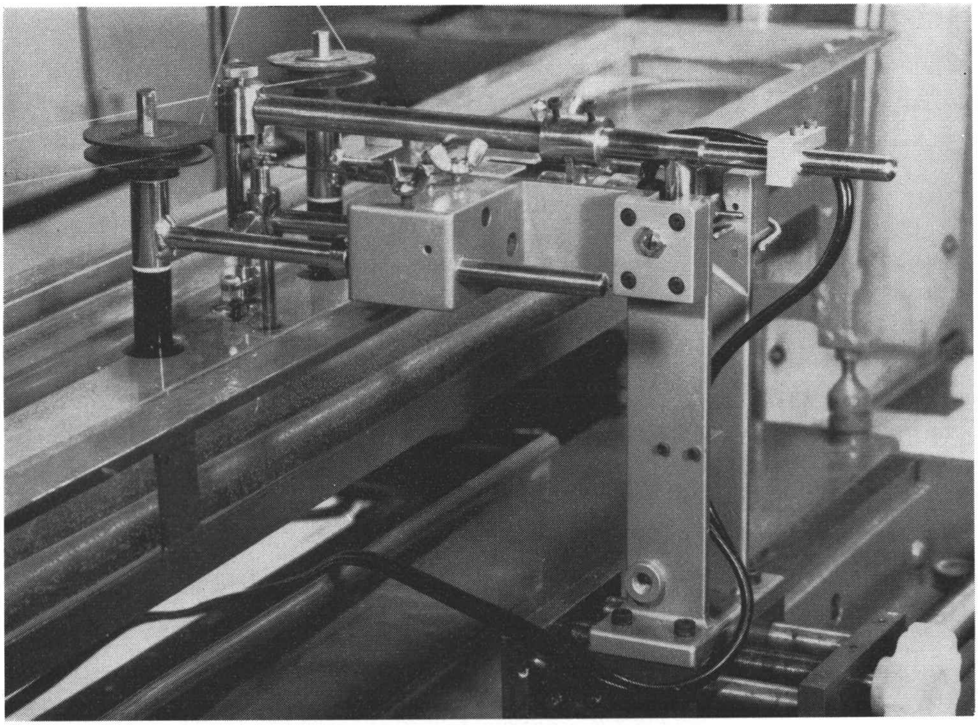


FIG. V-2.

FIG. V-3 shows a leaf-spring balance. When this instrument is applied, the spinning filament leaves the bath surface after the first roller; the stretch tensions are measured in air.

Both instrument give essentially the same results. The leaf-spring balance can more easily be calibrated. With both methods the speed of the rollers is measured by means of the signal of a photocel, the light path of which is interrupted by a vane on the axle of the roller.

The rollers themselves are driven by ropes and variable-speed motors.

The use of the Babinet compensator in this type of investigations is illutrated by the following photograph (FIG. V-4), in which is shown the idealized optical image, as obtained with the Babinet compensator, of a cylindrical material in different stages of inhomogeneity of birefringence.

The first picture gives the optical view when stretch is applied close to the nozzle,

the second picture the view when stretch is applied at a larger distance from the nozzle and

the last picture represents the view obtained on stretching at still larger distances.

A series of pictures showing the optical view of the spinning viscose filament at increasing distances from the nozzle is reproduced in the next photograph (FIG. V-5).

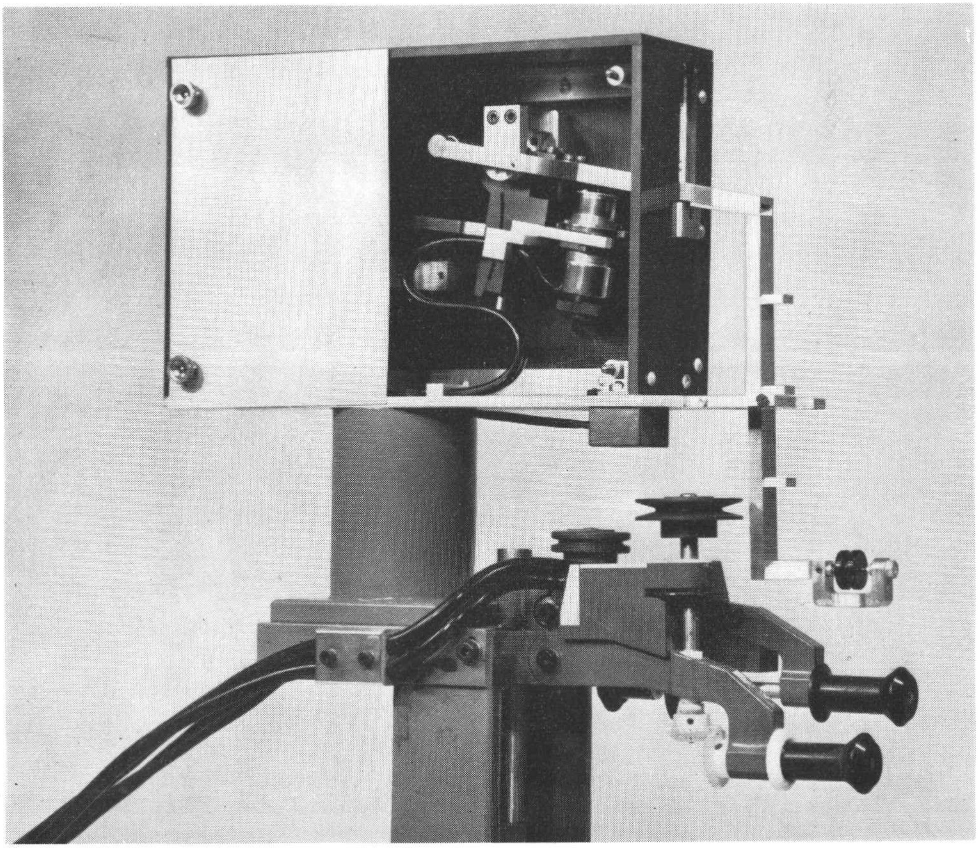
For the quantitative determination, the retardation is measured along the centreline of the filament in dependence on the distance from the nozzle.

The microscopic magnification actually used is 100 times. FIGS. V-6 and V-7 show some results: the graphs refer to experiments in which (FIG. V-6) the drawing-off speed and percentage of stretch applied were varied and in which (FIG. V-7) the viscose delivery was altered.

FIG. V-8 illustrates analogously the results obtained on messuring the stretch tensions at increasing distances from the nozzle; in this case the temperature of the spinning bath was varied.

Both the optical and the tensiometric method reveal that at a certain dis-

FIG. V-3.



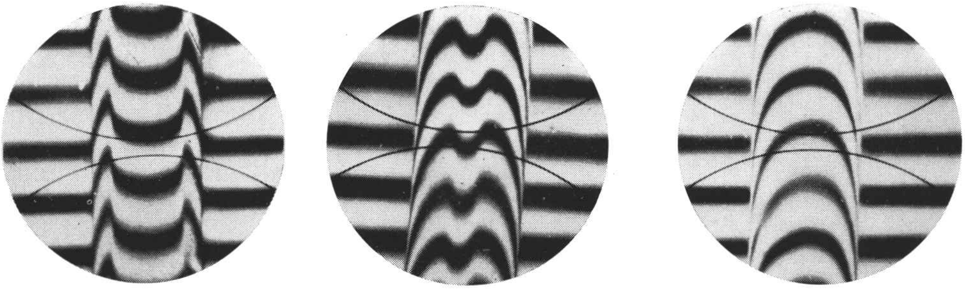
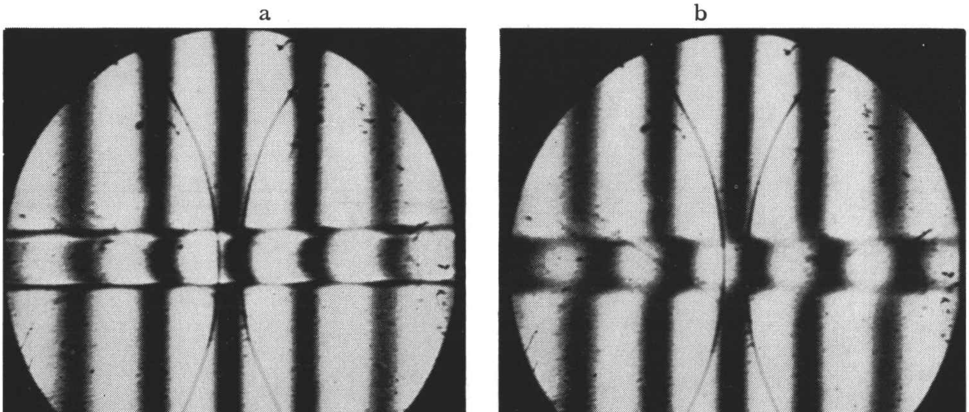


Fig. V-4.

Fig. V-5.



a

b

c

d

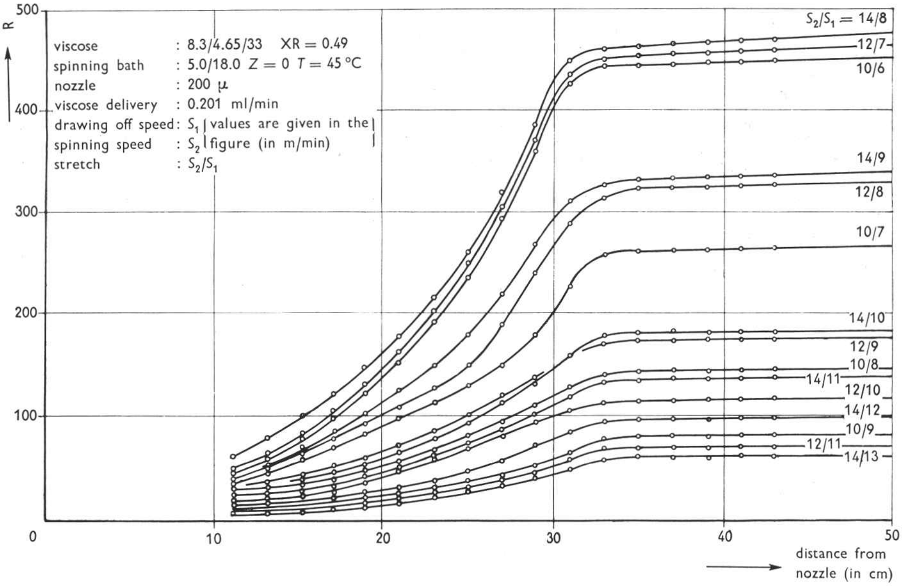


FIG. V-6 Retardation in the spinning filament in dependence on the position of the measuring system.
Measurements obtained on varying the drawing off speed and the stretch.

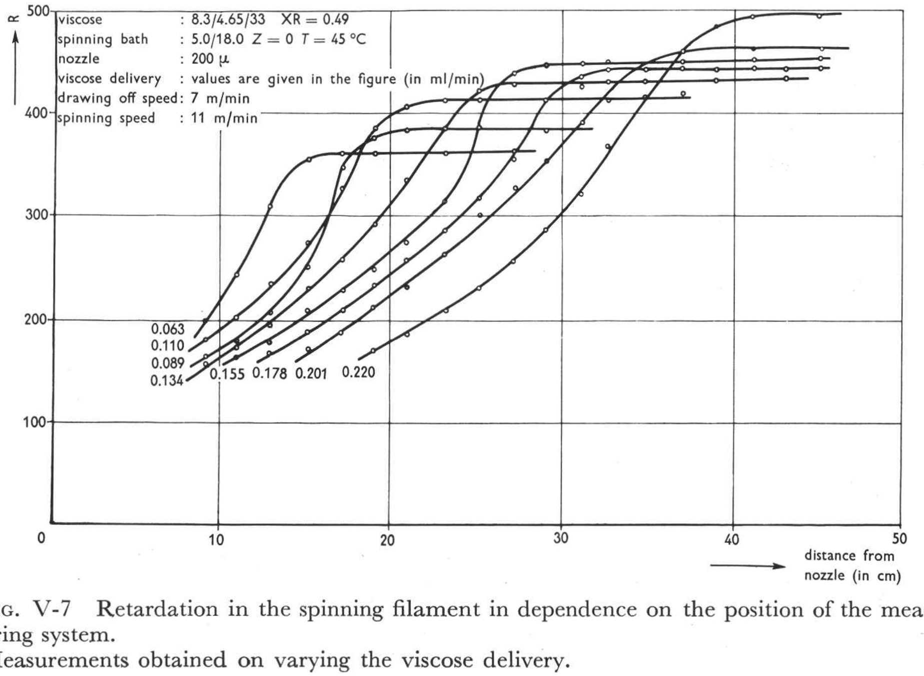
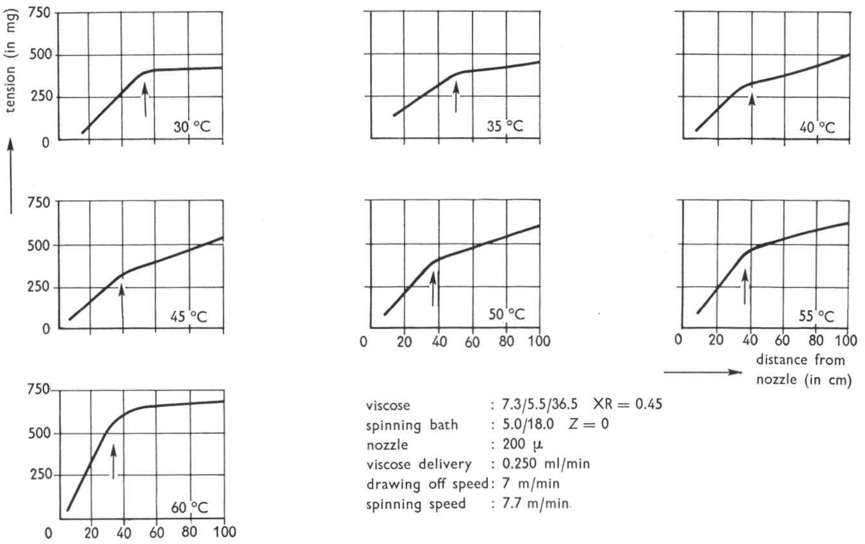


FIG. V-7 Retardation in the spinning filament in dependence on the position of the measuring system.
Measurements obtained on varying the viscose delivery.



viscose : 7.3/5.5/36.5 XR = 0.45
spinning bath : 5.0/18.0 Z = 0
nozzle : 200 μ
viscose delivery : 0.250 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min.

FIG. V-8 Tension-distance graphs obtained with different temperatures of the spinning bath.

tance from the nozzle the response of the spinning filament towards stretch changes more or less abruptly.

In a number of cases even two discontinuities were apparent in the graphs representing the response versus the distance from the nozzle.

We came to regard the distance from the nozzle, which corresponds with this discontinuity, as characteristic of the viscose spinning bath combination under investigation.

Some errors of the measurement

In general the use of the tensiometric method was preferred to the optical one: it gives a permanent, quickly obtainable record, is objective and not restricted in its applicability to spinning conditions which result in a circular cross-section of the spinning filament.

With both methods the difficulties encountered already in measuring the NP- and SP-distances considerably disturb the present type of measurements, since here the measurement involves a larger part of the spinning filament.

Expressed in terms of distance from the nozzle, the inaccuracy is estimated to be ± 5 cm.

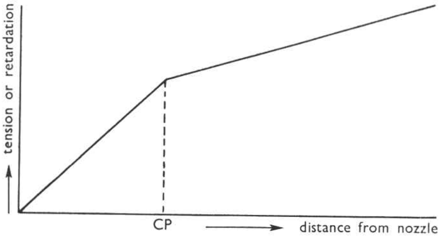
Experimental results. Zinc-free spinning baths

As mentioned in the preceding section, the optical method is limited to spinning conditions which result in circular cross-sections.

Therefore we want to start this account of our investigations with zinc-free spinning baths, to which both methods can be applied.

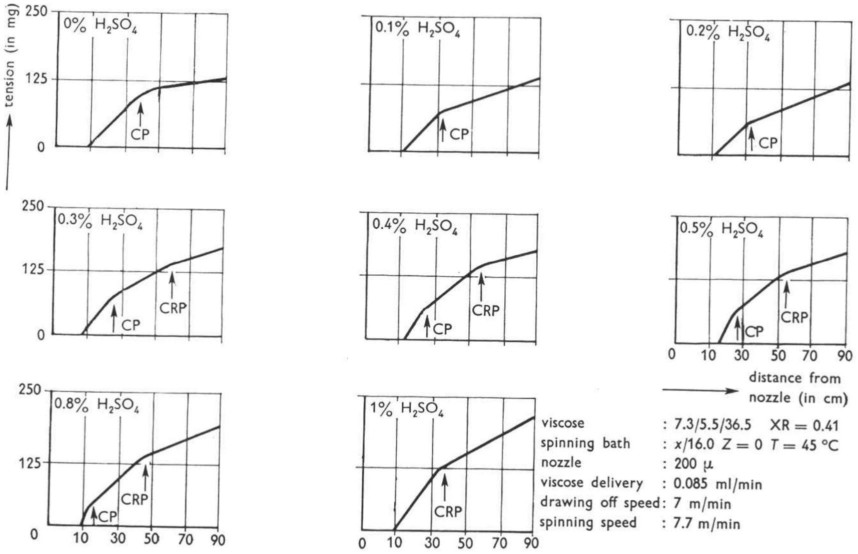
Experiments in which the H_2SO_4-content of the spinning bath was varied

On spinning in zinc-free baths containing salts, *e.g.* $(NH_4)_2SO_4$ or Na_2SO_4, and no or very little H_2SO_4, or in baths containing Na_2SO_4+NaOH, the repsonse of the spinning filament towards deformation shows, idealized, a picture like:



i.e. at a certain distance from the nozzle the increase of the stretch tension or the retardation changes more or less abruptly.

This distance will be labelled: the CP-distance. (The letter combination CP refers to the interpretation given later in this report; it is the *c*oagulation *p*oint).



viscose : 7.3/5.5/36.5 XR = 0.41
spinning bath : x/16.0 $Z = 0$ $T = 45$ °C
nozzle : 200 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. V-9 Tension-distance graphs obtained in acid-poor zinc-free spinning baths.

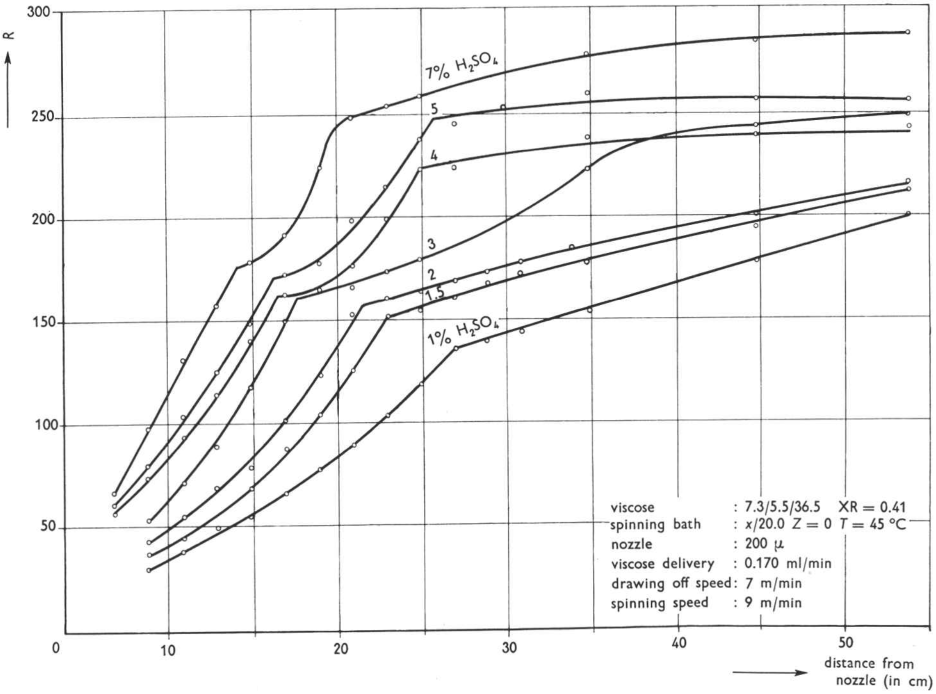
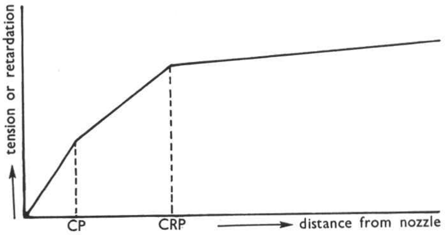


FIG. V-10 Retardation-distance graphs obtained with increasing H_2SO_4-content of the spinning bath.

When small amounts of acid are added to the bath, the CP-distance decreases and a second characteristic distance appears, which will be labelled: the CRP. (See FIGS. V-9 and V-10). (The letter combination CRP refers to the interpretation given later, it is the *p*oint where the original *c*oagulate is *r*einforced).



At still higher H_2SO_4-concentrations in the bath the CP-distance disappears. FIG. V-11 shows the results of CP_{tens} and CRP_{tens} determinations, in which we started with a spinning bath containing Na_2SO_4 and free NaOH.

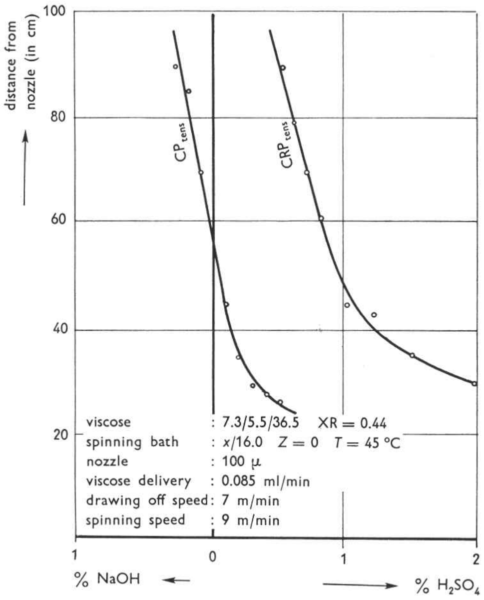


FIG. V-11 CP_{tens} and CRP_{tens} as functions of the H_2SO_4-content of the spinning bath.

When the acid concentrations of the spinning bath are more then about 10%, the optical method can not be applied any more: the spinning filament becomes opaque and very streaky. Investigation of the finished filament obtained at these acid concentrations shows that it is full of holes: it has a spongy structure; it is the acid concentration at which "rottenness" appears.

Generally the harmony between the tensiometric and the optical method is acceptable (taking into account the respective errors which can easily amount to ± 5 cm in the CP- and CRP-distance determinations) (FIG. V-12–13).

$$CP_{opt} \equiv CP_{tens}$$

$$CRP_{opt} \equiv CRP_{tens}$$

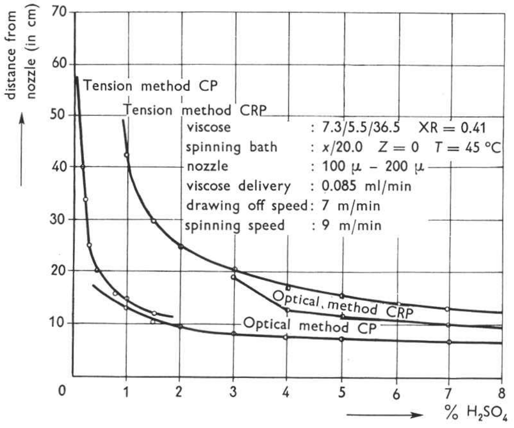


FIG. V-12 CP and CRP as functions of the H_2SO_4 content of the spinning bath.

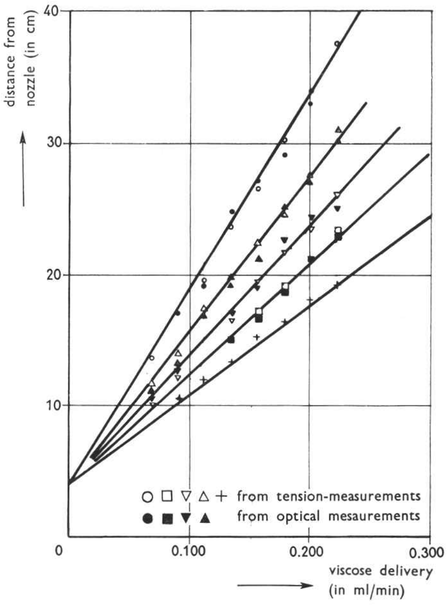


FIG. V-13 Uncorrected CP- and/or CRP-distances as functions of the viscose delivery.
Results obtained with different viscose spinning bath combinations.

In individual instances, however, there is not so good a harmony between both methods. This refers to spinning in acid-free and acid-poor baths (where CP_{tens} is larger than CP_{opt}); this is possibly due to the difficulties of the optical method.

Very often the optical method applied to the entire acid-range (0–ca. 10%) reveals only a single characteristic distance. From the dependence of this distance on Na_2SO_4-variations and XR-variations and from its confrontation with NP-determinations, it can be judged whether the discontinuity found represents the CP- or the CRP-distance.

Variations including the other parameters of the spinning process

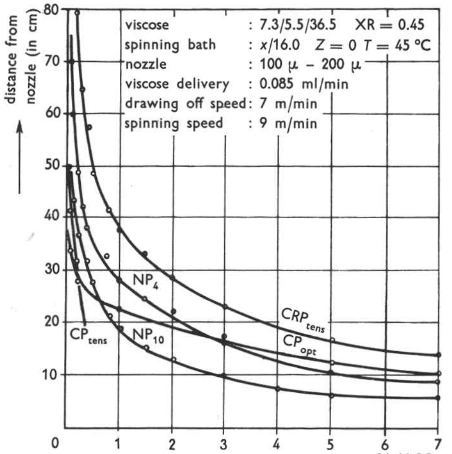
It has now been found that:

a. for a certain viscose spinning bath combination the distances CP and CRP are:
   1. independent of the drawing-off speed (compare Fig. V-6),
   2. linearly dependent on the viscose delivery (compare Fig. V-13),

   i.e. CP and CRP meet the requirements of a cylindrical diffusion process;

b. the CP-distance is dependent on:
   1. the XR of the viscose: the higher the XR, the larger the CP,
   2. the salt content of the bath: the higher the concentration, the smaller the CP,
   3. the type of salt used: in equimolecular amounts $(NH_4)_2SO_4$ leads to much smaller CP-distances than Na_2SO_4,
   4. the alkali content of the bath: the higher the NaOH-content, the larger the CP,
   5. neither the cellulose content of the viscose nor the DP;

c. the CP-distance is not tied up with a fixed pH-value (see *e.g.* Fig. V-14)*) The pH at the CP-distance is dependent on:
   1. the H_2SO_4-content of the spinning bath,
   2. the Na_2SO_4-content of the spinning bath,
   3. the XR of the viscose.



viscose : 7.3/5.5/36.5 XR = 0.45
spinning bath : x/16.0 Z = 0 T = 45 °C
nozzle : 100 μ – 200 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 9 m/min

Fig. V-14 CP, CRP, NP_{10} and NP_4 as functions of the H_2SO_4-content of the spinning bath.

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*) NP_{10}, NP_6 and NP_4 were determined as described in Chapter III and the pH at the CP-distance was obtained from graphs as those in Chapter III, Fig. 3.

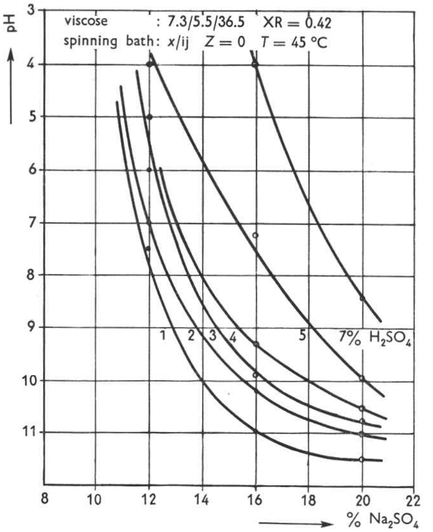


FIG. V-15 pH in the core of the spinning filament at the CP_{opt}-distance as a function of the Na_2SO_4 content of the spinning bath.
Results obtained on varying the H_2SO_4-content of the spinning bath.

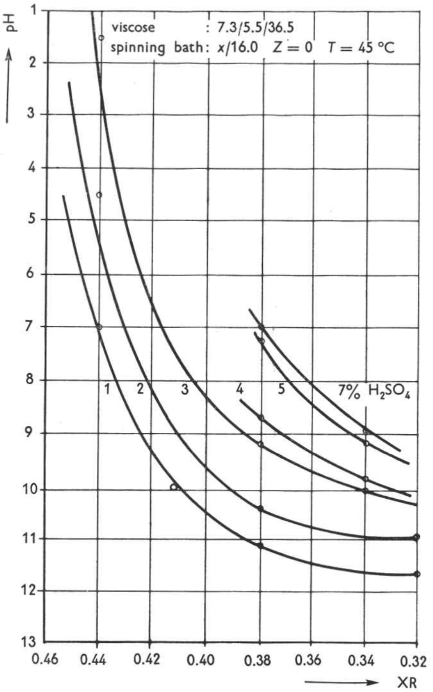


FIG. V-16 pH in the core of the spinning filament at the CP_{opt}-distance as a function of the XR of the viscose.
Results obtained on varying the H_2SO_4-content of the spinning bath.

As extreme pH-values were found 12 and 2. (Compare FIGS. V-14, 15 and 16).

d. The CRP-distance was found to be affected only by those parameters of the viscose spinning bath combination which also affect the neutralization process, *i.e.* mainly the alkali-acid balance.
The CRP-distance coincides with $NP_{\sim 2}$.

e. On spinning in various zinc-free baths, the tension values at the CRP-distance vary hardly at a certain viscose delivery and drawing-off speed and when a certain amount of stretch is applied.

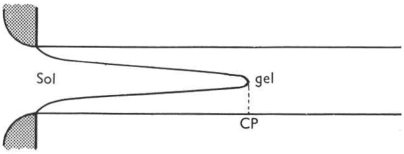
Interpretation of the experimental results obtained with zinc-free baths

The characteristics of the CP-distance suggest that it represents the sol→gel transition.

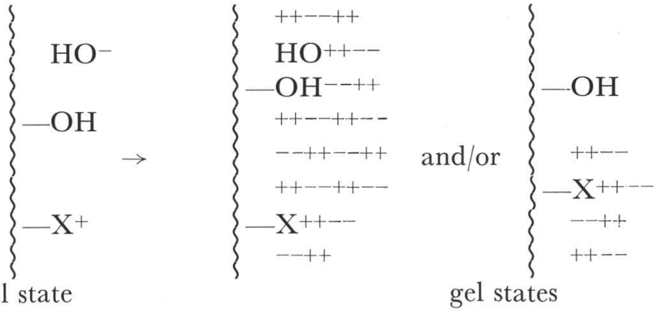
By analogy an argument is found for this in the solubility behaviour of cellulose xanthate (APPENDIX III), which also is affected by:

a. the XR of the cellulose xanthate
b. the pH of the medium
c. the type and amount of salts in the medium.

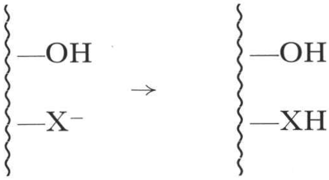
When this interpretation is accepted, the CP represents the distance from the nozzle where, under the influence of diffusion processes, the sol → gel transition, the coagulation process, has progressed to the centre line of the spinning filament: it is the coagulation point: CP.



Expressed in symbols it is the transition:

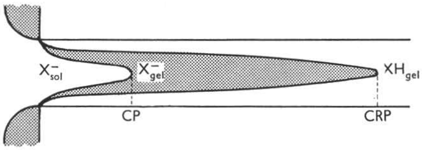


From the coincidence of the CRP with NP$_{\sim 2}$ the interpretation is derived that the CRP reflects the xanthate → xanthic acid transition



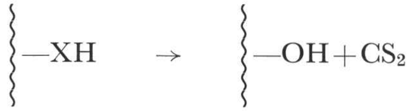
So this transition occurs in an already coagulated state (except in the extreme case when the coagulation is brought about by the xanthate → xanthic acid transition).

On the basis of the stretch tensions at the CRP (which are higher than those at the CP) and of the model description which (on the ground of the decreased charge density, *i.e.* decreased inter-chain repulsion) suggests a more coherent network, the CRP-discontinuity reflects a reinforcement of the already coagulated material: it is labelled the coagulate reinforcement point: CRP.



By describing the CRP-discontinuity as reflecting the transition to the xanthic acid state, we do not intend to say that at the CRP-distance the transition to the xanthic acid state is stoechiometrically complete. In fact the CRP-discontinuity is observed with spinning baths of such a low H_2SO_4-content (0.2–0.3%) that this leads to the conclusion that partial formation of the xanthic acid state already is sufficient to give rise to the CRP-discontinuity.

The cellulose xanthic acid starts to decompose (in a first order reaction-rate) immediately after its formation.



$$—XH \rightarrow —OH + CS_2$$

The cohesion forces of the network are presumably increased by the decomposition (decrease of steric repulsion, possibly additional H-bridge formation).

The effect of the temperature of the spinning bath (Fig. V-5) on the stretch tensions at and beyond the CRP-distance is tentatively understood as being tied up with this effect of the decomposition.

At low temperatures the stretch tensions beyond the CRP-distance remain at a rather constant level over the distances measured; apparently the decomposition does not play a role yet.

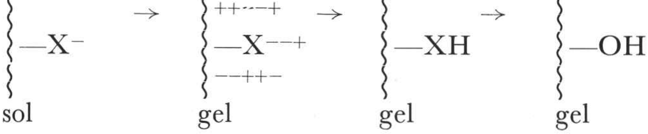
At high temperatures the stretch tensions beyond the CRP-distances also remain constant, though at a higher level; presumably the rate of decomposition is so fast that as soon as xanthic acid is formed, it is decomposed fully: the stretch tension at the CRP-distance reflects already the properties of the decomposed state.

At intermediate temperatures (40–55 °C), however, the stretch tensions beyond the CRP-distance still increase: to our understanding this reflects the conditions under which the rate of decomposition and the rate of diffusion are numerically comparable.

The optical method very often only discloses the sol → gel transition. Apparently the chemical changes occurring after the birth of the gel-state affect the stress-optical behaviour of the material not so much as the sol → gel transition. Optically, the material in the later stages still reflects the structure obtained at its birth.

The tension measurements on the contrary reveal all the changes affecting the coherence of the gel.

In the order



the inter-chain repulsion forces decrease, *i.e.* the cohesion forces of the network increase.

Summarizing, the following model picture emerges: the sol → gel transition leads to a network with primary-junction points, which persist through the next stages and determine the overall geometry and the overall optical deformation behaviour; subsequent chemical changes introduce secundary-junction points (without, however, basically altering the relative position of the primary junction points) by which the force necessary to obtain the deformation is determined.

This model corresponds with that developed by HERMANS and VERMAAS [1].

Literature

1. P. H. HERMANS and D. VERMAAS, Physics and Chemistry of cellulose fibers, 1946.

CHAPTER VI

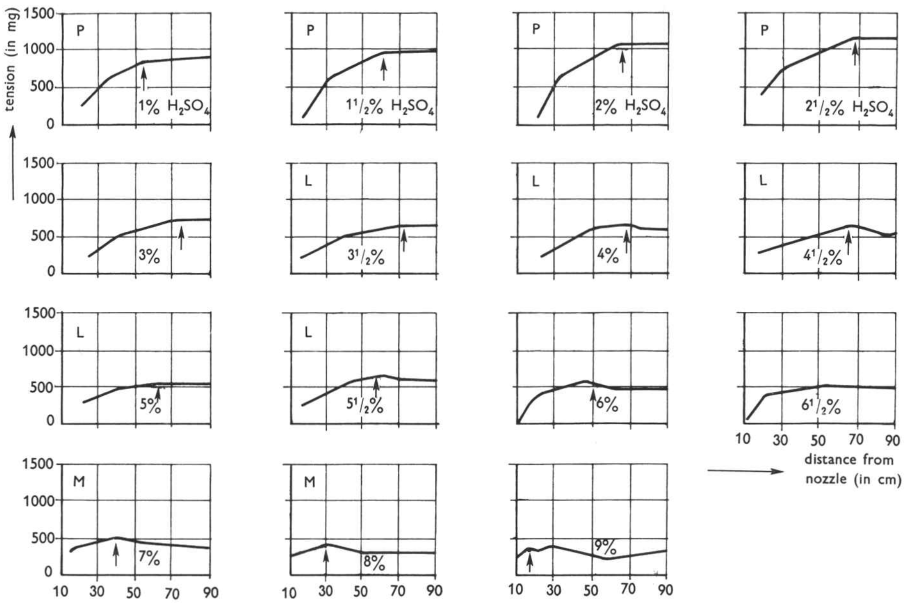
THE ROLE OF ZINC IN THE COAGULATION PROCESS

Experimental Part

Introduction

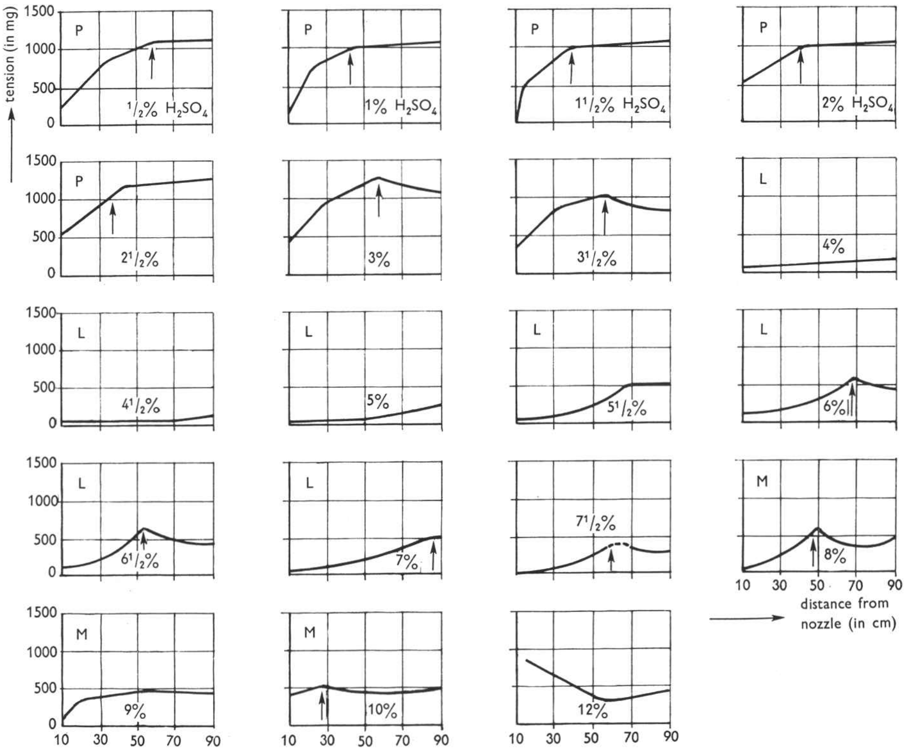
In order to investigate the course of the coagulation process on spinning in zinc-containing baths, the same technique was applied as described in CHAPTER V. However, only the tension-distance measurements could be carried out. The optical method failed owing to the more or less serrated cross-sections of the spinning filament.

In general, the graphs representing the tension-distance measurements,



viscose : 7.3/5.5/36.5 XR = 0.47
spinning bath : x/13.0 $Z = 4.0$ $T = 48$ °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-1 Tension-distance graphs obtained with varying H_2SO_4-content of the spinning bath.

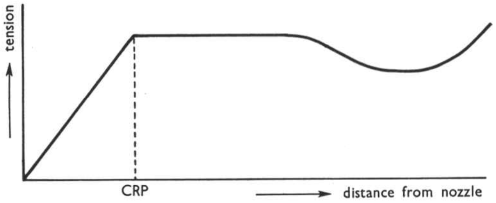


viscose : 7.3/5.5/36.5 XR = 0.43
spinning bath : x/18.0 $Z = 4.5$ $T = 45$ °C
Dope 0.11% 0 83
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG VI-2 Tension-distance graphs obtained with varying H_2SO_4-content of the spinning bath.

taken on these viscose spinning bath combinations show more variety and more detail than those referring to spinning in zinc-free baths. Compare FIGS. VI-1, 2, 3.

A composite reconstruction of the assembled tension-distance graphs shows a course like: *)



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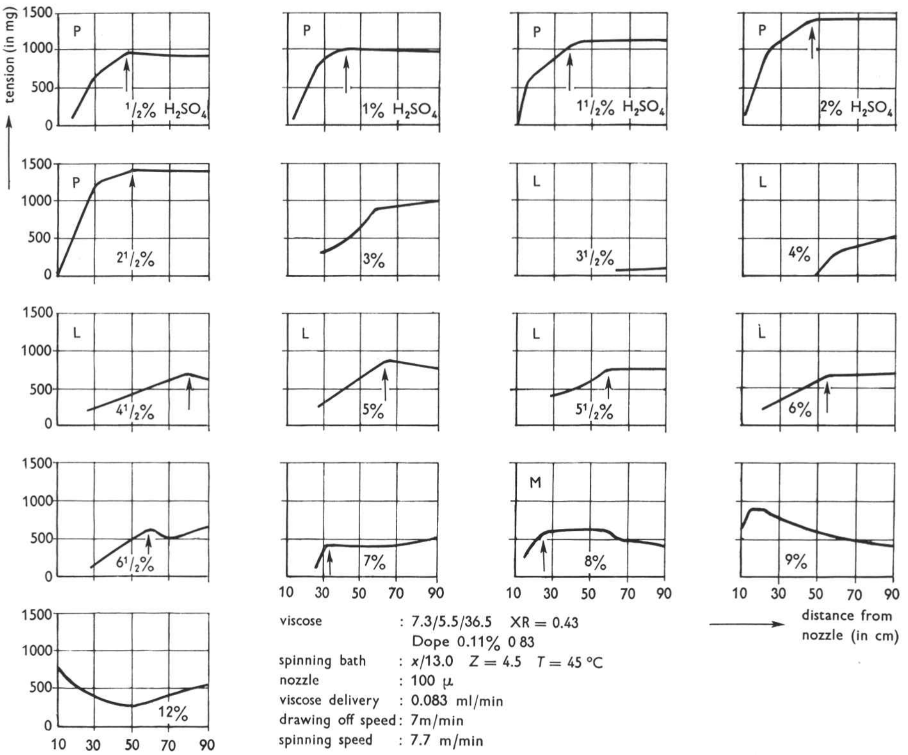
*) Between nozzle and CRP-distance there sometimes seems to be another discontinuity; in general, this could not be reproduced, however.



viscose : 7.3/5.5/36.5 XR = 0.43
Dope 0.11% 0 83
spinning bath : x/13.0 Z = 4.5 T = 45 °C
nozzle : 100 μ
viscose delivery : 0.083 ml/min
drawing off speed: 7m/min
spinning speed : 7.7 m/min

FIG. VI-3 Tension-distance graphs obtained with varying H_2SO_4-content of the spinning bath.

Under the different spinning conditions one or more of the features of the reconstruction are met. Our attention was in general directed towards the distance again labelled CRP, which was found to develop from the CRP in zinc-free spinning systems.

On testing the diffusion requirements, it was found that these CRP-distances behave in harmony with the diffusion spinning relations; for a certain viscose spinning bath combination the CRP-distances as obtained in zinc-containing spinning baths are also:

a. independent of the drawing-off speed,
b. linearly dependent on the viscose delivery.

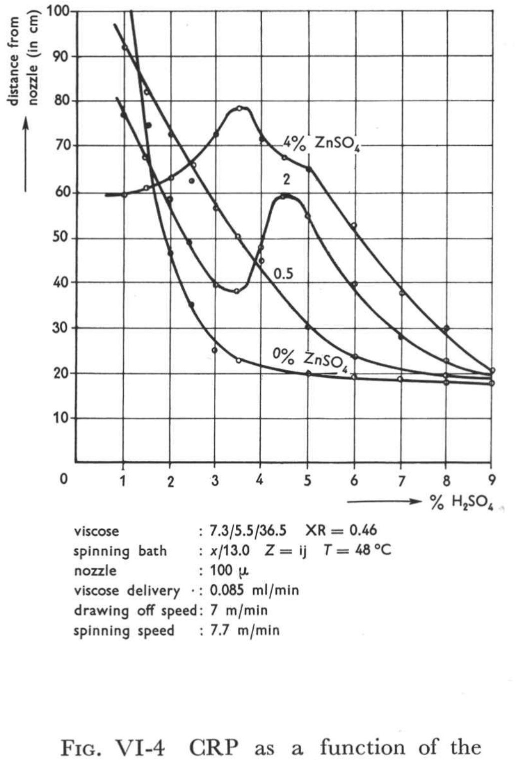
The CRP-distances are therefore a true characteristic of the diffusion spinning process.

Experimental results obtained on varying the viscose spinning bath combination

On investigating the effect of the parameters of the viscose spinning bath combination generally a series of measurements was carried out in which the H_2SO_4-content of the spinning bath was varied. Besides, in parallel experiments the $(SV)_{\text{lim}}$ was often determined.

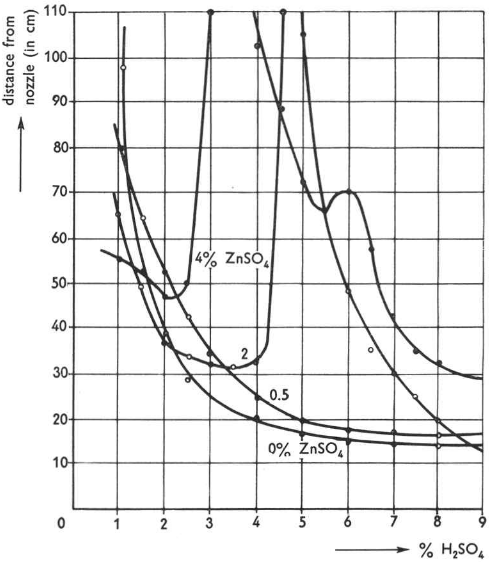
Some of the experimental data are represented graphically in FIGS. VI-4–13. The following comments may be made.

The CRP-distances obtained with zinc-containing spinning baths develop from the CRP-distances of zinc-free spinning systems. FIG. VI-4 shows this for the undoped process and FIG. VI-5 for the doped spinning.



viscose : 7.3/5.5/36.5 XR = 0.46
spinning bath : x/13.0 Z = ij T = 48 °C
nozzle : 100 µ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

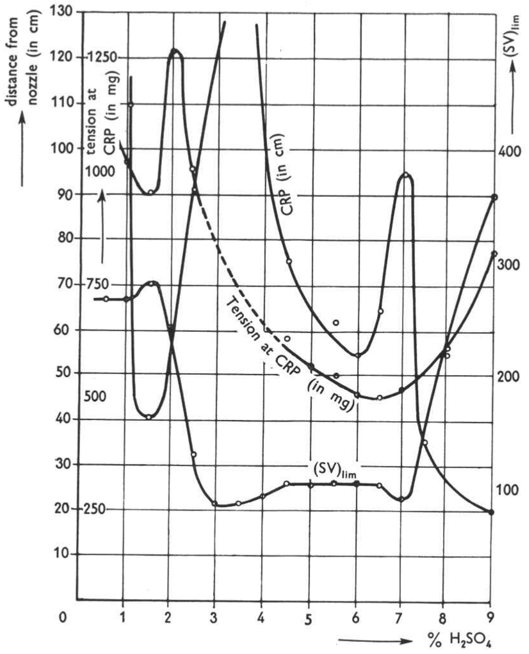
FIG. VI-4 CRP as a function of the H_2SO_4-content of the spinning bath. Results obtained on varying the $ZnSO_4$-content of the spinning bath.



viscose : 7.3/55./36.5 XR = 0.45
Dope 0.11% 0 83
spinning bath : x/13.0 Z = ij T = 45 °C
nozzle : 100 µ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-5 CRP as a function of the H_2SO_4-content of the spinning bath. Results obtained on varying the $ZnSO_4$-content of the spinning bath.

As shown in these figures, the CRP-H_2SO_4 graphs obtained with zinc-containing baths possess one or two relative maxima. On confronting the CRP-determinations with $(SV)_{\text{lim}}$-determinations of the same viscose spinning bath combinations (FIG. VI-6 is given as an example), it appears that both methods lead to the same differentiation of viscose spinning bath combinations into spinning regions.



viscose : 7.3/5.5/36.5 XR = 0.48
Dope 0.11% 0 83
spinning bath : $x/13.0$ $Z = 4.5$ $T = 45$ °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

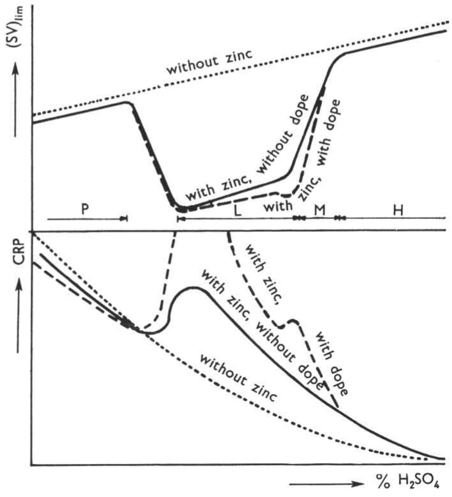
FIG. VI-6 CRP, Tension at CRP and $(SV)_{\text{lim}}$ as functions of the H_2SO_4 content of the spinning bath.

This shows up most characteristically in the appearance of the low-acid spinning region ($3\% < H_2SO_4 < 7\%$ in the example given), where the $(SV)_{\text{lim}}$-values are low (and are known to be correlated with the formation of skin cellulose or with the swelling value of a regularly spun and processed yarn) and the CRP-distances are high.

The effect of the dope shows up especially in this low-acid L-region: the CRP-distances are still larger; the $(SV)_{\text{lim}}$ is low over a wider range of acid-concentrations.

The CRP-distances, as a characteristic of the viscose spinning bath interaction at an early stage of the spinning process, already indicate the obtainable properties of the final product.

Schematically illustrated:

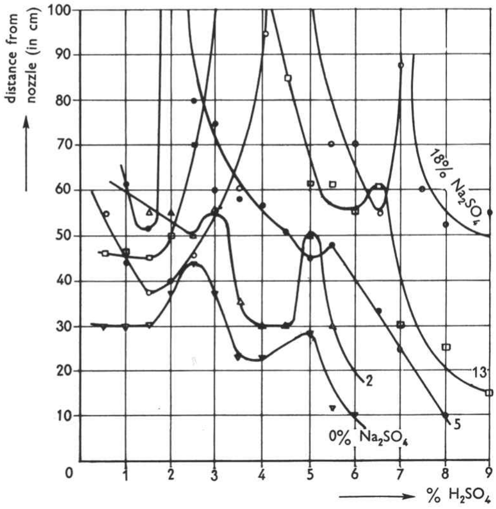


On combining the results of CRP- and $(SV)_{lim}$-determinations it is found that the spinning regions are mainly determined by the balance between:

a. the free alkali content of the viscose (cf. FIG. VI-15 in CHAPTER III)
b. the H_2SO_4-content of the spinning bath
c. the $ZnSO_4$-content of the spinning bath,

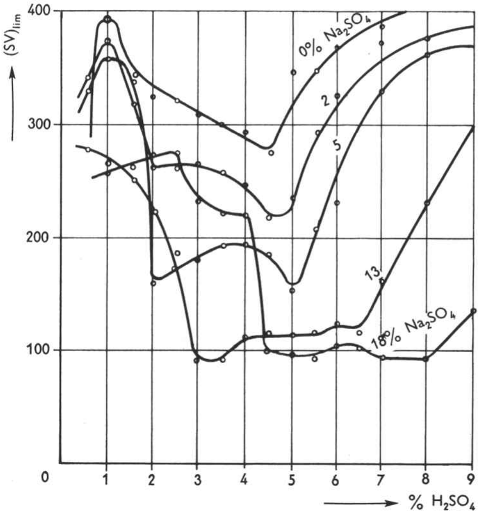
i.e. their appearance is coupled with the diffusion controlled neutralization process (cf. CHAPTER III).

Other factors are only of secondary importance; *e.g.* Na_2SO_4-variations



viscose : 7.3/5.5/36.5 XR = 0.40
Dope 0.11% 0 83
spinning bath : x/ij $Z = 4.5$ $T = 45$ °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-7 CRP as a function of the H_2SO_4-content of the spinning bath. Results obtained on varying the Na_2SO_4-content of the spinning bath.

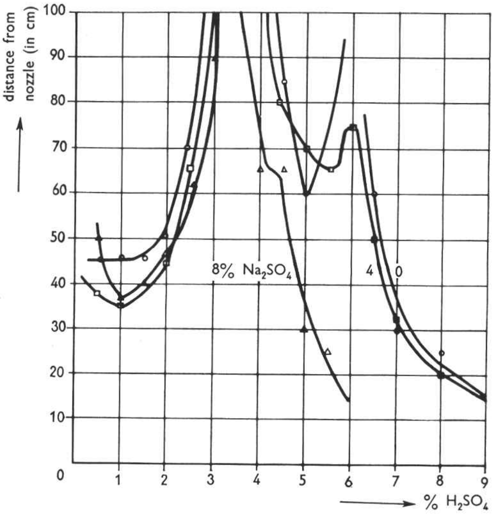


viscose : 7.3/5.5/36.5 XR = 0.42
Dope 0.11% 0 83
spinning bath : x/ij $Z = 4.5$ $T = 45$ °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min

FIG. VI-8 $(SV)_{lim}$ as a function of the H_2SO_4-content of the spinning bath. Results obtained on varying the Na_2SO_4-content of the spinning bath.

shift the regions somewhat along the acid axis (FIGS. VI-7, 8, 9). Tentatively this is understood as indicating the buffering action of the Na_2SO_4 on the ionization of H_2SO_4.

In particular the viscose buffer salts and the XR hardly play a role in describing the location of the spinning regions.



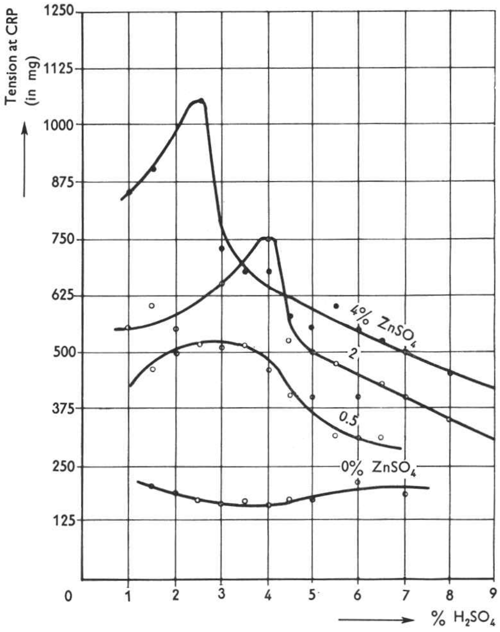
viscose : 7.3/5.5/36.5 XR = 0.42
Dope 0.11% 0 83
: ij% Na_2SO_4
spinning bath : x/13.0 $Z = 4.5$ $T = 45$ °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-9 CRP as a function of the H_2SO_4-content of the spinning bath. Results obtained on varying the amount of Na_2SO_4 added to the viscose.

The effect of zinc or zinc+dope does not only show up in the appearance of certain spinning regions and in the magnitude of the CRP-distance, but also in another aspect, *viz.* in the magnitude of the tension at the CRP and the course of the tension after the CRP.

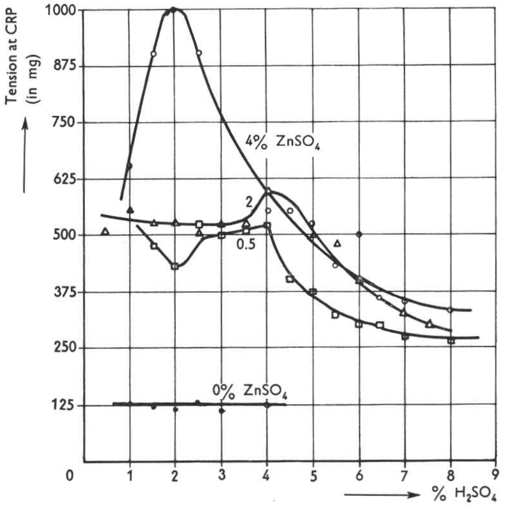
FIGS. VI-10 and 11 record for a number of series the results obtained on applying a fixed amount of stretch; generally the tensions are much higher than those obtained with zinc-free baths and appear to be highest somewhere in the acid-poor P-region (FIG. VI-12).

For a number of characteristic viscose spinning bath combinations the stretch (till breakage) vs. tension-curves were determined at the CRP-distance (FIG. VI-13).



viscose : 7.3/5.5/36.5 XR = 0.46
spinning bath : x/13.0 Z = ij T = 48 °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-10 Tension at CRP-distance as a function of the H_2SO_4-content of the spinning bath.
Results obtained on varying the $ZnSO_4$-content of the spinning bath.



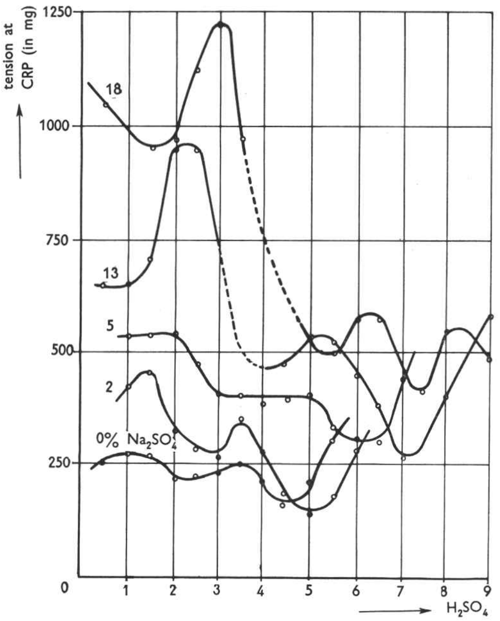
viscose : 7.3/5.5/36.5 XR = 0.45
Dope 0.11% 0 83
spinning bath : x/13.0 Z = ij T = 45 °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-11 Tension at CRP distance as a function of the H_2SO_4-content of the spinning bath.
Results obtained on varying the $ZnSO_4$-content of the spinning bath.

The curve representing the bath 2.5/16.0 Z = 4.5 relates to the acid-poor spinning region; this curve, if compared with the one for the bath 5.0/16.0 Z = 4.0, suggests that the high tensions observed in the acid-poor region with low percentages of stretch are caused by a yield-value behaviour.

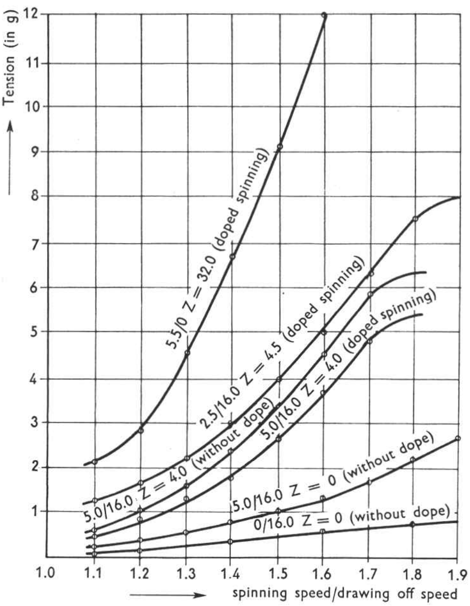
On considering the effect of zinc and/or zinc+dope in the various spinning regions, it was found that:

a. in the acid-poor region ($H_2SO_4 < 2^1/_2\%$ at $ZnSO_4 \simeq 4\%$) the tension distance graphs show a course similar to those obtained in zinc-free spinning;
the stretch tensions at the CRP, however are much higher (and also depend very much on the Na_2SO_4-content of the spinning bath); this is probably the reason why possibly preceding discontinuities cannot be "resolved";



viscose : 7.3/5.5/36.5 XR = 0.43
Dope 0.11%0 83
spinning bath : x/ij Z = 4.5 T = 45 °C
nozzle : 100 μ
viscose delivery : 0.083 ml/min
drawing off speed: 7 m/min
spinning speed : 7.7 m/min

FIG. VI-12 Tension at CRP distance as a function of the H_2SO_4-content of the spinning bath.
Results obtained on varying the Na_2SO_4-content of the spinning bath.



viscose : 7.3/5.5/36.5 XR = 0.43
: Dope 0.11%0 83
spinning bath : see figure T = 45 °C
nozzle : 100 μ
viscose delivery : 0.085 ml/min
drawing off speed: 7 m/min

FIG. VI-13 Tension at the CP or CRP distance as a function of the amount of stretch.
Results obtained with different viscose spinning bath combinations.

the tensions-at-the-CRP point to a "characteristic" acid content of the spinning bath at which they are maximum; the CRP-distances decrease somewhat with increasing zinc content. The presence of a dope does not appear in this region;

b. in the low-acid region ($2^1/_2\% < H_2SO_4 < 7\%$ at $ZnSO_4 \simeq 4\%$) the tension-distance graphs of the *doped-spinning process show that the filament possesses hardly any resistance towards deformation over a large distance from the nozzle*; (FIGS. VI-2 and 3) the CRP-distances (on spinning without or with a dope) increase with increasing zinc content; for low zinc concentrations ($Zn < 0.5\%$) this could be confirmed by the optical method.
The CRP-distances point to a "characteristic" acid content of the spinning bath, at which they are maximum; especially in the doped process there

is also a secondary maximum in the CRP-H_2SO_4 graphs (FIGS VI-5 and 6); one is inclined to subdivide the low-acid L-region into the
  a. $L_{principal}$-region, around the principal maximum in the CRP-H_2SO_4 graphs,
  b. $L_{secondary}$-region, around the secondary maximum.

  The stretch tensions at the CRP are generally higher than in the zinc-free process;

c. in the region of medium-acid concentrations ($7\% < H_2SO_4 < 10$–12%) the effect of zinc and/or zinc+dope gradually disappears (FIGS. VI-4 and 5); in a number of cases the tension-distance graphs even show a transient decrease of the stretch tension after the CRP-distance (FIGS. VI-1, 2, 3);
d. in the high-acid region ($H_2SO_4 > 10\%$) neither the CRP-distance nor the tensions suggest anymore any effect of zinc (FIGS. VI-4, 10).

From the experiments involving variations of Na_2SO_4 it appears that Na_2SO_4-variations:

a. in the acid-poor region hardly show up in the CRP-distances and $(SV)_{lim}$-values, but have a pronounced effect on the values of the tension-at-the-CRP (at low stretch percentages applied) (FIG. VI-12);
b. in the low-acid region hardly affect the CRP-distances at and around the principal maximum in the CRP-H_2SO_4 graphs (FIG. VI-7), but have a pronounced influence (this could be proved to be an osmotic deswelling effect) on the level of $(SV)_{lim}$-values (FIG. VI-8).

Variations of xanthate ratio (carried out in the range $0.25 < XR < 0.55$) are without effect on the CRP-distances.

In dope-free spinning the CRP-distances were found at NP-distances corresponding with pH $< \sim 2$. Specifically in the low-acid region, on spinning without a dope, zinc was found to have no effect on NP_{10}, NP_6, NP_4 (see CHAPTER III), but to displace the CRP-distance in a direction away from the nozzle. For doped low-acid conditions we are inclined to discard the indicator-colour change method as a measure of NP-distances; whereas the CRP-distances obey the diffusion requirements and are independent of the drawing-off speed, the distance from the nozzle at which *e.g.* the colour change of bromocresolpurple is complete (in vitro at pH ~ 6) is dependent on the drawing-off speed.

Interpretation of the experimental results obtained with zinc-containing baths

The problem to find an interpretation of the phenomena observed in experiments with zinc-containing baths was approached via considerations on diffusion processes and chemical reactions.

We did not succeed in obtaining a really consistent picture. This is not surprising, for in regard to stretch tensions one actually has to do with the sum-total of all different types of processes which have affected the gel-structure. Since only a few simplified systems were investigated, our approach of this complex system is both lacking in depth and in scope. Therefore the following paragraphs have a tentative character.

The tension-distance curves relating to the different spinning regions behave differently on varying the zinc sulfate content of the spinning bath. In our opinion this means that different mechanisms govern the different spinning regions.

In constructing the interpretation, our attention was again centered on the reactions which the xanthate group can undergo; all the experiments involving variations of the zinc sulfate concentration showed that the CRP-discontinuity in zinc-containing baths developed from the CRP-discontinuity in zinc-free baths, which was interpreted as the transition to the xanthic acid state.

In fact, this led us to the conclusion that also in zinc-containing baths the CRP-distance reflects the point where the diffusion process has resulted in (possibly only partial) formation of the xanthic acid state up to the centreline of the spinning filament.

The low-acid L-region.

The displacement of the CRP-distance in the low-acid L-region with increasing zinc-content (increasing CRP-distances result from increasing zinc-contents) *can then simply be interpreted as the consequence of the, transient, zinc-xanthate complex formation* (see CHAPTER IV, p. 54).

In harmony with this interpretation it was found that under dope-free spinning conditions the CRP is displaced towards lower pH-values.

This chemical interpretation of the CRP-discontinuity in zinc-containing baths as reflecting the transition to the xanthic acid state is furthermore in harmony with the effects of XR- and Na_2SO_4-variations on the CRP-distance. On comparing equivalent spinning conditions, both parameters *hardly affect* the CRP-distance (with the exception of the L_{sec}-maximum); so, physical phenomena (such as the sol → gel transition, which is dependent on both factors or the rate and magnitude of the osmotic deswelling which are dependent on the Na_2SO_4-content) do not seem to be decisive factors in determining the CRP-distance.

Accepting this interpretation, the conclusion is reached *that the dope effect in the low acid region is equivalent to an increased or more effective complex formation.*

The medium-acid M-region

The medium-acid M-region appears as *a typical transition* region between the low-acid L-region, where a maximum effect of zinc or zinc+dope is observed, and the high-acid H-region, where – presumably owing to the H^+—Zn^{++}—OH^--diffusion balance – no effect of zinc on the CRP-distance is observed anymore. In fact the yarns obtained in the M-region are inhomogeneous; when investigated with suitable means, such as dye-affinity tests and phase-contrast microscopy they show an outer skin and an inner core, whereas the yarns obtained in the H-region have a core character through the entire cross-section.

The acid-poor P-region

The CRP-determinations in the acid-poor P-region do not show the effect of zinc on the CRP-distance; apparently, either no complex formation occurs or the CRP-distance does not reflect the formation of the xanthic acid state. If it is taken into account that with increasing zinc contents the range of acid concentrations over which the P-region extends is decreased in favour of the low-acid L-region (even so far that at very high zinc contents the acid-poor region becomes nearly non-apparent), *the conclusion may be drawn that in the acid-poor P-region no zinc xanthate formation occurs.* Considering the results of the Zn^{++}—H^+—OH^--diffusion phenomena (CHAPTER III) this is unexpected:

1. the $(SV)_{lim}$ investigations with synthetic viscoses (prepared from cellulose xanthate+lye) revealed that the H^+—OH^--diffusion spinning relations determine the range of the spinning regions.
2. the model studies with lye-filled cylinders suggested that only the M-region has transition characteristics, but give no indication of a change of phenomena between P- and L-conditions.

Another element in constructing the interpretation is the stretch-tension-at-the-CRP-distance and the course of the tension-beyond-the-CRP-distance. On spinning in zinc-containing baths the stretch tensions at the CRP-distance are generally much higher than on spinning in zinc-free baths. Apparently the chemical definition of the gel-state (*viz.* that at the CRP-distance the xanthic acid state is formed) is not yet sufficient to fully define the physical structure properties.

A simple explanation would be that at the CRP-distance the diffusion has led to only partial xanthic acid formation, the remaining xanthate still being in the xanthate ion, and/or zinc xanthate state.*)

---

*) This is a sensible assumption; on determining the rate of the decomposition of K-ethyl-xanthate in these spinning bath media, the $t_{1/2}$-values found showed the presence of non-xanthic acid xanthate even under these equilibrium conditions.

The amount of xanthic acid formed at the CRP, or the proportion formed from the total xanthate, should then be sufficient to reveal the CRP-discontinuity; the remaining xanthate would still codetermine the stretch tensions observed.

Presumably the deformation modulus of the different gel states increases in the order:

$$—ZnX^+, —X^- < —XH < —ZnX_2 < —OH,$$

which follows from considerations on the role of charge effects and cross-linking effects on the coherence of the gel structure. In the case of zinc-free spinning processes the increase of the tension up to the CRP-distance is understood to reveal the increase in the amount of xanthic acid (the xanthic-acid state being more difficult to deform than the preceding xanthate-ion state), which continues till, at the CRP-distance, this process has reached the centre-line of the filament.

On spinning in zinc-containing baths, the increase of the tension to still higher levels, continuing until the CRP-distance has been reached, then reveals a dual character of the CRP-discontinuity:

1. zinc ions diffusing into the spinning filament together with the protons result in increasing ZnX_2-formation; this process is stopped when:
2. the diffusing protons have sufficiently decreased the pH to result in HX-formation.

If we accept this interpretation, the CRP-discontinuity marks the distance from the nozzle at which in the competition of the diffusing zinc-ions with the protons for the xanthate-group:

$$Zn^{++}+2X^- \rightleftarrows ZnX_2$$

$$H^+ + X^- \rightleftarrows HX$$

the balance turns in favour of the protons.

After the CRP-distance the replacement of zinc by protons as partners of the xanthate group still goes on; the temporary decrease of stretch-tension beyond the CRP-distance, observed in a number of viscose spinning bath combinations (particularly those in the M-region), is thought to reflect this process, till it is overtaken *e.g.* by the decomposition.

It seems even conceivable that this replacement of the remaining zinc xanthate has a diffusion-controlled stepwise mechanism:

$$ZnX_2+H^+ \rightleftarrows HX+ZnX^+$$

$$ZnX^+ + H^+ \rightleftarrows HX+Zn^{++}$$

In the majority of combinations of viscose and zinc-containing spinning bath, however, the temporary decrease in stretch-tension beyond the CRP-distance is not observed: the tensions at and beyond the CRP are high and remain on a high level.

If we accept that also in these cases xanthic acid is formed, the conclusion seems inevitable that the gel somehow retains the properties of the zinc xanthate state; *i.e.*, under suitable conditions the spinning mechanisms:

$$\text{viscose} \rightarrow \text{xanthate ion gel} \rightarrow \text{xanthic acid gel}$$

$$\text{viscose} \rightarrow \text{zinc xanthate gel} \rightarrow \text{xanthic acid gel}$$

lead to xanthic acid gels having structures reflecting the preceding state:

> *the gel structure is not necessarily a reversible property of the chemically defined state but can be frozen in.*

This is not a new concept but an application of a classical verdict – *viz.* the viscose-rayon endproduct has a memory of the moment of its birth – to a state already obtained in the spinning bath.

On attempting to interpret the high tensions observed in spinning in zinc-containing baths, an exception has to be made for the doped-spinning conditions. Our investigations showed that here, especially at the two maxima in the L-region, the resistance to stretch deformation is built up very slowly.

This seems to exclude the ZnX_2-state as a means for explaining the behaviour, but suggests that the ZnX^+-state determines the properties observed.

Then the two maxima possibly reflect the two diffusion-triggered reaction paths for ZnX^+-formation:

$$Zn^{++} + ZnX_2 \rightleftarrows 2ZnX^+$$

$$ZnX_2 + H^+ \rightleftarrows HX + ZnX^+$$

Remarks

In the preceding sections we have attempted to approach the tension-distance phenomena on the basis of chemical reactions triggered by diffusion processes.

We are aware that many more reactions are possible in the spinning process; the role of the viscose-buffer salts was *e.g.* entirely left out of the discussion. Also physical aspects were generally neglected. Their importance is suggested by the ambiguity of relating the gel properties to a chemical definition of the gel.

This is clearly demonstrated by the effect of Na_2SO_4-variations on the stretch tensions in the acid-poor P-region:

in the acid-poor P-region Na_2SO_4-variations have little effect on the CRP-distance, but (on spinning in zinc-containing baths) they are of decisive importance in codetermining the stretch tensions at the CRP (whereas on spinning in zinc-free baths no effect on the CRP-distance or the tension was found). Furthermore this cooperation of $Na_2SO_4+ZnSO_4$ becomes especially clear at a certain H_2SO_4-content of the spinning bath, but is revealed in stretch (till breakage) tension curves only at low percentages of stretch applied.

A satisfactory consistent interpretation of these phenomena could not be reached.

It is of practical importance that for a number of well-developed technological spinning processes the *CRP-distance was found to correspond with the bath length required for obtaining optimum mechanical properties*. This is understandable if it realized that the optical investigations showed that only at this or larger distances the filament responds homogeneously to stretch deformation.

CHAPTER VII

GENERAL DISCUSSION

Qualitative remarks

The phenomena reported and their interpretation reflect the fundamental importance of the diffusion in determining the course of the spinning process.

Even the CP- and CRP-distances (which as properties of the immobile cellulose component, are the derivatives of the diffusion process) were found to obey the spinning relations based on considerations on $\frac{t}{r_0^2}$. Presumably these spinning relations also result from a more advanced mathematical treatment of cylindrical diffusion processes with consecutive chemical reactions, but without the simplifications we made.

In regard to the phenomena in Müller-type spinning baths an important role is apparently played by the H^+—OH^- diffusion balance. This balance determines the spinning regions (compare Chapter III, Fig. 16, int. al. by regulating the diffusion of zinc ions) and in cooperation with the rate of other processes (diffusion of other species, *e.g.* $ZnSO_4$, chemical reactions), also codetermines, as we concluded, a number of intermediate states in the spinning filament and their pH-dependent life times.

The phenomena reported have furthermore revealed the possibilities and consequences of diffusion-controlled chemical reactions in affecting the physical state of the immobile cellulose component. It was concluded that in a number of cases the deformation properties of the spinning filament seemed to reflect and to follow the chemical reactions of the cellulose xanthate group.

This certainly does not cover all aspects of the coagulation process.

On the one hand there is the sol → gel transition in the xanthate state, which must have a more purely physical character (except in the extreme cases where it is coupled to a reaction of the xanthate group: zinc-xanthate formation or xanthic acid formation at high xanthate ratios).

On the other hand there is the consideration that the xanthic acid state is common to nearly all spinning processes as being the last state before the formation of regenerated cellulose. The deformation properties of the spinning filament beyond the CRP-distance and also the properties of the final product may vary widely, however.

In a number of instances we concluded therefore that the deformation properties seemed to indicate a "freezing in" of an early-formed structure, insusceptible to succeeding chemical reactions of the xanthate group.

For these cases the classical verdict – "the viscose rayon final-product has a memory of the moment of its birth" – has possibly even to be taken literally: the structure of the final-product is predestined by the firstly formed gel state.

Frozen in structure properties are not unfamiliar in cellulose chemistry. Vermaas [1], has found that the deformation properties of nitrated viscose filaments are to a certain extent comparable to those of the original, unnitrated filament.

Analogously, Richards [2] concludes that the effects of heterogeneous acetylation and methylation of isotropic cellulose on mechanical properties in the air-dry state are very small.

Saunders [3] has found that the deformation properties of acetate films are virtually unaltered by saponification.

Tentatively, one comes to think in terms of structure-organizing processes, coupled with the chemically distinguishable, intermediate states, having the character and aspects of crystallization and suppressed recrystallization phenomena and possibly involving yet another kinetic element:
the rate of the organizing process and the chance it gets, under the prevailing diffusion and reaction conditions, to affect the mass of material; the lifetime of the states may become an important factor.

It may be added that historically verdicts such as (Vermaas, [4]) "the original gel should not be too old" and "the lifetime of the state should not be too short" have found their way into viscose chemistry, though without coupling the state with a certain chemical description.

Assembling these considerations about the viscose spinning process and taking into account that stretch deformation leads to orientation anisotropy of the structure, one concludes that it is possible to describe the viscose spinning bath interaction in terms of consecutive and interacting

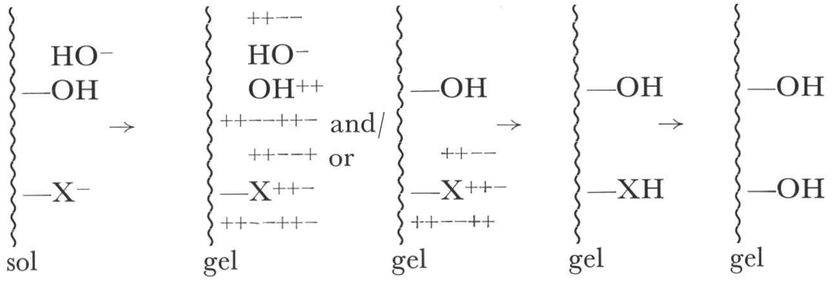
1. diffusion processes
2. chemical reactions
3. structure-organizing processes
4. orientation phenomena

Formulation of reaction paths

For a number of technological spinning processes the formulation of a reaction path seems possible, if the interpretation of the CP- and CRP-determinations is accepted. In general the first-appearing gel states are different.

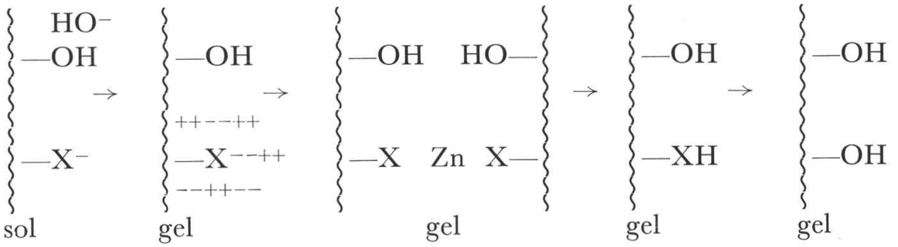
a. *Classical viscose spinning*

The classical viscose spinning process, carried out as a two-step process (using a salt solution as coagulation bath, regenerating afterwards) or with a one-step (salt and acid containing) Müller bath, becomes:



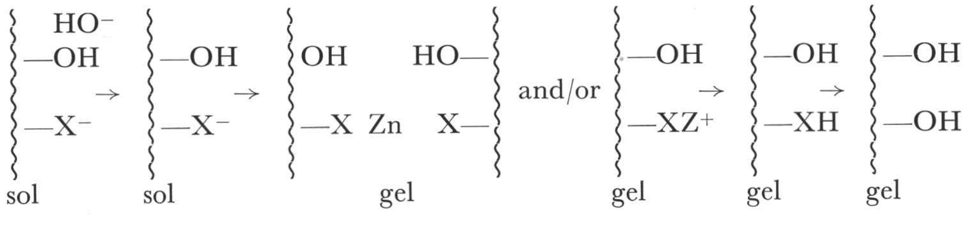
b. *Standard textile spinning*

When small amounts of *e.g.* Zn^{++}-ions are added to the Müller bath (as is done in regular textile spinning processes) the coagulated xanthate state reacts at least partly along the mechanism:



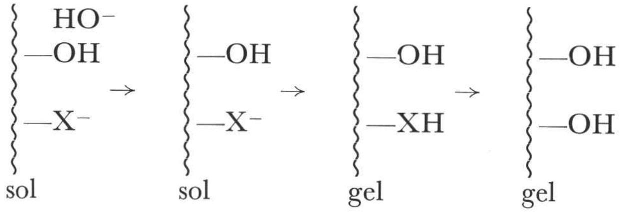
c. *Low-acid spinning*

At increased XR and zinc content, and under the proper H^+—Zn^{++}—OH^--diffusion conditions, *viz.* those of the tyre yarn spinning processes in the low-acid L-region, the mechanism becomes:



d. *Toramomen process*

As a contrast, in the Toramomen spinning process coagulation does not occur before the xanthic acid state is reached (as the viscose has a high XR, and a very dilute mineral acid bath of about room-temperature and containing hardly any salts is used as spinning bath):

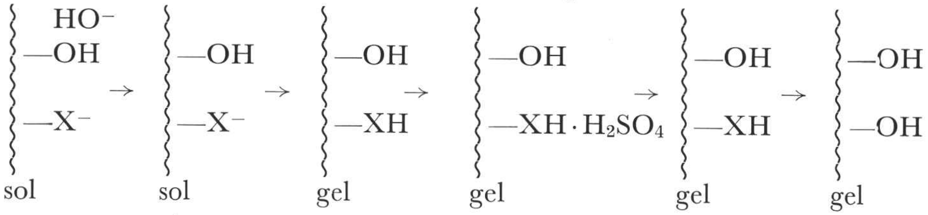


$$\begin{array}{l} \text{HO}^- \\ -\text{OH} \\ -\text{X}^- \\ \text{sol} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{X}^- \\ \text{sol} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{XH} \\ \text{gel} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{OH} \\ \text{gel} \end{array}$$

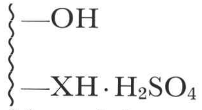
The low temperature of the Toramomen spinning bath is possibly required to give the xanthic acid state a long lifetime.

e. Lilienfeld process

Though outside the range of our investigations, it can be assumed that under Lilienfeld spinning conditions (*i.e.* with a spinning bath consisting of a rather concentrated H_2SO_4-solution), the reaction path becomes:

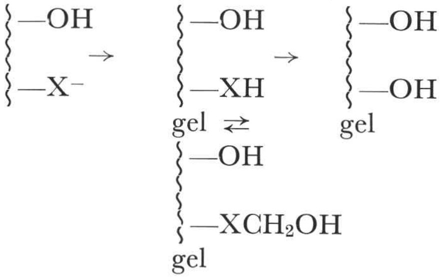


$$\begin{array}{l} \text{HO}^- \\ -\text{OH} \\ -\text{X}^- \\ \text{sol} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{X}^- \\ \text{sol} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{XH} \\ \text{gel} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{XH}\cdot\text{H}_2\text{SO}_4 \\ \text{gel} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{XH} \\ \text{gel} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{OH} \\ \text{gel} \end{array}$$

in which the  $\begin{array}{l} -\text{OH} \\ -\text{XH}\cdot\text{H}_2\text{SO}_4 \end{array}$ formulation reflects the empirical knowledge that the decomposition of the xanthic acid group in these conc. H_2SO_4-media is very much retarded; whether this is a pure medium effect or whether other effects, *e.g.* protonization of the xanthic acid group, play a role is an open question, however.

f. Spinning in the presence of formaldehyde

For spinning processes carried out in the presence of formaldehyde (which is known to interact with the xanthic acid group in a non-instantaneous equilibrium) a part of the reaction path is:



$$\begin{array}{l} -\text{OH} \\ -\text{X}^- \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{XH} \\ \text{gel} \end{array} \rightarrow \begin{array}{l} -\text{OH} \\ -\text{OH} \\ \text{gel} \end{array}$$

$$\begin{array}{l} -\text{OH} \\ -\text{XH} \\ \text{gel} \end{array} \rightleftarrows \begin{array}{l} -\text{OH} \\ -\text{XCH}_2\text{OH} \\ \text{gel} \end{array}$$

g. Doped spinning

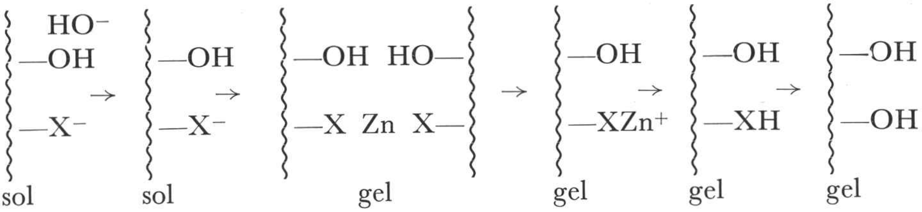
Accepting the interpretation that the doped low acid spinning conditions involve the ZnX^+-state, it should be noted that the latter can only be formed via the insoluble ZnX_2-state:
the amount of zinc required (which the diffusion has to bring into the spinning filament) increases in the order X^-—ZnX_2—ZnX^+.
Whether the reaction $ZnX_2 \rightarrow ZnX^+$

(a. $ZnX_2+H^+ \rightarrow ZnX^+ + HX$ or

b. $ZnX_2+Zn^{++} \rightarrow 2ZnX^+$)

leads to ZnX^+-properties will depend on the susceptibility of the insoluble ZnX_2-state.

If the doped low-acid spinning conditions are considered to be representative of the conditions of skin cellulose formation, the mechanism of skin cellulose formation becomes:



It may be mentioned that this formulation covers the different aspects of the spinning process only partially.

In fact it is known that for skin cellulose formation the spinning filament should undergo an osmotic dehydration at an early stage; this an important effect connected with the Na_2SO_4 in the spinning bath.

In this connection another question of interest is the technological experience as to the important role of the viscose buffer salts in the process of skin cellulose formation; possibly they also act as counterions for the ZnX^+-state: *e.g.* ZnX^+SH^- or $ZnX^+HCS_3^-$, which is possibly responsible for the yellow colour of the doped spinning filament.

In an analogous way the ZnX^+-state could interact with negative indicator ions, by which the pH-equilibrium:

negative indicator-ion$+H^+ \rightleftarrows$neutral indicator molecule

is affected and by which the SP- and NP-measurements are disturbed. (CHAPTER III). The NP-measurements with alizarin-Na (CHAPTER III, FIG. 14) (NP_{10} independent of drawing-off speed, NP_4 linearly dependent on drawing-off speed in the doped spinning process) are then understood to indicate that in the centreline of the spinning filament at pH ~ 10 ZnX^+ is not yet formed, but that at pH ~ 4 the indicator interacts with the ZnX^+-state (see also CHAPTER IV).

The nature of dopes

As is shown by the $(SV)_{lim}$ and tension-distance measurements, the dopes exert their effect on the spinning filament under the low-acid spinning conditions.

In interpreting the experimental phenomena it was suggested that the ZnX^+-state is involved.

The mechanism of the dope action however represents a still unsolved problem.

1. *Hypothesis of diffusion interference*

Historically, a number of hypotheses have been formulated (see *e.g.* SISSON [5]), which assume that the dopes exert their action by interfering with the H^+—OH^-—Zn^{++} diffusion process.

These hypotheses start from the observation that on addition of a dope the NP-values at finite drawing-off speeds are displaced away from the nozzle and in general pre-suppose an interaction between the diffusing components, H^+—OH^-—Zn^{++}, with the dope and with the non-cellulosic viscose buffer salts, particularly the Na_2CS_3; the overall effect should then be either a retarding effect on the proton diffusion ("barrier" hypotheses) or an accelerating effect on the Zn-diffusion ("carrier" hypotheses).

It seems to us, however, that there are a number of arguments against these hypotheses:

a. if the H^+—OH^-—Zn^{++} diffusion balance is involved, one expects an analogous result to be obtainable by altering the boundary conditions of the dope-free diffusion process:
   i.e. a change of concentrations of the bath components should act analogously; however, neither an increase of the $ZnSO_4$-concentration nor a decrease of the H_2SO_4-concentration (by which one eventually arrives at the acid-poor spinning conditions which result in an all-core yarn) imitates even the dope action as shown by *e.g.* skin core differentiation tests of the final product.

b. the study of the neutralization process in the spinning filament showed that the H^+—OH^- diffusion process is essentially unaltered by the dope (extrapolating the measurements to drawing-off speed $\rightarrow 0$).

2. *Hypotheses of structural regulation*

We venture the hypothesis that the dopes exert their action by interfering with the structure formation directly and not by interfering with the diffusion process.

By analogy this seems possible: skin formation is not only favoured by the addition of a dope but also in the dope-free process:

a. by increasing the cellulose content of the viscose, both on using "natural" viscoses and on using "synthetic" viscoses (obtained by dissolving pure cellulose xanthate in lye).
   From natural viscoses with a cellulose content of 12–15% an all-skin yarn can be obtained, under low-acid spinning conditions.

b. by increasing the XR; an effect which is also found with synthetic viscoses on increasing the XR to values of ~ 0.70.

This hypothesis is moreover based on the observation (obtained on examining many different dopes by means of $(SV)_{\mathrm{lim}}$-, CRP- and skin-core tests) that for dope action a minimum molecular volume of the dope is required, which possibly suggests a type of "plasticizer" action of the dope. (Compare *e.g.* the lower homologues of amines with the higher ones; analogously the lower dithiocarbamates are less active than the higher ones).

It is suggested that the dopes exert their action during the transition to the ZnX^+-state, either topochemically by keeping the chains in the ZnX_2-state far enough apart to permit newly arriving Zn^{++}-ions to result in ZnX^+-formation, or more physically, by increasing the "susceptibility" of the gel so as to undergo the structural reorganization to the ZnX^+-state.

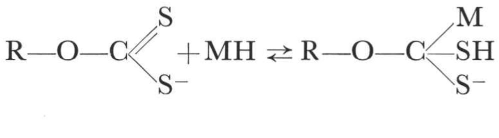
For the dopes possessing a free pair of electrons an interaction with the cellulose xanthate chain seems possible by H-bridge formation with the alcoholic OH-groups. This possibly competes with the interchain H-bridge formation during the gel-organizing process.

3. *Hypothesis of mixed complex formation*

The formation of mixed complexes between xanthate group, dope and Zn-ions presents itself as another possibility:

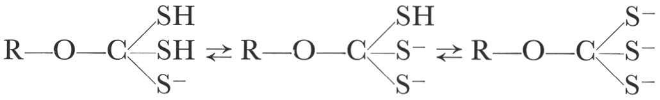
dope-Zn—X, *i.e.* as a competing partner for the ZnX^+-state.

A related possibility has been formulated by Toms [6] who concludes that the xanthate group reacts with compounds with an active hydrogen under formation of an ortho-ion:



$$\mathrm{R{-}O{-}C}\begin{array}{l} /\!\!/\mathrm{S} \\ \\ \backslash\mathrm{S^-} \end{array} + \mathrm{MH} \rightleftarrows \mathrm{R{-}O{-}C}\begin{array}{l} /\mathrm{M} \\ {-}\mathrm{SH} \\ \backslash\mathrm{S^-} \end{array}$$

MH represents *e.g.* an amine or H_2S. In alkaline media these ions possibly dissociate further, *e.g.* for H_2S:



$$\mathrm{R{-}O{-}C}\begin{array}{l}\mathrm{SH}\\ \mathrm{SH}\\ \mathrm{S}^-\end{array} \rightleftarrows \mathrm{R{-}O{-}C}\begin{array}{l}\mathrm{SH}\\ \mathrm{S}^-\\ \mathrm{S}^-\end{array} \rightleftarrows \mathrm{R{-}O{-}C}\begin{array}{l}\mathrm{S}^-\\ \mathrm{S}^-\\ \mathrm{S}^-\end{array}$$

Taking into account the role of the diffusion and the number of reactions in which the xanthate group, the zinc-ions, the dopes and other viscose components possibly partake. the restricted and tentative character of the interpretation of the phenomena discussed should be stressed again.

Literature

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2. G. N. Richards, J. Appl. Pol. Sc. **5** – 545 (1961).
3. D. W Saunders, collaborator Brit. Rayon Res. Inst., private communication.
4. D. Vermaas, Text. Res. J. **32** – 353 (1962).
5. W. A. Sisson, Text. Tes J. **30** – 153 (1960).
6. B. A. Toms, private communication.
   G. Ingram and B. A. Toms, J. Chem Soc. (1957) – 4328.

CHAPTER VIII

SUMMARY

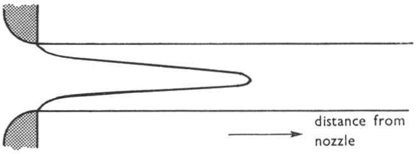
In the spinning of viscose a number of unit-processes can be distinguished; *e.g.* the neutralization and acidification, the coagulation, the decomposition or regeneration, *etc.*

So far as they are connected with the transport of matter into or out of the spinning filament, they are kinetically coupled with and dependent on the diffusion; besides, at least one of these unit-processes, the decomposition-reaction, is known to have a finite reaction rate.

The investigations reported in this thesis are in particular related to the role which diffusion processes and chemical reactions play in determining the course of the spinning process.

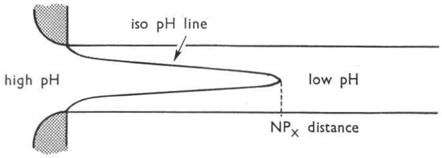
From existing theories about cylindrical diffusion processes with consecutive reactions of the diffusing components, a number of relations between the parameters of the viscose spinning process were derived (CHAPTER II). *E.g.*:

a. The equi-concentration points in the spinning filament, governed by a cylindrical diffusion process with consecutive instantaneous reaction of the diffusing components, lie on a bell-shaped surface of rings having their centres in the centreline of the spinning filament.



b. For a given viscose spinning bath combination the distance from the nozzle at which a certain diffusion-controlled quasi-stationary state will be found is linearly dependent on the amount of viscose delivered through the nozzle hole and is independent of the drawing-off speed.

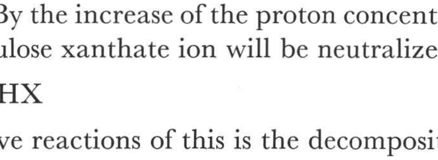
An investigation into the course of the neutralization process in the spinning filament was carried out (CHAPTER III) by spinning a monofilament from a viscose to which a pH-indicator had been added. The experimental results were generally found to be in good harmony with the theoretical predictions based on the diffusion process, in which the diffusing and reacting partners are assumed to be the H^+ and OH^--ions. The above figure *e.g.* represents then an experimentally found iso-pH line in the spinning filament; the distance from the nozzle, at which the colour change of the indicator throughout the filament has been completed, has been labelled the neutralization point distance: NP_x (the pH of colourchange of the indicator has been added as an index).



For certain spinning conditions, however, *viz.* on spinning in zinc sulfate-containing baths, notably in the presence of a modifier or dope, the colour change phenomena of the indicator were in disagreement with the above-mentioned theoretical predictions; though it seems that this discrepancy between theory and experiment is connected with the formation of a certain structural modification of regenerated cellulose (so-called skin cellulose), an unambiguous interpretation of these phenomena could not be obtained.

From model experiments with alkali-filled cylindrical media, which therefore contain neither the cellulose xanthate nor the viscose buffer salts and which were placed in solutions of the same composition as that of regular spinning baths, we learned that under certain conditions the zinc ions diffuse into the cylinder synchronously with the protons, the rate being determined by the protons. Under these conditions (which in some respects are comparable with the conditions under which skin cellulose can be formed) the front of the zinc ions coincides with pH ~ 8, and a precipitate of $Zn(OH)_2$ is formed in the range $6 < pH < 8$.

In terms of a spinning cylinder this is represented by



The changes of medium brought about by the diffusion lead to a number of chemical reactions of the immobile cellulose xanthate and are in turn coupled with these reactions. By the increase of the proton concentration in the spinning filament, *e.g.* the cellulose xanthate ion will be neutralized:

$$H^+ + X^- \rightleftarrows HX$$

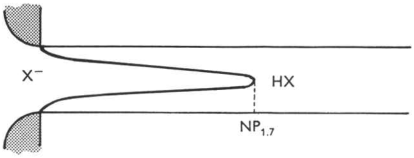
One of the concecutive reactions of this is the decomposition:

$$HX \rightarrow ROH + CS_2.$$

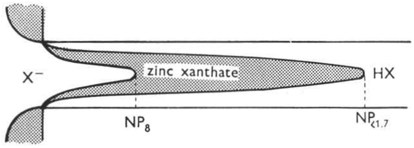
In vitro model experiments (CHAPTER IV), which mainly involve a study of the decomposition kinetics of K-ethylxanthate in acidic media in the presence of zinc-ions, showed that, moreover, complex equilibria between xanthate ions and zinc ions have to be taken into account. (For some different zinc ethylxanthate complexes the equilibrium constants could be determined:

$$\begin{aligned} X^- + Zn^{++} &\rightleftarrows ZnX^+ \qquad && pK_{\text{compl}} \simeq 1.3 \\ 3X^- + Zn^{++} &\rightleftarrows ZnX_3^- \qquad && pK_{\text{compl}} \simeq 4.7). \end{aligned}$$

Taking into account the competitive effect of these complex equilibria on the position of the acid dissociation equilibrium, one may conclude that the formation of the xanthic acid state in the spinning filament is displaced away from the nozzle by the complex formation. Schematically pictured:



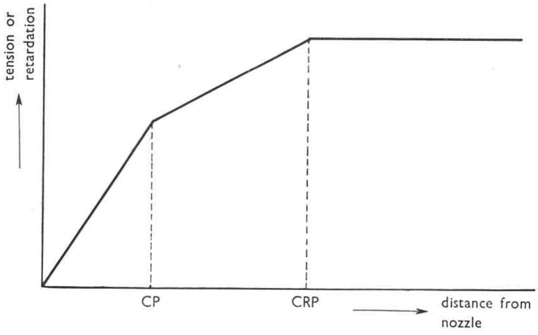
Xanthic acid formation in the spinning filament in the *absence* of complex formation with zinc ions (on the assumption that pK_{diss} (cell. xanthic acid) = pK_{diss} (ethyl xanthic acid), the value for the latter being $pK_{\text{diss}} = 1.7$).



Xanthic acid formation in the spinning filament under such conditions that zinc xanthate *complexes can be formed.*

We then carried out an investigation on a monofil spinning machine into the stretch-optical and stretch-tension behaviour of the spinning filament, starting from the idea that different "states" (sol state, gel state, and possibly even different gel states) will have a different stretch-optical or stretch-tension behaviour. The method of investigation consisted in spinning a monofilament, applying stretch at varying distances from the nozzle and measuring the corresponding stretch-tension or optical retardation values. By using for the latter purpose a microscope with a Babinet compensator it is even possible to measure differentially over the cross-section.

The results obtained with zinc-free spinning baths (CHAPTER V) show the presence of one or two characteristic distances as schematically reproduced in the following picture:



Both characteristic distances, CP and CRP, were found to meet the requirements of a cylindrical diffusion process (*i.e.* they are liniarly dependent on the viscose delivery and independent of the drawing-off speed).

On varying the viscose spinning bath combinations, the CP-distance furthermore appeared to be dependent on those factors which also affect the solubility behaviour of cellulose xanthate (*e.g.* the xanthate ratio of the viscose, the type and amount of spinning bath salts).

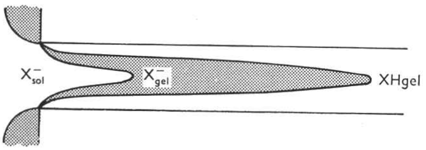
The CRP-distance, however, was found to be only dependent on those parameters of the viscose spinning bath combination which also affect the neutralization process, *i.e.* mainly the alkali-acid balance.

For zinc-free baths the CRP-distance was found always to coincide with $NP_{\sim 2}$.

On the basis of the various experimental results the CP-distance was interpreted as corresponding with the distance from the nozzle at which the sol→gel transition, as controlled by the changes of medium brought about by the diffusion, was completed up to the centre line of the spinning filament; this sol → gel transition apparently takes place while the cellulose xanthate state is still preserved. The CP-distance is the coagulationpoint distance.

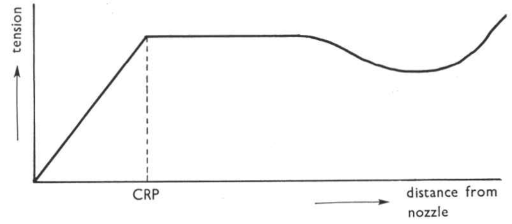
Analogously, the CRP-distance corresponds with a diffusion-controlled process by which the original coagulate is reinforced (= coagulate reinforcement point); it has been interpreted as the transition from the cellulose xanthate state to the cellulose xanthic acid state.

So, the following picture for the spinning filament appears:



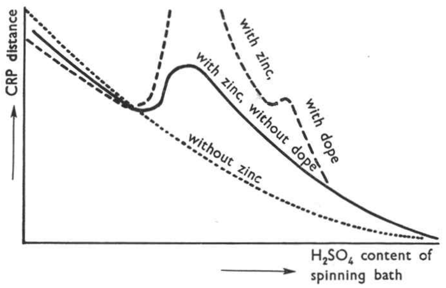
When spinning was done in zinc-containing baths (Chapter VI), only the method based on tension measurements could be applied; the optical method requires circular cross-sections, which generally are not obtained with zinc-containing baths.

The graphs representing the tension-distance measurements relating to the zinc-containing baths show in general more variety and more detail than those referring to spinning in zinc-free baths; the level of the tension values is generally much higher.



The characteristic distance, again called CRP, was found to be a true characteristic of the diffusion spinning process and appeared to develop from the CRP-discontinuity in zinc free spinning systems, which was interpreted as the transition to the xanthic acid state.

In agreement with the complexing effect of zinc ions on xanthate ions it furthermore appeared that under some conditions (notably in the so-called low-acid L-region) the CRP-distance was found at larger distances from the nozzle than under spinning conditions without zinc in the spinning bath.



We did not succeed in obtaining a consistent interpretation of the various experimental findings. So our investigations with these zinc-containing spinning baths largely have a phenomenological character; however, this led to the view that the gel structure is not necessarily a reversible property of the chemically defined state, but may have a "memory" of earlier states.

In a general discussion (Chapter VII) this conclusion is given a generalized basis by postulating that besides diffusion processes and chemical reactions, structure organizing processes with the character of crystallization and recrystallization processes play a role in determining the course of the spinning process and the properties of the final product.

CHAPTER IX

SAMENVATTING

In dit proefschrift wordt verslag gedaan van een aantal onderzoekingen over de wisselwerking tussen viscose en spinbad in het viscose spinproces.

Na een inleidend HOOFDSTUK I over het viscose spinproces wordt in HOOFDSTUK II een modelbeschouwing gegeven over het spinproces uitgaande van bestaande theorieën over cilindrische diffusie met opvolgende chemische reactie tussen de diffunderende componenten.

De conclusies van deze modelbeschouwing worden vervolgens in HOOFDSTUK III toegepast in een onderzoek over het neutralisatieverloop in de spinnende draad. Dit onderzoek werd uitgevoerd op een monofil-spinmachine door viscoses te verspinnen waaraan een pH-indicator is toegevoegd. Aannemende dat de diffunderende en reagerende partners de H^+- en OH^--ionen zijn, konden de experimentele resultaten in het algemeen aanvaardbaar geïnterpreteerd worden, in het bijzonder echter met uitzondering van de waarnemingen verkregen bij het zgn. doped spinproces. In aansluiting hierop werd een modelonderzoek verricht met dikke cilindrische staven over de invloed van de zuur (in het spinbad)-alkali (in de viscose) verhouding op het transport van zinkionen de draad in.

De milieu-veranderingen, die door de diffusie teweeg gebracht worden, leiden ook tot een aantal reacties van het immobiele cellulose-xanthogenaat. Hierop wordt ingegaan in HOOFDSTUK IV, waar de resultaten van een in vitro onderzoek worden vermeld, uitgevoerd met behulp van K-aethyl-xanthogenaat, betreffende reacties die de xanthogenaat-groep kan aangaan met protonen en met zink-ionen.

Dit onderzoek voerde tot de conclusie dat de vorming van zink-xanthogenaat in de spinnende draad slechts in een bepaald pH-gebied mogelijk is (en dat dus nergens over de gehele doorsnede van de spinnende draad zink-xanthogenaat aanwezig kan zijn) en dat door het complex-karakter van zink-xanthogenaat de xanthogeenzuurvorming in de spinnende draad naar gebieden met lagere pH verschoven wordt (i.e. van de dop af).

Het voorgaande impliceert dat chemisch te onderscheiden vormen van cellulose-xanthogenaat geacht worden te kunnen optreden in de spinnende draad op ruimtelijk te onderscheiden plaatsen.

Al dan niet gekoppeld aan de chemische omzettingen zal ook het fysische gedrag van de spinnende draad beïnvloed worden door de milieu-veranderingen. De Hoofdstukken V en VI zijn hieraan gewijd. Hierin worden de resultaten vermeld van een onderzoek, uitgevoerd op een monofilspinmachine, waarbij het gedrag van de spinnende draad t.o.v. verstrekking nagegaan werd, in afhankelijkheid van de afstand tot de dop, door het meten van strekspanning en strek-dubbele breking.

Bij de interpretatie van deze metingen aan de spinnende draad werd in het bijzonder de gedachtengang ontwikkeld dat de milieu-veranderingen, teweeggebracht door de diffusie, een aantal chemische en fysische processen inleiden, waardoor het gedrag en de toestand van de spinnende draad mede beïnvloed worden.

Aannemende dat verschillende "toestanden" van de cellulose-xanthogenaat in de spinnende draad (sol-toestand, gel-toestand en mogelijkerwijze zelfs verschillende gel-toestanden) kunnen optreden en verschillend zullen kunnen reageren op de aangelegde verstrekking, kon uit de experimentele waarnemingen dan afgeleid worden waar de sol → gel overgang en waar de xanthogenaat → xanthogeenzuur overgang in de spinnende draad optreedt. Deze laatste vindt als regel plaats in een reeds gecoaguleerde gel-toestand:

xanthogenaat-sol → xanthogenaat-gel → xanthogeenzuur-gel

Beide overgangen bleken te voldoen aan een aantal criteria van het cilindrische diffusie-proces.

Speciaal uit de waarnemingen verkregen bij onderzoek van spinomstandigheden waarbij met zink-houdende baden gewerkt werd (Hoofdstuk VI), werd verder afgeleid dat de eigenschappen van het xanthogeenzuur-gel mede bepaald worden door de reactie-weg waarlangs dit gel verkregen is.

In een algemene discussie (Hoofdstuk VII) wordt deze conclusie gegeneraliseerd door te stellen dat behalve diffusie-processen en chemische reacties ook structuur-ordenende processen met het karakter van kristallisatie- en rekristallisatie-processen mede van invloed zijn op het verloop van het spinproces en op de eigenschappen van het eindprodukt.

Voor een aantal technologische spinprocessen wordt ten slotte getracht de reactieweg te formuleren.

APPENDIX I

Some historical developments

The large number of parameters governing the rayon spinning process offer the opportunity of exploration and development of the spinning conditions in many different directions.

In our opinion the inherent variety represents one of the natural values of the rayon spinning process.

The following list of patent publications, which is of necessity a selection, marks some of the historical developments concerning the viscose spinning bath combinations and the properties of the product spun.

C. F. Cross, E.J Bevan and C. Beadle	The preparation of viscose	Brit. Pat. 8700/A.D. 1892
C. H. Stearn	The spinning of viscose through an orifice into a precipitating NH_4Cl-solution	Brit. Pat. 1020/A.D. 1898
C. H. Stearn	The manufacture of films from viscose	Brit. Pat. 1022/A.D. 1898
M. Müller	The use of baths made up from H_2SO_4 and containing metal sulfates	Ger. Pat. 187 947 (1907)
E. Thiele and C. A. Ernst	Stretch spinning	Brit. Pat. 8083/A.D. 1902 U S. Pat. 808 148 (1905)
S. S. Napper	Müller baths with small amounts of $ZnSO_4$	Brit. Pat. 406/A.D. 1911
Glanzfäden A. G. and E. Schulke	Crimped yarns and fibres	Ger. Pat. 312 304 (1917) Ger. Appl. S 55 138 (1920)
L. A. van Bergen and W. P. Dreaper	Müller baths with high $ZnSO_4$-contents	Neth. Pat. 169 53 (1923) Brit. Pat. 239 254 (1924)
L. Lilienfeld	Spinning baths containing at least 50% H_2SO_4	Aut. Pat. 124 684 (1925)
J. J. Polak and J. G. Weeldenburg	Kation-active surfactants as spinning aids	Neth. Pat. 39 956 (1935)
S. Tachikawa	Cotton-like products from extreme unripe, diluted viscoses spun in diluted H_2SO_4-solutions of low salt content	Aut. Pat. 206 259 (1943)
G. M. A. Kayser	Spinning in the presence of formaldehyde	Neth. Pat. 60 647 (1945)

N. L. Cox	The spinning of viscoses to which extra amounts of Na_2CS_3 are added	U.S. Pat. 2 581 835 (1946)
N. L. Cox	The spinning of viscoses containing quaternary N^{IV} compounds	U.S. Pat. 2 536 014 (1946)
R. Mac Laurin and W. O. Israel	The spinning of viscoses containing ethoxylated amines	U.S. Pat. 2 593 466 (1948)
D. Vermaas	The spinning of solutions of cellulose xanthate containing sodium zincate	Neth. Pat. 76 456 (1951)

APPENDIX II

The formation of zinc cellulose xanthate in the spinning filament

In an attempt to verify the conclusion regarding the appearence of zinc xanthate in the spinning filament, an investigation was carried out in the AKU-laboratory by DR. A. M. VAN DER VEN, in which the filament was analyzed as to the presence and content of zinc.

For this purpose the spinning filament, after leaving the spinning bath, is sampled with the aid of two rollers; the first, on which the filament is given one wrap, is turning in an appropriate quenching bath; the second is used for collecting the yarn.

Quenching is carried out by means of distilled water. After the yarn has been collected, it is washed in water till a constant value for the zinc content is obtained.

It is assumed that in this way only the immobilized zinc is determined and that adhering spinning bath or soluble, mobile, zinc-containing reaction products are effectively removed. After boiling the sample for 1 hour in 2 2 N H_2SO_4, the zinc is determined complexometrically.

Some of the results obtained with a viscose-spinning bath combination in the low acid L-region (where *e.g.* the $(SV)_{lim}$-H_2SO_4 graphs reveal a clear effect of zinc) are shown in Figs. APP. II-1, 2, 3.

Fig. APP. II-1 records the zinc data found on varying the distance from the nozzle, where the yarn is quenched. Since at a distance = 0, *i.e.* at the nozzle, no zinc can be present in the filament, the graphs suggest a maximum at a

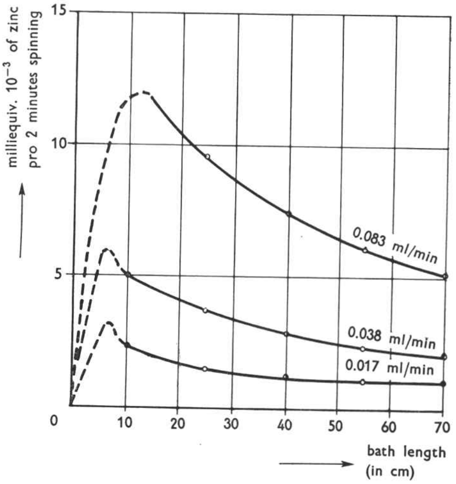


FIG. App. II-1 Zinc content of the undecomposed filament as a function of the bath length. Results obtained on varying the viscose delivery.

viscose : 7.3/5.5/36.5 XR = 0.44
Dope 0.11% 0 83
spinning bath : 4.5/13.0 $Z = 4.5$ $T = 45$ °C
nozzle : 100 μ
drawing off speed: 5 m/min

rather small distance from the nozzle. Theoretically, such a course is expected if the zinc content is governed by a diffusion process+subsequent immobilization by cellulose xanthate in the spinning filament (see CHAPTER IV). Sampling could not be carried out, however, at smaller distances, owing to disintegration of the filament.

On varying the viscose delivery (Fig. APP. II-2), and sampling at distances proportional to the delivery the zinc content increases linearly in dependence on the viscose delivery.

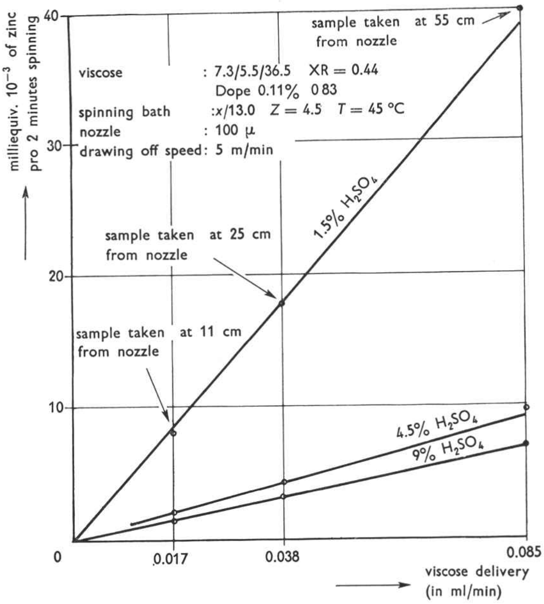


FIG. App. II-2 Zinc content of the undecomposed filament as a function of the viscose delivery.
Results obtained on varying the H_2SO_4 contant of the spinning bath.

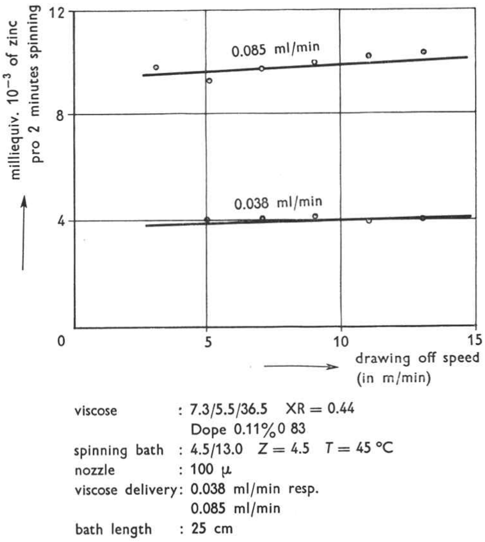


FIG. App. II-3 Zinc content of the undecomposed filament as a function of the drawing off speed.

On varying the drawing-off speed (Fig. APP. II-3) at a certain viscose delivery, the zinc content of samples taken at a certain distance from the nozzle appears to be independent of the drawing-off speed.

So, the results obtained are in harmony with the diffusion spinning relations.

As quenching bath also a solution of 5 N NaCl, saturated with $NaHCO_3$, has been used. However, the zinc contents determined in this way are much lower; presumably the zinc cellulose xanthate acts as an ion-exhanger.

Washing the regular sample with a buffer solution of pH 3–4 (0.1 N Na-acetate+acetic acid) instead of with distilled water hardly affected the zinc data obtained in this spinning region: so, $Zn(OH)_2$ was probably not present in the regular sample.

When in the low acid L-region a viscose spinning bath combination with dope and such a combination without dope were compared, no effect of the dope was found in the zinc contents. Apparently, neither the diffusion of zinc nor its immobilization by cellulose xanthate is affected by the presence of a dope.

In a further attempt to characterize the penetration depth of the zinc ions, cross-sections of the washed yarn sample were stained for 10–15 seconds with a 1% solution of pyrocatecholviolet and afterwards treated with a 0.1 mol phosphate buffer solution of pH 9. When this procedure was carried out with yarns spun under the conditions of the low acid L-region (immersion lengths 25 cm, 40 cm and 60 cm), the following microscopic observations were made:

Without staining, the cross-sections show a differentiation between a pale yellow outer layer and a clearly visible, slightly darker core. The staining with the indicator results in orange-coloured cross-sections. On applying the buffer solution, the core of the filaments becomes intensely blue, in contrast with the yellow-orange colour which the indicator has at this pH and which is found in a surrounding outer layer. As checked by experiments in vitro the blue color indicates the presence of zinc ions, under these pH-conditions.

Except for the imperfections of the sampling procedure, these results can be considered to prove the presence of zinc up to the centre of the filament.

Increasing the immersion length results in a smaller zinc-containing core.

In the low acid L-region again no difference was found, in regard to the presence of zinc irrespective of the presence or absence of a dope during spinning.

In the acid-poor P-region no zinc could be detected in this way; in the medium-acid M-region (experiments were carried out with ~9% acid) zinc was only found in the core, when sampling was done after short immersion lengths (1.5 cm).

APPENDIX III

The solubility of cellulose xanthate

For determining the solubility of cellulose xanthate, model filaments were spun in a coagulating bath of 2 mol $(NH_4)_2SO_4$, washed in this bath for 5–10 min. and blotted between filter paper.

Samples 10 cm long were put into test tubes containing ca. 15 cm³ of the medium to be studied; occasionally the test tubes were gently shaken.

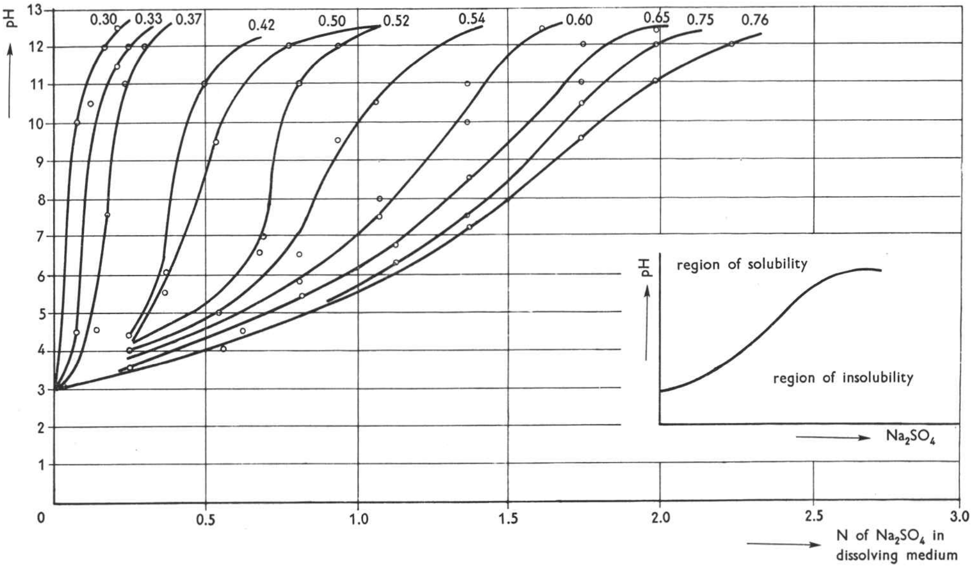


FIG. App. III-1 The solubility of cellulose xanthate in dependence on pH and Na_2SO_4 content of the dissolving medium.
Results obtained on varying the XR.

Solubility is observed visually after about 15 min; dissolving is defined as the vanishing of the filament. In this way the solubility of a small amount of cellulose xanthate in a large amount of solvent is determined. The maximum obtainable concentration of solute is not taken into consideration.

The media were composed of buffer solutions, *viz.*:

for pH 3 – 6: 0.1 N acetic acid + 0.1 N Na-acetate
for pH 6 – 9: 0.1 N prim. + 0.1 N sec. Na-phosphate
for pH 9 – 13: 0.1 N sec. Na-phosphate + 0.1 N NaOH,

to which electrolytes had been added.

After the addition of the salts the pH-values of the media were measured with a glass-electrode pH-meter. The pH of the media was varied by values of $^1/_2$.

Fig. App. III-1 records graphically some of the experimental results: the pH at insolubility is given against the normality of Na_2SO_4 of the medium at different xanthate ratios of the cellulose xanthate (half a pH-value higher, solubility is observed).

The upper region represents dissolving conditions.

Solubility was found to be dependent on:

1. the XR of the cellulose xanthate
2. the pH of the medium
3. the type and amount of salts in the medium.

The solubility in the various sulfate solutions investigated increases in the order $NH_4^+ < K^+ < Na^+$, Mg^{++}, compared on a normality basis.

Solubility is resticted to pH-values $> \sim 3$, *i.e.* the xanthate-ion state.

At high pH-values ($> \sim 13$) the measurements indicate the relative unimportance of the XR and salts. It is suggested (*cf.* Tait c.s. [1]) that this might be caused by an interaction between the hydroxyl ions and the hydroxyl groups of the cellulose chain.

Literature

1. C. W. Tait, R. J. Vetter, J. M. Swanson en P. Debye, J. Pol. Sc. **7** – 261 (1951)

LEVENSBERICHT

Op aanbeveling van de Senaat volgt hier van de schrijver een kort levensbericht.

Hij werd op 19 januari 1924 te Amsterdam geboren en bezocht na de lagere school te Oosterbeek het Stedelijk Gymnasium te Arnhem.

Het eindexamen-β werd door hem afgelegd in 1942. Vanaf 1945 studeerde hij scheikunde aan de Rijksuniversiteit te Utrecht. In 1947 legde hij daar het candidaatsexamen af.

De studie zette hij voort aan de Rijksuniversiteit te Leiden, alwaar hij in 1950 het doctoraalexamen met als hoofdrichting organische scheikunde aflegde.

In de jaren 1949–1950 was hij tevens als assistent verbonden aan de afdeling voor physische chemie.

Tot 1953 bleef hij daarna eerst als assistent, later als hoofdassistent verbonden aan de afdeling voor theoretische organische chemie van de Rijksuniversiteit te Leiden.

In 1953 trad hij in dienst bij de Algemene Kunstzijde Unie N.V. te Arnhem.

STELLINGEN

1.

Het is mogelijk een aantal belangrijke aspecten van het viscose-spinproces te beschrijven op basis van diffusie-processen, chemische reacties en structuurordenende processen.

Dit proefschrift.

2.

Bij beschouwingen over de wisselwerking tussen viscose en spinbad moet er mede rekening gehouden worden dat zink-cellulose-xanthogenaat het karakter van een complex heeft.

Dit proefschrift.

3.

Het lijkt in principe mogelijk de kinetiek van door diffusie geïnitieerde reacties nader te bestuderen d.m.v. een spinproces met variërende aftreksnelheid.

Dit proefschrift.

4.

Uit een oogpunt van moleculaire structuur is een spectroscopisch onderzoek in het zichtbare en nabije U.V.-gedeelte van het spectrum van het di-anisylstikstofoxyde radicaal en verwante verbindingen interessant, daar het mogelijk lijkt dat in deze groep verbindingen neutrale moleculen, radicalen, positieve en negatieve ionen met nagenoeg hetzelfde kern-skelet kunnen optreden.

5.

De geometrische structuur van aromatische ethers, bij welke een COC-hoek van ca. 120° gevonden wordt, werpt de vraag op of aan de ether-zuurstof een sp^2-hybridisatie moet worden toegeschreven.

6.

De bewering van BUNN, dat molaire cohesie-energie-waarden van betekenis zijn bij de classificatie van smeltpunten van polymeren, is fundamenteel onjuist.

C. W. BUNN, J. Pol. Sc. 16 - 323 (1955).

7.

Door in methyleenchloride opgeloste polycarbonaten, op basis van bisphenol A, met loog te behandelen kan het moleculair gewicht stijgen. Dit behoeft niet noodzakelijk verklaard te worden, als door SCHINK gedaan, met de vorming van intermediaire verbindingen met een eind-standige -O-COOH groep.

F. SCHINK, J.f. prakt. chem. **17** - 107 (1962).

8.

Bij de grensvlak polycondensatie van bifunctionele zuurchlorides en diamines kan de viscositeit van het gevormde polymeer hoger zijn dan overeenkomt met de toegevoegde hoeveelheid monofunctioneel zuurchloride. Het is onwaarschijnlijk dat dit toegeschreven moet worden, als gedaan door Onyon en White, aan de vorming van vertakte ketens.

P. F. Onyon en E. B. White, Makrom. Chem. **54** - 143 (1962).

9.

De door Hoste en Gillis vermelde waarde voor de moleculaire extinctiecoëfficiënt van het uit SeO_2 en 3,3′-diamino-benzidine gevormde piazoselenol volgt niet uit de in hun publikatie vermelde gegevens.

J. Hoste en J. Gillis, Anal. Chim, Acta **12** - 158 (1955).

10.

De door Lyselius en Samuelson ontwikkelde methode van onderzoek en beschouwingswijze en de door hen hieruit getrokken conclusies betreffende de verdeling van xanthogenaat-groepen over de 6 dan wel 2,3 posities van cellulose in viscose zijn niet zonder meer in overeenstemming met elkaar.

A. Lyselius en O. Samuelson, Sv. Papperstidning **64** - 815 (1961).

11.

Voor de uitvoering van een deelproces met een kinetisch karakter, waarvan het produkt geen evenwichtstoestand bereikt, verdient het gebruik van parallel opgestelde produktie-eenheden de voorkeur (uit een oogpunt van totale proces-beheersing) boven het gebruik van één enkele grote produktie-eenheid.

12.

Analoog aan de diffusie- en spin-relaties, welke in dit proefschrift beschreven zijn, kunnen betrekkingen opgesteld worden voor de warmtegeleiding in cilindrische, niet-turbulente systemen.
Enkele conclusies hiervan zijn:

a. Voor smelt-spinprocessen, waarbij in afhankelijkheid van de temperatuur overgangen in de spinnende draad plaats vinden (b.v. vloeibaar → vast), geldt dat de afstand van de spinplaat, waar deze overgangen gevonden worden, lineair afhankelijk is van de dosering per spinplaat-gat en onafhankelijk van de aftreksnelheid.
b. Voor een geïdealiseerde (d.w.z. met een uniforme binnenwand-temperatuur) uit uniforme pijpen opgebouwde warmte-wisselaar voor niet-turbulent stromende massa's geldt, dat de lengte van alle pijpen tezamen een, slechts van de proces-omstandigheden afhankelijk, constante is. Deze constante is onafhankelijk van de gekozen pijp-diameter en lineair afhankelijk van de dosering aan de warmtewisselaar.

13.

Voor de verdere ontwikkeling van de Nederlandse Industrie is de mondigheid van de gehele groep van werknemers van essentieel belang.