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Literature Review on Possible Alternatives to Tar for Antiskid Layers

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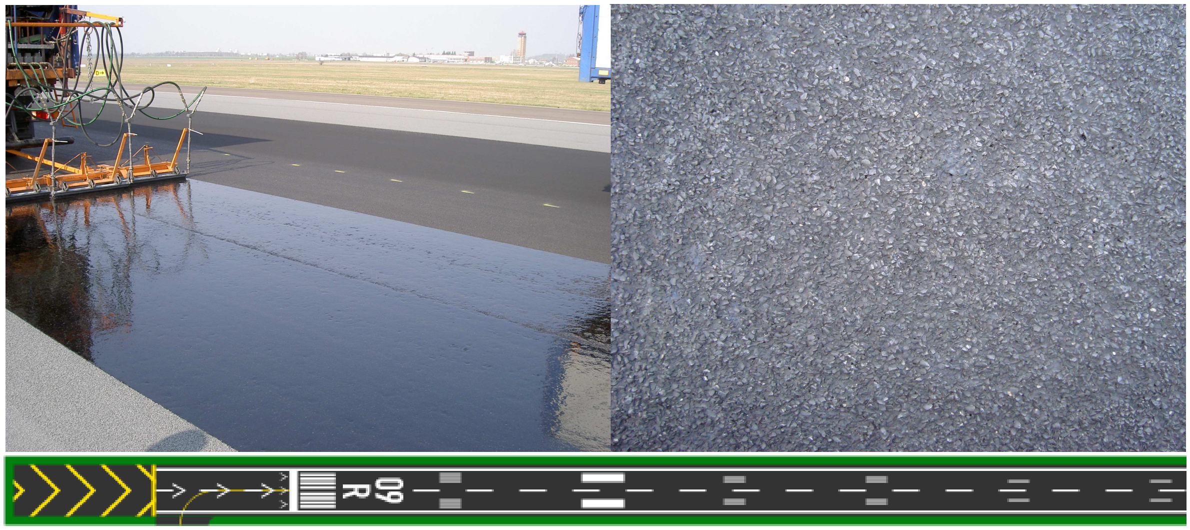

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Literature Review on
Possible Alternatives to Tar for Antiskid Layers

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Abbreviations

CLSM	Confocal Laser Scanning Microscopy
D.O.L	Design Objective Level
DSC	Differential Scanning Calorimetry
EVA	Ethylene Vinyl Acetate
FAA	Federal Aviation Administration
FTIR	Fourier Transform Infrared Spectroscopy
ICAO	International Civil Aviation Organization
LWT	Loaded Wheel Test
MMT	Montmorillonite
OMMT	Organomodified Montmorillonite
OPC	Ordinary Portland Cement
PAHs	Polycyclic Aromatic Hydrocarbons
PAV	Pressure Aging Vessel
PCN	Polymer-Clay Nanocomposite
PMA	Polymer Modified Asphalt
PMBs	Polymer Modified Bitumens
SBS	Styrene Butadiene Styrene
SBR	Styrene Butadiene Rubber
TEM	Transmission Microscopy
TFOT	Thin Film Oven Test
TGA	Thermo Gravimetric Analysis
VOCs	Volatile Organic Compounds
WTAT	Wet Track Abrasion Test
XRD	X-ray Diffraction

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Introduction

Coal tar is derived from crude coke oven tar that is a by-product of the combustion of coal in steel manufacturing. The crude coke oven tar is then refined, through distillation, into a number of products, including various grades of road tar (RT). RT-12 grade refined coal tar, which conforms to the requirements of EN 13847 [EN 13847, 2001]. These grades are used to produce coal tar emulsion pavement sealers.

[http://www.asphaltstore.com/products_page.aspx?cid=5]

Unlike asphalt pavements with bitumen as binder (which can be damaged and eventually destroyed by the effects of thermal and UV induced oxidation, erosion caused by moisture, gasoline and oil drippings, salt and chemicals), coal tar emulsion pavement sealers, due to the refined tar's unique chemical and molecular structure, are inherently resistant to these elements and provide protection superior to asphalt based pavement sealers. Regular application of coal tar emulsion pavement sealers will protect the pavement surface and extend the service life of the pavement.

[http://www.asphaltstore.com/products_page.aspx?cid=5]

In airports, there are different areas such as runways, taxiways, aprons and parking areas. For runways, good skid resistance and water drainage of the surface layer is necessary [Airfield uses of asphalt, EAPA 2003]. Tar, because of its good adhesion properties and other advantages as mentioned above, is widely used in thin, high skid resistance surfaces.

Figure 1 Construction of antiskid layer on the airfield

Tar however is toxic and carcinogenic because of its high benzene content. This material did not meet the Dutch environmental standards. In the Netherlands and many other countries, the use of tar in pavement applications is not allowed anymore because of the environmental concerns. The only temporary exception for the use of tar is for the earlier mentioned antiskid layers for airport applications (See Figure 1), will not be allowed anymore after 2010. Therefore, alternatives for tar-bearing antiskid layers are under investigation for a number of years.

On one hand, alternatives should of course satisfy the basic requirements of enough friction between tire and surface and enough macro-texture to prevent aquaplaning. On the other hand, alternatives should have the same or even better properties compared to tar-bearing antiskid. Alternatives must at least have the following properties [Argue 2005，and Shoenberger 2007]:

1. very good adhesion properties of the system and surface;
2. good skid resistance and surface water drainage for good braking while avoiding aquaplaning;
3. good resistance to aviation fuel and kerosene (paraffin), impermeable to most liquids;
4. ageing of the binder is seen as a cause of failure of the antiskid layers, so good ageing properties are very important for a durable performance;
5. good mechanical properties (flexible, stiffness, fatigue and permanent deformation resistance);
6. being able to withstand a temperature of 100 ℃ for a minimum of one minute;
7. good resistance to weathering.

Until now, little researches were focusing on antiskid layers. So it is hardly to get the exact requirements for alternatives. Evaluations on antiskid layer should be carried out before alternative selections can be made.

Table 1 Test results comparing coal tar emulsions and bitumen emulsions

Test	Coal Tar Emulsion	Bitumen Emulsions
Gas Resistance	Pass	Failure
Motor Oil Resistance	Pass	Failure
Kerosene Resistance	Pass	Failure
Scrub Resistance (Durability test)	4000 cycles	2400 cycles
Water re-absorption	1.00%	3.2%
Odor	Some	None
Skin Irritant	yes	yes
Photosensitive	yes	no
The water re-absorption test is an indicator for durability since water attacks seal coatings causing re-emulsification. Low numbers are better; The photosensitivity is that causes burning to some workers.		

[http://www.pavecoat.com/coal_tar_vs_asphalt.html]

Bitumen emulsions, with good performance and durability under a wide range of climatic and traffic conditions, are widely used for industrial areas or for specific applications. Compared with coal tar emulsion (See Table 1), bitumen will always be less odorous and cause far less burning to the workers, but performance is less with regards to protection against UV radiation, gas, oil, chemicals, color retention, and water absorption.

Bitumen emulsions have several advantages:

1. low temperature during application and storage, cost-effective;
2. the low temperature of application and storage minimizes hazards from fuming and improves safety;
3. storage and applications at low temperatures minimize the use of energy.
4. bitumen emulsions have a lower impact on the environment in terms of pollution and toxicity relative to tar-bearing materials.

Additives are known to improve the properties of bitumen emulsions in special road applications. Polymer (SBS, SBR and EVA), clay (illite, kaolinite and montmorillonite) and epoxy modified bitumen/bitumen emulsions were successfully used in South Africa and Australia.

At the same time, waterborne coatings, polyurethanes and epoxy modified bitumen, with good adhesion, fuel, water and chemical resistance, are widely used for roofing, building construction and pavements. They are also possible alternatives to tar.

This paper presents a literature review on the properties and the use of bitumen emulsion and modified bitumen emulsions in the road making industry, together with the current researches and findings about waterborne coatings, polyurethanes and epoxy modified bitumen. This literature review aims to give general ideas for finding a reasonable material to replace tar-bearing antiskid surfaces which are used on runways nowadays.

Part I Antiskid Runways and Current Researches

1. Antiskid Runways and Tar

1.1 Antiskid Runways

A runway (See Figure 2) is a strip of pavement on an airport, on which aircraft can take off and land. [http://en.wikipedia.org/wiki/Runway]

The runway pavement surface is prepared and maintained to maximize friction between tyre and road surface. There are several ways to realize this. One way is applying a grooved asphalt surface. To minimize hydroplaning following heavy rain, the pavement surface is usually grooved so that the surface water film flows into the grooves and the peaks between grooves will still be in contact with the aircraft tires [http://en.wikipedia.org/wiki/Runway; Kim, 2009]. Existing pavements may have surfaces that are not suitable for sawing grooves. A survey should be conducted to determine if an overlay or rehabilitation of the pavement surface is required before grooving [FAA, 150/5320-12C, 1997].

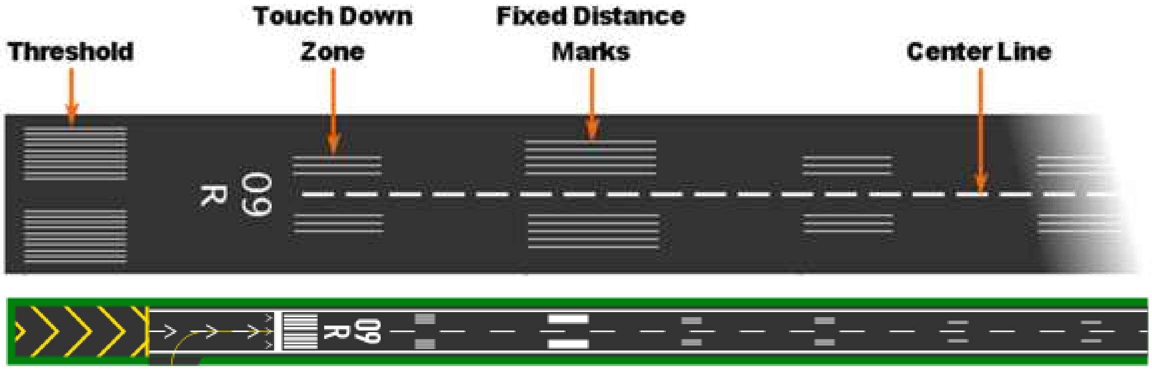


Figure 2 Runway diagram

Another way to maximize friction is using chip or slurry seals. These solutions include the antiskid surface. Antiskid is a tar-bearing bituminous surface coating that protects the underlying (asphalt) pavement construction and has excellent surface friction and texture properties [van Leest, 2005].

The aggregate for antiskid surfaces shall either be natural or manufactured angular aggregate and shall be composed of clean, hard, durable, uncoated particles, free from lumps of clay and all organic matter. In state of Wisconsin, the aggregate shall meet the gradation shown in Table 2. [Wisconsin, 1998]

Table 2 Gradati 和 on of aggregates for antiskid runways

Sieve size	Percentage by weight passing sieves
2.36	100
1.18	97-100
0.85	85-100
0.60	15-85
0.40	2-15
0.15	0-2

Asphalt surfacings normally suffer from ageing as a result of the oxidative action of solar radiations, oxygen, etc. Due to ageing, the wearing course might ravel i.e. loss of aggregates from its surface might occur.

Unlike grooved asphalt surfaces, antiskid surfaces with coal tar emulsions can improve this aging resistance. Furthermore, it can provide a fuel resistant surface, without causing an unacceptable reduction in the friction characteristics of the pavement [Engineering Brief, 2005]. The rubberized coal tar pitch emulsion seal coat was often used for tar-bearing antiskid surfaces for runways. These coal tar pitch emulsions should consist of coal tar pitch emulsion, water, latex rubber and aggregate in proportions. In state of Wisconsin, the tar emulsion mixture design should meet the requirements given in Table 3 [Wisconsin, 1998].

Table 3 Design criterion for antiskid runways

Test property	Purpose	criterion
Brookfield Viscosity posies @ 77℉	Incompatibility between latex and coal tar	10–90
Brookfield Viscosity poises @ 77℉	Workability of composite mix	10–90
Scuff Resistance torque @ 8 hours	Rate of set	>100 in-lbs
Scuff Resistance torque @ 24 hours	Final scuff	>8 hr. torque
Freeze–Thaw @ 5 cycles @ 10 cycles	Cracking	<1 <3
Adhesion Rating	Loss of adhesion	= 5A
Fuel Resistance	Fuel penetration Loss of adhesion	No penetration or loss of adhesion

1.2 Properties of Tar

Tar is a viscous black liquid derived from the destructive distillation of organic matter (e.g. coal and petroleum). Tar was a vital component of the first sealed, or "tarmac", roads. The streets of Ba ghdad were the first to be paved with tar from the 8th century AD. It was also used as seal for roofing shingles and to seal the hulls of ships and boats [http://en.wikipedia.org/wiki/Tar]. Coal tar was formerly used as one of the primary ingredients of asphalt pavements. Today, petroleum derived binders and sealers are commonly used. These sealers are used to extend the life and lower maintenance cost associated with asphalt pavements. [http://en.wikipedia.org/wiki/Coal_tar].

1.2.1 Advantages of Tar

Two basic types of pavement sealers for runway surfacings are currently on the market; refined coal tar-based and bitumen-based. [Austin, 2007]

Refined coal tar, a byproduct of the coking process used for steel production, is a very complex mixture of chemicals, quite different in its molecular structure from bitumen. Some of the constituents are in a class of chemicals described as Polycyclic Aromatic Hydrocarbons (PAHs). Being stable in molecular structure, these chemicals repel oil and gas, and provide a barrier coat to protect asphalt surfaces from the destructive elements of weather and chemicals. [Austin, 2007]

Coal tar-based pavement sealers are typically used at airports for plane parking, aprons, taxiways and runway areas. The Federal Aviation Administration Advisory Circular 150/5370-10A Standards for Specifying Construction of Airports includes a requirement for Item P-629, Coal-Tar Sealer/Rejuvenator, which requires pavement sealers to contain at least 35% coal tar pitch for acceptance on asphalt runway pavements. The reason for this requirement is that coal tar-based pavement sealers offer a greater degree of resistance to jet fuel than bitumen-based sealers. [Austin, 2007]

Coal tar has a great advantage over bitumen that it has better chemical resistance than bitumen Coatings. Coal tar coatings hold up better under exposure to petroleum oils and inorganic acids. Another outstanding quality of coal tar coatings is their extremely low permeability to moisture. [http://www.truthaboutcoaltar.com]

1.2.2 Disadvantages of Tar

Coal tar was used for antiskid surfaces on airfields, providing a good water and fuel resistance. Unfortunately, it is toxic and carcinogenic because of its high benzene content. So many countries all over the world have been eliminated its usage. Because of PAHs, this material did not meet the Dutch environmental standards and is not allowed since 1990. In the Netherlands and many other countries, the use of tar in pavement applications is not allowed anymore because of the environmental concerns. For the Netherlands however, only temporary exception for the use of tar is on antiskid layers for airport applications. But after 2010, it will not be allowed for airport pavement applications anymore.

This forces us to find alternatives and develop runway surface layers that don’t contain tar but are comparable to coal tar antiskid in terms of material properties and cost effectiveness, and meet all current statutory requirements.

2. Current Researches for Finding Alternatives

2.1 Statutory Requirements

The statutory requirements for antiskid runways surfacing that currently apply in the Netherlands take the following aspects in account [van Leest, 2004]:

1. skid resistance
2. texture depth
3. the environment

Skid resistance: Legislation in the Netherlands governing skid resistance is identical to that contained in the ICAO Manual and the FAA Advisory Circular with regard to the Design Objective Level or D.O.L Depending on the type of equipment, the type of measuring tyre and the test speed, the skid resistance values required on a newly laid surface are shown in Table 4.

Table 4 Required skid resistance values on newly laid surfaces in the Netherlands

		Dutch legislation (newly laid)		**FAA and ICAO design Objective level**		**Experiences With asd**
Type of equipment		SFT and BV11		SFT and BV11		SFT
Type of measuring tyre		smooth	Aero profile	smooth	Aero profile	smooth
Test speed	65 km/h. 1mm water	0.82	0.70	0.82	0.70	
	95 km/h. 1mm water	0.74	0.60	0.74	0.60	0.81-0.96
	120 km/h. 1mm water					0.74-0.87

Unlike the ICAO Manual, the D.O.L. is normally applied in the Netherlands as requirement immediately after a surface is placed. ICAO only applies the D.O.L. as a target value.

Texture depth: The requirements set in the Netherlands for the texture depth are also the same as those in the ICAO Manual and the FAA Advisory Circular. To restrict the danger of aquaplaning, etc., the average texture depth for newly laid surfaces (determined using the sand patch test) must be at least 1 mm

The environment: Since 1st January 2001, materials used for road pavements must meet the requirements laid down in the building materials decree. This contains composition values (mg/kg dry material) and emission levels (mg/m^2 per 100 years) for various types of impurities. For the content of 10 substances containing PAHs, the maximum composition value is 75 mg/kg dry material.

2.2 Current Pre-selections

A CROW working committee has been set up in the Netherlands to establish whether there are any existing surface layers or coatings that are qualitatively comparable to tar-bearing antiskid surfaces. The precondition for the selection of the alternatives is that they must be existing products and must be proven techniques for surface layer systems that have already been used on runways. Six alternative systems for surface layers and coatings were selected, and compared with tar-bearing antiskid runways [van Leest, 2004]:

1. epoxy-based surface coating;
2. surface coating with a tar-less bituminous binder;
3. surface coating based on a 2-component synthetic binder;
4. SMA (graded as 0/11, 0/14 or 0/16 mm);
5. supergrip (a thin surface layer with an open structure, SGP);
6. mechanically treated asphaltic surface layers (grooved asphalt).

Three kinds of investigations were performed in this research:

1. in situ measurements of the bonding level of a surface coating to the underlying asphalt layer.
2. in situ measurement of raveling resistance using the raveling tester developed by KOAC-NPC.
3. laboratory tests on submerged cores using the steel brush test to determine the chemical resistance.

2.2.1 Bonding Test

This test was only conducted on surface coatings. Holes with 9 centimeter diameter were drilled in the pavement to a depth of 20 mm so that the drill bit passes through the surface coating. Steel plates with pull-hooks were stuck to the dry surface with a quick-hardening adhesive. Once the adhesive was dry, the antiskid layer was removed and the tensile force measured. Figure 3 shows the setup that was used.

Three surface coatings were included. Average failure stresses are presented in Table 5. The tar-less bitumen coating were pulled entirely free from the underlying pavement. In the case of the epoxy coating, the aggregate was pulled away from the surface coating that stuck to the underlying layer. The results of the coating on epoxy basis are comparable to tar-bearing antiskid. The results for the tar-less coating on bitumen basis were clearly poorer.

Figure 3 Setup for bonding tests and kinds of surface coating

Table 5 Average failure stress

Material	Average failure stress/ Mpa
surface coating with epoxy binder	1.34
surface coating with tar-less modified bitumen	0.64
Tar-bearing antiskid	1.14

2.2.2 Raveling Test

The raveling test is used to expose the pavement surface to repeated shear stresses. A ring–shaped rubber load plate (outside diameter 200mm, inside diameter 100mm) is placed on the asphalt and rotated repeatedly. The frequency of this rotation can be varied between 0 and 25 Hz. The weight of the apparatus was set at approximately 500 kg (based on a friction coefficient of 0.5-0.7). Figure 4 shows the setup that was used for raveling test.

Figure 5 shows the results of raveling tests on three kinds of coatings at the same rotation frequency and rotation time. The raveling resistance of bituminous binder coatings without tar is the poorest.

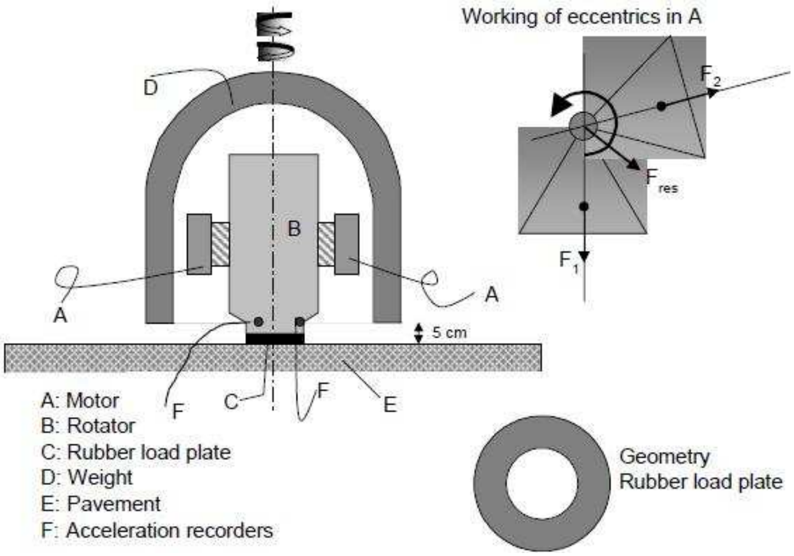


Figure 4 Asphalt raveling tester setup

Figure 5 Results of raveling test on three kinds of coatings

2.2.3 Steel Brush Test

The test procedure of the steel brush test (chemical resistance test) is as follows:

1. all extracted cores are sawn to the same height (60mm);
2. all test samples are weighed;
3. for each paving material, 3 cores are submerged in Kerosene (1 hour). The submersion times are based on practical experience. When kerosene is spilled on the runway, it will be quickly removed from the surface, normally in less than one hour.
4. after drying, the test samples are brushed with a steel brush (see Figure 6) at a pressure of 600 kPa for 90 seconds. Each test sample is weighed every 30 seconds and the loss of weight is determined.

Figure 6 Setup for steel brush test

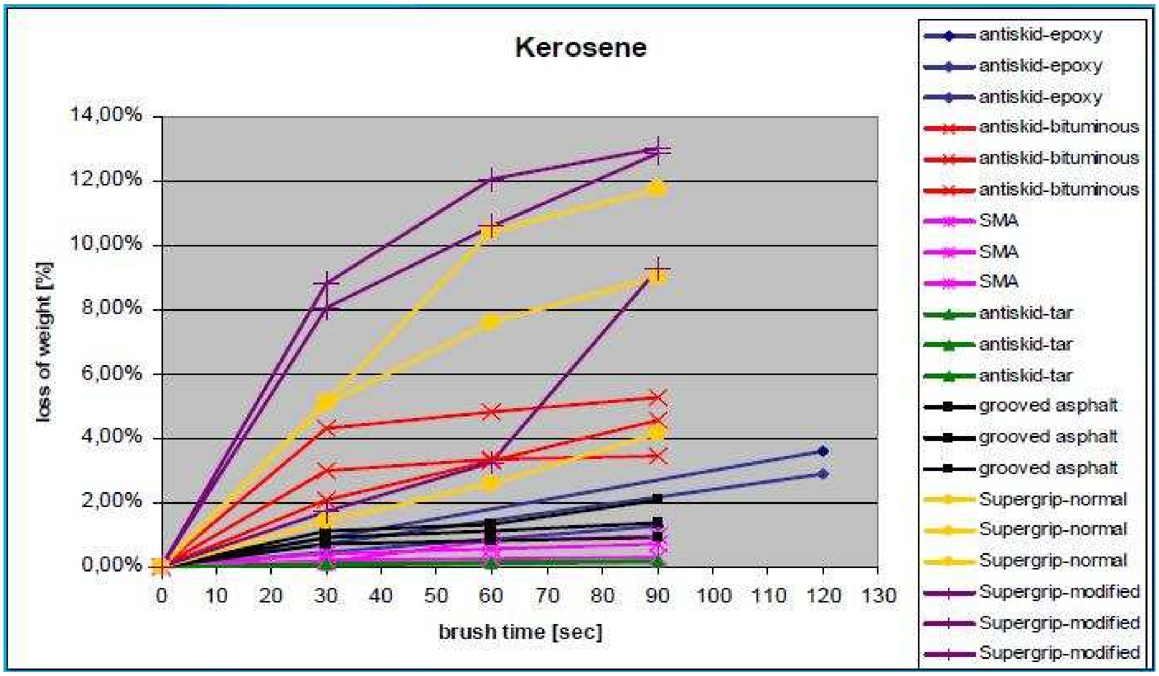


Figure 7 Results of steel brush tests on surface coatings

Figure 7 shows the results of the kerosene resistance test, where the tar containing antiskid is the reference. The tar containing antiskid had the best kerosene resistance results but SMA scored well too. Both tar-less surface coatings (with epoxy and modified bitumen) show significantly poorer results compared to antiskid.

The results of the bonding test, raveling test and steel brush test was done by the CROW group have shown that none of the selected possible alternative surface layers that have been tested achieved the same results on all properties as the tar-bearing antiskid. The alternative coatings are comparable on skid resistance and texture depth, but their raveling and chemical resistance is substantially lower [van Leest, 2004]. These results suggested us to develop a new kind of material.

2.3 New Materials: Modified Bitumen

As the CROW group research shows, none of the selected alternatives can give a performance as good as tar-bearing antiskid, we need to find new materials that meet the statutory requirements and have the same raveling and chemical resistance as the tar-bearing antiskid.

2.3.1 Sealoflex

A special kind of Polymer Modified Asphalt (PMA), Sealoflex, was developed by Ooms [Put, 2006], the Netherlands. Sealoflex is a type of bitumen which is modified with an elastomer called Styrene Butadiene Styrene (SBS). This type of modification is quite common with other manufacturers, but Sealoflex distinguishes itself by the use of "Seal-O-Mat Gellation technology" which gives the product superior handling and aging properties compared to other PMBs. [http://www.oomsindia.com/visitfactory.htm]

Sealoflex is coal tar free and jet fuel resistat. It was applied on many airports (e.g. Amsterdam Schiphol Airport) and showed an excellent resistance towards jet fuel spillage on the runway. Standard Hot Mix Asphalt mixtures may lose up to 10% weight after 24 hour soaking in jet fuel, and Standard Polymer Modified Asphalt (PG 76-22) may lose up to 4.5% weight after 24 soaking in jet Fuel. Sealoflex jet fuel resistant asphalt mixture however loses less than 0.5% by weight (See Figure 8). [Sealoflex Airport Projects; Sealoflex]

Figure 8 Compacted samples after 24 hours immersion in jet fuel

2.3.2 Citgoflex

The polymer modified bitumen developed by CITGO Company, known as Citgoflex [Rooijen, 2004] was developed and used for tests on a distressed taxiway at La Guardia Airport (USA) in August 2002. A visual inspection was carried out in October, 2003. No measurable rutting was observed, and there was no evidence of cracking, raveling or fuel-induced damage in the pavement.

Laboratory studies were carried out to characterize the jet fuel resistant PMA (Citgoflex, PMA JR) and compare its performance with that of standard Penetration Grade bitumen (Pen 40/60) and a PMA (PMA S) with proven good performance. [Rooijen, 2004]

The resistance to jet fuel (or any other fluid) can be assessed by keeping bitumen specimens immersed in jet fuel for a certain period of time (e.g. 24 hours) and by measuring the loss of weight (only one side of the specimen is kept immersed in the fluid and the loss of weight is measured after the chemically treated side has been mechanically "brushed" during two minutes with a steel brush). The loss of weight typically ranges from less than 0.5 % for asphalt mixtures with jet fuel resistant bitumen (Citgoflex, PMA JR) to more than 10 % for asphalt mixtures with standard bitumen.

The values for Penetration and Softening Point of the bitumens are shown in Table 6. Based on these properties it can be concluded that all three bitumens are to some extent softened by jet fuel. The effect is largest for Pen 40/60 bitumen (300% increase in Penetration) and the smallest for Citgoflex (20 % increase in Penetration).

Table 6 Bitumen properties before and after jet fuel immersed

Bitumen types		**Penetration at 25 ℃/ 0.1 mm**	**Softening Point R&B/ ℃**
Pen 40/60 bitumen	Fresh	55	50.5
	Recovered (no conditioning)	50	51.6
	Recovered (immersed in jet fuel)	148	40.1
PMA S	Fresh	61	101.5
	Recovered (no conditioning)	50	97.5
	Recovered (immersed in jet fuel)	79	92.0
Citgoflex	Fresh	56	86.0
	Recovered (no conditioning)	54	82.0
	Recovered (immersed in jet fuel)	65	79.0

2.4 Other New Materials

New technology allows waterborne epoxy and polyurethane coatings to have a good adhesion and a high chemical resistance at prices competitive to conventional coatings. Detailed information about these kinds of materials will be discussed in Part III.

3. Conclusion

At the moment, there are no materials available that can replace tar for antiskid layer. In recent years, several kinds of research have been carried to find alternatives and some products, especially modified bitumen and modified bitumen emulsion, have been produced for use on runways. Sealcoat manufacturers have been quite successful refining the performance of bitumen based formulations by adding rubber or latex additives (e.g. Sealoflex and Citgoflex) which enhance water and fuel resistance and improve durability. These researches show a possible use of bitumen emulsion to replace tar because of the significantly properties improvement after modification.

Unfortunately, being a petroleum derivative, bitumen has a natural affinity for petrochemicals, so it can be easily dissolved by them. Curing time is another disadvantage, because runways and taxi ways should be available as soon as possible after construction or maintenance. Unfortunately, bitumen emulsion always need 2-6 hours for curing before they get their full strength.

Considering the disadvantages of modified bitumen emulsion, some other new materials with good adhesion and chemical properties need to be evaluated.

Part II Bitumen Emulsions and Modified Bitumen Emulsions

4. Bitumen Emulsions

4.1 Bitumen and Bitumen Emulsions

4.1.1 Bitumen

Mankind has been using bitumen in a range of applications for over 5000 years. Today, the main use of bitumen is in the road industry for construction and maintenance. Bitumen is difficult to work with at ambient temperatures since it is a highly viscous material under these conditions. It can, however, be transformed into a workable state by either applying heat (hot mixes), by blending with petroleum solvents (cutback mixes) or by emulsification with a surfactant in water to form bitumen emulsion [Gorman, 2004].

Bitumen is a complex colloidal system that consists of a mixture of hydrocarbons and heteroatoms, including saturated aliphatic groups, naphthenic groups or cycloparaffins, aromatic rings and aliphatic groups with olefinic double bonds [Gorman, 2004].

For bitumen to be made workable by heating, it must be heated to temperatures between 150 ^{o}C and 180 ^{o}C, at which stage it can be mixed with other components, such as mineral aggregate. Asphalt mixtures prepared in this way are known as hot asphalt mixtures. Working with bitumen at these temperatures is very dangerous, with a risk of serious burns. It also requires costly equipment for the heating, storage and application of the bitumen, as well as mixing it with the aggregates. [Gorman, 2004]

In contrast, bitumen emulsions can be applied without the need for heating (although they are still prepared at high temperatures).

4.1.2 Bitumen Emulsions

An emulsion is a thermodynamically unstable heterogeneous system including at least two immiscible liquid phases one of which is dispersed in the other in the form of droplets whose diameter is generally greater than 0.1 micrometers. The minimum stability inherent to this type of system may be increased by adding appropriate agents, such as surfactants or finely divided solids [TRB-EC102, 2006].

Emulsions can be formed by any two immiscible liquids, but in most emulsions one of the phases is water. Oil-in-water (O/W) emulsions are those in which the continuous phase is water and the dispersion (droplet) phase is an “oily” liquid. Water-in-oil (W/O) “inverted” emulsions are those in which the continuous phase is oil and the disperse phase is water. Emulsions can have more complex structures. In multiple emulsions, the disperse phase contains another phase which may not have the same composition as the continuous phase (See Figure 9) [TRB-EC102, 2006].

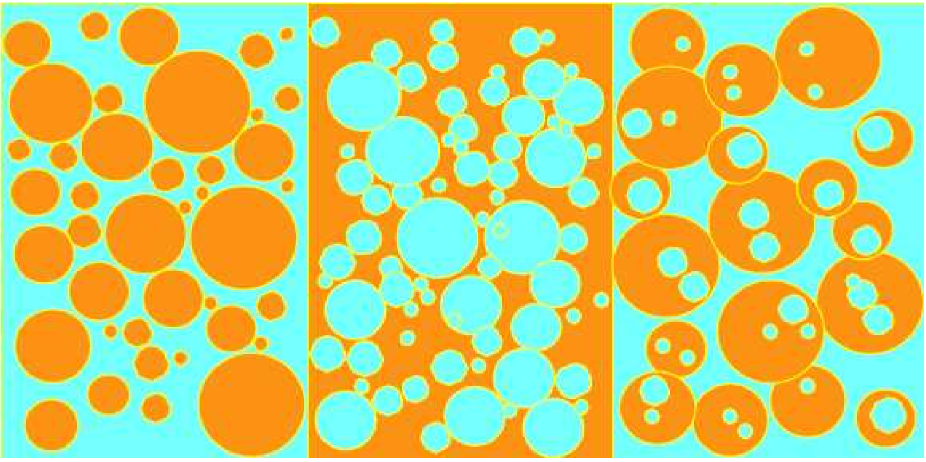

(1) (2) (3)

Figure 9 Types of emulsions

(1) O/W emulsion (2) W/O emulsion and (3) multiple W/O/W.

Bitumen emulsions are heterogeneous systems with two or more liquid phases, made up of a continuous liquid phase (water) and at least a second liquid phase (bitumen) dispersed in the former as fine droplets [TRB-EC102, 2006].

With viscosities in the range of 0.5-10 Pas at 60 °C, bitumen emulsions have a considerable lower viscosity than bitumen itself (100-4,000 Pas), allowing it to be used at lower temperatures. Low temperature techniques for construction and maintenance reduce emissions, reduce energy consumption, avoid oxidation of the bitumen, and are less hazardous than techniques using hot bitumen. They are also more economical and environmentally friendly than cold techniques using cut back asphalts. The environmental benefit of bitumen emulsions is particularly positive when used for in-place or on-site techniques which avoid the energy usage and emissions associated with heating, drying, and haulage of aggregate. The construction of a road with cold techniques has been calculated to consume approximately half the energy of one of similar bearing capacity made with Hot-Mix Asphalt (HMA) [Kennedy. 1997]. An Environmental Impact Analysis (EIA) technique called “eco-efficiency” has been applied to emulsion maintenance techniques (micro-surfacing and chip seal) and it was concluded that the emulsion system had less environmental impact than a thin hot-mix overlay [Takamura, 2001].

Emulsions are water-based and in many cases can be diluted further with water for applications such as dust control and priming. They are also compatible with hydraulic binders like cement and lime as well as water-based polymer dispersions like natural and synthetic latex. When mixtures of cement, latex, and bitumen emulsion cure, a composite binder is produced with a structure that cannot be duplicated with hot bitumen and with significantly improved properties compared to pure bitumen [Takamura, 2001; Brown, 2000].

Standard bitumen emulsions are normally considered to be of the O/W type and contain from 40% to 75% bitumen, 0.1% to 2.5% emulsifier, 25% to 60% water plus some other minor components. The bitumen droplets range from 0.1 to 20 micron in diameter. Emulsions with particle sizes in this range are sometimes referred to as macro-emulsions.

4.2 Nomenclature of Emulsions

4.2.1 Classification

Bitumen emulsions are classified according to the sign of the charge on the droplets and according to their reactivity. Cationic emulsions have droplets which carry a positive charge. Anionic emulsions have negatively charged droplets. Rapid-setting (RS) emulsions set quickly in contact with clean aggregates of low-surface area, such as the chippings used in chip seals (surface dressings). Medium-setting (MS) emulsions set sufficiently less quickly allowing them to be mixed with aggregates of low surface area, such as those used in open-graded mixes. Slow setting (SS) emulsions will mix with reactive aggregates of high surface area. RS emulsions are reactive and are used with unreactive aggregates; SS emulsions are unreactive and are used with reactive aggregates. The actual setting and curing time in the field will depend on the technique and materials being used as well as the environmental conditions [TRB-EC102, 2006].

In the naming of emulsions according to ASTM D977 and D2397, cationic RS, cationic MS, and cationic SS emulsions are denoted by the codes CRS, CMS, and CSS, whereas anionic emulsions are called RS, MS, and SS, followed by numbers and text indicating the emulsion viscosity and residue properties. For example SS-1H would be a slow-setting (i.e., low reactive) anionic emulsion with low viscosity and a hard bitumen residue. CRS-2 would be an active cationic emulsion of high viscosity. The QS (quick-setting) and CQS (cationic quick setting) designations for quick-setting emulsions have been introduced for emulsions intermediate in reactivity between MS and SS, which do not need to pass the cement mix test, and are used primarily in quick-setting slurry surfacing applications [TRB-EC102, 2006].

4.2.2 European Standard

The new European Standard EN 13808 uses a maximum of seven terms in the identification of a bitumen emulsion. These terms describe the following properties of the emulsion: Particle Polarity; Binder Content; Binder Type and Breaking Behavior. Their use is illustrated in Table 7 [EN 13808].

Table 7 Denomination of the abbreviation terms for cationic bitumen emulsions

Position	Letters	Denomination	Supporting document
1	C	Cationic bituminous emulsion	EN 1430 (particle polarity)
2 and 3	2 digit number	Nominal binder content in %(m/m)	EN1428 (water content) or EN1431 (recovered binder + oil distillate)
4 or 4 and 5 or 4 and 5 and 6		Indication of type of binder	EN 12591(specification for paving grade bitumen)
	B	Paving grade bitumen	
	P	Addition of polymers	
	F	Addition of more than 2%(m/m) of flux based on emulsion	
5 or 6 or 7	1 to 7	Relative breaking behavior	EN 13075-1 (breaking value)

Examples for abbreviation terms:

C 69 B 3: Cationic bitumen emulsion with a nominal binder content of 69% produced from paving grade bitumen and having a Class 3 breaking value.

C 40 BF 3: cationic bitumen emulsion with a nominal binder content of 40% produced from bitumen, containing more than 2 % flux, and having a Class 3 breaking value.

C 69 BP 3: Cationic bitumen emulsion with a nominal binder content of 69% produced from bitumen, containing polymers and having a Class 3 breaking value.

C 60 BPF 6: Cationic bitumen emulsion with a nominal binder content of 60% produced from bitumen, containing polymers and more than 2% flux and having a Class 6 breaking value.

4.3 Emulsifiers

An emulsion prepared by homogenizing two pure immiscible liquid components will rapidly result in phase separation. To prepare a stable emulsion, an emulsifier must be added that facilitates emulsification of the two immiscible phases and promotes stability.

Water molecules at the interface between oil and water have higher energy than those in bulk water. The result is an interfacial energy or tension which acts to minimize the interfacial area. The production of emulsion involves the creation of a large interfacial area between the bitumen and water, approximately 500 m^2 per liter. Emulsifiers are surface active agents (surfactants).

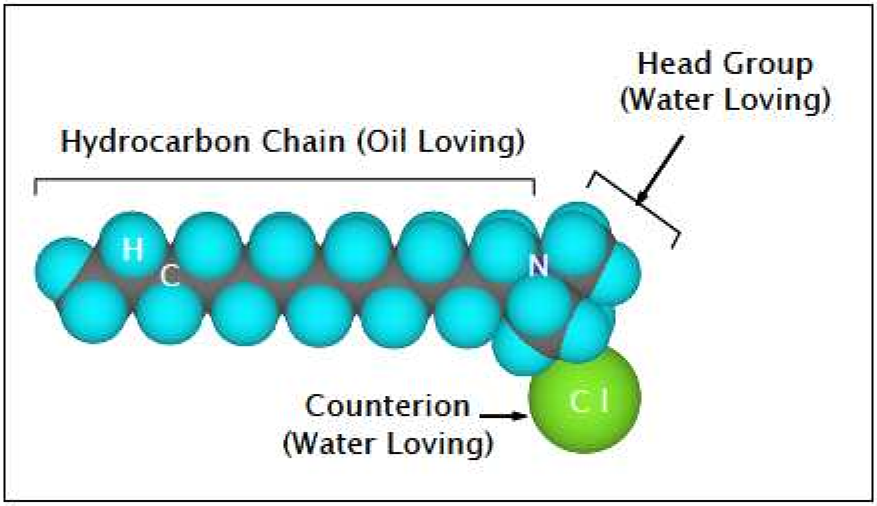


Figure 10 Cationic emulsifier molecule

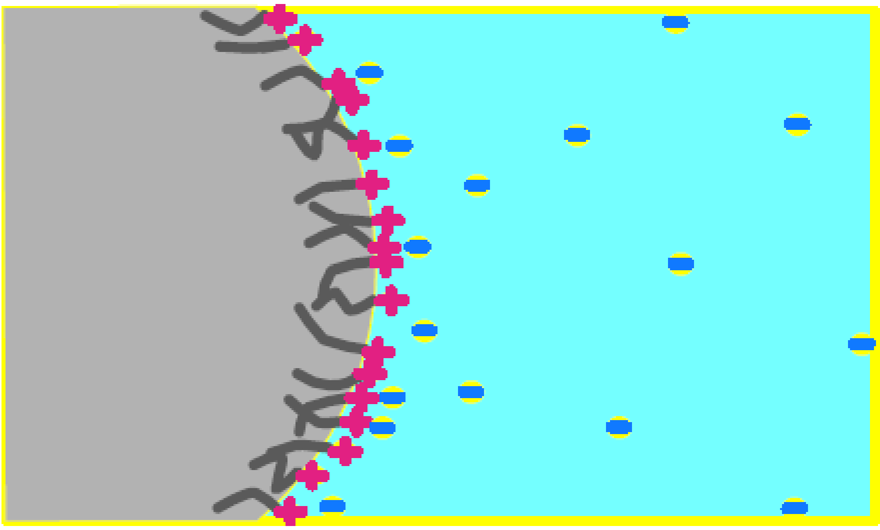


Figure 11 Origin of charge on bitumen droplets

A typical emulsifier has a hydrophilic “head” group (water-loving) and lipophilic (oil-loving, hydrophobic) hydrocarbon “tail” in the same molecule (See Figure 10). The hydrocarbon chain of the emulsifier ion orientates itself on the surface of the bitumen droplet, so that the hydrocarbon chain is firmly bound to the bitumen, with the ionic portion located at the surface of the droplet (See Figure 11). These both reduce the energy required to emulsify the bitumen and prevents coalescence of the droplets once formed. The choice and concentration of emulsifier also largely determines the charge on the bitumen droplet and the reactivity of the emulsion produced. [TRB-EC102, 2006]

Emulsifiers can be classified into anionic, cationic, and nonionic types depending on the charge their groups adopt in water.

4.3.1 Cationic Emulsifiers

In cationic emulsifiers, the electrovalent as well as the polar head group is positively charged and imparts a positive charge to the surface of the bitumen droplets.

Table 8 Typical cationic compounds commonly used as emulsifiers

Type of compound	**characteristics**	**Example of chemical structure**	**Emulsion class**
Monoamines	Appearance at room temperature: paste. Seldom used alone as emulsifier. Has to be reacted with acid.	$R\text{-}NH_2$	Rapid setting
Diamines	Appearance at room temperature: paste or liquid, highly efficient, used alone or in combination with other compounds. Has to be reacted with acid.	$R\text{-}NH\text{-}(CH_2)_3\ NH_2$	Rapid setting
Quaternary ammonium compounds	Appearance at room temperature: liquid. Used alone or in combination with other compounds. Does not require reaction with acid, except when low pH is desirable	 $R\text{-}\overset{\overset{Cl^-}{\oplus}}{N}(CH_3)_2\text{-}(CH_2)_3\ \overset{\overset{Cl^-}{\oplus}}{N}\ (CH_3)_3$	Medium and slow setting
Alkoxylated amines	Appearance at room temperature: liquid. Seldom used alone, but useful as component in formulated emulsifier. Required reacted with acid.	 $R\text{-}N\begin{matrix} CH_2\text{-}CH_2\text{-}OH \\ CH_2\text{-}CH_2\text{-}OH \end{matrix}$	slow setting
amidoamines	Appearance at room temperature: paste or liquid. Can be used alone or in combination with other compounds. Has to be reacted with acid.	 $R\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}NH\text{-}(CH_2)_3\ NH\text{-}(CH_2)_2\text{-}NH_2$	Rapid to medium setting

R represents the hydrophobic portion of the emulsifier and is usually a long chain hydrocarbon consisting of 8 to 22 carbon atoms. [Scan Roads, 1983]

Cationic emulsions constitute the largest volume of emulsions produced worldwide; they are produced from the following types or mixtures: monoamines, diamines, quaternary ammonium compounds, alkoxylated amines, and amidoamines. They are represented in Table 8 [Shell, 2003].

Most of these are supplied in a neutral basic form and need to react with an acid to become water soluble and cationic in nature. Therefore, cationic emulsions are generally acidic with a pH<7. Hydrochloric acid is normally used to react with the nitrogen atom to form an ammonium ion; this reaction can be represented as follows:

$$\mathrm{R-NH_2+HCl \rightarrow R-NH_3^{+}Cl^{-}}$$

Amine +Acid ⟶ Alkylammonium chloride

Quaternary ammonium compounds do not require any reaction with acids as they are already salts and water soluble but the water phase pH can be adjusted with acid if required to modify the performance of the emulsion.

Requirements for cationic emulsified bitumen are given in Appendix A.

4.3.2 Anionic Emulsifiers

In anionic emulsifiers, the electrovalent and polar head group is negatively charged and imparts a negative charge to the surface of the bitumen droplets.

$$\mathrm{R\text{-}COO^{-}Na^{+}}$$

Anionic emulsifiers constitute the second largest volume of emulsion produced worldwide and are usually stabilized with fatty acids or sulphonate emulsifiers.

Fatty acids are insoluble in water and are made soluble by reacting with alkali, normally sodium or potassium hydroxide, so that anionic emulsions are alkaline with a pH >7.

$$\mathrm{R\text{-}COOH \quad + \quad NaOH \quad \rightarrow \quad R\text{-}COO^{-}\ Na^{+} + H_2O}$$

Fatty acid + Sodium hydroxide ⟶ Soap + Water

Sulphonates are usually supplied as water soluble sodium salts. Further neutralization is not required but an excess of sodium hydroxides is used in order to keep the pH of the emulsion higher than seven and also to ionize the natural acids contained in the bitumen.

4.3.3 Nonionic Emulsifiers

Non-ionic emulsifiers are not produced in significant quantities and are normally only used to modify both anionic and cationic emulsions. Typical nonionic emulsifiers include nonyiphenolethoxylates and ethoxylated fatty acids.

4.4 The Manufacture of Bitumen Emulsions

Bitumen emulsions are made by mixing hot bitumen with water containing emulsifying agents and by applying mechanical energy sufficient to break up the bitumen into droplets. It is clear that the manufacturing process can not only affect the physical properties of the emulsion but also affects the performance of the emulsion.

4.4.1 Continuous Plants

Most bitumen emulsions are manufactured with a continuous plant (See Figure 12) using a colloid mill (See Figure 13).

The colloid mill consists of a high-speed rotor rotating at 1000 to 6000 revs/min in a stator. The clearance between the rotor and the stator is typically 0.25 to 0.5 mm and is usually adjustable. Both the gap between rotor and stator and the peripheral rotor speed influence the particle size distribution of the bitumen droplets. The droplets size increases either by increasing the gap or reducing the peripheral rotor speed.

The viscosity of the bitumen entering the colloid mill should not exceed 0.2 Pa·s. Bitumen temperatures in the range 100 ^{o}C to 140 ^{o}C are used in order to achieve this viscosity with the penetration grade bitumen that is normally used in emulsions. To avoid boiling the water, the temperature of the water phase is adjusted so that the temperature of the resultant emulsion is less than 90. As the bitumen and emulsifier solutions enter the colloid mill they are subjected to intense shearing forces that cause the bitumen to break into small globules. The individual globules become coated with the emulsifier which gives the surface of the droplets an electrical charge. The resulting electrostatic forces prevent the globules from coalescing [Shell, 2003].

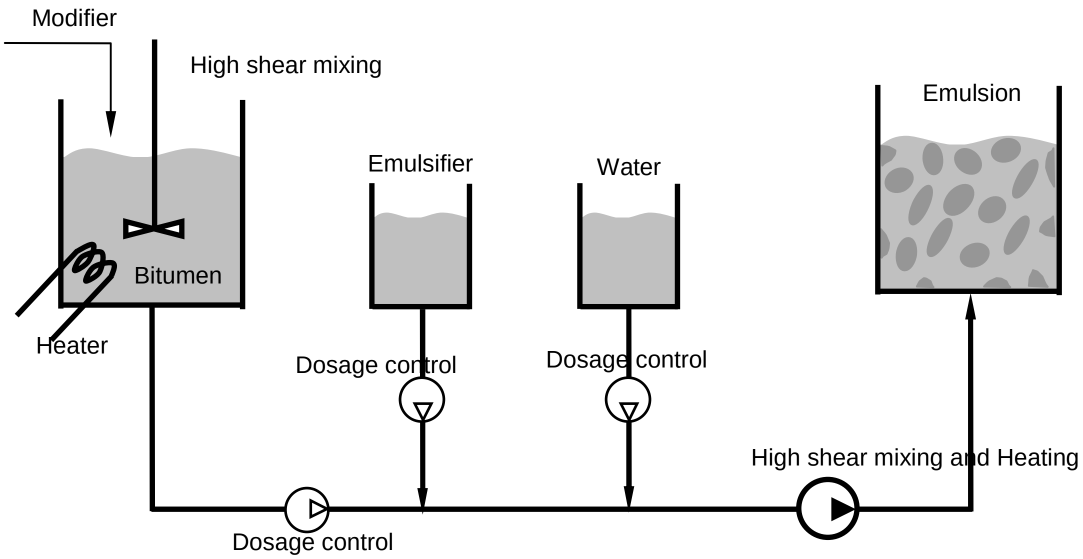


Figure 12 Principle diagram of a continuous plant

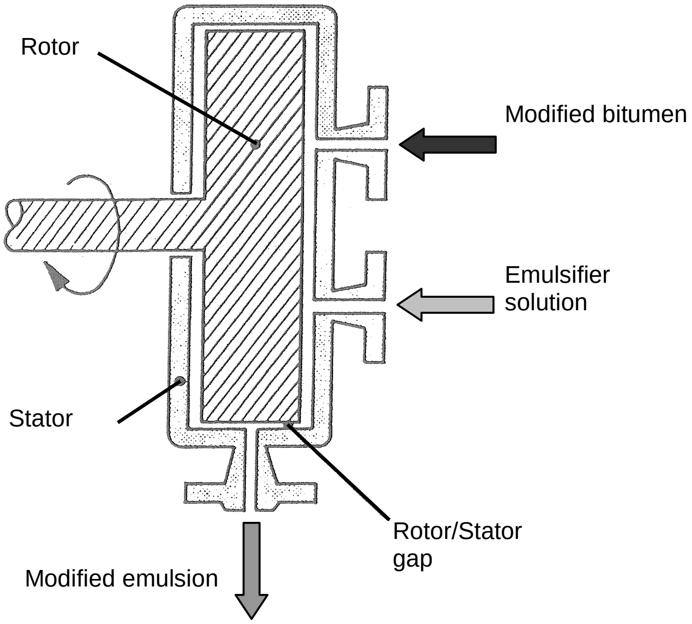


Figure 13 Principle diagram of a colloid mill

The continuous plant has no batch tanks, the bitumen and emulsifier solution come directly from the supply. The emulsifier solution is prepared automatically and in accordance with the selected formulation by injecting emulsifier, acid and stabilizer into the water line, where the reaction between the emulsifier and the acid takes place before the water enters the mill.

The water is heated to a suitable temperature by a continuous heater. The continuous plant requires emulsifiers that easily disperse in water in order to allow fast reaction with acid. A pH-probe, attached to the water line just before the mill, controls the dosage.

The main advantages of continuous plants over batch plants are [Scan Roads, 1983]:

1. quick change from one emulsion type to another;
2. less labor and less handling cost;
3. health hazards related to chemicals are almost eliminated;
4. higher utilization by elimination of the batch process.

4.4.1 Batch Plants

In a batch plant (See Figure 14), the emulsifier solution and bitumen are prepared at the right amounts and temperature in batch tanks. Bitumen is usually kept in a storage tank and pumped over to a batch tank. The modifier is added and mixed with the bitumen. The batch tanks are filled to levels that will give the correct bitumen content to the emulsion. The temperatures of the batches have to be adjusted before production starts. A batch tank is often designed so that the amount of liquid can be read from a level indicator. In this case there is no need for metering pumps, and ordinary pumps can be used instead.

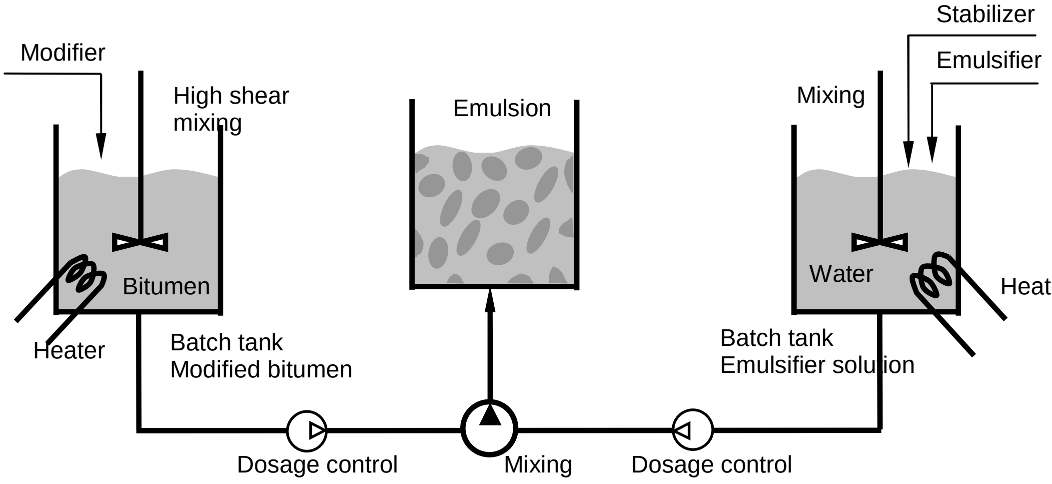


Figure 14 Principle diagram of a batch plant

Water and bitumen are passed through the mill until the batch tanks are empty. Since the amounts of bitumen and water are chosen before the production starts, the bitumen content of the emulsion will be as decided.

A batch plant can be used for the production of small volumes of emulsion, but is also used to produce large amounts. The type of mixer which is used is chosen to suit the consistency of the end product; it may be a high-speed propeller for low-viscosity road emulsions or a slow Z-blade mixer for paste-like industrial emulsions.

4.5 Properties of Bitumen Emulsions

The most important properties of bitumen emulsions are:

1. stability;
2. viscosity (or, more accurately, rheology);
3. breaking;
4. adhesion.

There are conflicting requirements for the properties of bitumen emulsions. The ideal emulsion would be stable under storage, transport and application conditions but would break rapidly very soon after application leaving a binder having the properties of the original bitumen adhering strongly to the road and the chippings. It would have a low viscosity to allow early handling and application and would flow to minimize irregular spraying but would not flow due to road irregularities, camber or gradient.

4.5.1 Emulsion Stability

Emulsions are inherently unstable. Over a period of time, which may be hours or years, the bitumen phase will eventually separate from the water phase.

Settlement: Settlement is a process, where the bitumen phase, or part of it, moves towards the bottom of the emulsion container (Figure 15). The fact that an emulsion settles does not mean it is unstable—gentle agitation often brings the emulsion back to its original quality. If, however, the stability is poor, settlement may lead to coalescence and breaking of the emulsion, in which case agitation can no longer restore the quality of the emulsion. The degree of settlement of an emulsion gives an indication of its shelf life.

Figure 15 The settlement of bitumen emulsions

Settlement in an emulsion is due to the gravity force and the difference in density between the two phases. Even if this difference is small, settlement may still take place if the emulsion contains big droplets and the bitumen content is lower than 65%. The speed at which a droplet moves depends on the bitumen content of the emulsion and decreases with increasing bitumen content. In emulsions containing more than 65%, settlement is normally negligible. Some methods used to reduce or prevent settlement are [Scan Roads, 1983]:

1. reducing the density of the bitumen phase by adding solvent;
2. increasing the viscosity of the water phase by adding a thickening agent;
3. preventing flocculation by change of types and concentrations of stabilizer and emulsifier or by changing the pH;
4. reducing the size of the droplets for example by better milling or change of emulsifier;
5. improving storage conditions, for example by keeping the emulsion at higher temperature than the ambient temperature.

In some cases the bitumen droplets can rise to the top which is called creaming. This can happen when the bitumen density is lower than the density of the water phase.

Flocculation and Coalescence: (See Figure 16) Flocculation is a process where the droplets start adhering to each other. Very often there is a large central droplet with smaller droplets surrounding it. The bitumen droplets in the emulsion have a small charge. The source of the charge is the emulsifier, as well as ionisable components in the bitumen itself. These small charges on the droplets normally provide an electrostatic barrier to their close approach to each other (like charges repel). However, when two droplets do achieve enough energy to overcome this barrier and approach closely then flocculation will happen. This flocculation may sometimes be reversed by agitation, dilution, or addition of more emulsifier.

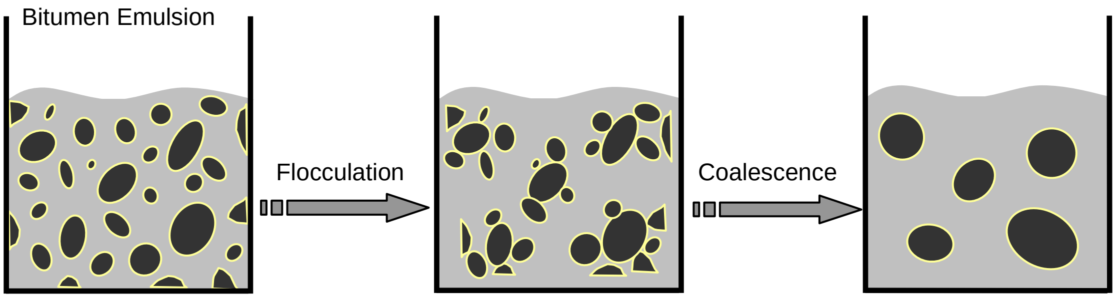


Figure 16 Flocculation and Coalescence of bitumen emulsions

When droplets in an emulsion merge to form bigger droplets, this is called coalescence. Flocculation is often followed by coalescence. Coalescence can start because of mechanical action such as agitation, pumping or vibration. Coalescence occurs in the breaking process and is depending on the aggregate type. Coalescence cannot be reversed.

Factors which force the droplets together such as settlement under gravity, evaporation of the water, shear or freezing will accelerate the flocculation and coalescence process, as does anything which reduces the charge on the droplets. Lower viscosity bitumens coalesce more rapidly than high viscosity bitumens. Of course, eventually we want the emulsion droplets to coalesce after the bitumen emulsion has come in contact with the aggregate and been placed on the roadway. [TRB-EC102, 2006]

4.5.2 Emulsion Viscosity

Viscosity of a fluid is defined as the resistance to flow. It is usually measured with an orifice viscometer (Engler, Redwood II or standard tar viscometer) in which the shear rate is relatively low. [Shell, 2003]

In general, in any flow, layers move at different velocities and the fluid's viscosity arises from the shear stress between the layers that ultimately oppose any applied force. For straight, parallel and uniform flow, the shear stress, τ, between layers is proportional to the velocity gradient, $\partial u/\partial y$, in the direction perpendicular to the layers.

$$\tau = \eta \frac{\partial u}{\partial y} \quad \text{or} \quad \tau = \eta \frac{\partial \delta}{\partial t} \tag{1}$$

Here, the constant η is known as the coefficient of viscosity (dynamic viscosity). $\partial \delta$ is the shear strain and $\frac{\partial \delta}{\partial t}$ is the shear rate. The SI physical unit of dynamic viscosity is the pascal-second (Pa·s), which is identical to kg·m^{-1}·s^{-1}.

In many situations, we are concerned with the ratio of the viscous force to the inertial force, the latter characterized by the fluid density ρ. This ratio is characterized by the kinematic viscosity, defined as follows:

$$\upsilon = \eta / \rho \tag{2}$$

Where η is the dynamic viscosity (Pa·s) and ρ is the density (kg/m^3), and υ is the kinematic viscosity (m^2/s).

The physical unit for kinematic viscosity is the stokes (St).

$$1 \text{ centistokes} = 1 \text{ mm}^2 \cdot \text{s}^{-1} = 10^{-6} \text{m}^2 \text{s}^{-1} \tag{3}$$

In principle, there are three ways to increase the viscosity of an emulsion.

1. By increasing the concentration of the disperse phase (bitumen): at low bitumen contents, the effect is small. At high bitumen contents, a small increase in concentration can induce a dramatic change in viscosity which may be uncontrollable.
2. By increasing the viscosity of the continuous phase: the viscosity is highly dependent on the aqueous phase composition. In the case of conventional cationic road emulsions, the viscosity can be increased by decreasing the acid content or increasing the emulsifier content. Additives intended specifically as viscosity modifiers can also be used.
3. By reducing the particle size distribution range: the particle size distribution of the emulsion can be changed by increasing the flow rate through the mill or decreasing the viscosity of the bitumen in the mill. At a bitumen content greater than 65% where the globules of the bitumen are packed relatively closely together, inducing a change in the particle size distribution by changing the flow rate has a marked effect on viscosity. At contents less than 65%, the viscosity of the emulsion is virtually independent of the flow rate.

Emulsion viscosity is almost independent of the viscosity of the disperse phase (bitumen). It is possible to produce emulsions of hard bitumens (<10 pen) which are readily pourable at 10 ^{o}C. The manufacturer must be able to produce emulsions with the desired viscosity. The viscosity must be predictable and remain within certain limits throughout the storage life of the emulsion.

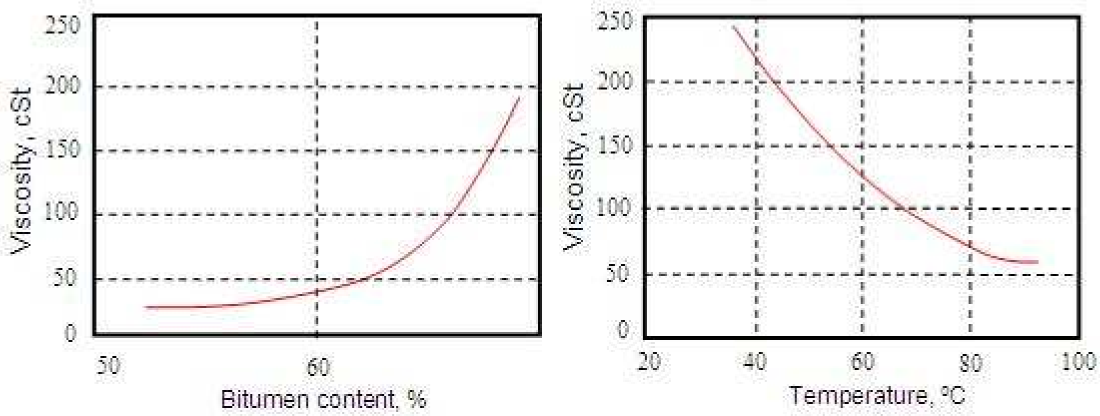


Figure 17 Example of relationship between viscosity and bitumen content, and relationship between viscosity and temperature

The viscosity is influenced by many factors. The most important are the bitumen content, the temperature of the emulsion, and the droplet size distribution (Figure 17). Type and dosage of emulsifier, type and dosage of stabilizer, salt content and viscosity of the bitumen also have an influence on the viscosity of the emulsion. [Scan Roads, 1983]

4.5.3 Breaking of Emulsions

The emulsion contains emulsifier molecules in both the water and on the surface of the droplets. If the concentration of the emulsifier ions is high the ions will form micelles. In a stable emulsion a state of equilibrium exists between the ions in solution and the ions on the surface of the droplets.

The equilibrium is disturbed by the removal of emulsifier ions from the solution, the balance will be restored by ions released from the micelles if there are some available, or by ions released from the surface of the droplets. In the latter case, the stability of the emulsion will decrease which may be enough to start the coalescence process and eventually will lead to the breaking of the emulsion. This is what happens when an emulsion is applied on a mineral aggregate surface. The electrical charges on the stone surface rapidly absorb a number of the emulsifier ions from the water phase of the emulsion, thus reducing the number of emulsifier ions on the droplets to such an extent that the breaking process starts

(See Figure 18). A point is reached where the charge on the surface of the droplets is so depleted that rapid coalescence take place. The aggregate is now covered with hydrocarbon chains and, therefore, the liberated bitumen adheres strongly to its surface. [Shell, 2003]

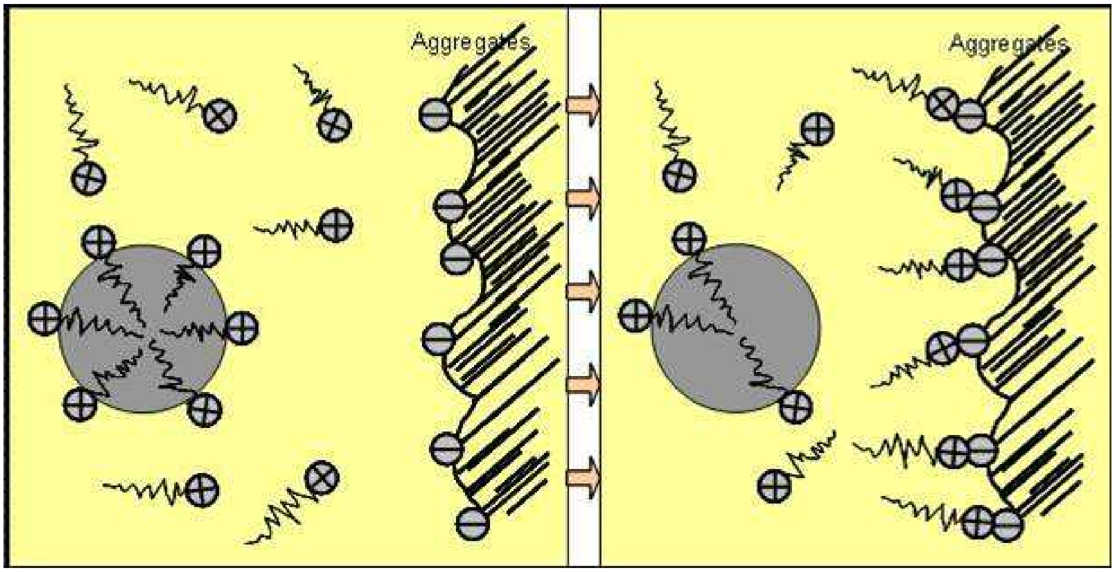


Figure 18 Schematic diagram of the breaking process for cationic bitumen emulsion

The setting or breaking of a bitumen emulsion can be divided into three distinct phases.

Phase 1: The emulsion is stable and the distance between the dispersed particles is sufficient to prevent contact or possible coalescence.

Phase 2: There is a close approach between the droplets which can be caused by destabilization of the emulsifier phase, evaporation of the water phase or mechanical action. This phase is called the flocculation phase.

Phase 3: Due to the close proximity of the bitumen droplets, they fuse and flow together. The coalescence of the droplets results in a continuous film of binder, with some minute water droplets initially being trapped in the coalesced layer.

The rate of setting and curing depends on the reactivity of the emulsion towards the aggregate and environmental conditions such as ambient temperature, wind velocity and humidity. When a certain intermediate state of coagulation has been reached, mechanical action such as rolling will also promote further coagulation of the emulsion.

Breaking Agent: The use of a breaking agent can accelerate the breaking of an emulsion. For surface dressing emulsions, it is possible to spray a chemical breaking agent either simultaneously with the emulsion or just after the emulsion has been applied to the road. Care is required in the use of breaking agents. Applying too little will have no effect, applying too much may break the emulsion but adversely affect its adhesion. Poor distribution of a breaking agent can have similar effects. [Shell, 2003]

Aggregate: Aggregates have a specific surface charge in the presence of water. Acidic aggregates such as quartzite and granite contain silica and have a strong negative charge in the presence of water. These negative charges attract the positively charged cationic bitumen particles, leading to destabilisation of the surfactant system and subsequent coagulation of the bitumen particles (See Figure 19). This breaking mechanism is absent when anionic emulsions are used with acidic aggregates, and in this case the coagulation can only take place by evaporation of the water phase. [Louw, 2004]

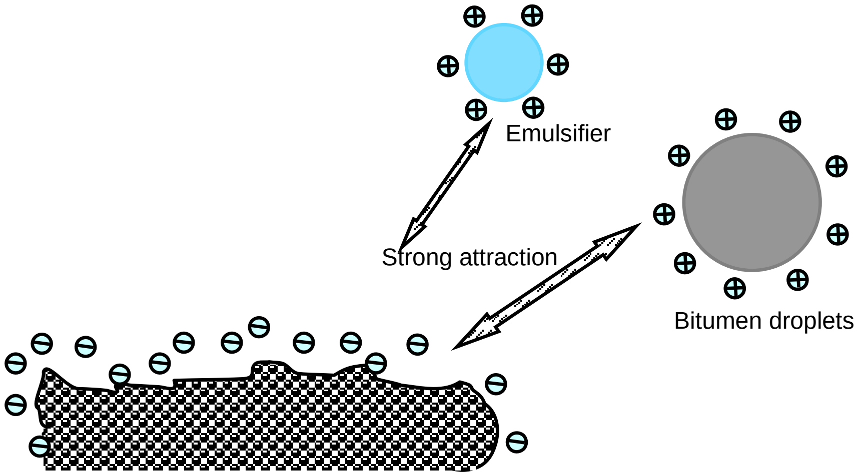


Figure 19 Attraction between cationic emulsion particles and aggregates

Aggregates are sometimes classified as alkaline or acidic. Limestone is an example of an alkaline aggregate and among the acidic ones are granite and quartzite. Aggregates rarely consist of one pure mineral and even a pure mineral may have both alkaline and acidic components. If aggregates are arranged according to the content of silica, SiO_2, carbonate and $CaCO_3$, a diagram can be drawn (See Figure 20). This diagram can also give a rough idea on the relative number of positive and negative charges on the surface of the aggregate.

The influence of the aggregate is not only its chemical nature. Many aggregates may also be contaminated with clay particles, which even in small quantities will increase the breaking rate. Aggregates physical form has a considerable influence on the breaking rate. Dusty aggregates will cause a more rapid breaking than clean aggregates. This is due to the large surface area of the fines which gives a large number of electrical charges.

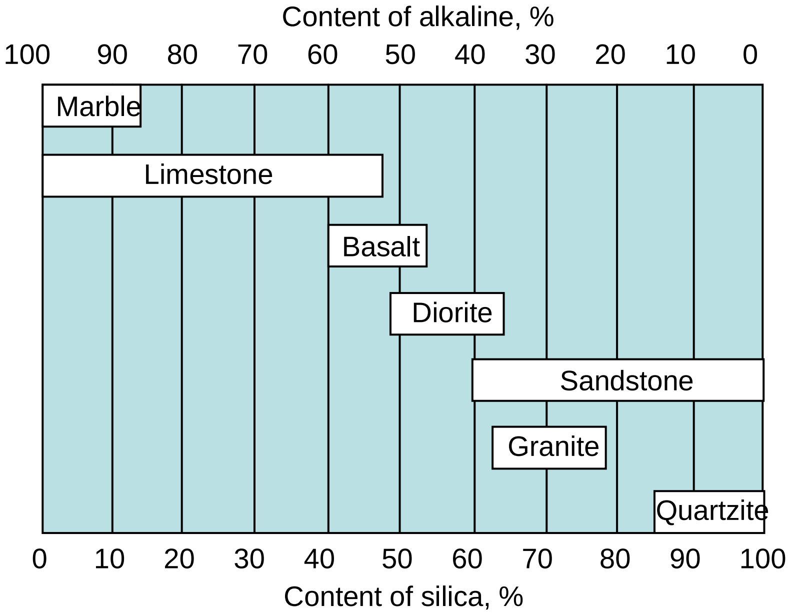


Figure 20 Classification of aggregates

Since most aggregates used in road construction have a majority of negative charges on its surface, cationic emulsions are generally more suitable than anionic.

4.5.4 Emulsion Adhesion

It is very important in all applications where bitumen is used as an adhesive between solid surfaces that the bitumen "wets" the surface to create the maximum contact area. For anionic emulsion with acidic aggregate, e.g. silica, it is the inorganic cation (K^+ or Na^+) in the emulsifier which is absorbed on the surface of the silica. This cation does not give an oleophilic property to the surface on which it is absorbed, and moreover has no surface active effect. The resulting adhesion is therefore poor.

Table 9 summarizes the results of cationic and anionic emulsions with the two types of aggregates.

Table 9 Results of cationic and anionic emulsions with two types of aggregates

Emulsion	**Aggregate**	**Results**	
		Breaking rate	**Adhesion**
Anionic	Acidic	Slow	Poor
Anionic	Alkaline	Medium	Good
Cationic	Acidic	Fast	Excellent
Cationic	Alkaline	Fast	Good

On the other hand, a cationic emulsion breaking on an acidic or basic aggregate results in a strong absorption of the organic cation ($R\text{-}NH^3$) on the surfaces. This cation gives oleophilic properties to the surface on which it is absorbed, and has a water displacing effect resulting in strong adhesion of the deposited bitumen film to the aggregate surfaces. In this way, cationic emulsifiers act as anti-stripping agents after breaking of the emulsion. [Scan Roads, 1983]

4.6 Test Methods of Bitumen Emulsions

Since bitumen emulsions are used for many different applications, many test methods are available to classify emulsions to determine the appropriateness for a specific use. In appendix B the test methods of bitumen emulsions and emulsion mixtures are summarized.

5. Modified Bitumen Emulsions

Various additives, like polymers, cements and clay, are known to improve the properties of bitumen emulsions for special road applications.

5.1 Polymer Modified Bitumen Emulsions

Over the years, many polymer products have been used in highway construction. All of the products listed under elastomers are considered rubbers, either natural or synthetic (e.g. SBR, SBS, and Neoprene). Plastomers used in highway construction are typically classified as paraffins (e.g. LDPE, EVA) [Gardiner, 1995]. Typical polymers are listed in Table 10.

Table 10 Typical Polymers

Type	**Form**	**Chemistry**
Block copolymer	Crumb or powder	SBS (Styrene-Butadiene-Styrene)
Random copolymer	Latex	SBR (Styrene Butadiene Rubber)
copolymer	Crumb or powder	EVA (Ethylene Vinyl Acetate)
Homo-polymer	Preblended with AC	LDPE (Low Density Polyethylenes)
copolymer	Crumb or powder	EMA (Ethylene Methacrylate)

There are many ways of blending polymers into the bitumen. Alternatively it can be done indirectly in the case of modified bitumen emulsions. The final modified bitumen/polymer blend can be described in only four ways. [Nootenboom, 1991]

1) Polymers can be a separate phase dispersed in the bitumen. This occurs when the polymer is incompatible with the bitumen. These products are generally unstable with very poor storage characteristics.
2) Bitumen can be a separate phase dispersed in the polymer. This only occurs at a high level of polymers (>12%). These materials are used in industrial products such as roof sealers etc.
3) Polymers can form a network within the bitumen. This is typical for the popular type of

polymer modified bitumen generally used in road construction. The long polymer molecules become entangled to form an elastic net. The elastic structure changes the mechanical properties of the bitumen such as ductility, softening point, viscosity, etc.

4) Polymers can be molecularly bound to the bitumen. This has the advantage that bitumen and polymer are chemically linked and form a homogeneous material. The methods of productions are closely guarded trade secrets.

The use of Polymer Modified Bitumen Emulsions has increased dramatically in the road maintenance industry.

5.1.1 Chemistry of Polymer Modifiers

SBR is a copolymer of styrene, or vinyl benzene, (CH_2=CH-C_6H_5) and butadiene (CH_2=CH-CH=CH_2). SBR is relatively easily to use to modify bitumen emulsions. Modifying hot bitumen with SBR latex is more difficult and care needs to be taken to control frothing caused by the aqueous phase of the latex boiling off [Zacharias. 1991].

SBS has an ordered block structure of the general triblock form A-B-A. The A component is a thermoplastic polymer block (e.g. polystrene) with a glass transition point above room temperature. The B component is an elastomeric polymer block (e.g. polybutadiene) with a glass transition temperature well below room temperature [Gardiner, 1995]. These binders have application in most forms of road construction. In surface treatments, good cohesion, low temperature susceptibility, excellent elasticity (even at very low temperature) and good adhesion allow these surfacing to be used even on very heavy trafficked roads. [Zacharias. 1991].

EVA is a copolymer of ethylene (C_2H_4) and vinyl acetate ($C_4H_6O_2$). The inclusion of the vinyl acetate is used to decrease the crystallinity of the ethylene structure and to help make the plastomer more compatible with the bitumen cements. EVA is noted improving the workability and rutting resistance of hot mix asphalt，it improves four essential properties of the binder, cohesion, temperature susceptibility, rheological behavior and adhesion.

5.1.2 Properties of Polymer Modified Bitumen Emulsions

Polymer modified bitumen takes advantage of distinctly different physical properties of the bicontinuous phases of the bitumen and polymer network as shown in Figure 21, which compares the complex modulus of unmodified bitumen and a dried styrene-butadiene rubber, SBR, latex film at a wide temperature range from -60 ℃ to 80 ℃.

The latex film is flexible even below -30 ℃ and maintains its stiffness at an elevated temperature of above 80 ℃, due to the high molecular mass of this polymer, which yields sufficient amounts of polymer chain entanglement. The complex modulus changes only by a factor of 10 between -20 ℃ and 80 ℃. In contrast, complex modulus changes 100000 times over the same temperature range of -20 ℃-60 ℃ for the unmodified bitumen. [Takamura, 2003].

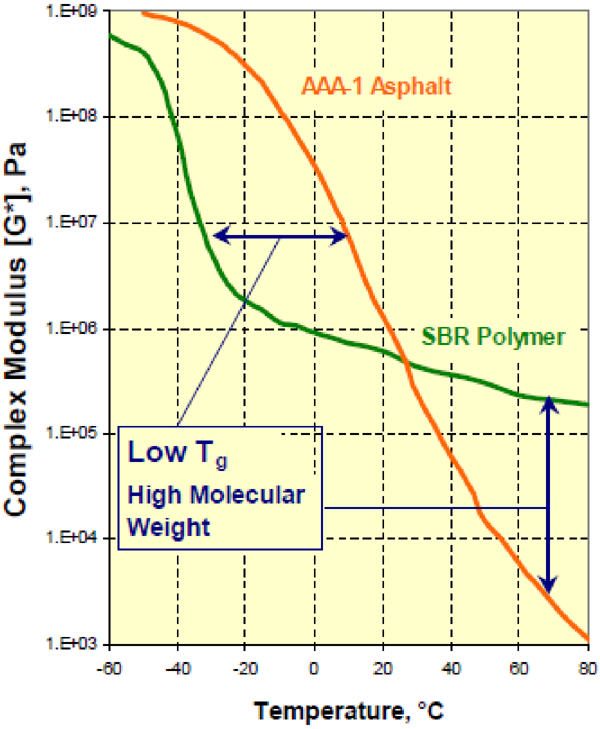


Figure 21 Complex modulus of MRL AAA-1 bitumen and dried SBR latex film

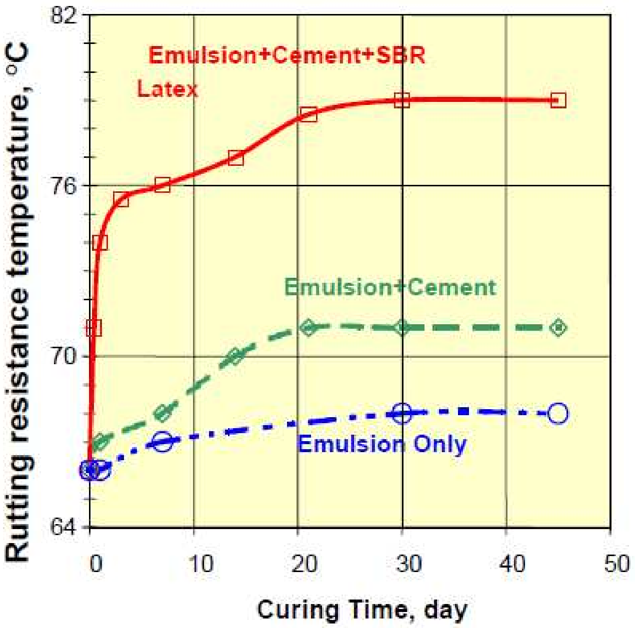


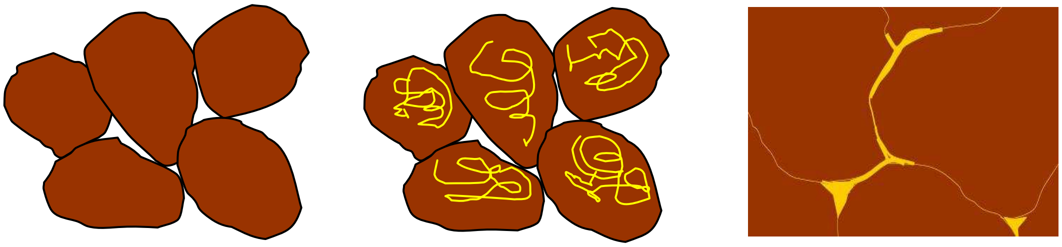
Figure 22 Rutting resistance temperature of emulsion and modified emulsions

From Chris Lubbers` research (See Figure 22), the rutting resistance temperature (Temperature at $G^*/\sin(\delta)=1\text{kPa}$, where G^* is complex modulus and δ is phase angle) of emulsion type mixtures is increased after modification, especially after modification with cement or SBR together. The rutting resistance temperature becomes much higher after modification with cement together with SBR [Lubbers, 2008].

Even though bitumen droplets deform and consolidate, their boundaries do not completely disappear even after full drying of the asphalt emulsion. This is due to the high asphalt viscosity at ambient temperature, as shown in Figure 23. Repeated high strains results in the observed sharp reduction in the binder strength. The unmodified residue would fracture through bitumen droplet/droplet boundaries (See Figure 23 A).

In an SBS modified bitumen emulsion, the SBS polymer is present within the bitumen droplets of the emulsion. The polymer significantly enhances elastic properties of the bitumen through the polymer network formation in the bitumen. However, the SBS polymer modification does not address potential fracture through bitumen particle/particle boundaries under repeated high strains or stresses (See Figure 23 B).

In SBR latex modified bitumen emulsions after curing the pure polymer films are surrounding the bitumen droplets. These polymer films are highly elastic even at very high elongation. The high strains or stresses applied to the emulsion residue will be concentrated in these polymer membranes. These flexible membranes absorb external stresses without causing fractures to brittle bitumen droplets at low temperature. This microscopic polymer network is the reason for the observed excellent fatigue resistance of the emulsion residue modified with the cationic SBR latex (See Figure 23 C). [Takamura, 2003]



A: Unmodified B: SBS Modified C: SBR Latex modified

Figure 23 Schematics of fully cured unmodified, SBS modified and SBR latex polymer modified bitumen emulsions

The mechanical adhesion of four emulsions was analyzed with the Vialit Plate Shock Test, by A.S. Kucharek [Kucharek, 2008; NEN-EN 12274-3]. These four emulsions were cationic rapid-setting and were prepared using a commercially available emulsifier for CRS-2 emulsions, at identical dosages. One is nonmodified (CRS-2) and 3 are polymer modified, all containing the same polymer content of 3 wt% to the emulsion. The difference between these 3 emulsions lies in the type of polymer modification: one is modified using SBR latex (CRS-2P Latex) while the second is made by modifying the asphalt with SBR prior to emulsification (CRS-2P PMA). The third contains the same 3% SBR level but half is contained in the binder and half is contained as latex (CRS-2P Comb).

Table 11 Adhesivity at 24 hours cure by Vialit Plate Shock Test

Adhesivity/ %	**Limestone**	**Granite**	**Traprock**
CRS-2	100	100	100
CRS-2P Latex	100	100	100
CRS-2P PMA	93	100	100
CRS-2P Comb	100	100	100

Table 11 shows that the four emulsions showed 100% adhesivity to the granite and the traprock chips, after 24 hours. With the limestone chip, the CRS-2P PMA show some degree of failure. This means that the adhesion properties of CRS-2P PMA are lower than others.

With the Frosted Marble Cohesion Test (see appendix C, [Howard, 2009]), the cohesion properties were also evaluated in this research [Kucharek, 2008]. Results are shown in Table 12. CRS-2 and CRS-2P PMA have consistently higher cohesion values than the other emulsions. The cationic emulsions containing latex have lower initial cohesion values compared to the others, but they are the fastest cohesion gainers. The difference observed between the latex and the PMA cationic emulsions is because of the difference in polymer morphology. The PMA emulsion contains SBR polymer in the binder therefore, with breaking of the emulsion (rapid by design), the cohesion build up can take advantage instantly of the polymer presence. This seems to be especially effective during the first 2-3 hours of its curing time. With the emulsions containing latex, the SBR particles are creating a honeycomb structure with curing of the residue. This morphology is very effective but it needs almost complete curing of the binder before it can deliver its full mechanical benefit. The combination CRS-2P shows relatively low cohesion after two hours but has the highest cohesion of all emulsions after 4 and 6 hours. All 4 cationic emulsions display similar cohesion values after 24 hours.

In Jones' research [Jones, 1988], the Loaded Wheel Test (LWT) (ISSA TB-109), Wet Track Abrasion Test (WTAT) (ASTM D3910) and Cohesive Test were performed on various emulsion mixtures. The results (See Table 13) indicate that polymers enhanced the cohesion and other properties of bitumen emulsions. The SBR latex performs well in virtually all the laboratory tests.

Table 12 Cohesion by Frosted Marble Test

Cohesion/ kg·cm	**2 Hrs**	**4 Hrs**	**6 Hrs**	**24 Hrs**
CRS-2	9	10.83	12.23	21.92
CRS-2P Latex	4.4	7.8	11.6	22.42
CRS-2P PMA	11.2	13	16.4	23.8
CRS-2P Comb	6.6	18.6	19.6	23.8

Table 13 Test results of various polymers modified emulsions

Polymer	**Cohesion/ kg·cm**		**WTAT loss/ g/sq ft**		**Vertical Displacement/ %**
	30min	**60min**	**1 hour**	**6 day**	
Natural	16	18	15	41	7.8
SBR	16	21	11	15	1.3
SBS	12	17	23	28	8.6
EVA	13	16	51	56	11.2

The microstructure of 180/200-penetration bitumen refined from Middle Eastern crude and latex elastomer polymer modified bitumen emulsions were analysed by using Confocal Laser Scanning Microscopy (CLSM) [Forbes, 2001]. The percentage of latex polymer modifier is 3%. The polymer was added by four different methods: (1) pre-blending the polymer into the bitumen at 180 ^{o}C for 1 h before emulsifying; (2) co-milling the latex polymer through the mill with the bitumen and emulsifier solution phases; (3) adding the latex polymer into the emulsifier and water solution; (4) post-adding the latex polymer to the prepared emulsion.

As Figure 24 shows, the dark particles are bitumen particles and do not fluoresce. The pictures also shows the polymer network formed by: (A) post-adding latex polymer to the manufactured emulsion; (B) addition of the latex into the emulsifier solution phase and emulsifying with the bitumen; (C) comilling the latex with the bitumen and emulsifier solution phases; (D) and (E) latex polymer preblended into hot bitumen (D) before emulsification and (E) binder after emulsification. In (A), (B) and (C), the polymer encapsulates the bitumen droplets (the dark bitumen droplets are surrounded by a bright polymer phase). In (D) the polymer distribution is coarse and uneven; indicating incompatibility between the polymer and bitumen, whereas in (E) the polymer distribution is much more even but has a different microstructure compared to the latex addition methods in (A) , (B) and (C).

From these CLSM pictures, we can see that emulsified binders appear to have a more homogeneous distribution of polymer compared to hot polymer-modified binders. Pre-adding polymer latex into hot bitumen is not good for the dispersion of polymers.

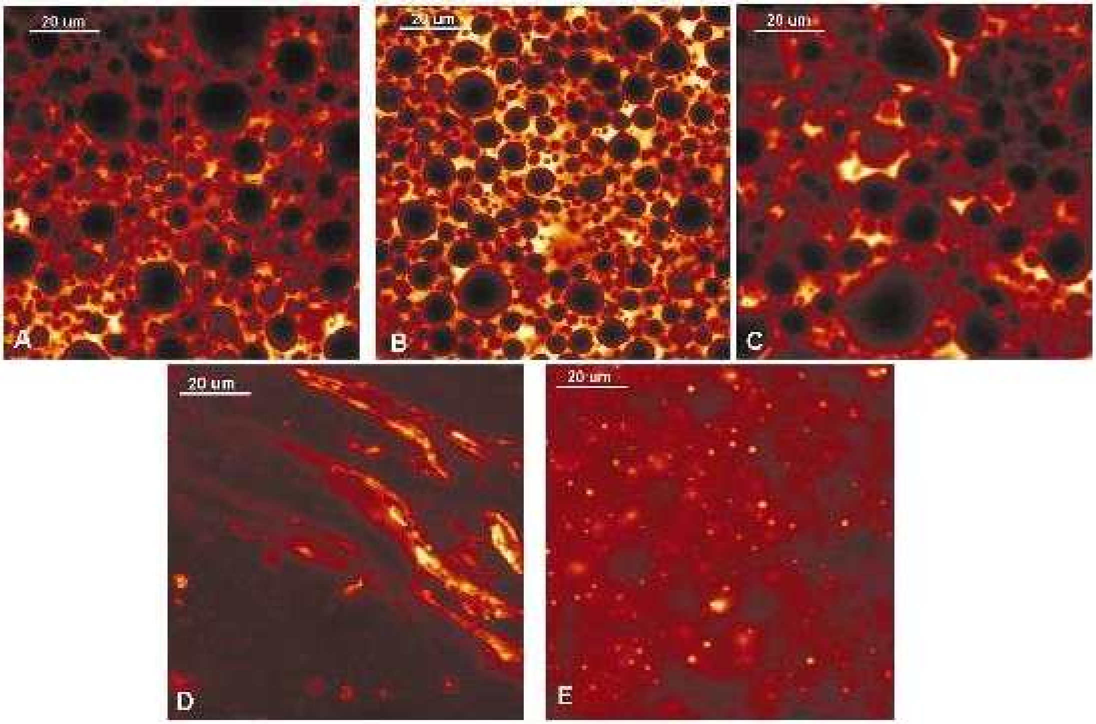


Figure 24 CLSM images of residual modified binder after evaporation of the emulsion water phase and showing the polymer network structures.

5.2 Cement Modified Bitumen Emulsions

Portland cement was used primarily as filler in warm-mixed bituminous mixtures to prevent stripping of the binder from previously dried aggregate. It was used to enhance the coating of wet aggregate with bitumen or tar [Oruc, 2007].

The resilient modulus of emulsion mixtures with and without cement modifications was determined by means of the resilient modulus test [Oruc, 2007]. Specimens of emulsion mixture were first tested after 3 days and periodically, as the specimens cured. The tests were carried out throughout 365 days at various periods. The specimens were tested at 25 ^{o}C. Pulse period and rise time were set to 1000 and 40 ms, respectively. The results of these tests are shown in Figure 25.

Results indicated that the resilient modulus of the emulsion mixtures increased steadily over several months, in contrast with the hot mix which showed no change. The rate of resilient modulus increase of the emulsion mixtures increased with the amount of cement added. The work further revealed that the ultimate resilient modulus was achieved after curing and the rate of resilient modulus gained increased with increasing cement content up to 6%.

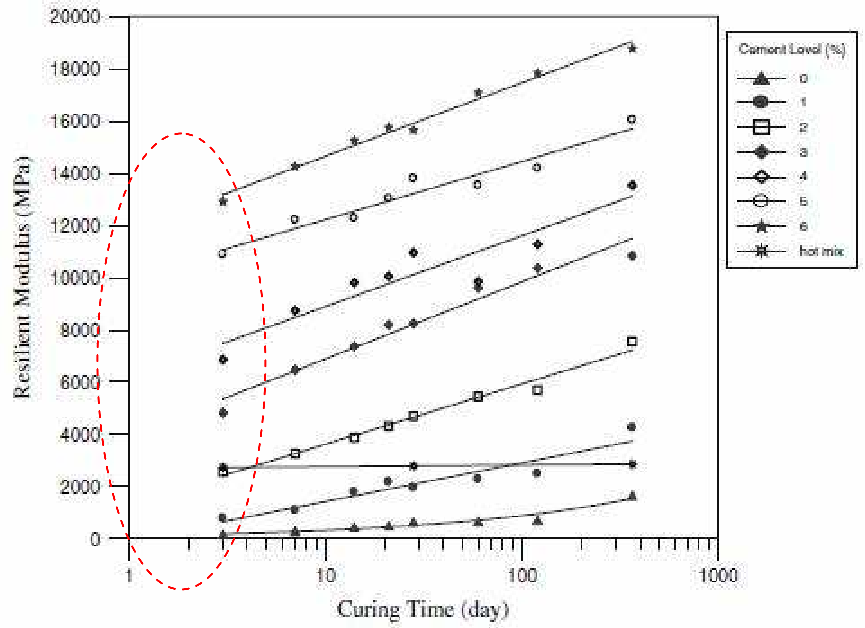


Figure 25 Effect of cement on resilient modulus

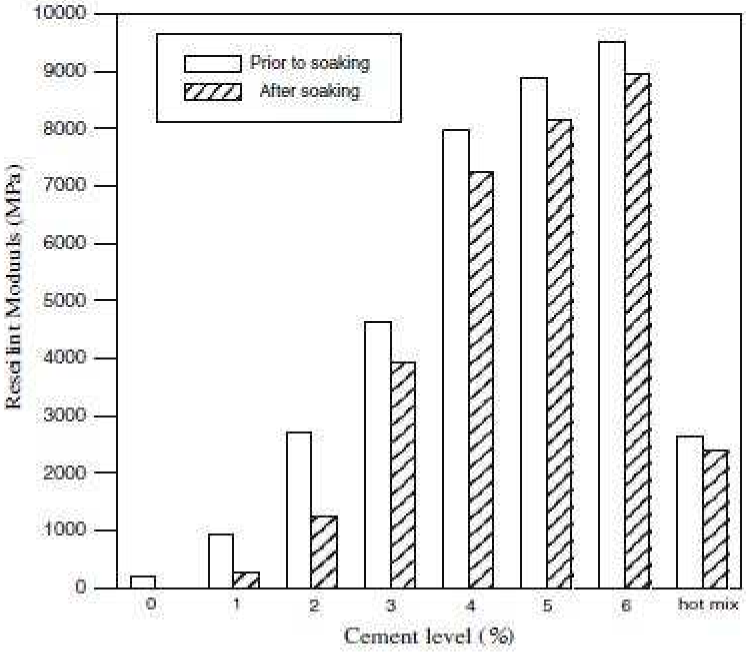


Figure 26 Effect of cement level on the resistance to water damage

The effect of cement on the resistance to water damage of mixtures has also been reported by Seref Oruc [Oruc, 2007]. Specimens of the emulsion mixtures were tested at 25 ^{o}C after 3 days curing time. Then, the specimens were soaked for 1 day under water at 50 ^{o}C. The ratio of the resilient modulus prior to soaking and after soaking was determined. Results of the tests are shown in Figure 26. The results indicate that without cement, emulsion mix specimens failed after sixth hour of conditioning. The resistance to water damage of the emulsion mix increased by the addition of cement. The ratio is 0.91 for hot mixture. The ratio obtained for the emulsion mixture with 3% cement is 0.85 even after only 3 days of curing. The results indicate that cement is an effective adhesion agent for emulsion mixtures.

Additions of Ordinary Portland Cement (OPC) decrease the rate of water loss, improve the adhesion properties and water resistance. Stiffness modulus, permanent deformation resistance and fatigue strength are all improved by OPC addition. [Brown, 2000; James, 1996]

Figure 27 shows the results about the effect of OPC on stiffness modulus as determined by Brown [Brown, 2000]. From Figure 25 and Figure 27 we can find that the minimum curing time for cement modified bitumen emulsion is far more than 24 hours. It takes about 1year to achieve fully cured specimens. This disadvantage of cement modified bitumen emulsion suggests that it is impossible for rapid setting emulsion application.

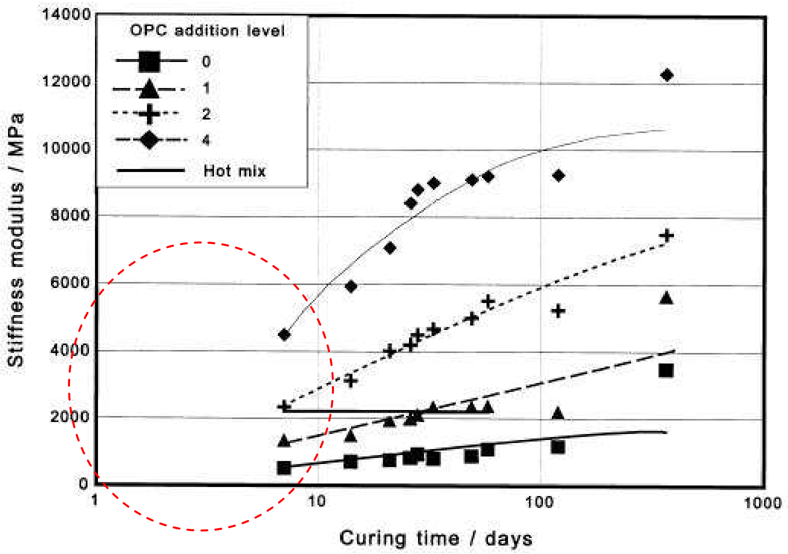


Figure 27 Effect of OPC on stiffness modulus

5.3 Nanoclay Modified Bitumen and Emulsions

Clay is a naturally occurring material composed primarily of fine-grained minerals, typically formed over long periods of time by the gradual chemical weathering of rocks (usually silicate-bearing) by low concentrations of carbonic acid and other diluted solvents [http://en.wikipedia.org/wiki/Clay]. The details of the crystal structure of these materials are of great importance in understanding its physical and chemical properties.

5.3.1 Structure of Clay

In nanotechnology, "nanostructure" refers specifically to those found in minerals and especially to layered silicates. The most preferred and widely used silicates are organically modified smectite clays with a 2:1-type layer structure such as montmorillonite, saponite, etc [Ammala, 2007]. All these layered silicates have the same crystalline structure and normally have a thickness D_0 of about 1 nanometer and a length of about 50-1000 nanometers [Itagaki, 2001]. Each layer is built up of three sheets, two octahedral sheets on the outside of the layer and one tetrahedral sheet in the middle of the layer. Therefore this group of materials is referred to as 2:1 layered silicates. The sheets on the outside are made of interconnected SiO_4 tetrahedrals, while the inner sheets have octahedral configurations and contain metal cations like Al^{3+} or Mg^{2+} and hydroxyl groups. Figure 28 shows a schematic drawing of a 2:1 layered silicate.

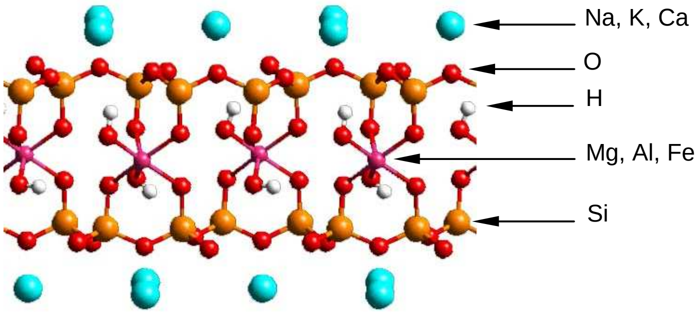


Figure 28 Schematic drawing of a 2:1 layered silicate and element

Sometimes not all octahedral sites are occupied by cations. This results in negatively charged silicate layers. So cations like Na^+, Ca^{2+} or K^+ act as counter charges in the inter-gallery space and can provide a strong ionic bond between adjacent layers. The several types of 2:1 layered silicates only differ in the amount and kind of metal cations incorporated in the crystal [Martin Antonius van Es, 2001]. The organic cations lower the surface energy of the silicate surface and improve wetting with the polymer matrix. Sometimes, the organic cations may contain various functional groups that react with the polymer to improve adhesion between the inorganic phase and the matrix.

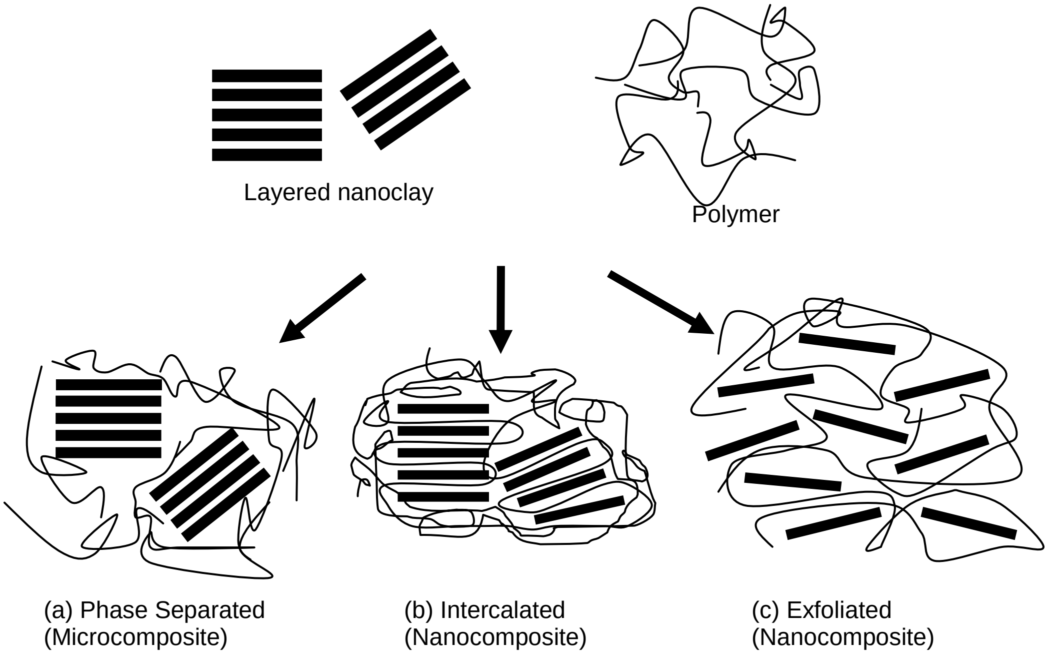


Figure 29 Schematic diagrams of different morphologies of clay in composite

Depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when layered silicate is associated with a polymer [Alexandre, 2000]. A simple phase separation of clay in the composite (Figure 29 a) makes the composite behave as traditional microcomposite. Once one or more polymer chains enter the intergallery of the nanoclay, an intercalated structure (Figure 29 b) is obtained. Furthermore, complete nano-dispersion of the silicate layers of nanoclay in a polymer matrix results in an exfoliated structure (Figure 29 c). In most cases, nanocomposites exist between the intercalated and the exfoliated. XRD and TEM are employed to identify intercalated structures and characterize the nanocomposite morphology.

5.3.2 Nanoclay Modified Bitumen

Several kinds of clay (Kaolinite, Illite, etc) were used for making modified bitumen.

Two types of nanoclay, Nanofill and Cloisite were adopted as a modifier to bitumen [Ghile, 2006]. Results indicated that the Cloisite nanoclay modifications when applied at 6 wt% content to 40/60 bitumen increased the stiffness, the rutting resistance of the standard binders and the indirect tensile strength and fracture energy values of dense asphalt mixtures. The nanofill (6%) modification improved the short and long term ageing resistance of a 70/100 bitumen. However, the standard binders/mixtures showed better fatigue resistance than the nanoclay modified binders/mixtures especially at low test temperatures.

The improvement in properties of both binders and mixtures was not large. The relatively high amount of used nanoclay (6% by weight) made the financial consequences too high to consider application. However the improvement was strongly believed to be related to the chemical additive of the nanoclay and further studies on the chemistry of the nanoclay and bitumen and further development of the nanoclay technology was recommended to utilize the full potential of the nanoclay modification.

Yu adopted Na-form MMT and organomodified montmorillonite (OMMT) to modify bitumen [Yu, 2007]. The results showed that the addition of MMT and OMMT to bitumen increased both the softening point and viscosity of the modified bitumen. Modified bitumens exhibited higher complex modulus, lower phase angle and higher rutting resistance. Compared with MMT, OMMT has greater effects in improving softening point and rutting resistance, because of the formation of an exfoliated structure in the OMMT modified bitumen. The storage stabilities of modified bitumens were very good when the clay content is less than 3wt%.

The effect of Organophilic Montmorillonite on the thermal-oxidative aging properties of bitumen has been researched [Yu, 2008] and results showed that the change of the complex modulus and phase angle after TFOT is smaller after modification (See Figure 30). This indicates that the ageing resistance of bitumen was enhanced by the barrier effect of the lamellas of OMMT.

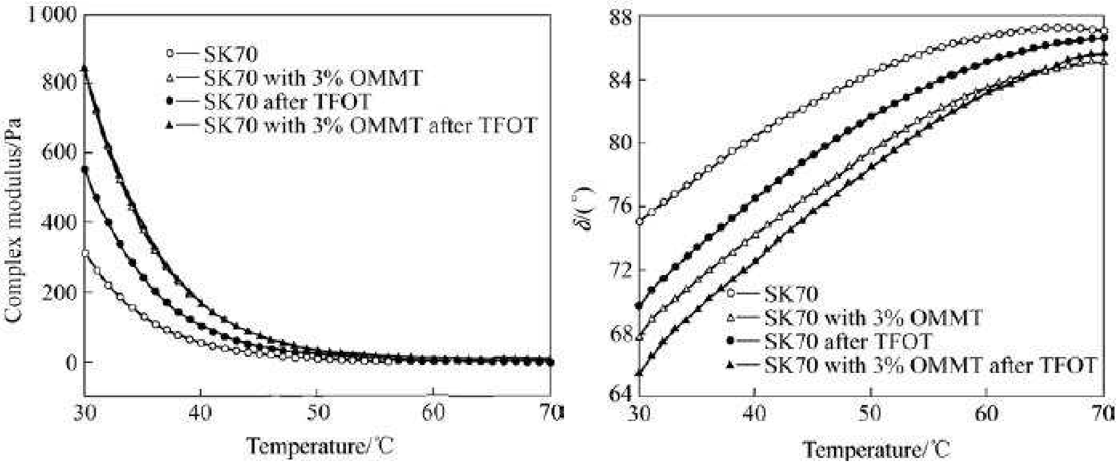


Figure 30 Complex Modulus and Phase Angle Vs Temperature of virgin and OMMT modified bitumen before and after TFOT

Another layered silicate, rectorite, was introduced into bitumen by Yu's group [Yu, 2007]. The effects of organophilic rectorite (OREC) on the change of the rheological properties of bitumen due to ageing were investigated, through TFOT and PAV testing. The results showed that the softening point and viscosity were increased after the introduction of OREC.

After TFOT and PAV, the increment of softening point and viscosity of 3% OREC modified bitumen is 5.8 and 33%, while it is 13.8 and 51% for standard bitumen. This shows the addition of OREC also improved the aging resistance of bitumen.

Because SBS is not totally compatible with bitumen, Kaolinite Clay (KC) was added to improve the storage properties [Ouyang, 2005].

The high-temperature storage (163 °C, 48 hours) stabilities of SBS/KC compound modified bitumens are presented in Table 14. Obviously, for bitumens modified with SBS in the absence of KC, the differences in the softening points and viscosities were large, which imply that the phase separation of the SBS/bitumen mixture was serious. When the KC content in the SBS/bitumen/KC mixture was 1.2%, the storage stability of the SBS/KC compound modified bitumen was improved significantly. When the content was 0.4% or 2%, the modified bitumen was unstable. Bitumen modified by directly adding SBS and KC, was still unstable even when the KC content was 1.2%. So it can be concluded that SBS/KC compound is critical to obtain the high temperature storage stability of SBS modified bitumens.

Table 14 Effect of KC content on the high-temperature storage stabilities of SBS/KC compounds modified bitumens

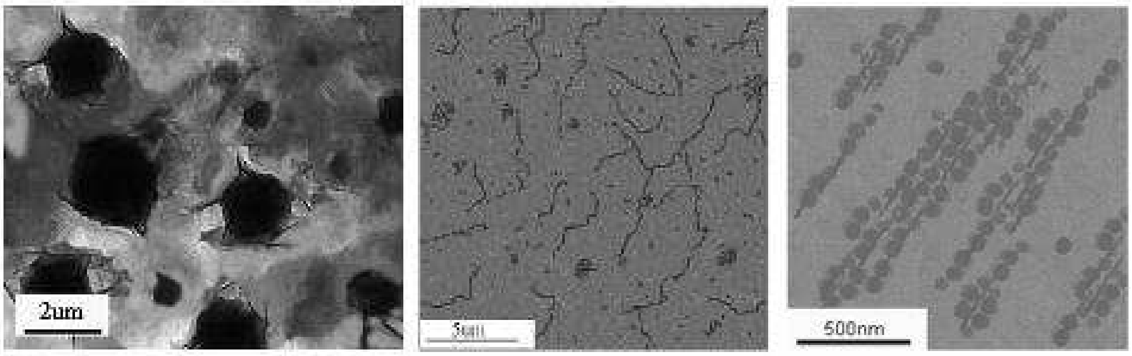
Material	**Formulation**				
Bitumen, % (w/w)	96.0	95.6	94.8	94	94.8 [a]
SBS/KC compound, % (w/w)	4/0	4/0.4	4/1.2	4/2	4/1.2
Top viscosity (135 °C) (Pa·s)	0.88	0.93	0.87	0.58	0.93
Bottom viscosity (135 °C)	0.70	0.76	0.85	1.05	0.80
Top/bottom ratio of viscosity	1.25	1.22	1.03	0.56	1.17
Top softening point (°C)	59.5	64.0	58.2	52.5	64.5
Bottom softening point (°C)	51.0	53.0	58.0	84.5	55
Top-bottom (°C)	8.5	11.0	0.2	32	9.5
[a] SBS and KC added directly.					

At present, only a few researches have been done on nanoclay modified bitumen emulsion.

5.3.3 Nanoclay Modified Emulsions

Three types were selected for nanocomposite resin preparation, Boehmite needles, Laponite discs and Cloisite 30B clay plates [Nobel, 2007]. PNC resin dispersions containing these three clays were analyzed by transmission microscopy (TEM) to characterize the dispersion of the inorganic nanoparticles and resin particles. Images of water borne emulsions are shown in Figure 31, all concentrations are 6 wt%.

The dark irregular shaped areas represent the resin particles frozen in the surrounding aqueous environment (See Figure 31 (a)). At a concentration of 6 wt% the MMT particles are visible on the resin surface. TEM images of Laponite containing water borne nanocomposite resins reveal the formation of long strings and smaller clusters of resin particles while the individual Laponite particles could not be observed (See Figure 31 (b)). This string formation could be caused by the interactions between the Laponite particles and the resin particles. Laponite particles are by nature hydrophilic. Organo-modification has made them more hydrophobic. If (stacks of) Laponite particles are located on the resin/water interface they might form bridges between neighbouring resin particles, creating in this way long strings of resin particles or “raspberry like” structures. TEM images of water borne nanocomposite resin emulsions containing Boehmite indicate a complete and random emulsion of Boehmite particles while the resin particles are paired at the surface of the needles; a high aspect ratio of the particles causes alignment of the needles (See Figure 31 (c)). [Nobel, 2007]



(a) (b) (c)

Figure 31 TEM micrographs of water borne polymer nanocomposite (WB PNC) emulsions (a) Containing C30B; (b) Laponite and (c) Boehmite

Nobel studied the effect of adding these three types of clays to the dispersions of resin (the paint medium) in water and to resin in an organic solvent. Nobel saw the best chance of commercial application for the needles, which are the particles that have seen the least research so far. Compared with natural nanoparticles the artificial needles offer the advantage of moving freely through the solution without sticking together. According to Nobel the strength of nanoparticles is that they form a bridge between macroscopic properties and molecular structures. Boehmite needles for example, improve the adhesion between the needles and the other ingredients of the coating. In combination with the alignment of the needles at the surface of the coating the additional molecular adhesion results in the coating’s improved resistance to impact and scratching.

6. Nanotechnology and Nanoclay Modified Bitumen Emulsion

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. A nanometer is one-billionth of a meter. A sheet of paper is about 100,000 nanometers thick; a single gold atom is about a third of a nanometer in diameter. Dimensions between approximately 1 and 100 nanometers are known as the nano-scale. Unusual physical, chemical, and biological properties can emerge in materials at the nano-scale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules. [http://www.nano.gov]

As the mechanical behavior of bitumen and/or bitumen mixture depends to a great extend on structural elements and phenomena which are effective on a micro- and nano-scale, nanotechnology has been used in some areas of manufacturing bitumens.

6.1 Application of Nano-technology in Bitumen Research

Generally, it can be assumed that nano-science and -technology have a great potential to advance bitumen pavement technology in the field of materials design (development and optimization), materials manufacturing (nano-technological production) and pavement, construction, materials properties (multifunctionality and sustainability), materials testing and pavement monitoring with sensors and chemo-physical modeling of the material behavior down to a nano-scale. [Partl, 2003]

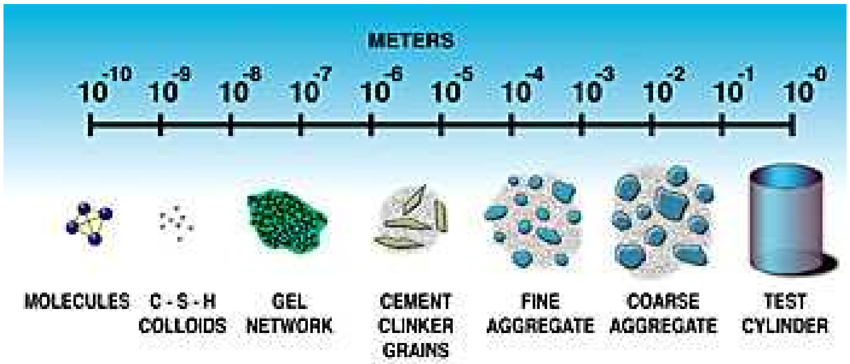


Figure 32 Nano-technology in bitumen mixtures

Both Portland cement and bituminous mixture are nano-structural materials, with the binder material consisting of a gel composed of calcium-silicate-hydrate colloidal particles in the 1 to 100 nm range. [Resperion, 2008]

Given the composite nature of asphalt mixture, the potential for improvements in the engineering properties of asphalt mixture through the application of nano-technology is significant. The mechanical behavior of bituminous materials depends to a great extent on structural elements and phenomena which are effective on a micro- and macro-scale. The nano-modification of materials is start with engineering modifications to the molecular structure with an aim to affect the bulk properties of the materials. The nano-modification of bituminous materials has the potential to open up whole new uses and classes of bituminous materials. [Resperion, 2008]

Most of the current bitumen modifiers in the market do not work on a nano-scale. They don't do anything to the chemistry of the bitumen, rather just improving specific properties such as binding and flexibility. Nano-scale modifiers can react with bitumen and change the chemistry and the molecular structure of the bitumen. This catalytically reaction may cause better properties. [Resperion, 2008]

6.2 Possible Properties of Nanoclay Modified Bitumen Emulsion

In figure 33, the aggregate surface coating after curing are shown that develop when using bitumen emulsion and nanoclay modified emulsion.

For bitumen emulsion, factors such as fuel, water and even ultraviolet radiation can have an immediate affection. These can decrease the adhesion properties because of the worse resistance to outside influences. As Figure 33 shows the main difference after curing between bitumen emulsion and nanoclay modified bitumen emulsion is that in the surface coating of nanoclay modified emulsion, the clay layers are dispersed in the binder. Unlike bitumen and polymers which are petroleum derivatives and can be dissolved by petrochemicals to a certain extent, these clay layers can stop the outside influences, resulting in the coating's improved resistance to outside factors and adhesion.

One difference between bitumen and tar is the fact that tar contains up to 5 mass% fine particles, which are not soluble in toluene. These particles can behave like special filler. For tar a much smoother transition between binder and filler can be observed than for bitumen where a gap in the very fine particle size exists [Partl, 2003]. These fine particles have a size in micrometer rather than in nanometer. Nevertheless they may have similar influences to emulsion as nanoclay may have.

As section 5.3.2 in part II shows, nanoclay modifications can improve the aging resistance of bitumen in the short term and long term. The current researches indicate that a clay modifier can improve the storage stability of modified bitumen. These advantages suggest that nanoclay may also give the same improvement to bitumen emulsion. This could make nanoclay modified bitumen emulsion a possible alternative to tar for antiskid runways.

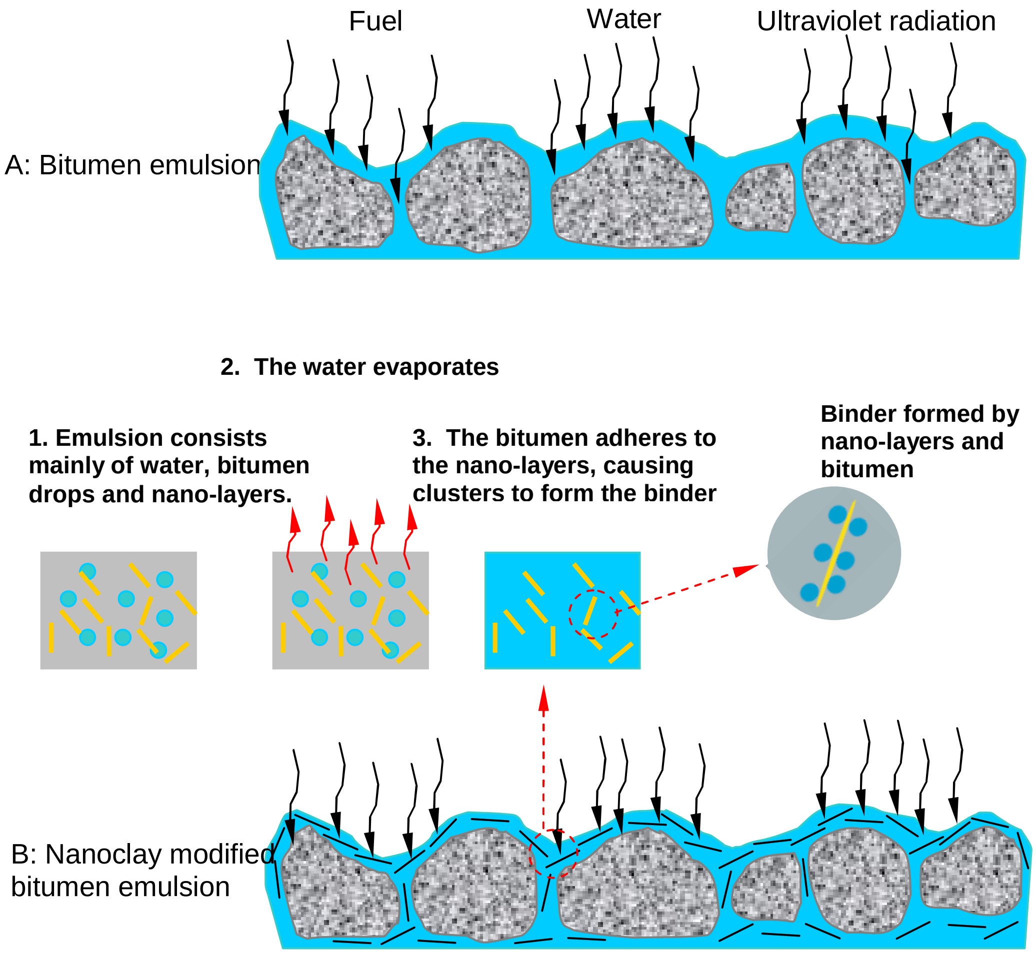


Figure 33 Possible difference on (fuel, water and ultraviolet radiation) resistance between bitumen emulsion and nanoclay modified emulsion

Part III Other Possible Alternatives

Surface treatments on runways should be available to aircraft traffic as soon as possible. Bitumen emulsions have disadvantages like the needed curing time and it is always not sure when curing is ended. This implies that aircraft operation can not take place during a significant amount of time (probably up to 1 day) which makes emulsion applications not very attractive for busy airports. Therefore other kinds of possible materials need to be investigated.

Waterborne generally defines the broad category of coatings that utilize water as the main volatile liquid component. It has good adhesion and fuel, water and chemical resistance [Mirgel, 1993; Weiss, 1997]. Epoxy asphalt and epoxy modified bitumen emulsion have already been used for pavement surface and performed significantly better than normal asphalt mixtures.

7. Waterborne Coatings

Two methods can be employed to form a film of resin on a substrate. The first involves using a liquid resin and a liquid hardener which are mixed together and applied to the substrate. The second method comprises a solution of resin and hardener in a solvent which is designed to evaporate once the material has been applied in a thin film. A solvent-free or 100% coating is produced by the first method whereas the second is referred to as a solvent-based coating. Each system has its advantages and disadvantages, a summary of which is outlined in Table 15 [http://www.azom.com/Details.asp?ArticleID=1100].

Table 15 Solvent Based versus Solvent Free Systems

Property	Solvent Free	Solvent Based
Max. Film Thickness (one application)	Unlimited	75 microns
Cure Speed	Comparable	Comparable
Moisture Susceptibility During Cure	High	Low
Pot Life	Short	Long
Mixing Accuracy	Must Be Accurate	More Tolerant
Water Resistance	Very Good	Very Good
Film Strength	Strong but can be Brittle	More Flexible
Film Shrinkage on Cure	Virtually None	Up to 70%

The comparison in Table 15 shows that solvent based systems have several advantages. So in the past, most industrial coating manufacturers were using organic solvents. But solvent based systems are potentially hazardous, providing a source of volatile organic compounds (VOCs). In order to improve protection of the environment, most industrial nations have issued laws demanding a reduction in the use of organic solvents. For coatings this means that the solid content needs to be increased or the organic solvent should be changed to water. [Mirgel, 1993]

Waterborne coating systems usually contain up to 80% water with small amounts of other solvents, such as glycol ethers. Most regulations require waterborne coatings to have a VOC content of less than 3.5 pounds per gallon.

Waterborne systems have been known for many years and their field of application has been predominantly in the building and construction market. However, many industrial applications require a higher performance, the standard having been set by solvent borne systems, especially with polyurethanes, which cannot be fulfilled by this kind of waterborne system. In view of the need to reduce the organic solvent content and increase the performance of waterborne systems, the transfer of polyurethane chemistry to the aqueous coatings was an obvious step. [Mirgel, 1993]

New technologies in waterborne systems provide unique technical solutions to overcome well known problems, like good adhesion to concrete, water resistance and acidic resistance. With the waterborne two-Component technology, coating manufacturers can formulate high-performance coatings without a cosolvent and achieve the same or even better properties.

7.1 Waterborne Polyurethane Resins

7.1.1 Polyurethane and Waterborne Polyurethane

Polyurethane (PU) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization by reaction between a monomer containing at least two isocyanate functional groups with another monomer containing at least two hydroxyl (alcohol) groups in the presence of a catalyst.

Polyurethane resins are formed from the reaction of an isocyanate with compounds containing active hydrogen. The active hydrogen can arise from a hydroxyl group (such as those contained in polyester, alkyd, epoxy, and acrylic polymers), a carbonyl group, or an amine. The formation of urethane groups, such as shown in Figure 34, can be accelerated through the use of tertiary amine or organic tin catalysts. [Weiss, 1997]

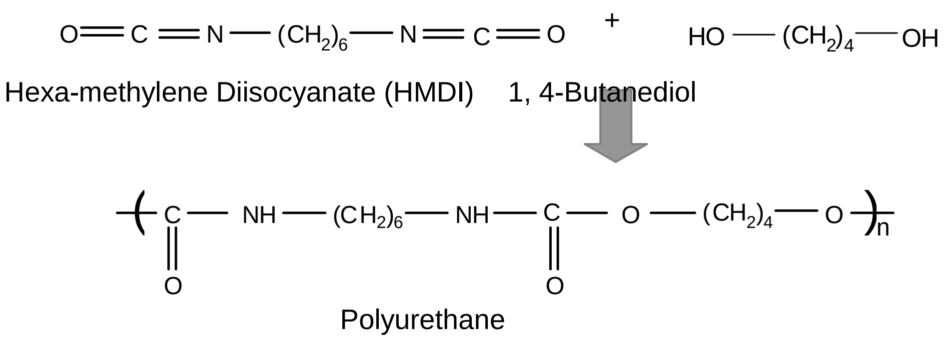


Figure 34 The reaction of an isocyanate with a compound containing hydroxyl functionality results in the formation of a polyurethane

Polyurethane is the generic term for the cured product which is formed from a chemical reaction between a polyol resin and a polyisocyanate hardener. When the two components are mixed the hydroxyl groups (-OH) in the resin react with the isocyanate groups (N=C=O) in the hardener and a three dimensional molecular structure is produced. Only one isocyanate group can react with one hydroxyl group so there is an ideal ratio of hardener molecules to resin molecules which will give optimum mechanical properties. Despite this fact, it is possible to vary this ratio slightly either way in order to modify the mechanical properties of the system. This is because the isocyanate hardener is also capable of cross-linking with itself in the presence of atmospheric moisture. More hardener than the optimum ratio will produce coatings which are harder, more brittle and have greater resistance to chemical attack. Less hardener will have the opposite effect: the film will be more flexible and its resistance to weathering will decrease. Therefore it follows that a polyurethane coating can accommodate a degree of variance in the mixing ratio but not without this having some effect on the properties of the final film. [http://www.azom.com/Details.asp?ArticleID=1100]

Polyurethanes are widely used in high resiliency flexible foam seating, microcellular foam seals, durable elastomeric wheels and tires, high performance adhesives and sealants.

Waterborne Polyurethane resins are coatings and adhesives that use water as the primary solvent. Aqueous polyurethane dispersions can be tailor-made and show many of the features of conventional solvent-born coatings and many technological advantages, such as low viscosity and good applicability. Polyurethanes obtained from aqueous dispersions have superior properties when compared with similar materials obtained from organic media.

7.1.2 One-component Polyurethane Resins

One-component polyurethane foams are used predominantly in the building sector. Usually, for manufacturing these products, an isocyanate group-containing prepolymer (isocyanate prepolymer) is filled into a pressure vessel together with one or more blowing agents and conventional additives. The foaming prepolymer, brought out of the pressure vessel by the user, is cured under the action of the ambient moisture. At the same time, the reaction of the isocyanate groups, present in the prepolymer, with the water of the ambient moisture is used for the polymerization of the prepolymer. [US Patent 6414045, 2002; Mirgel, 1993]

Because the reaction partner, water, depends on the ambient conditions (temperature, humidity, air movement), such one-component polyurethane foam compositions react very sensitive to the absence of an adequate amount of the reactant, water. This problem arises particularly when the one-component polyurethane foams are used at low temperatures. [US Patent 6414045, 2002]

7.1.3 Two-component Polyurethane Resins

Two-component polyurethane systems have been used very successful in the past because they combine high performance with air drying properties unlike any other coating system.

2-component Polyurethane coatings consist of two separate components. One is a water dispersible, soluble polymer (e.g. acrylic, polyester) which contains hydroxyl groups that can react with the isocyanate groups and can also contain the necessary pigments, extenders, additives and organic cosolvents. The second component consists of the polyisocyanate, with or without organic solvents. These two components are kept separate and should not be combined until just before application. The mixing can be achieved by means of two-component spray equipment (with the advantage of no shelf-life restrictions), or mechanically mixing by hand. [Mirgel, 1993]

Once the two components are mixed, several types of reaction start to compete:

NCO + OH → urethane

NCO + H_2O → urea + CO_2

NCO + COOH → amide + CO_2

NCO + urethane → allophanate

NCO + urea → biuret

NCO + amine → substituted urea

The main competing reactions are the crosslinking reaction (NCO + OH) and the undesired (NCO +H_2O) reaction which leads to generation of carbon dioxide.

After mixing of the two components, larger particle sizes can be found (1000 nm, polyisocyanates) emulsified by small particles (50-100 nm) of the OH-component. During the rapid consumption of the NCO groups the number of the large particles decreases and finally a homogeneous film is obtained. As well as the OH component, the nature of the polyisocyanate influences the properties of the coating. Generally, the basic monomer diisocyanate used for the polyisocyanate (HDI, IPDI, Desmodur W of Miles Corporation, Pittsburgh, PA, TMXDI, etc.) has the same effect on the coating in the waterborne systems as in the solventborne systems. The linear aliphatic hexamethylene diisocyanate exhibits higher flexibility and higher resistance to water, solvents or chemicals than the cycloaliphatic diisocyanates. [Mirgel, 1993]

The initial stage of film-formation process for waterborne polyurethane resin is physical drying. This drying consists of water evaporation till the polymer particles coalesce and polymer chains start to interdiffuse and react. These waterborne resins will remain soft and tacky until most of the water has evaporated and the particles start coalescing. There are several factors that can influence this process: [Noble, 1997; Huybrechts, 2000]

1. the amount of water to be evaporated till the particles start to touch each other (temperature and humidity will influence this step);
2. the viscoelasticity of the polyol and cross-linker will affect the coalescence process. The viscoelastic properties will depend on T_G, polarity and molecular weight as well as the presence of solvents or plasticisers;
3. in case the particles are ionically or non-ionically stabilized, the ease with which repulsive forces on the particles can be overcome.

7.1.4 Properties of Waterborne Polyurethane Resins

Waterborne Polyurethanes are fully reacted urethane polymers dispersed in water. These products contain no residual free isocyanate. They are now being widely used in the coatings and adhesives industries.

Waterborne polyurethanes are environmental friendly. They provide a tough, durable yet highly flexible seal. The advantages associated with polyurethane coatings are their high tensile strength, excellent weathering characteristics and chemical/mechanical resistance. These advantages have allowed polyurethane coatings to obtain a dominant market share in both the aerospace and cars refinish industries.

The modulus, tensile strength, and hardness, thermal and water resistance of waterborne polyurethane can be enhanced by organoclay layers (Cloisite or OMMT nanocomposite) dispersed in nanometer-scale. Table 16 shows how the tensile strength of waterborne polyurethane resins can be improved by adding OMMT nanocomposite. It reaches a maximum value of 43.1 MPa at 2 wt% OMMT content. This is 65% higher than resins with zero percent OMMT. Figure 35 shows that the storage modulus of OMMT nanocomposite modified waterborne polyurethane resin is much higher than if no OMMT is used. Under 100 ℃ the strength clearly increases with an increase of OMMT content. These results reveal that OMMT effectively improves the modulus of polyurethane. Notably, the storage modulus with 3 wt% OMMT at 80 ℃ still reaches 20.3 MPa. This is an increase with about 200% compared to polyurethane with zero percent OMMT at 80 ℃ (6.7MPa). [Kim, 2003; Deng, 2007]

Table 16 Effect of OMMT on tensile strength of waterborne polyurethane resin

OMMT content/ %	0	1	2	3	4	5
Tensile strength/ MPa	26.6	37.1	43.1	42.0	37.4	36.3

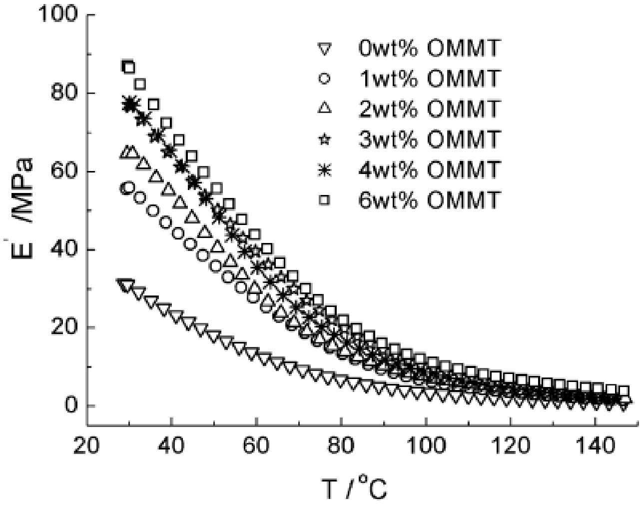


Figure 35 Effect of OMMT on the storage modulus of waterborne polyurethane resin

Table 17 Properties of the Addagrip's 1000 System resin

Roughness ratio	Without surface treatment	0.69	
	After application of this resin	0.75	
Water resistance Absorption of samples in water	Without surface treatment	4.19 %	Reduction 95.4 %
	After application of this resin	0.19 %	
Fuel resistance Absorption of samples in fuel	Without surface treatment	5.26 %	Reduction 75.2 %
	After application of this resin	1.31 %	

Over the last seven years Addagrip's 1000 System resin, a two-component polyurethane resin designed by Addagrip Surface Treatments UK Ltd for sealing and protecting asphalt surfaces from erosion caused by frost damage, chemical attack and aviation fuel spillage, has been used to carry out durable and extensive repairs to the concrete runways of two Polish airports. In 2001 they used this kind of resin in Radom airport and the surface is still perfect, see Table 17. It shows that apply this polyurethane resin onto the pavement surface can prevent further deterioration prolonging the life. [www.addagrip.co.uk]

7.2 Waterborne Epoxy Resins

7.2.1 Epoxy Resins

Epoxy is a copolymer, that is, it is formed from two different chemicals. These are referred to as the "resin" and the "hardener". The resin consists of monomers or short chain polymers with an epoxide group at either end. Most common epoxy resins are produced from a reaction between Epichlorhydrin and bisphenol-A (See Figure 36), though the latter may be replaced by similar chemicals, such as glycerol and other aliphatic polyols. The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA). When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked, and is thus rigid and strong. Polyamide, amido/amine and aliphatic/aromatic amine hardeners react with epoxy resins upon mixing to provide films that are extremely resistant to chemicals. [http://en.wikipedia.org/wiki/Epoxy; K. D. Weiss, 1997]

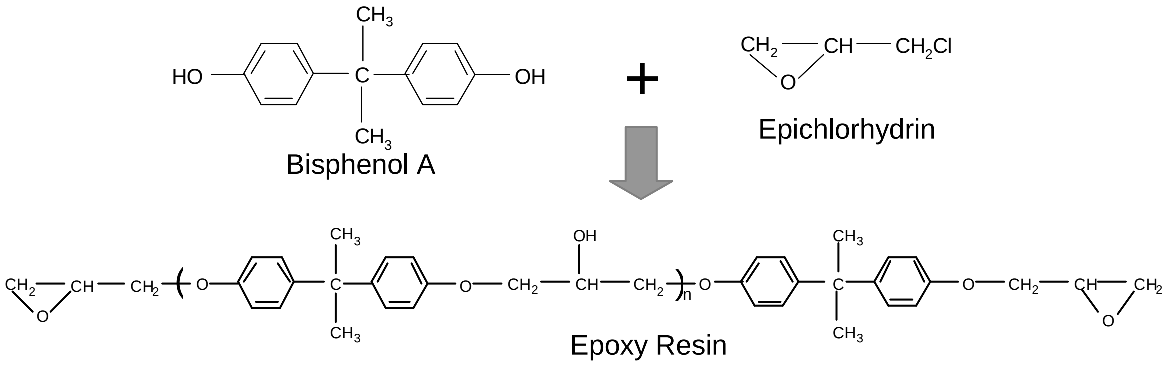


Figure 36 An epoxy resin formed by reacting Bisphenol A with Epichlorhydrin

Many epoxy products also contain additives such as organic solvents, fillers such as fiberglass or sand, and pigments. When epoxy resin systems are used, single molecules (monomers) of the epoxy resin chemical and the curing agent combine to form long chains of molecules (polymers). This process of polymerization is called "curing", and can be controlled through temperature and choice of resin and hardener compounds; the process can take minutes to hours. Some formulations benefit from heating during the cure period, whereas others simply require time, and ambient temperatures [http://en.wikipedia.org/wiki/Epoxy].

7.2.2 Waterborne Epoxy Resins

Waterborne epoxy resin is a kind of stable resin material prepared by means of dispersing epoxy resin in the form of particles or droplets into the dispersion medium based on water as a continuous phase. The viscosity of waterborne epoxy resin can be discretionarily adjusted. The operation method is not only convenient but also causes no pollution to the environment and no harm to human body. After adding a proper amount of curing/solidifying agent, advantages like high strength, high-temperature resistance, fatigue resistance, and high anti-aging ability will be achieved. [Zhang, 2007]

Epoxies can be made dispersible in water by copolymerization with polymers containing polar functional groups, such as those present in acrylic and methacrylic polymers. Waterborne epoxy resin is a coating formulation that utilizes water as the main volatile liquid component. Paint containing an epoxy resin dispersed in a water medium would be correctly described as a waterborne epoxy resin.

Waterborne epoxy coatings were commercially introduced about 40 years ago, mainly as an environmentally friendly replacement to solvent-borne epoxies in countries with strong environmental and worker safety regulations.

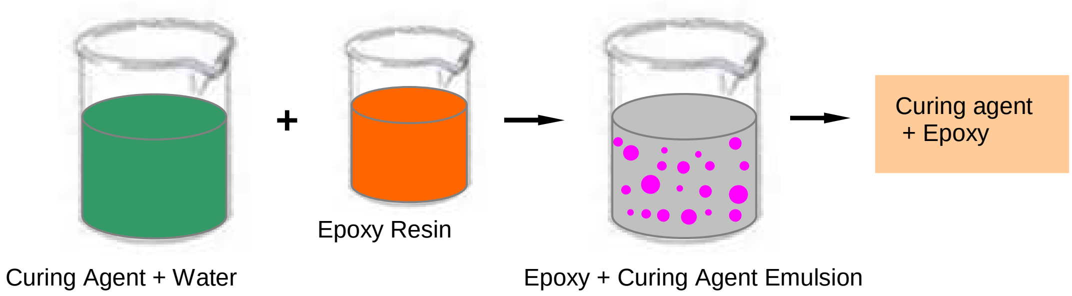
Waterborne epoxy resins (waterborne epoxy coatings) are used as ambient cure epoxy coatings. These non-hazardous, two-part epoxy coatings are developed for heavy duty service and use less energy than heat-cured powder coatings. The coating dries quickly providing a tough, UV resistant, protective coating with excellent ultimate hardness, and good mar and abrasion resistance. They are designed for rapid dry protective coating applications. Ambient cure 2 part waterborne epoxy coatings provide excellent physical properties in exterior applications. These products have excellent adhesion. [http://en.wikipedia.org/wiki/Epoxy]

Waterborne epoxy coatings evolve in two fundamentally different kinds. Type I systems are based on liquid bisphenol A/F epoxy resins, with an EEW (Epoxy Equivalent Weight) <250. Type II systems are based on higher molecular weight, solid epoxy resin dispersions (See Figure 37). [Rufo, 2005; Dubowik, 2007]

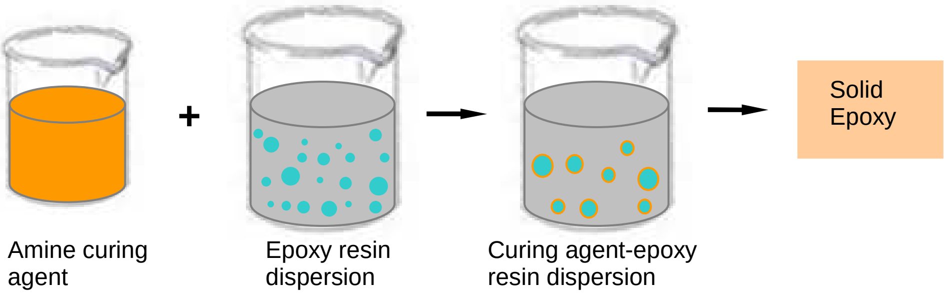
In type I systems the curing agent not only crosslinks the epoxy resins in the final film, but in the liquid state often also serves as the emulsifier for the epoxy resin. As a result, in this system, immediately after mixing the emulsion particles contain both curing agent and epoxy resin, although there is usually also some amine in the aqueous phase. In contrast to the Type II systems described below, there is clearly less phase separation of the curing agent and resin. After application, water evaporates and the particles coalesce. Good coalescence is normally not an issue due to the low molecular weight of the ingredients and consequently high rates of diffusion, and coatings generally form that possess relatively uniform film morphology.

Type I systems can often be formulated to zero VOC coatings with high hardness but low flexibility and low impact resistance. The pot life of such systems is usually short, typically 2 hours.

To overcome the limitations of the Type I approach, waterborne systems based on higher molecular weight solid epoxy resins were developed. Solid epoxies are supplied pre-dispersed at 50-55% solids in water and co-solvent, and always containing an emulsifier. To aid in processing and to overcome the poor flow and coalescence of solid epoxies, 5-10% glycol ether is added to the dispersions, thereby eliminating any possibility for zero VOC formulations.



Type I waterborne epoxy



Type II waterborne epoxy

Figure 37 Mixing process for two typical epoxy systems

With these systems the dispersed resin particles contain only solid epoxy resin. Therefore the curing agent must migrate from the aqueous phase into the dispersed epoxy particles for the crosslinking reaction to occur. As the coating coalesces, there is a greater tendency for films with heterogeneous film morphology to develop. Stained cross sections of certain Type II coatings viewed through transmission electron microscopy have shown particle boundaries to be amine rich, further suggesting the presence of un-reacted epoxy resin in the particle cores.

7.2.3 Properties of Waterborne Epoxy Resins

In general, epoxies have excellent adhesion, excellent chemical and heat resistance and excellent mechanical properties.

Due to their properties, waterborne epoxy resins have a wonderful application prospect. Especially in terms of the application of epoxy resin in combination with cement mortar, the introduction of hydrophilic groups into epoxy resin makes this high performance organic-and-inorganic compound available with the high performance epoxy resin as preconditions. The outstanding advantage of a waterborne epoxy resin lies on that this compound can be cured at atmospheric temperature and humidity with reasonable curing time. It can be mixed with such common materials as cement mortar and concrete to enhance the early strength, impact resistance and waterproof ability of above mentioned materials. This is incomparable for many other types of waterborne polymers.

The structure of epoxy-based coatings leads to high chemical resistance, thermal stability, good adhesion, and superior toughness. Some epoxies offer greater chemical and corrosion resistance than alkyd resins. [Weiss, 1997]

Organophilic montmorillonites were introduced to waterborne epoxy resin, and results indicated that properties like drying time as well as mechanical properties (hardness, resistance and adhesion) were positively affected by these layered nanofiller. [Kowalczyk, 2008]

7.3 Comparisons between Epoxy and Polyurethane

Epoxy resins consist of a linear chain molecule with a reactive epoxy group at each end of the chain. Each particular type of epoxy resin varies in terms of its detailed structure and the length of the chain between the epoxy groups. The actual properties of the final epoxy resin coatings are very much dependent on the type of resin and hardener used.

Table 18 Relative Performances of Epoxy and Polyurethane Systems

Property	Epoxy	Polyurethane
Adhesion	Excellent	Good
Water Resistance	Excellent	Good
Cure Speed	Good	Excellent
Susceptibility to moisture during curing	Little to Considerable	Considerable
Abrasion Resistance	Good	Excellent

Generally speaking polyurethane systems cure faster than their epoxy counterparts. They can however, be difficult to use when cured in moist conditions at low temperatures because of the affinity of the isocyanate for moisture. This may result in inadequate curing and premature embrittlement.

The main role of all these alternatives is to protect the surface of the runway, and to enhance its raveling resistance. In order to be considered effective it must give the desired protection against environmental and mechanical damage during an as long as possible period time. In order to achieve this level of performance good adhesion to the surface and a resistance to moisture, fuel and ultraviolet radiation are essential.

It is apparent (See Table 18, [http://www.azom.com/Details.asp?ArticleID=1100]) that epoxy systems are particularly suitable for use as the alternative for tar-bearing antiskid runways because of their good adhesion and water resistance.

8. Epoxy Asphalt

An epoxy asphalt mixture is a polymer concrete made from a slow curing, epoxy asphalt binder that is mixed with aggregates. The epoxy asphalt binder is a two-phase chemical system in which the continuous phase is an acid cured epoxy and the discontinuous phase is a mixture of specialized asphalts, which makes the mixture’s performance different from traditional asphalt mixtures [Chen, 2009]. This kind of binder is unlike conventional asphalt; it does not become brittle at low temperature and does not melt at high temperature.

It was originally developed in the late 1950s by Shell Oil Company as a material designed to withstand the damage jet fuel could impart on pavements. In 1967, it was used to strengthen the surface of San Francisco Bay's mile-long San Mateo-Hayward Bridge. After more than 40 years, the bridge's surface is reported to be in excellent condition. The cured epoxy asphalt mixture has an extremely high temperature stability and strength, excellent fatigue and anti-bleeding properties, and superior rutting resistance.

8.1 Properties of Epoxy Asphalt

Marshall Stability values of epoxy asphalt mixtures tend to increase with the curing time. The Marshall Stability value of a cured specimen can be as high as 37.0 kN (See Figure 38). Even at the beginning of curing, the stability value is more than 10 kN. [Luo, 2007]

Epoxy asphalt is a material with a stiffness that can be applied in thin surface layers. When used on roads, it sets quickly enough for normal traffic in the early life even without full curing, which enables the roadway to be reopened within two hours [Alabaster, 2007]. It performs well on steel bridge decks, as its low porosity helps to prevent deck corrosion. When weight is a consideration, a thin coating of epoxy can be applied. Application does not require special equipment.

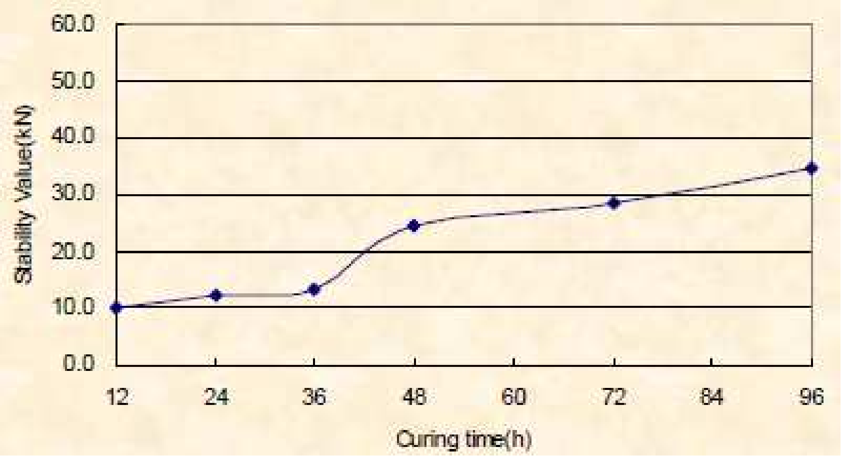


Figure 38 Marshall stability-curing time curve of epoxy asphalt mixture at 60 ℃

Table 19 Marshall Stability test for different kinds of asphalt mixtures

Mixture type	**Marshall Stability/ kN**		**Retained Stability**
	Standard condition	Conditioned at 60 ℃ for 48 h in a water bath	
Epoxy asphalt mix	36.1	35.7	98.9
SMA 10	5.6	4.4	78.6

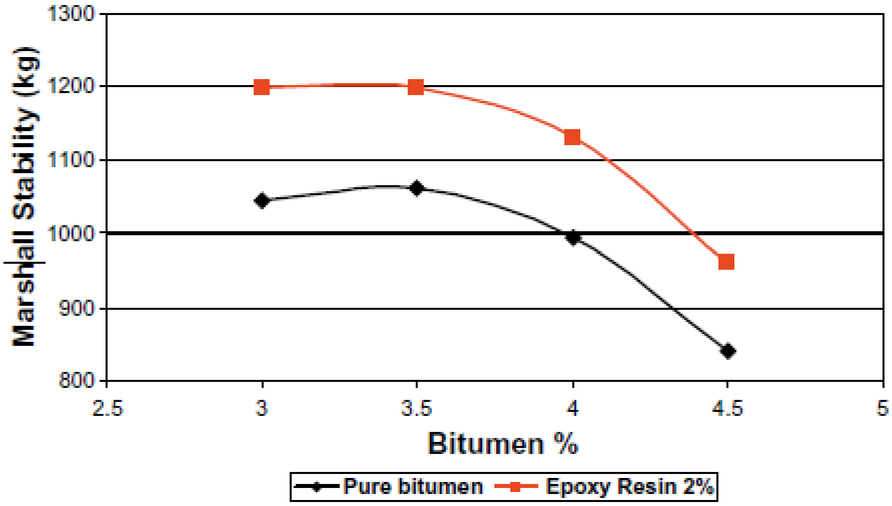


Figure 39 Marshall Stability of pure bitumen and epoxy asphalt

Table 20 Indirect tensile strength test for different kinds of asphalt mixtures

Mixture type	**Indirect tensile strength at 25 ℃/ kN**		**Retained Stability**
	Standard condition	Conditioned at -18 ℃ for 16 h, then at 60 ℃ for 24 h in a water bath	
Epoxy asphalt mix	31.9	25.8	80.9
SMA 10	7.4	5.6	75.7

The Marshall Stability test and Indirect Tensile Strength test were used to evaluate the moisture sensitivity of epoxy asphalt mixture. From the results in Figure 39, Table 19 and Table 20, it can easily be seen that the epoxy asphalt mixture performed significantly better than the SMA mixture. The results show that the epoxy asphalt mixture is less susceptible to moisture damage. Fatigue properties of the epoxy asphalt mixture and asphalt mixture was evaluated by beam fatigue test using a sinusoidal mode with 5 kN maximum load and 10 Hz frequency. Fatigue test results in Table 21 show that the fatigue life of the epoxy asphalt mix is more than three times greater than that of SMA10. [Cubuk, 2009; Luo, 2007]

Table 21 Fatigue life for different kinds of asphalt mixtures

Mixture type	**Load cycles/ times**	**Condition of the samples**
Epoxy asphalt mix	12 000 000	No damage
SMA 10	3 200 000	Cracking in the middle of the sample

The low temperature properties were evaluated by three point bending test on epoxy asphalt mixture, SMA and mastic asphalt mixture (MA). Table 22 shows the results. It indicates that the stiffness modulus of epoxy asphalt mixture decreased with an increasing temperature. At the same temperature of -15 ℃, epoxy asphalt mixture has the highest tensile strength and stiffness modulus value. It can be concluded that the epoxy asphalt mixture performed significantly better in terms of strength at low temperature, while its deformation characteristic (strain at failure) was similar to that of other mixes. [Luo, 2007]

Table 22 Bending test results for different kinds of asphalt mixtures AT

Mixture type	**Temperature/ ℃**	**Damage strength/ MPa**	**Maximum strain**	**Bending stiffness modulus/ MPa**
Epoxy modified asphalt mix	-20	20.54	2.26×10-3	10172
	-15	20.29	2.60×10-3	7808
SMA 10	-15	7.51	2.06×10^{-3}	3477
MA		13.56	3.63×10^{-3}	3736

Epoxy asphalt is reported to be extremely durable as well as flexible. Tests performed by the California Department of Transportation showed that surfaces with epoxy asphalt obtained maximum skid resistance. The Washington State Department of Transportation also tested epoxy asphalt against another road surfacing product and found that the epoxy asphalt surface make less noise. It was determined that the epoxy asphalt resisted well and don’t need maintenance for a longer period of time.

Epoxy asphalt is used in high-performance systems that are fully capable of resisting the stresses imposed by traffic on the most difficult sites. Binders used in such systems are classified as “thermosetting” as the epoxy resin components cause the binder to cure by chemical action and it is not subsequently softened by high ambient temperatures or by the spillage of fuel. An epoxy asphalt layer thus acts as an effective seal against the ingress of oil and fuel.

An asphalt mixture and epoxy asphalt mixture were put into diesel. After the same time, the asphalt mixture almost dispersed while epoxy asphalt mixture was still in good condition (see Figure 40). This shows that epoxy asphalt mixture presents a nice fuel (or diesel) resistance.

Figure 40 Effect of Diesel Immersion [Elliott, 2008]

According to several researches, advantages for epoxy asphalt can be listed as follows: [Elliott, 2008; Chen, 2009; Alabaster, 2008]

1. more resistant to low temperature cracking because of its higher tensile strength and flexibility, the temperature influences on the fracture resistance of epoxy modified asphalt mixture is not as significant as that of thermo-plastic HMA;
2. more resistant to fatigue cracking;
3. stiffer (higher modulus) at service temperatures, with greater load spreading ability;
4. less susceptible to water induced damage; sufficiently resistance to the action of fuel spillage and blast from jet-type aircraft;
5. more resistant to rutting and ageing;
6. excellent adhesion properties, more resistant to surface abrasion from tyre action.

8.2 Epoxy Modified Bitumen Emulsion

Bitumen emulsions modified by waterborne epoxy resin and a compound containing SBR were investigated. [Zhang, 2007] In this research, modified bitumen emulsion was manufactured by twice thermal mixing method. First, a mixture of water, epoxy resin emulsion, SBR latex and emulsifier was prepared by mixing water-epoxy resin emulsion with SBR latex (normal temperature) and a hot emulsifier solution (60~70 ℃) by means of an emulsification machine. Then this mixture was put immediately together with melting bitumen (120~130 ℃) into the emulsification machine for emulsification.

The different test results for bitumen emulsion and kinds of modified bitumen emulsion are shown in Table 23. These results indicate that asphalt emulsion modified by the compound of waterborne epoxy resin and SBR latex has better performances on adhesion, stability and other mechanical properties.

Table 23 Test results for bitumen emulsion and modified bitumen emulsions

Types		**Bitumen emulsion**	**Waterborne epoxy modified bitumen emulsion**	**SBR modified bitumen emulsion**	**Bitumen emulsion modified by epoxy and SBR**
Storage stability/ %		3.0	2.7	2.7	2.6
Viscosity/ Pa·S		18.6	38	32	40
Adhesion	granite	Good	Good	good	excellent
	limestone	Good	excellent	excellent	excellent
	basalt	excellent	excellent	excellent	excellent
Residue	Penetration/ 0.1 mm	99	81	74	62
	Softening point/ °	46	53	49	55
	Ductility/ cm	fracture	4.3	8.4	9.7

In Chen's research, colloidal nano-silica particles were added into waterborne epoxy coating by direct blending. In this literature, they found that nano-silica particles can improve the scratch resistance significantly. The hydrophilic nanoparticles also need surface modification to improve the mechanical properties of waterborne coatings, similar to how they work in solvent-based coatings [Chen, 2009]

Conclusions

As this literature review shows, there are several types of materials that can be considered as a possible alternative to tar-bearing antiskid, such as modified bitumen emulsion, waterborne epoxy resin, waterborne polyurethane resin, epoxy asphalt and epoxy modified bitumen emulsion. The possible properties of the selected alternatives are showing in Table 24.

Table 24 Possible property of several possible alternatives

Alternatives	Possible Properties	
Nanoclay (or with polymer) modified bitumen emulsion	advantages	Low temperature for application and storage; Good fuel, water and ultraviolet radiation resistance Good aging properties; Good storage stability;
	disadvantages	Slow curing, Less adhesion; The dispersion of nanoclay layers may has complicated influence;
Epoxy asphalt/ epoxy modified bitumen emulsion	advantages	Low temperature for application and storage; Less temperature sensitivity; 2 hours curing is enough for Open to traffic; Good fuel, water and chemical resistance; Quieter, flexible; Excellent adhesion, good aging properties; Good resistance to low temperature and/or fatigue Cracking; Much more stable under high temperature;
	disadvantages	Mixed before application; good temperature control needed; Long curing time (normally needs several days for full curing);
Waterborne epoxy resin	advantages	Low temperature application and storage; Good fuel, water and chemical resistance; Good adhesion and thermal stability; Can be modified by nanofiller;
	disadvantages	Slow cure (based on ambient temperature and humidity); Mix proportions are critical;
Waterborne polyurethane resin	advantages	Low temperature for application and storage; Good fuel, water and chemical resistance; Good adhesion and thermal stability; Can be modified by organoclay;
	disadvantages	Slow cure (based on ambient temperature and humidity); Mix proportions are critical;

When comparing the advantages and disadvantages shown in Table 24, modified bitumen emulsion, epoxy asphalt or epoxy modified bitumen emulsion might be the best one because of their outstanding properties.

Currently, there are many companies are working on these pavement/building surfacing materials, such as BASF, Ciba, Bolidt, DUPONT, and ICOPAL.

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Appendix A REQUIREMENTS FOR CATIONIC EMULSIFIED BITUMEN [1]

NOTE 1—CQS–1H emulsions shall meet the requirements outlined in Practices D 3910.
NOTE 2—CQS-1h is used for Quick Set Slurry Seal systems.

Type	Rapid-Setting				Medium-Setting				Slow-Setting				Quick Setting	
Grade	**CRS-1**		**CRS-2**		**CMS-2**		**CMS-2h**		**CSS-1**		**CSS-1h**		**CQS-1H**	
	min	Max	min	max	min	max	min	max	min	max	min	max	min	max
Test on emulsions：														
Viscosity, Saybolt Furol at 25 ℃ (77℉) SFS									20	100	20	100	20	100
Viscosity, Saybolt Furol at 50 ℃ (122℉) SFS	20	100	100	400	50	450	50	450						
Storage stability test, 24-h, % [2]		1		1		1		1		1		1		
Demulsibility, 35 mL, 0.8 % dioctyl sodium sulfosuccinate, %	40	…	40	…										
Coating ability and water resistance：														
Coating, dry aggregate					good		good							
Coating, after spraying					fair		fair							
Coating, wet aggregate					fair		fair							
Coating, after spraying					fair		fair							
Particle charge test	positive		positive		positive		positive		positive		positive		positive	
Sieve test, % [2]		0.10		0.10		0.10		0.10		0.10		0.10		0.10
Cement mixing test, %										2.0		2.0		N/A
Distillation:														
Oil distillate, by volume of emulsion, %		3		3		12		12						
Residue, %	60		65		65		65		57		57		57	
Tests on residue from distillation test:														
Penetration, 25 ℃ (77℉), 100 g, 5 s	100	250	100	250	100	250	40	90	100	250	40	90	40	90
Ductility, 25 ℃ (77℉), 5 cm/min, cm	40		40		40		4 0		40		40		40	
Solubility in trichloroethylene, %	97.5		97.5		97.5		97.5		97.5		97.5		97.5	

[1] ASTM D 2397–05 Standard Specifications for Cationic Emulsified Bitumen. 2005
[2] This test requirement on representative samples is waived if successful application of the material has been achieved in the field.

Appendix B TEST METHODS FOR BITUMEN EMUIONS AND BITUMEN EMULSION MIXTURES

Tab. 1 test methods for bitumen emulsions and emulsion residues

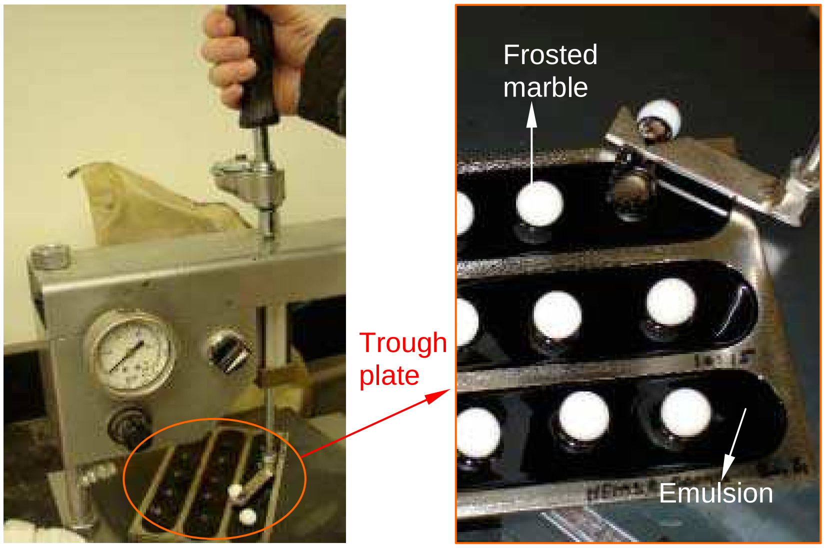
bitumen emulsion	properties	test methods	properties	methods
	Viscosity	DSR Efflux time (EN 12846) Dynamic Viscosity (EN 14896)	**Particle size distribution**	Fluorescence Microscopy Laser light scattering instrument
	Sieve test	EN 1429	**PH value**	EN 12850
	Cement mixing test	EN 12848	**Particle Charge**	EN 1430
	Breaking value	EN 13075-1	**Setting tendency**	EN 12847
Emulsion Residue	**Ductility (25 ºC. 5 cm/min)**	EN 13589	**Tensile stress**	EN 13587
	Penetration	EN 1426	**Elastic recovery, 25 ºC**	EN 13398
	Softening Point (ºC)	EN 1427	**Evaporation Residue, 163ºC**	Distillation test (ASTM D69)
	Dynamic Viscosity	EN 12596	**Recovery by evaporation, 50 ºC**	EN 13074

Tab. 2 test methods for bitumen emulsion mixtures

Adhesion	Frosted marble cohesion test Modified cohesion test Loaded wheel test Vialit plate shock test (EN 12272-3)	**Water resistance**	EN 15816，EN 15817
		Fuel resistance	EN 12697
		Raveling resistance	Wet Track Abrasion Test ()

Appendix C Frosted Marble Cohesion Test

A modified cohesion tester was the primary piece of equipment used for this test. The standard cohesion tester foot was replaced with a 50 mm hooked foot. The hooked foot was rotated horizontally with a torque wrench to dislodge a 14.3 mm acid etched (i.e., frosted) glass bead (i.e., marble) from asphalt emulsion contained in a trough plate. The emulsion depth is 1.6 mm and corresponds to an application rate of 1.5 L/m2. The average torque required to dislodge 5 frosted marbles was recorded as the chip retention strength. The test is conducted within a trough plate containing 3 rows that each held 5 frosted marbles. The average of the five results per row is reported as one test.



Test Procedure:

1. Replace the 28.6 mm diameter cohesion tester foot with the 50 mm hooked foot and adjust to contact the frosted marbles slightly below the center of the marble. Lock in place with the jamb nut. Adjust air pressure to 70 kPa to minimize friction
2. Add 9.0 + 0.2 g of chip seal emulsion to each of the three, 1.6 mm deep troughs of the plate. Place on a level surface and allow the emulsion to seek a level position. When the emulsion is level, place the acrylic template directly over the trough plate and add 15 frosted marbles (5 per trough). The template may be removed in a few minutes or when the initial set occurs; it is merely for alignment.
3. Cure specimens.
4. After each specified curing period, the trough plate was positioned on the cohesion tester base with the hooked foot for 2-point static contact. The trough plate was held firmly in place while the torque wrench was applied to the upper rod end and twisted with a firm but smooth horizontal motion through a 30 to 45 degree arc in about half of a second. The

torque required to dislodge the marble was read by the follow up pointer and recorded. The average torque values of five successive tests in each trough for the curing period stated was recorded as the chip retention strength. All 3 rows per trough were tested in one interval. Each row contained a different emulsion.

5. After the test, the residual bitumen in the trough may be removed and tested for moisture or solvent content.