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ROAD CHEMICALS, SELECTION, TEST METHODS AND FUTURE TRENDS

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SYNOPSIS

It is important to recognise functioning and performance of chemicals used in bitumen road construction in order to achieve highest attainable field results.Cationic surfactants doped to bitumen secure a physico-chemical bond between bitumen and electro-negatively charged aggregates, this is applied in cutback bitumen, road oiling, bitumen emulsions and hot mix.

This paper is an introduction to the use of "surfactants" in bituminous materials and will deal more specific with applications of cationic surfactants in cut-back bitumen and bitumen emulsions.

The data and opinions presented are based on experience gained in the European market,

Approximately 70-80% of W.European produced cutback bitumen and bitumen emulsions is applied in surface dressing technology. Primarily for ecological reasons a switch from cutback bitumen to bitumen emulsions happened. The review of the W. European countries using cutback bitumen or bitumen emulsion in surface dressing shows a fragmented picture. Cutback bitumen compared with bitumen emulsion differs in application field, failure risk and strength build-up, Economy is quite the same.

Evaluation of performance of cationic surfactants in cutback bitumen include passive, active and dynamic adhesion tests. Performance testing of bitumen emulsions for surface dressing is done by filler index test (break time), shake stability test (power of the emulsifier) and passive plus active adhesion tests.

The future trend will be a higher performance within existing technologies.

1. INTRODUCTION

Road construction is a costly affair. Road engineers do their best to achieve highest performance at balanced costs. It is in the interest of all of us to achieve highest technical performance - failures are more costly. Specifications should be established allowing a freedom in choice of materials, however, securing required technical performance.

With the introduction of cationic surfactants in 1950-1960 a major step forward in technology of bitumen based roads has been made. When incorporated into the bitumen binder, the chemical adhesion agent promotes adhesion of the binder to the road surface, be it wet or dry. Cationic chemicals possess a physico-chemical positive charge. The higher the "cationicity" the stronger will be the adhesive power towards an electronegative charged surface, eg aggregates. Cationic surfactants can be neutralised with acids to their salts which are water soluble. These cationic emulsifiers will travel in an electric field to the negative poles. Herman von Helmholz established a method to measure the speed of travelling in such a field and called it zeta potential. The higher the speed of travel, the higher the zeta potential and the more cationic is the surfactant. Experimental work is described by Dybalski (1).

2. APPLICATION

The use of cationic surfactants is practicised in the following technologies:

(1) cutback bitumen (surface dressing) (7)
(2) road oiling (road/base/surface)(5)
(3) bitumen emulsions (8)
(4) hot mixes (2, 3, 4).

Addition of cationic surfactants to a hot mix is done in those cases where lack of adhesion/binding strength in the hot six is noticed. A comparison in strength between a hot mix including end excluding an adhesion agent should be made. A comparison of 19arshall Stability of the hot mix with and without immersion testing (48 hours, 40 C water) should show noticeable differences in strength. After water immersion, mm. 70% of the original strength should remain. A reduction in the loss of strength on soaking is noticed if the correct adhesion agent is used in the hot mix.

One literature place (2) claims that the addition of adhesion agents to hot sixes ives an improved cohesion of the mix. In a so-called splitting force test (Anderson, R.I.L.E M. symposium, Dresden 1966) the force is measured to split the hot mix specimen Adhesion agents increase the stiffness of the mix and increased force is necessary to split the mix.

Road Oiling is a special technology used in cold climates in Norway, Sweden and Finland. Heavy petroleum fractions, known as road oil (500 ePa's at 40-50 degrees celsius) are mixed at 90^0C with aggregates. Amine adhesion agents are used in the road oil and secure a thorough, irreversible bonding with the aggregates. Road oil based roads are subject to tough winter conditions,

Imitation of displacement forces is a criterium for securing permanent success. Water and pumping effects, traffic, temperature cycling, and bitumen oxidation, deterioration and stress cracking determine life time of road oil based roads (13).
Stripping could be divided in three steps:

(a) Water goes through weak spots in the bitumen coating and penetrates the aggregates
(b) Water occupies the surface and parts of the aggregate by forcing the bitumen back and off the surface. Stripping starts.
(c) The bitumen only covers small parts of the surface and lose finally its bond to the aggregate. Stripping developed more or less.

The actual displacement forces are imitated in a test with water + road oil + aggregate under vibrating conditions and are used as correlation to practical traffic circumstances (6).

The same principle would be basically valid for surface dressings and can be used as an indicator for possible longtime failures.

Surface dressing technology either with cutback bitumen or with bitumen emulsion consumes a lot of cationic surfactants. Surface dressing, if applied well, will bring an aggregate mosaic embedded in bitumen as surface coating on top of an existing road. The strength of the surface dressed road comes from the right mosaic formation plus the proper embedding in bitumen. It means aggregate size and shape selection is important. Spraying the right, well dosed quantity of bitumen to secure this embedding is necessary (7).

3. SURFACE DRESSING

Two ways of applying the bitumen binder are available; cutback bitumen or bitumen emulsions. Both possess advantages and disadvantages. Primarily for environmental reasons bitumen emulsions replaced cutback bitumen. Energy conservation and atmospheric pollution cause great concern. Fuel savings that can be realised by using bitumen emulsions instead of cut-back bitumen is estimated at 2-3% of total hydrocarbon pollutants. Another element of concern is firehazards with cutbacks(12).

Historical reasons and personal preferences determine very much whether one sticks to either the one or the other, or to change. -

Following is a summary what the different countries are doing:

		Cutback Bitumen %	Bitumen Emulsion %
Norway	(2)	100	0
Sweden	5)	80	20
Denmark	(2)	90	10
U.K.	(25)	20	80
Holland	(15)	30	70
Germany	(25)	30	70
Belgium	(8)	80	20
France	(100)	10	90
Spain	(20)	20	80
Italy	(5)	80	20
Australia	(5)	70	30
New Zealand	(5)	90	10

In brackets you will find the approximate amount of emulsions produced compared with France in percentages. So if France produces 1 mt per year, the U.K. produces 0.25 mt per year.

What are the preferred technologies (8) used in the different countries in relation to cationic chlemicals?

3.1 Technology

Norway	Road oiling: 0.8% Duomeen T adhesion agent in oily bitumen + aggregate mix.
Sweden	Road oiling: 0.8% of special amine mix.
Finland	Road oiling: as Norway.
U.K.	Emulsions: 70% surface dressing with 68-70% emulsion, 30% mix grades + tack coat.
Holland	Tar/bitumen (40/60) in surface dressing. Bitumen emulsions: 80% surface dressing, rest tack coat, no mix grades.
Germany	Bitumen emulsion: 70% tack coat, rest surface dressing
Belgium	Surface dressing with cut back. Emulsions in tack coat mainly.
France	The emulsion country. Double surface dressing. Cutback bitumen in surface dressing on hills
Spain	The slurry seal country. Surface dressing with emulsions.
Italy	Minimal surface dressing and slurry sealing.
Australia	Surface dressing mainly with cutback bitumen, some emulsion.
New Zealand	Mainly cutback bitumen in surface dressing.
U.S.A.	Tendency to forbid the use of cutback bitumen surface dressing-energy concious (9,12)

The conclusion is that we meet a fragmented world of application technology.

3,2 Cutback vs Emulsion Surface Dressings

The differences between cutback bitumen and surface dressing can be summarised as follows:

(a) Application of bitumen emulsions in surface dressing is more critical than with cutback bitumen. Failures with cutback bitumen mainly happen, if material is sprayed at too low temperatures. The viscosity of the binder is then too high to wet the aggregate surface properly resulting in lack of adhesion.

Failures with bitumen emulsions in surface dressing happen more often. Bitumen emulsions have one drawback of technical deficiency. The break of the emulsion onto the aggregate is managed very well. The emulsion which stays in between the aggregates breaks via a water elimination path (sun, wind). This is the so called 'cheesy state'. It is responsible for the lack of early build-up of strength of the mosaic embedding. In colder climates especially this can be a problem and the cause of failures.

(b) Cutback bitumen usually gives earlier strength to chipping embeddings in the binder compared to bitumen emulsions. For circumstances requiring "earliest open to traffic" or situations where high speeds can be expected soon after the laying of the surface dressing mat, this can be of importance.

(c) In hilly areas mainly cutback bitumen is used. The explanation is that a fast increase in the viscosity of the binder will better secure a fixing of the chippings in the binder.

(d) Ecological reasons cause bitumen emulsions to get preference. The loss of cutback solvent to the atmosphere is wasting energy. In Europe no restrictions exist. In some states in the U.S.A. there is a strong lobby to switch to environmentally acceptable bitumen emulsions.

(e) From point of view of economy cutback bitumen meets approximately the cost/ performance of bitumen emulsions. Bitumen emulsions contain 30-35% water, approximately 0.2% emulsifier, 0.2% auxiliary chemicals. They require the investment in an emulsion factory. The estimated depreciation costs for a 5.000-10.000 tons factory are approximately DFL. 0.10/kg (USS 0,04/kg emulsion).

The higher application rates, 20-25% of bitumen emulsion versus cutback bitumen in the surface dressing, balance the cost-price advantage of the water content. The disadvantage of an investment for a bitumen emulsion factory retards progress in recessive times facing overcapacity in production facilities already present.

The estimate is that we will face a fairly steady situation in the next 3-5 years without major switches in technologies in the different countries.

4. TEST METHODS

Laboratory test methods vary from country to country. Whatever method is chosen, it should be as near as possible to practice and be of a realistic design. Preferably the aggregate for the particular application should be used. Laboratory test methods chosen should be quantitative. Lastly simplicity and low test costs are required. We distinguish as test methods:

(a) passive adhesion. The influence of water displacing an established bond between mineral surface and bitumen is established;
(b) active adhesion. The active adhesion agent displaces moisture from the surface of the mineral aggregates and establishes a bond between the mineral surface and the bitumen;
(c) dynamic adhesion. The degree of adhesion and strength of the bond between mineral aggregate and bitumen is evaluated by shaking with water. The strength of the established bond can be assessed for different adhesion agents and aggregates.

4.1 Cutback Bitumen in Surface Dressinq

One of the best known tests is the Immersion Wet Tray Test developed by U.K. T.R.R.L.

It is a simple active adhesion test giving a first screening. Basically aggregates are dipped through a water layer into the cutback bitumen (200 secs, 8S 3690). After ten minutes the aggregates are removed from the binder and the percentage of binder retained on the chippings is assessed visually. The presence of a good cationic adhesion agent in the binder will give a displacement of water from the aggregate surface and so binding of bitumen to aggregate surface.

The French passive test methods model actual sealing practice better than U.K. T.R.R.L. test method (10). Cutback bitumen at operation temperature (100-130^{0}C) is mixed with dried aggregates giving 5% residual bitumen onto the aggregates. After air curing at 20^{0}C for 24 hours the coated aggregates are divided in two parts:

(a) put under water for 16 hours at 20^{0}C requirement: mm. 90% coating left;
(b) put under water for 16 hours at 60^{0}C requirement: mm. 75% coating left.

This test could be modified to an active adhesion test if pre-wetted aggregates are used and the cutback bitumen operation temperature is lowered.

A simple active adhesion test is described in German DIN 52006. Aggregates 100 g.) are mixed at 25^{0}C with delonised water (1.5 g.) followed by cutback bitumen (15 g.). After mixing (2 mm.) a water layer of 1 cm is put over the mix.

This is left for 24 hours. Usually aggregate coating is examined.

Many authors report that the viscosity of the binder used in the test-methods has a great influence on the de-coating appearance of the aggregates (14). Binder viscosities in the laboratory tests should be the same as used in actual practice.

Dynamic adhesion testing is of ultimate importance (6).

It will simulate traffic influences for an aggregate/bitumen surface dressing mat which is subjected to the reciprocating action of water pumping under wheel loads. The forces exerted on the aggregate bitumen mozaic due to water, traffic,temperature changes, are enormous. It is obvious that the lifetime of a surface dressing mat is influenced by these factors. No publication is known which gives immediately a proven relationship between laboratory test methods and field experiences for cutback bitumen in surface dressing. Laboratory test methods in relationship to field experiences are done in Northern Europe for road oiling (13) and prove the necessity for dynamic adhesion testing (6, 13). What looks like a perfectly successful surface dressing can turn into a failure after several years under dynamic loading conditions as well met in road oil technology,

The application of a dynamic test method brings qualitative test results. Specifications and conclusions drawn from a dynamic test method should be related to a proven adhesion agent. The final limits to be settled for are a forward guarantee for highest performance to be expected in the field later on.

Two laboratory test methods are useful and worth further study:

(a) a Danish method. Aggregate is mixed with sufficient cutback to give a complete surface coating. This is done at temperatures related to field application. The coated aggregate is cooled to 25^{0}C and put into a jar. The jar is filled for 50% with water and rolled for 25 hours at 80 RPM. A visual examination of the remaining coating on the aggregate surface follows;

(b) a Norwegian method. Statens Vegvesen Oslo-Norway has issued active, dynamic adhesion test for evaluation of road oil performance. Although this method is not in use for surface dressing performance evaluation, basically it should give comparable results.

By using this dynamic testing method -in which binder-coated aggregate is shaken in water - the strength of the established bond can be assessed for different adhesive agents and aggregates.

A road oil aggregate mixture, prepared under the same conditions as can be expected in practice, is put in a beaker and an excess of water is added. The beaker is placed in a vibrating machine. Every two hours an Inspection follows. Water is removed, surface coating left is checked and fresh water added. Vibration (275 strokes/mm) continues until 95% displacement is obtained.

The time taken in reaching this value is a measure of adhesion. Testing can be continued for days without interruption. Both wet and dry aggregate can be used as starting material. For every test series a reference material must be used (reference adhesion agent and/or aggregate).

Following graphs are giving reviews of typical results achieved:

I. Evaluation after Storage in Road Oil for 5 Hours at 120 C (Coverage %)

Adhesion Agent	2h	4h	6h	8h	10h	12h	14h	16h	20h	24h
1.0% Armeen HT	100	100	100	100	100	100	100	100	100	100
0.8% Duomeen T Fl*	100	100	100	100	100	100	100	100	100	100
0.6% Duomeen T Fl	100	100	100	100	100	100	100	100	100	95

Vibrating machine at Low Speed

**as reference standard: hydrogenated -tallow propylene diamine flake*

II.

Adhesion Agent	1h	1.5h	2h	3h	4h	5h	6h	7h	8h	10h	24h
1.0% Armeen HT	100	90	90	85	85	85	60	60	50	40	5
0.6% Duomeen T Fl*	100	90	90	90	85	50	40	40	40	30	5

Vibrating machine at High Speed

III. Adhesion Tests on Road Oil I After Storage 5 Hours at 120 C (% Coverage)

Adhesion Agent	0h	2h	4h	6h	8h	10h	12h
None	5						
0.5% Duomeen T Fl*	90	90	85	80	60	45	30
0.5% Product C	85	80	50	20			
0.8% Duomeen T Fl*	100	100	100	95	90	85	80
0.8% Product C	100	95	95	90	80	10	

IV. Adhesion Tests on Road Oil II. After Storage 5 Hours at 12O C (% Coverage)

Adhesion Agent	0h	2h	4h	6h	8h	10h	12h	14h	16h	18h	20h	22h	24h
0.8% Duomeen T Fl*	95	95	95	95	95	95	90	80	80	70	60	40	20
0.8% Product C	95	95	95	95	95	90	50	35	20	20	15	10	10
0.8% EN 408	95	95	95	95	95	95	85	85	60	60	50	30	15
1.0 %EN408	95	95	95	95	95	95	95	90	90	90	60	60	50

V. Adhesion Tests on Road Oil I, After Storage 3 Days at 130^{0}C (% Coverage)

Adhesion Agent	0h	2h	4h	6h	8h
0.8% Duomeen T Fl*	90	85	70	50	30
0.8% EN 408	90	95	95	90	70

VI. Adhesion Tests on Road Oil II, After Storage 7 days at 130 C (%Coverage)

Adhesion Agent	0h	2h	4h	6h	8h	10h
0.8% Duomeen T Fl*	90	50	50	50	50	10
0.8% EN408	95	95	90	95	85	60

4.1.1 In Summary.

(a) The speed of vibrating machine is important and determines ultimate bitumen coating displacement.

(b) Storage time/temperature of the adhesion agent in the binder influences test results.

(c) The type of road oil (both meeting the same specification but from different suppliers) used in the tests has a clear influence on final test results.

(d) A comparison against a standard (for road oiling hydrogenated tallow propylene diamine is taken as standard) with proof of good (field) performance can be established and used as general test criteria. Rejection of alternative adhesion agents is done on the basis of failure to meet the performance achieved with hydrogenated tallow propylene diamine in dynamic laboratory testing.

4.2 Bitumen Emulsion in Surface Dressing

Storage stability is needed for emulsions transported over short and long distances. The stability should be as high as possible during storage and transport. On the other hand the bitumen should be deposited on the aggregate as soon as possible after the spreading of the emulsion onto the road. A contradicting requirement.

Sensitive test methods have been developed to check bitumen emulsion performance for use in road surface dressing.

4.2.1 Breaking Index of Bitumen Emulsions (11)

Reference aggregates, Portland cement (anionic emulsions), siliceous fine aggregate (cationic emulsions) is added continuously to a beaker with 100 g. emulsion at a rate of 0,3-0,5 g/s using a funnel.

The mixture is constantly stirred and addition of the aggregate is stopped when the emulsion-aggregate system has the appearance of a lump. The amount of added aggregate per 100 g. emulsion is calculated and is termed the "breaking index" of the bitumen emulsion.

Basically this test is the same in a modified way as in DIN 52047, West Germany.

4.2.2 Adhesion of Binder in the Presence of Water (10)

This is the same test as done for cutback bitumen. Also here 5% residual binder should finally be covering the aggregate surface.

4.2.3 Shake Stability/Stability to Transport

Bitumen emulsions are made with a varying amount of emulsifier and at different pH's. A typical range includes emulsifier levels of 0,05-0,10-0, 1 5%.

The shake stability test is carried out by taking a sample of each emulsion (so g.) in 250 ml. bottle and shaking it for 1 and 2 hours at 275 strokes/ minutes at a displacement of 25 cm. The bottle contents are filtered through a 250 micron sieve and the residue of broken material recorded. Typical results to be expected:

Emulsion Breakage (%)

		1 Hour	2 Hours
Emulsion	1	s	s
	2	9	s
	3	3	11
	4	2	2

s = severe breakage in bottle

This test gives a relative indication of the emulsification power of different emuisifiers at a specific uselevel. Due to the use of an unusual low concentration (up to 0,05%) emulsifier in the test, it is possible to distinguish between "emulsification power" of comparable emulsifiers.

4.2.4 Rapid Break of Emulsion - Early Rain Resistance (Method Used by German and Swiss Customers)

Mix 200 gr. of available aggregate (as used in typical surface dressing application) with 20 gr. fast-breaking emulsion.

Continue mixing with a spatula until all the emulsion breaks on the aggregates. The aim is to achieve a break-time of maximum 60 seconds.

Immediately after the breaking of the emulsion on the aggregate is a achieved, the coated aggregates will be held for two minutes under running tap water. The first time a black rinse water will come off. After S minute interval the rinse under tap water is repeated. After three rinses clear water should come off the aggregates.

This is recognised as a practical method testing rapid break of the emulsion onto aggregates as well as earliest resistance against possible rain and subsequent wash-off of bitumen from aggregate surface.

Other interesting test methods related to bitumen emulsions are a Swedish coagulation test (Sweden 671.795) and a German wetting ability test for tack coat emulsions (DIN 52046).

This review of test methods summarises the most important test methods which are in use in Western Europe. The mentioned test methods are covering the best available technology and their use will secure highest attainable performance in road construction.

An exchange of experience gained with different evaluation techniques can be beneficial to all involved in road construction.

5. FUTURE TRENDS TO BE EXPECTED ARE:

(1) The introduction of more sophisticated products meeting higher test demands required for road surface dressing technology.
(2) A reluctance to change present road technologies (cutback versus bitumen emulsions, hot mix versus cold mix) due to recessive times, vast over-capacities and lack of money.
(3) Development of special technologies for (smaller) heavy-duty applications.

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