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CATIONIC BITUMEN EMULSIONS:- THEORY AND APPLICATIONS

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SYNOPSIS

The paper is a review of the use of cationic bitumen emulsions in road construction and repair.

The chemistry and theory of cationic bitumen emulsions and the factors influencing breaking behaviour during application are considered.

The use of cationic bitumen emulsions allows control of the emulsion break behaviour and the emulsifiers provide an anti-stripping effect in the final application.

The advantages of emulsions over cut-back binders are detailed. Emulsions are less hazardous to use than cut-back binders, and can be applied in a wider range of conditions.

An asphalt additive to improve basic asphalt properties is introduced.

1. WHAT ARE CATIONIC EMULSIONS?

Cationic bitumen emulsions can be used for a wide range of applications (Table 1). The four main application areas are surface dressing, tack coats, slurry sealing, and cold mixing.

i) Surface Dressing

Road maintenance technique, that involves the restoration of a deteriorating road wearing course, before the main fabric of the road foundations are irreparably destroyed, (see section 5).

ii) Tack Coats

Provide a thin adhesive film of bitumen between an existing road pavement and overlay, or between courses in road construction. Overlay materials include hot rolled asphalt wearing courses, Macadams and slurry seal. Tack coats are also used in patching and inlay work, where further functions of priming and waterproofing are necessary.

Tack coat forms an adhesive and cohesive bond between the bituminous overlay and the existing pavement, reducing the risks of slippage between the two courses, and allowing traffic stresses to be distributed uniformly. The problems caused by surface dust on the road are minimised. A further advantage of a tack coat, is during the paving or rolling of the new overlay, pushing and sliding are reducing, thereby allowing for improved compaction, with a resultant increased life expectancy of the surfacing.

Figure 5

Samples of Surface Dressing, typically used in road construction and maintenance

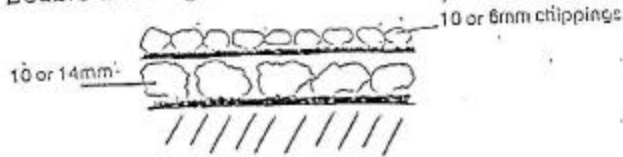
TRADITIONAL



Pad Coat



Double dressings



'Racked in' system

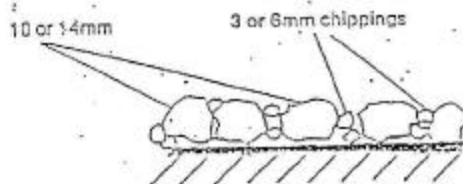


Table 1

Application Areas of Cationic Bitumen Emulsions

APPLICATION	SUITABLE EMULSION TYPES	
Surface dressing	60-70%	rapid setting
Tack coats	40%	rapid or medium setting
Slurry seal	60%	slow setting
Mixes, open-graded	60%	medium setting

Mixes, dense-graded	60%	slow setting
Penetration macadam, grouting	60-70%	rapid setting
Sub-base and base sealing of cement mixes	40-60%	rapid or medium setting
Sub-base and base sealing	60-70%	rapid setting
Retreading	60%	medium setting
Stone coating	60%	medium or slow setting
Mist spraying	40%	rapid or medium setting
Concrete curing	40%	rapid or medium setting

iii) Slurry Sealing

This is a technique for road repair in which a fluid mix of finely grained aggregate bitumen emulsion and water is applied to the road surface. On the road this slurry sets quickly to provide a new wearing surface, (the seal).

The thickness of the seal is normally 2-15 mm (can be up to 40 mm) and the final surface has a texture, wearing and load bearing characteristics similar to those of fine cold asphalt, depending on the aggregate and grading used. The seal is impenetrable to water and so ensures protection against ingress of water and is ideal for sealing existing surfaces which are cracked, fissured or pitted. The seal also provides a contribution to riding quality (noise reduction) and an improved resistance to skidding.

iv) Cold Mixing

Traditionally, deferred set Macadam (hot mix) are produced by coating mixed aggregates with hot bitumen, flux oils being added to adjust the binder viscosity and so extend the storage life of the finished product.

These materials are mainly used in trench reinstatement and remedial patching. The Macadam may be stockpiled for a period of time before laying, and must remain workable, while at the same time providing good stability when laid. The disadvantages of this method are:-

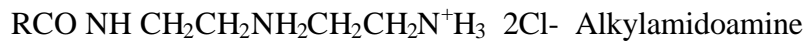
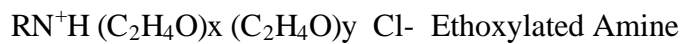
- a) The necessity of heating the aggregate to the temperature required to ensure its dryness and so facilitate adequate coating.
- b) The operating temperatures that are necessary, give rise to a fire hazard, which is associated with the use of relatively low flash point flux oils.
- c) The probability of loss of volatile oils from the flux, giving rise to unpredictable properties with regard to workability.

The development of cold mixing has to a great extent overcome these disadvantages and given certain additional benefits:-

- a) Cationic emulsions, may be used at ambient temperatures with aggregates, which need not be completely dry.

- b) Lower costs are incurred due to a considerable saving on fuel for heating purposes.
- c) Operating at lower temperatures for cold mixing gives a greater margin of safety, even though these emulsions may contain fluxing oil.
- d) Not only may cold mix be stockpiled for long periods, but it may also be packaged in small containers and stored. This facilitates the treatment of very small areas quickly, cleanly and economically.
- e) Cationic emulsions are characterised by positively-charged bitumen droplets, which result from the use of emulsifiers having positively-charged head groups, (Figure 1).

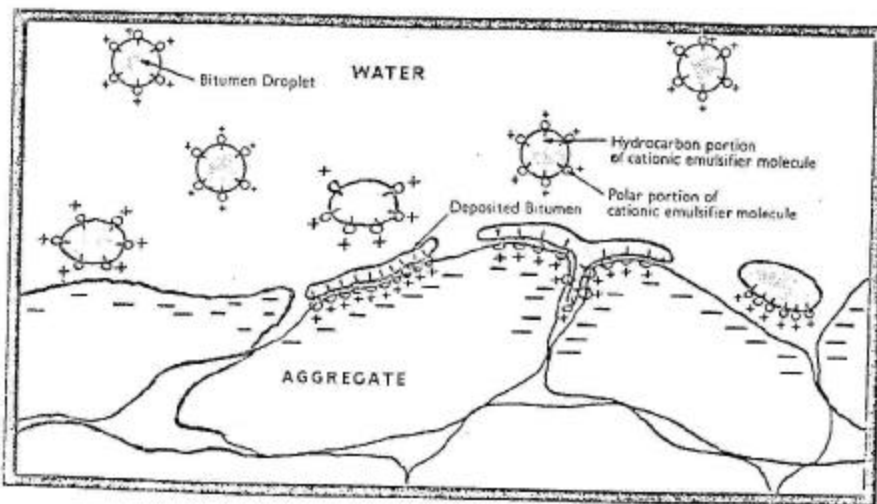
Figure 1 : Typical Chemical Structures of Cationic Emulsifiers



R = C9-C18 alkyl

Figure 2

Bitumen Deposition from Cationic Emulsion

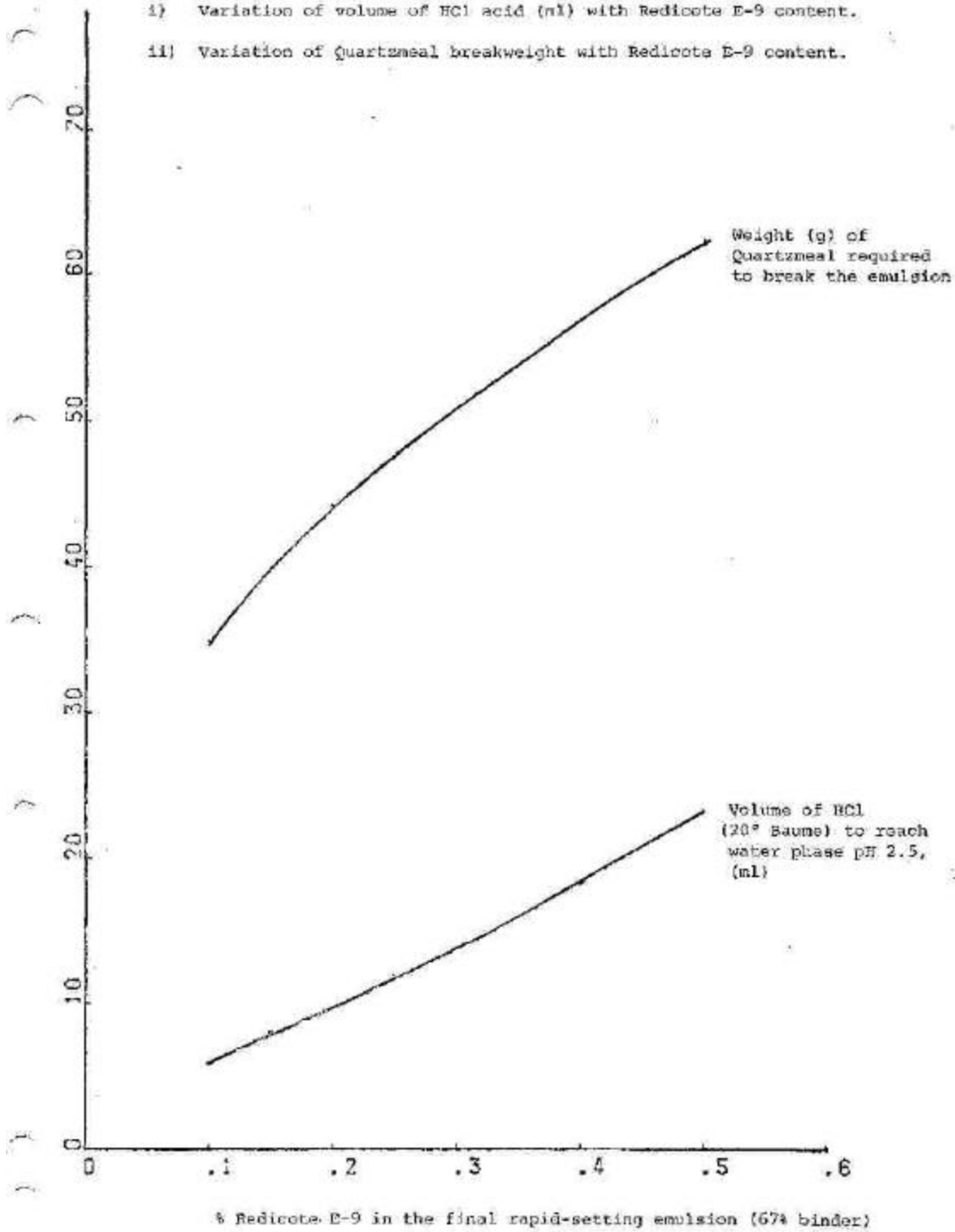


2. **GENERAL REQUIREMENTS OF BITUMEN EMULSIFIERS**

- i) To produce a good emulsion with the correct droplet size.
- ii) To stabilise the emulsion and prevent changes on storage.
- iii) To control the break behaviour during application.
- iv) To provide good adhesion between bitumen and aggregate.

Figure 3

- i) Variation of volume of HCl acid (ml) with Redicote E-9 content.
- ii) Variation of Quartzmeal breakweight with Redicote E-9 content.



3. Why CATIONIC EMULSION?

Anionic, nonionic and cationic emulsifiers are all available, which will successfully emulsify bitumen and provide storage stable emulsions.

Cationic emulsifiers offer additional advantages, which arise from the fact that most naturally occurring aggregates are negatively-charged in aqueous media, and have a capacity to adsorb cationic emulsifiers, (Figure 2).

Choice of emulsifier type, and emulsion formulation enables the rate of breaking of the emulsion to be controlled.

The emulsifiers remain in the cured seal and are concentrated at the interface between bitumen and aggregate and act as antistripping agents.

4. **CONTROL OF EMULSION BREAKING**

The breaking of an emulsion in contact with aggregate is initiated by;

- i) Adsorption of emulsifier onto the aggregate until the emulsifier remaining at the bitumen droplet surface is insufficient to prevent coagulation.
- ii) Neutralisation of emulsion acidity by reactive aggregates and fillers leading to a loss in positive charge on the bitumen droplets and therefore coalescence occurs.

So the rate of breaking depends, for example;

- a) The adsorption capacity of the aggregate for emulsifier

This is related to the aggregate type and grading. The fines content and type of fines present can have a disproportionately large influence, (Table 2).

- b) The reactivity of aggregates to emulsion acidity

Aggregates like limestones which react with acids, will clearly have the largest effect on emulsion breaking.

Additives like lime can have the effect of accelerating breaking.

Table 2
Cation Exchange Capacity of Aggregates

Size Fraction		CEC meq/100
Slurry seal aggregate		
1.7-6.7	mm	0.09
1.0-1.7	mm	0.22

0.5-1.0	mm	0.29
0.3-0.5	mm	0.27
0.15-0.3	mm	0.55
0.075-0.15	mm	0.61
-0.075	mm	5.0
Kaolinite		3-15
Montmorillonite		70-100

Pre-wetting of the aggregate with cationic surfactant or metal salts can reduce the adsorption capacity and so increase the break time of the emulsion. This technique is used in cationic slurry seal.

c) The concentration of emulsifier (and acid)

The higher the level of emulsifier (and therefore acid) used, than the more that has to be adsorbed (neutralised) by the aggregate, before emulsion destabilisation occurs, (Figure 3).

d) The chemical type of emulsifier

Some emulsifiers, produce emulsions in which the stabilising charge, on the bitumen droplets, is less sensitive to acid concentration than others, and so emulsion breaking is less rapid, (Figure 4).

e) Temperature

Like any chemical reaction, breaking of cationic emulsions is slower at lower temperatures.

To facilitate a comparison between the use of cationic bitumen emulsions and cut-back binders, an in-depth analysis will be made of the application area of surface dressing.

5. CATIONIC EMULSIONS FOR SURFACE DRESSING

Cationic emulsions for surface dressing are 70% binder content, applied hot (80-90C), or 60-65% binder content, applied cold. The emulsion must set rapidly to anchor the chippings to the road surface, (Figure 5).

Comparison with cut-back binders (Table 3)

Both properly formulated cut-back binders and rapid-setting cationic emulsions can give excellent performance in surface dressing.

However, cationic emulsions have an environmental advantage, because they are sprayed at lower temperatures than cut-backs and their lower solvent content leads to less fumes and smell, which can be a hazard to workers and an annoyance to residents in built-up areas.

The main advantage of cationic emulsions is that the adhesion agent is built-in. The adsorption of emulsifier onto the aggregate, which is responsible for emulsion breaking, also provides the anti-stripping effect. This means that emulsions can be used in damp conditions and at lower temperatures, without the need for expensive coated chippings.

Of course effective anti-stripping agents are available for cut-back bitumens and their use is often specified by national or regional authorities. But anti-stripping agents can degrade on prolonged storage in hot cut-back binders and it may not be clear how much additional anti-stripping agent to add, to compensate for this degradation.

The chemistry of cationic bitumen emulsifiers and amine adhesion or wetting agents for cut-back or hot binders is similar, but the products are rarely identical or interchangeable.

The requirements of the two products are quite different, (Table 4).

Table 3
Comparison of emulsion and cut-back bitumen

CATIONIC EMULSION	CUT-BACK BINDER
- Sprayed 80-90 0C	-Sprayed 140-160 0C
- Low Solvent Content	-High Solvent Content
- Low Fire Hazard	-Fire Hazard
- Breaks by Chemical Reaction	-Solvent Evaporation
- Possible in Damp Conditions	-Not Recommended in Damp Conditions
- Coated Chippings Not Required	-Coated Chippings Recommended when Spraying at Low Temperature or with Viscous Binder.
Built-In Adhesion Agent Unaffected by Emulsion Storage	-Effective Adhesion Agent Available but can Degrade during Binder Storage

Table 4
Requirements of emulsifiers and adhesion agents

CATIONIC EMULSIFIER	ADHESION AGENT
Must withstand Acid Water Phases at 60 0C.	Must withstand Storage in Hot Binders at 90-1600C
Must give Good Quality Emulsions	
Can be Formulated in Water or Water/ Alcohol Solvents.	Must Not Contain Volatile/ Harmful Components up to

	160 0C
Used in Factory Situation	Must be Convenient to Use in the Field
Soluble in (Acid) Water	Bitumen Soluble
Must Give Good Antistripping Effect	Must Give Good Antistripping Effect

Typical use levels of adhesion agents in cut-backs for surface dressing are 0.5-1.5%, compared to typically 0.3% (on binder) for surface dressing emulsions. The higher level required for the cut-back system reflects:-

- i) Insurance against losses due to hot storage.
- ii) Slow migration of adhesion agent from bulk binder to binder-aggregate interface, so more is require to ensure "active" adhesion.

The adhesion promoting action of cationic emulsifiers is often overlooked, although emulsion adhesion tests are specified in some national standards, (ref. 2 and 3).

Adhesion of the cured seal is increased by increasing emulsifier level.

Good performance in the key area's of emulsion break behaviour and adhesion in the cured seal, is just as important as the physical properties of the emulsion, usually specified in national standards.

6. **DISADVANTAGES OF CATIONIC EMULSIONS**

Even though cationic bitumen emulsions have many advantages over cut-back binders, they also have certain disadvantages:-

- i) Climatic

A regular water supply is required and this can be a great problem in very hot countries, where water can be in very short supply. Also aggregates in arid regions are often very dry and cationic emulsions work most effectively, in may applications¹ (especially mixing) with moist aggregate.

- ii) Stability

Emulsions are inherently unstable with limited shortage life, (generally maximum 6 to 12 months).

- iii) Plant

Emulsion manufacture requires specialised plant and quality control procedures.

- iv) Bitumen

Special emulsifier grade binders are needed to make the best quality emulsions.

This is a problem, because due to the increasing severity of the oil refining processes employed throughout the world, it is well recognised that the quality of bitumen, has greatly decreased over the last twenty years.

Akzo Chemie have developed an asphalt improvement additive, REDICOTE AP, that can upgrade poor quality asphalt, to emulsifier grade.

7. ASPHALT IMPROVEMENT ADDITIVE (REDICOTE AP)

Asphaltenes (solubility classification) in bitumen are generally considered to exist in the colloidal state, with maltenes acting as the disperse phase. Figure 6 represents the average hypothetical structure of an asphaltene from a Venezuelan crude oil, and Figure 7 is the possible schematic microstructure of an asphaltic oil, (bitumen).

Therefore, by the very nature of colloidal systems, the physical and chemical properties of asphalt are significantly influenced by the asphaltene/maltene ratio. Resins are the most important fraction in maintaining the colloidal equilibrium.

Thus, if a bitumen consists of a high concentration of asphaltene micelles! then its resultant use in emulsions and cut-back binders gives very poor results.

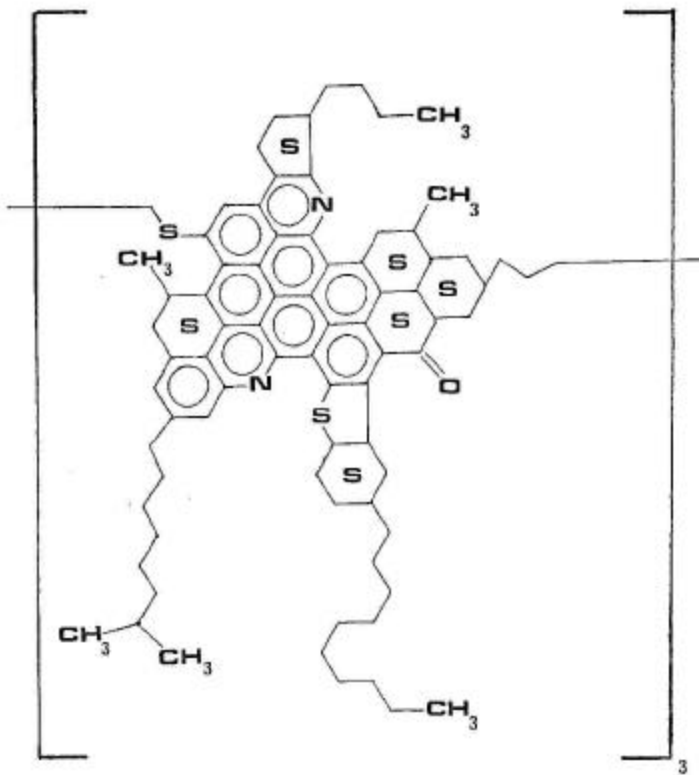
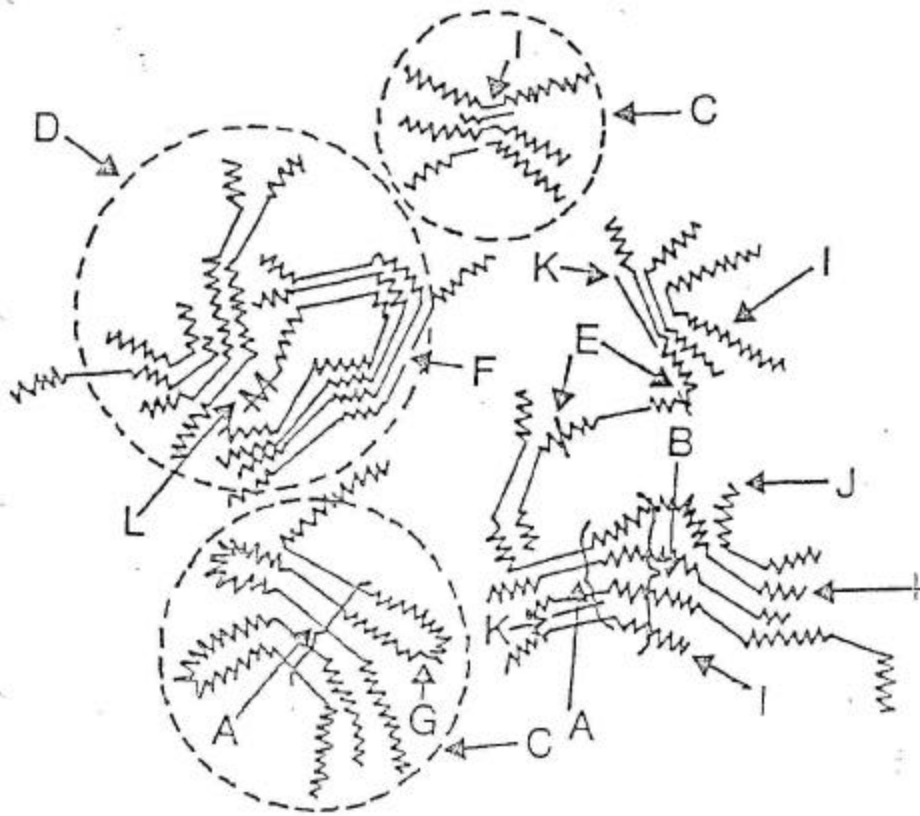


Figure 6 Hypothetical Structure of asphaltene from Venezuelan Crude.

Figure 7

Possible macrostructure of an asphaltic oil



Key

A	Crystallite	B	Chain bundle
C	Particle	D	Micelle
E	Weak link	F	Gap and hole
G	Intracluster	H	Intercluster
I	Resin	J	Single layer
K	Petroporphyrin	L	Metal

REDICOTE AP is an additive, that when added to asphalt, improves its basic This improvement, is considered to be due, to the reduction in asphaltene micelles, contained within the asphalt, by Redicote AP

i) Emulsification

When emulsified, a treated asphalt exhibits a smaller, more uniform particle size, which gives greatly improved storage stability and increased emulsion viscosity, (Table 5).

ii) Oxidation

Basic asphalt parameters, like oxidation, viscosity etc.. are improved by addition of Redicote AP, (Table 6).

iii) Adhesion

Treated asphalt exhibits enhanced coating and anti-stripping properties, especially with hard to coat aggregates, important in hot mix and anionic emulsions.

iv) Compatibility

Asphalt, when composed of blends from two or more different sources, as well as asphalt/polymer blends, exhibit greater compatibility and uniformity when treated with Redicote AP.

References

1. Lane, AR., 1970, The Stability of Oil and Water Emulsions (Thesis), University of Bristol.
2. DIN 52006 (I).
3. AFNOR NF T66-018.

Table 5 : Properties of CRS-2 Emulsions prepared with Redicote E-9

Emulsion	%solids	Particle Size (μ)	Viscosity, SSF 50C	Storage Settlement	
				5 days	21 days
A (no Redicote AP)	68.7	44% <1	158	3.0	15.6
	69.5	51% 1-10	174	2.2	16.1
	70.2	5% >10	216	2.1	15.2
B (0.5% Redicote AP)		88% <1	262	0.8	2.3
		12% 1-5	308	0.6	1.9
			341	0.6	1.6

Table 6: Rolling Thin Film Oven Test (ASTM D2872)

	Viscosity (mpa.s)		Ageing Index
	Initial	After	
Asphalt A	746	1736	2.33
without Redicote AP	212	1367	1.92
0.5% Redicote AP			
Asphalt B			
without Redicote AP	3720	17149	4.61
0.5% Redicote AP	3682	9720	2.64
Asphalt C			
without Redicote AP	4370	33387	7.64
0.5% Redicote AP	5300	32966	6.22