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Adhesion Agents for Use in Hot Mixes and Cut-Back Bitumens

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1. INTRODUCTION

Bitumen is the glue that holds asphalt pavement together. Depending on the application a greater or lesser part of the stress may be supported by the binder aggregate bond. Whatever the application of bitumen for road construction and repair the integrity of the bitumen aggregate bond is essential for the durability of the roadway.

In surface repair treatments like surface dressing a lack of adhesion between bitumen and aggregate will be manifested as stripping loss of aggregate from the wearing surface of the road. In thick layers of dense or open-graded asphalt, lack of adhesion may show as a reduction in stability [1] and load carrying capacity, and fatting up of the surface.

The strength of the bitumen - aggregate bond depends, at the molecular level on the interaction of chemical groups in the surface of the aggregate with groups in the bitumen. The aggregate surface is hydrophilic and typically contains groups like silanol. Bitumen is essentially a non-polar material but contains small amounts of polar groups such as: carboxylic acids, anhydrides, quinolines, ketones and sulphoxides which occur as parts of the large macromolecular "asphaltene' compounds. The polar compounds in bitumens depend on the source and processing of the bitumen. High penetration binders are generally richer in the napthenic acid components than low-penetration (harder) binders. Studies have shown that the polar components in bitumen are concentrated at the aggregate - binder interface, but there is also evidence that some of these groups are relatively easily displaced by water and so may not prevent stripping in wet conditions[2].

As refinery processes become more severe, the surface active components in the bitumen are destroyed by thermal cleavage and the natural adhesive properties of the binder are reduced. This paper is concerned with the deliberate addition of surface - active chemicals to the bitumen (adhesion agents, antistripping agents, wetting agents) to improve the bonding of bitumen to aggregate.

2. THEORETICAL BACKGROUND OF ADHESION AGENTS

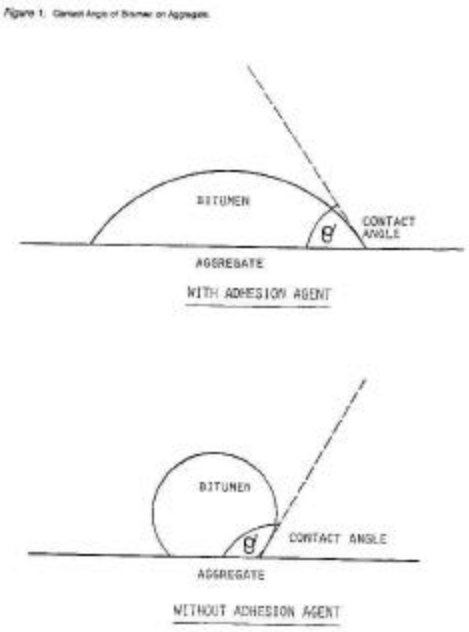
There are three aspects of the formation and integrity of the bitumen bond: spreading of bitumen over dry aggregate; spreading of bitumen over wet aggregate ("active" adhesion); and resistance of the bitumen film to displacement by water ("passive" adhesion).

2.1 DRY AGGREGATE

The work required to spread a liquid over a dry flat surface depends on the (advancing) contact angle (θ) and the surface tension of the liquid (σ).

$W = \sigma_{1,2} (1 + \cos\theta)$

In a practical system of bitumen - aggregate where mechanical energy (of mixing) is introduced and the aggregate sample is not smooth, the situation is clearly more complex, but we can nevertheless expect the factors of contact angle and surface tension to be important. These factors along with fluid viscosity also govern the kinetics of the spreading process.



Contact angle (see Figure 1) is a measure of the (net) interaction of bitumen with aggregate. A large contact angle means that it is more difficult for the bitumen to spread and coat the aggregate. In particular, it becomes more difficult' for the bitumen to penetrate into the small pores and crevasses on the aggregate surface necessary for so-called micro-mechanical" adhesion, or for the bitumen to flow through dust particles on the aggregate surface. The more viscous the binder (lower the temperature), the slower the spreading and the more severe is the problem. Adhesion agent absorbs at the bitumen - aggregate interface and reduces the contact angle. The effect of adhesion agents is to help coat the aggregate, wet out fines adhering to the aggregate surface and help the binder enter the microscopic crevasses on the aggregate surface. The effect of adhesion agents is particularly helpful with viscous binders (e.g. polymer - modified binders) or to compensate for too low temperature of application, mixing and/or compaction.

The adhesion agent also helps prevent the bitumen receding from the mineral surface when the mechanical energy supplied by mixing is removed.

2.2 ACTIVE ADHESION

Active adhesion is the ability of fluid to spread over a wet surface and to displace water. Displacement of water will be favored by a low contact angle a and a low interfacial tension

between bitumen and water. Because of the hydrophilic nature of mineral surfaces it is more difficult for the non-polar bitumen to spread on a wet surface than on a dry surface, and the process is usually impossible without adhesion agent.

Adhesion agents act through both a reduction of bitumen - water interfacial tension and their effect on the bitumen - aggregate contact angle in water. For example the interfacial tension is reduced from 34 to 17 dyne/cm by the addition of Duomeen T (tallowdiamine); and the contact angle (on glass) from 1200 to 180 [3].

2.3 PASSIVE ADHESION

Passive adhesion is the ability of the bitumen -mineral bond to resist being displaced by water.

Water will not readily displace bitumen because, over a period of time, surface active components of low mobility diffuse through the bitumen to the interface, and strengthen the bitumen - aggregate bond. Also, after cooling and loss of solvents, binder viscosity increases, making displacement more difficult.

3. CHEMISTRY OF ADHESION AGENTS

Adhesion agents are based on alkylamines, diamines and polyamines and their derivatives (see Figure 2). They may be liquids, paste or solids. Usually they are supplied as liquids for easy dosing, or as free flowing pastilles or flakes. For addition to hot binders the adhesion agents should not contain volatile, harmful components. For use in the field the solid products have some advantages: easy handling of 10-20 kg sacks; splashing avoided, spilled material easily swept up; free flowing even at very low temperatures when liquids may freeze. Liquids are preferred for easy dosing and pumping when added at the factory/refinery.

The bond between bitumen and aggregate is ensured because of the chemical reaction between the cationic amine adhesion agent and electronegative mineral surfaces.

4. APPLICATIONS OF ADHESION AGENTS

4.1 DENSE MIXES

When void volume is so low that water penetration into the asphalt cannot occur, displacement of binder by water is only a surface problem. The use of adhesion agents in impervious mixes is to improve binder distribution during mixing, to prevent flow of binder from the aggregate surface and to improve binder quality.

When water can penetrate the mix (which may be possible at quite low void volumes, especially in waterlogged ground conditions), the use of adhesion agents ensures stability is maintained [4].

4.2 OPEN MIXES

Mixes with high voids content, e.g. 'draining" asphalt, are particularly susceptible to stripping as well as flow of bitumen off to smooth hydrophillic aggregates even in dry conditions.

Field studies using specially prepared macadam patches have shown the advantage of using adhesion agents [5].

Any mixing operation done with aggregate which may not be dry (e.g. road oil mixes) needs an adhesion agent so that water can be displaced from the aggregate surface (active adhesion). Without an adhesion agent adequate mixing does not occur.

4.3 SURFACE DRESSING (CHIP SEALING)

Surface dressing is a repair technique in which a thin layer of cut-back bitumen is sprayed onto a road surface and chippings rolled into the binder. Adhesion agents are required to ensure good active adhesion if the aggregate is damp and to prevent stripping during the life of the seal.

5. SELECTION OF ADHESION AGENTS

The correct adhesion agent for a particular aggregate binder combination can be selected on the basis of laboratory tests. The test may be specific to a particular application or general tests of adhesion or anti-stripping properties between aggregate and binder (Table 1). Test methods for adhesion agents have been reviewed [6].

Table 1. Laboratory Evaluation of Adhesion Agents Test Methods.

Test Method/Application	Summary of Method	References
Static Immersion (passive) hot mixes	Dry aggregate is coated with binder, immersed in hot or cold water, stored, then coverage estimated.	1,2
Static Immersion (active) cold mixes, road oiling, surface dressing	Wet aggregate is mixed with binder, immersed in hot or cold water, stored, then coverage estimated.	2,3,4
Dynamic Immersion (passive) hot mixes	Dry aggregate is coated with binder, covered with water, then shaken or rolled before estimating coverage.	5
Dynamic Immersion (active) cold mixes, road oiling, surface dressing	Wet aggregate is mixed with binder, covered with water, then shaken or rolled before estimating coverage.	6,7
Plate/Tray Tests (active) surface dressing	Chippings are pushed through a water layer into binder. After a period of time the chippings are removed and examined for coverage.	8,9
Plate/Tray Tests (passive) surface dressing	Chippings are pushed into a layer of binder deposited on a plate or tray, allowed to cure and removed and examined for coverage. In the Vialet plate test chippings are knocked off the plate by the impact of steel balls.	10,11 12,13 14
Marshall stability or modified Marshall stability hot and cold mixes	Marshall stability or modified marshall stability is determined on mixes, with and without moisture conditioning.	15,16
Immersion Wheel Tracking	Slabs of compacted macadam are subjected to abrasion by rubber coated wheels under water.	17

Table 2. Effect of Aggregate Type on Adhesion Agent
Usage in Surface Dressing Method: TRRL Tray Test Binder 200 Pen Bitumen.

Aggregate	Concentration of Duorneen T[a] required to give 90% adhesion
Limestone	1.3%
Slag	1.0%
Quartzite	0.5%
Granite	1.0%
Red Whinstone	1.0%

a tallowdiamine

Some typical results by various methods are shown in Table 2.

6. HEAT STABILITY

Adhesion agents can degrade in hot binders, the rate of degradation depends on temperature, the chemical type of adhesion agent and the binder (Table 3).

Table 3. Degradation of Adhesion Agents in Hot 200 Pen Bitumen Analysis by GLC Storage Temperature 140°C.

A: Venuezualen bitumen acid value 2.0 mgKOH/g
B: Mexican bitumen acid value 0.4 mgKOH/g

Product	Bitumen	Time (h)	Level Remaining %	Coverage of aggregate in immersion adhesion test Greywacke Chips
Redicote N422[a]	A	0	1	100
		6	0.91	100
		24	0.61	100
		72	0.59	100
		156	0.28	100
	B	0	1	100
		6	0.94	95
		24	0.86	95
		72	0.75	95
		156	0.51	95
Duomeen T[b]	A	0	1	100
		6	0.61	100
		24	0.11	95
		72	0.01	95
		156	-	90
	B	0	1	100
		6	0.85	100
		24	0.33	95
		72	0.03	80
		156	-	60
None	A,B	-	-	5

a) alkylamidopolyamine b) tallowdiamine

The main mechanism for degradation is that amine groups in the adhesion agent may react with acidic groups in the binder to form amido-compounds. Primary and secondary amine groups are lost more rapidly than tertiary amine groups. High acid value binders cause more rapid loss in adhesion agent efficiency. As the amine adhesion agent is degraded, the acid value of the bitumen is reduced, confirming the reaction with acid components in the binder (Table 4). However, not all components in the binder which contribute to the binder acid value may be reactive to amines. At high temperatures, oxidation of adhesion agents becomes an important degradation route.

Some adhesion agents are more resistant to degradation (heat stable agents like Redicote N422 or N60) and should be specified when the adhesion agent is to be stored in hot binders for extended periods (Table 5).

The adhesion agent evaluation tests (see above) should be performed after an appropriate period of storage in hot binder. No adhesion agent should be stored in hot binder for longer than is necessary.

7. USE OF BITUMEN EMULSIONS IN ROAD CONSTRUCTION AND REPAIR

The use of cationic emulsions can overcome adhesion problems with aggregate because the emulsifier acts as an adhesion agent in the cured seal.

Throughout the world, cut-back bitumens and straight-run binders compete with bitumen emulsions for use in the various methods of road construction and repair.

Table 4. Effect of Polyamine Adhesion Agent (1% level) on the Acid Value of Binder During Storage at 1400C
Binder: 200 Pen Venuezualen Bitumen.

Storage Time hours	Acid Value mgKOH/g
0	2.0
6	1.2
24	0.7
72	0.7

Emulsions have advantages and disadvantages:

Advantages:

- safe: applied at lower temperatures, low fumes,low fire hazard.
- cationic emulsions have 'built-in' adhesion agent (i.e. emulsifier).
- can be used successfullv in cold, damp conditions.
- can be conveniently modified by polymers.
- low temperature handling of bitumen reduces ageing and oxidation during processing, and the built-in adhesion agents cannot degrade.
- allow special repair techniques such as slurry sealing.

Disadvantages:

- require water supply since they contain 30% water.
- aggregates in arid regions are often very dry and emulsions work most effectively in many applications (especially mixing) with moist aggregate.
- special emulsifier grade binders are needed to make best quality emulsions.
- emulsions are inherently unstable with limitedstorage-life.
- emulsion manufacture requires specialized plant and quality control procedures.

The choice of emulsion depends on the availability of water and climatic conditions. Emulsion use is particularly important for repair techniques in France. Germany, Netherlands, Spain and the British Isles, but less important in Scandinavia, Africa, the Middle East and Australasia [7].

8. CONCLUSIONS

Adhesion agents are widely specified by local and national agencies for use in various road construction and repair processes because of their beneficial effect on the integrity of the bitumen -aggregate bond. Laboratory test procedures are available which allow the efficiency of different products to be compared and the most cost-effective product for a particular application to be identified. In practice, adhesion agents may be stored in hot binders for extended periods before use. During this period some loss of efficiency will result as the adhesion agent reacts with acid components in the binder or is oxidized. This expected storage in binder must be considered when evaluating adhesion agents.

Use of cationic bitumen emulsion overcomes this problem, since the emulsifier acts as an adhesion agent in the cured seal and does not degrade during the storage of the emulsion. However, emulsions have disadvantages for arid climates.

9. ACKNOWLEDGEMENTS

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10. REFERENCES

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Table 5. Effect of Hot Storage of Untreated Binder on Active Adhesion.

Application : Road Oiling Mix
Binder : Road Oil ex. Norsk Fina
Aggregate : 10 mm gravel ex. Sandvik
Storage Temp.,C : 120
Method : Method 263, SVL, Norway

Additive	Level %	Coverage %	
		5h storage	7d storage
Untreated	0	0	0
Duomeen T flake[a]	0.8	95	50
Redicote N408 [b] flake	0.8	95	95
Redicote N422C	0.8	95	95

a) hydrogenatedtallowdiamine
b) alkylamidopolyamine
c) alkylamidopolyamine