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"A GAS CHROMATOGRAPHY METHOD FOR THE DETERMINATION OF
ANTI-STRIPPING AGENTS IN HOT BINDERS AND THE
SIGNIFICANCE OF THIS TECHNIQUE TO SURFACE DRESSING

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ABSTRACT

This paper charts the development of a gas chromatographic technique, which can measure the degradation or disappearance of free residual anti-stripping agents in hot binders.

A combination of this technique and controlled surface dressing field trials was used to monitor the several different complex relationships, which occur at a bitumen-aggregate interface, during actual road construction or repair techniques.

INTRODUCTION

Whatever the application of bitumen in road construction or maintenance, the integrity of the bitumen aggregate bond is essential for ensuring the durability of the road-pavement. Historically, the failure of this bond could only be observed by actual aggregate stripping in surface dressing or a reduction in the load bearing capacity of a hot mix¹. No one analytical technique has been available to monitor, at the molecular level, the physico-chemical bond between the binder and electronegatively charged aggregate surfaces. The strength of this bond is dependent on the level of surface active groups (carboxylic acids, anhydrides, quinolines, ketones, sulphoxides, etc.) contained within a binder. This level is determined by the source and thermal process history of the binder, where the more severe the refinery processing, the greater the reduction in its natural adhesive properties. Plancher et al have shown that these polar groups are concentrated at the bitumen-aggregate interface, but some

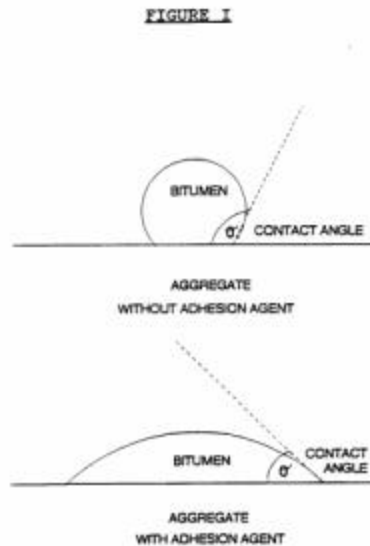
of these groups are easily displaced by water and may not prevent binder stripping in wet conditions².

Bitumen in the presence of water has little affinity to adhere to aggregate.

The deliberate addition of surface active chemicals to a binder (adhesion agents, anti-stripping agents, wetting agents) is known to improve the bonding of a binder to an aggregate. This improved adhesion is shown by the ability of the binder-aggregate bond to resist water ingress (passive adhesion) and to displace water from the surface of wet aggregate (active adhesion).

MECHANISM OF ADHESION

The theoretical background of anti-stripping agents has been well covered elsewhere, (3-5), but Figure I gives a **pictorial representation** of the mode of action, where the addition of an anti-stripping agent to a bitumen, allows the binder to spread and adhere to the surface of an aggregate.



Commercial anti-stripping agents can be based on alkylamines, diamines, polyamines and their derivatives, (Figure II). A strong bond between the bitumen and aggregate is ensured, because of the chemical reaction between the nitrogen atoms of the anti-stripping agent and the electronegative surface of the aggregate.

FIGURE II

R - NH₂ Fatty Amine

R - NHCH₂CH₂CH₂NH₂ Fatty Diamine

R - CONHCH₂CH₂NHCH₂CH₂NH₂ Alkylamidopolyamine

R - CONHCH₂CH₂CH₂N (CH₃)₂

Alkylamidoamine

R = C₁₂ TO C₂₀ Alkyl

ANALYSIS OF ANTI-STRIPPING AGENTS IN BITUMEN

Anti-stripping agents degrade in hot binders, and the rate of degradation is dependent on the storage temperature and the chemical type of anti-stripping agent. The main degradation reaction involves the amine groups in the anti-stripping agent reacting with the acidic groups in the bitumen. High acid value binders cause a more rapid loss in anti-stripping agent efficiency, and primary and secondary amine groups degrade faster than tertiary amine groups.

This degradation mechanism coupled with the complex nature of bitumen make the analysis of anti-stripping agents in hot binders very difficult. Donbavard and Kerr developed a method, where an anti-stripping agent is extracted in isopropanol and titrated with dilute hydrochloric acid,⁶ but no method existed in the literature for the direct measurement of an anti-stripping agent in a hot binder.

DEVELOPMENT OF A CAPILLARY GAS CHROMATOGRAPHY METHOD FOR THE ANALYSIS OF ANTI STRIPPING AGENTS IN BITUMEN

Anti-stripping agents manufactured by Akzo Chemicals were originally required to be analysed in bitumen in order to study degradation rates in different acidity bitumen types at temperatures varying between 100 to 160⁰C and at storage times from 0 to 72 hours. Because of the number of samples generated a relatively quick and reliable method was needed with good sensitivity in order to determine anti-stripping agents at levels down to 0.05%.

Several analytical procedures are able to achieve that sensitivity, but the bitumen matrix caused massive interference. As a consequence spectroscopic and titrimetric procedures were eliminated.

Separation of the amine from the bitumen would allow the use of the above techniques but attempts with sorbent extraction and liquid - liquid extraction were unsuccessful.

Chromatography was chosen as the most likely analytical technique to succeed.

Some initial work with HPLC was successful but problems were encountered with separation of the amine when different types of bitumen were encountered.

Capillary GC was tried and found to give relatively easy elution of the amine adhesive agents from a 0.1~ DB5 capillary. Originally it was expected that bitumen, being a relatively high boiling compound, would not cause any coelution problems with the amine. However, because

bitumen must be injected at fairly high concentration levels, the minor levels of volatile residues caused problems with co-eluting peaks. For this reason, a Nitrogen Phosphorous Detector (NPD) was used, which eliminated the interference and allowed specific detection of nitrogen containing peaks. The following chromatography conditions were developed.

Column 10 metre 0.32 m ID 0.1m DB5 capillary

Injection :- 1ml of approx 0.02g bitumen/ 10 ml toluene on column

Detection :- NPD at 350C

Temperature Programme:- 130 to 330C at 15C/min

P = 0.6 kg/cm² Helium

Quantitation of the amine was by the use of an external standard, where a straight line graph for the weight of amine injected versus peak area was obtained.

The main problem with this method was column efficiency loss caused by the build up of non eluting bitumen at the head of the column having to be flushed every 4-5 injections to remove the bitumen. Other problems that transpired during this period was adsorption and tailing of some amines because of their high polarity.

Also, later work with road oils had even higher levels of volatile components which eluted with the amine peaks, although no problem was found with interference because the NPD was used, it was found that their components were quenching the response of the amine peak.

All the above problems resulted in developing the following method.

FINAL CAPILLARY GLC CONDITIONS

Column:- 15 metre 0.32 mm ID 1.0m DB5 capillary

Injection:- 325C operated in splitless mode with Split shut for 20 secs (Split flow 200 ml/min).

Detection:- NPD at 320C

Flow:- 1.0 kg/cm² of Helium

**Temperature Programme: -
40 C/min from 60 to 130C. 20C/min from 130C to 300C (6 minutes)**

Injection volume 1ml

Changing from a 0.1 μ to a 1.0 μ thickness phase prevented peak tailing and adsorption problems of certain polar amines.

By changing from an on-column to a splitless injection system prevented any involatile bitumen component from entering the column, which instead remained in the glass liner not visibly effecting column performance.

However, by changing from on-column to splitless it is not so easy to carry out external standard analysis because injection reproducibility is not so good, therefore, for this reason an internal standard had to be used.

The quenching effect of the road oils was overcome by standard addition of a known amount of amine to the road oil.

By analysing the sample before the addition of an amine and after the addition of an amine, the quenching effect can be assessed on an added level of amine and therefore, the quenching effect on the actual sample can be assessed and consequently allowed for in the percentage free residual anti-stripping agent calculation.

This method detects the "free" residual anti-stripping agent, but the (undetected) amine which has reacted with the bitumen acids is still partly effective as an anti-stripping agent.

EXPERIMENTAL EXAMPLE

For ease of explanation, an example of the analysis of a bitumen containing Redicote® N422 (an amidoamine) is presented:-

a) Sample Preparation

An internal standard is weighed accurately into toluene at a concentration of approximately 0.08g / 500 ml. The standard can be changed depending on the chemical type of the anti-stripping agent, (if known).

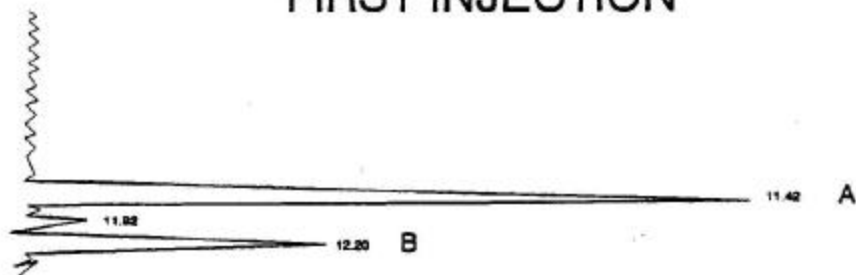
The binder to be analysed for Redicote N422 content is weighed accurately at a concentration of approximately 0.1g in 10ml of the previously prepared toluene solution.

This solution is then injected using the developed GLC conditions. A typical First Injection Chromatograph is shown in Figure III.

A known solution of Redicote N422 is then prepared accurately at an approximate concentration of 0.1g/10ml in toluene. 50 μ l of this solution is added to the original bitumen/internal standard solution and re-injected. A typical Second Injection Chromatograph is also shown in Figure III.

FIGURE III

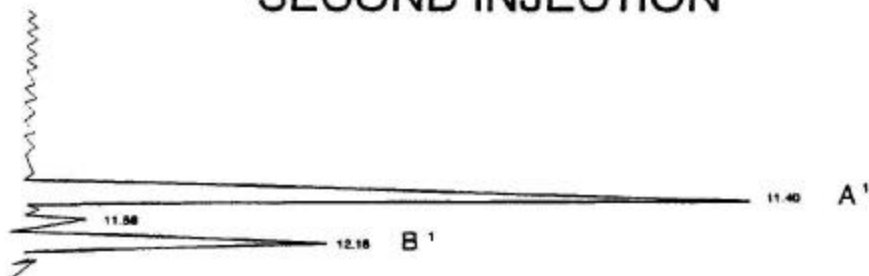
FIRST INJECTION



RETN TIME	PEAK HT	PEAK AREA
11.42	4.874	26.391
11.92	.262	1.529
12.20	1.646	12.028

A = Internal Standard
B = Redicote [®] N422

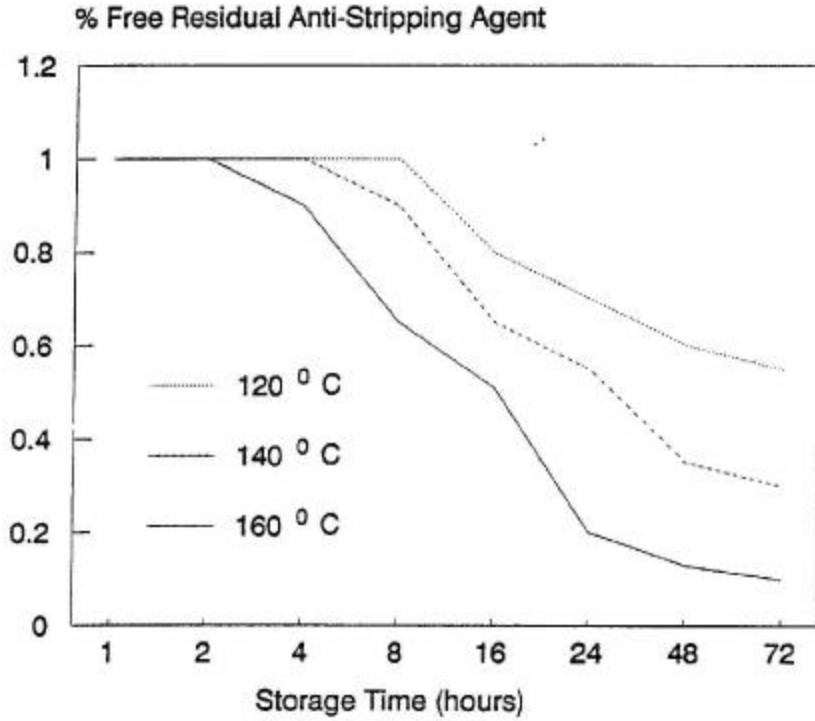
SECOND INJECTION



RETN TIME	PEAK HT	PEAK AREA
11.40	4.887	25.182
11.88	.383	2.011
12.18	2.770	17.346

A' = Internal Standard
B' = Redicote [®] N422 plus a known addition of
Redicote [®] N422

FIGURE IV



1.0% Anti-Stripping Agent Addition Level
 Venezuela 200 pen Bitumen, (4mg KOH/g)

b) % Redicote(R)N422 Calculation

	Weight of Bitumen(g)	Peak Area of internal standard	Peak Area of Redicote(R) N422 peak
Sample	0.1501	26.391	12.028
Sample+50µl of known Redjcode(R) N422 solution	0.1501	25.162	17.346

* Known extra addition level of Redicote(R)N422 = 0.000539g

* as % of the bitumen = 0.395 % added

- * allowing for the difference in the injection volume using the peak area of the internal standard, the corrected peak area for the Redicote(R)N422 can be calculated as follows:-

$$(25.162/26.391) \quad \times \quad 12.028 = 11.468$$

- * Peak area due to the added Redicote N422 = $17.341 - 11.468 = 5.878$
- * % Redicote(R)N422 in the original sample = $(11.468/5.878) \times 0.359 = 0.70\%$

ie. The initial bitumen sample contained 0.70% Redicote N422

Therefore, this analytical technique can be used to determine a temperature performance profile for an anti-stripping agent, (Figure IV).

CONTROLLED SURFACE DRESSING FIELD TRIALS

A series of Surface Dressing Road Trails were carried out in September 1989 on the A52, Belfast to Nutts Corner Road in Northern Ireland. The work was carried out by John McQuillan Contracts Limited for the Department of the Environment for Northern Ireland, Roads Service, Research and General Services Section, in conjunction with the Highway Engineering Research Section of the University of Ulster and Akzo Chemicals.

Materials

Table 1 shows the various combinations of materials which were assessed. Sections 1 to 6 were used to evaluate the complex relationship between binder application rate and film thickness. It was anticipated that the results obtained in conjunction with results already obtained in the University of Ulster Laboratory would lead to the development of a rational design method for surface dressing and, hopefully, see an end to the current practice of using more binder per square metre than recommended in Road Note 39 - and thus better value for money.

The manufacturers of wetting agents (or adhesion agents) used for surface dressing have for many years advocated the use of their products in the Surface Dressing process. Consequently by carrying out trial sections 11 and 12 in conjunction with the remaining sections where untreated binder would be used, it would be possible to test the manufacturer's claims for their product and monitor its performance, both during the initial stage when water was to be sprayed on the new dressing and in the long term, to assess whether the durability of the treated binder was actually improved as laboratory tests have indicated.

PERFORMANCE MONITORING OF THE SURFACE DRESSINGS

To monitor the performance of the various sections of the road trial surface dressings over the first nine months of service a number of methods of assessment were used, these included Time

Lapse Photography (TLP), the AASHO visual assessment technique and detailed physical and chemical analysis of recovered binders.

Binder Tests

The samples of binder were analysed in the laboratory and Table 2 shows the results of the Standard Tar Viscometer tests on the cutback bitumen samples, and the Redwood No.2 Viscometer results for the K1-70 emulsions. Details of the binder as supplied are also given. Whilst it is noted that the sample of cutback bitumen taken on 8 September has a value of 126 seconds, this value is within the limits of 80 to 130 given in Table 3 of B53690: Part 1: 1982.

Figure 1 shows results of Sliding Plate Microviscometer analysis of the four samples of cutback bitumen. It would appear that the increased concentrations of adhesion agent have had little effect on the viscosity I temperature relationship of the cutback bitumen used on 2 September. The results for the binder used on 8 September bear out the STV result.

Analysis of Binder Recovered from the road surface.

On the 14th December 1989 samples of stone and binder were scraped off the surface of the road on seven of the trial sections. Two samples were taken from each section, by taking scrapings from five 50 mm square areas along the City bound nearside wheel track, close to the photographed areas. The material from each of these areas being divided equally between two glass sampling jars.

Care was taken to ensure that as much of the binder as possible was removed from the road surface, without removing any of the old road surface material. A hammer and sharp chisel were used for this purpose. The sampling jars were then carefully labelled and returned to the laboratory where the binder was separated from the aggregate without the use of solvents.

The recovered binder was then analysed using the Sliding Plate Microviscometer over a range of temperatures from 15 degrees Centigrade to 30 degrees Centigrade. The averages of the results are shown in the form of Log Viscosity I Temperature Curves in Figure 2.

The penetration of each binder at **25 degrees Centigrade was then** determined using the Carre and Laurent Nomogram.

The binder viscosity results obtained on the 14th December 1989 represent the viscosity of the binder on the road at the particular sections and wheel tracks concerned at the beginning of the most critical period in the early life of the dressings.

TABLE 1: PROPOSED SURFACE DRESSING TRIAL SECTIONS (BELFAST - NUTTS CORNER ROUNDABOUT).

Section	Specific.	Bitumen	Flakiness	% Dust	Adhesion agent
1	D.O.E	Cutback	FI - 10	2	--
2	U.O.U	Cutback	FI - 10	2	--
3	D.O.E	Emulsion	FI - 10	2	--
4	D.O.E	Cutback	FI - 24	2	--
5	U.O.U	Cutback	FI - 24	2	--
6	D.O.E	Emulsion	FI - 24	2	--
7	D.O.E	Emulsion	FI - 10	0.5	--
8	D.O.E	Cutback	FI - 10	0.5	--
9	D.O.E	Cutback	FI - 10	2	--
			Racked in		
10	D.O.E	Emulsion	FI - 10	2	--
			Racked in		
11	D.O.E	Cutback	FI - 10	2	0.5%
12	D.O.E	Cutback	FI - 10	2	1.0%
15	D.O.E	Cutback	FI - 10	2	--

Table 2: SAMPLED BINDER-VISCOSITY RESULTS.

SAMPLE	STV at 400 secs. as supp.	STV at 400 secs. as samp.	REDWOOD No. 2 at 855 secs. as supplied
CB100 +0.2% N422	1/9/89 92	2/9/89 98	
CB100 +0.5% N422		2/9/90 99	
CB100 +1.0% N422		2/9/90 100	
K170 EMULSION			2/9/90 16
CB100 +0.2% N422	7/9/89 84	8/9/89 126	

Fig 1. Cutback Bitumen Viscosity / Temperature

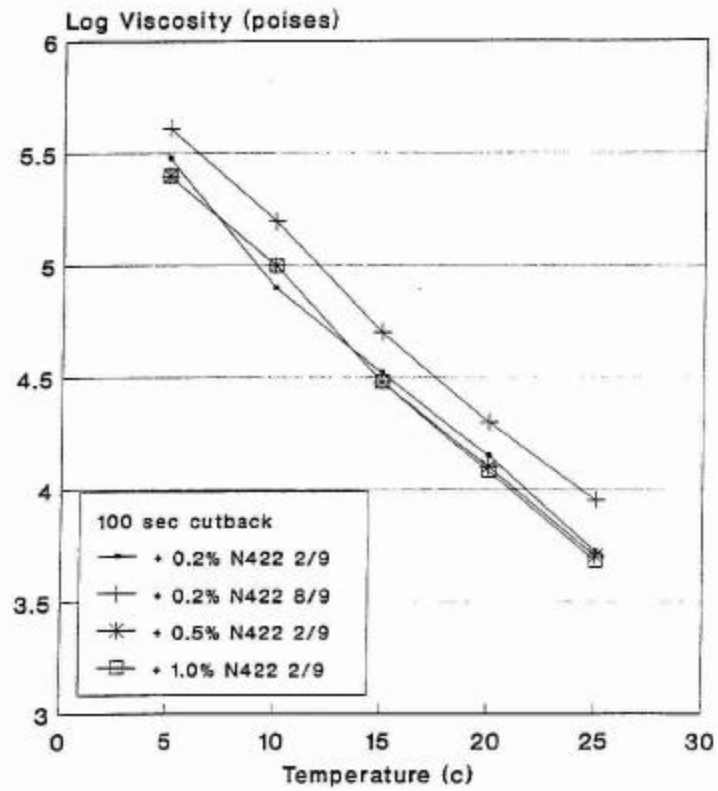
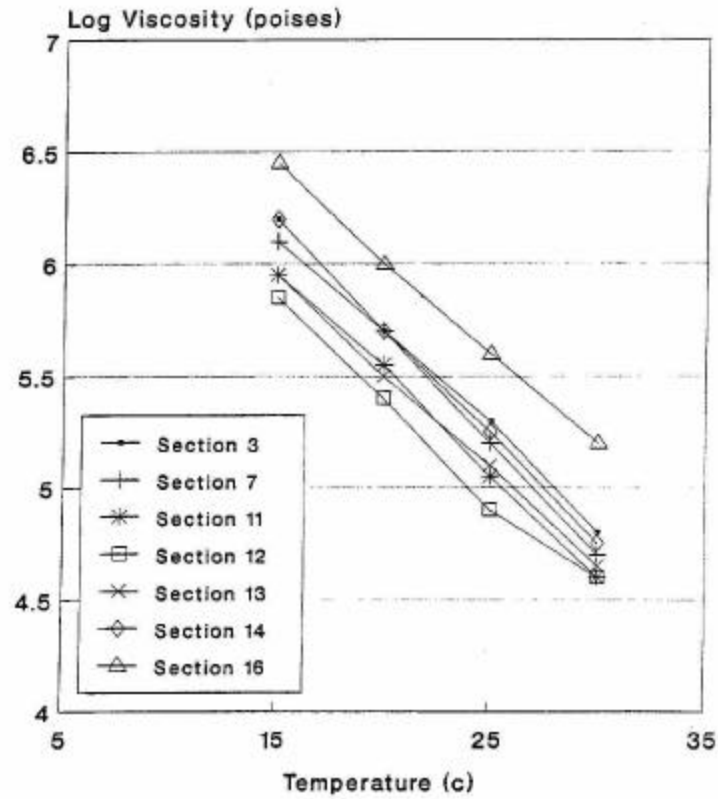
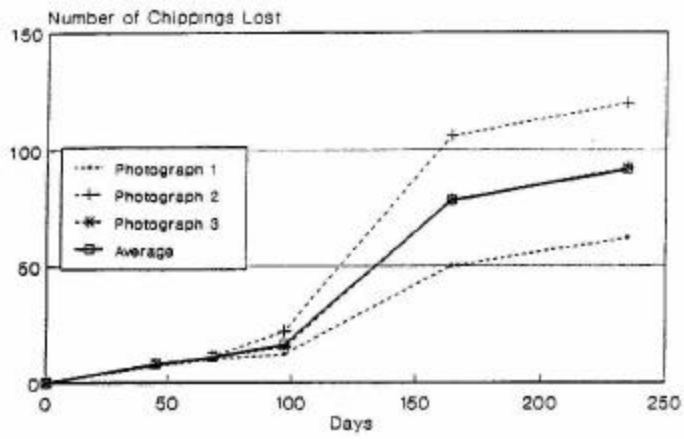


Fig 2. Binder Recovered from Road Trials
Temperature / Viscosity



Recovered 14 December 1989

Cumulative Loss of Chippings with time from Section 15



Cumulative Loss of Chippings with time from Section 11

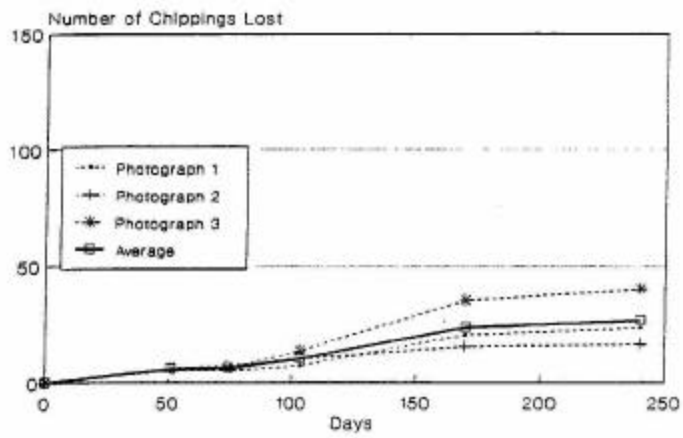
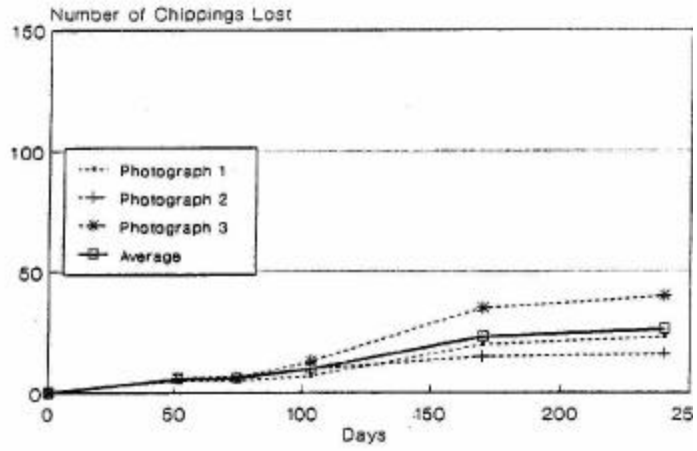


Figure 3

Cumulative Loss of Chippings with time from Section 11



Cumulative Loss of Chippings with time from Section 12

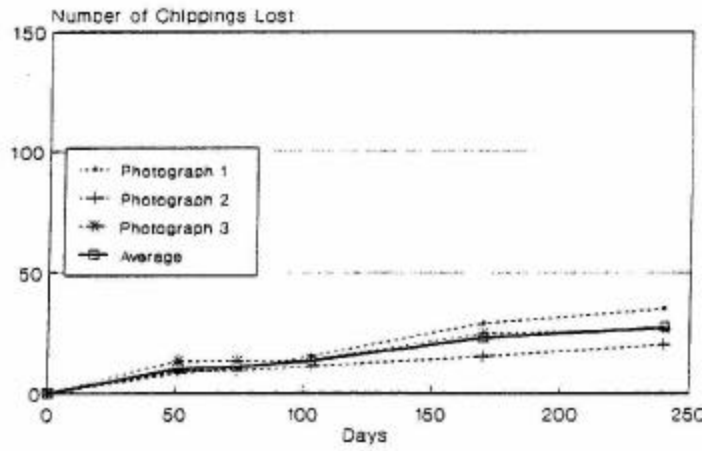
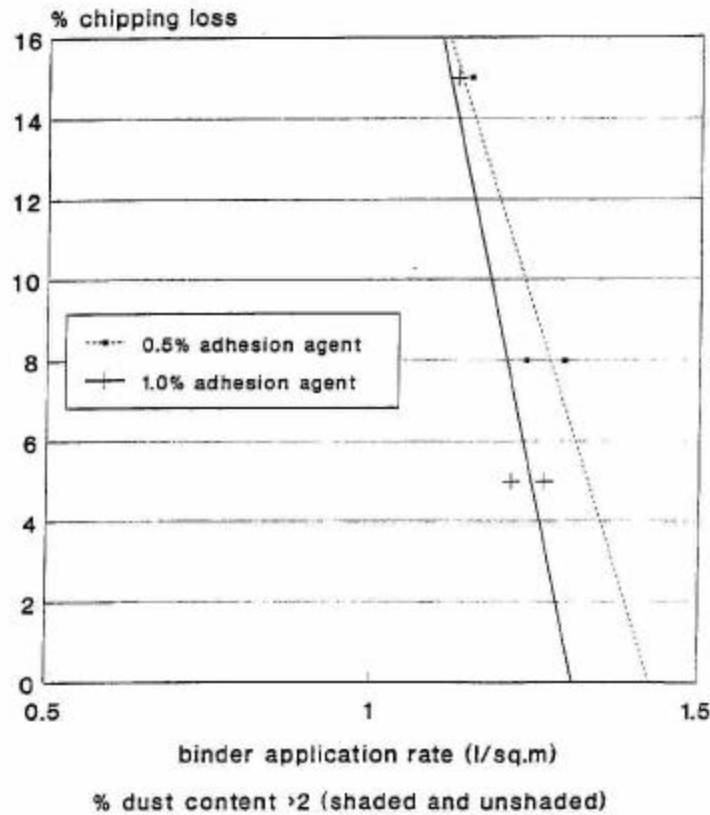


Figure 4

Fig 5. Effect of Binder Application Rate on Cubic Chip Loss with varying Adhesion Agent Concentration



DISCUSSION

In order to relate the performance of the trial sections to the variables such as dust content, binder application rate, binder type, binder viscosity, adhesion agent concentrations, aggregate shape, racking - in, traffic, weather and shading affects, each of these factors were correlated with the loss of chippings at various stages in the early life of the surfacing.

The adhesion agent concentration was increased from the basic 0.2 percent, normally added by the supplier for cutback bitumen used for surface dressing, to 0.5 percent in section 11 and to 1.0 percent in section 12. The agent used was Redicote N422, a heat stable amine derivative manufactured by Akzo Chemicals Ltd.

Figure 3 compares the cumulative chipping loss, as assessed by the TLP method, against time for section 15 and section 11. The binder application rates for these sections were 1.271 and 1.208 litres per square metre, respectively. The chipping dust contents were 1.925 and 3.18 percent respectively. Both sections used cubic unwashed chippings. The binder used in section 15 was 100 second cutback with 0.2 percent N422 while that used on section 11 had 0.5 percent. Figure 3 clearly demonstrates that section 11 has performed much better than section 15, even through the chipping dust content was higher and the binder application rate was slightly lower. similarly

Figure 4 which compares the performance of section 11 to section 12, shows a slight improvement in the performance of section 12 as compared to section 11. However the chipping dust content was slightly lower at 2.29 percent and the binder application rate was slightly higher at 1.238 litres per square metre. Therefore it is difficult to attribute this slight improvement to the increase in adhesion agent concentration alone. The improvement between the performance of binders with 0.5 percent agent and 1.0~percent agent is certainly not as marked as the improvement between 0.2 percent and 0.5 percent.

In Figure 5, the percentage chipping loss as assessed by the AASHO/TB method has been plotted against binder application rate for adhesion agent concentrations of 0.5 percent and 1.0 percent with chipping dust contents greater than 2 percent. It would appear that the optimum binder application rate for this situation may have been 1.3 litres per square metre for binder with 1.0 percent adhesion agent, and 1.35 litres per square metre for binder with 0.5 percent adhesion agent.

By far the most important point to note with respect to the performance of the adhesion agent sections is that even though chipping dust contents were over 2 percent, and in some cases over 3 percent, the adhesion agent sections have not performed badly, and remain in the top three sections with regard to performance.

ANALYSIS OF BITUMEN SAMPLE S FROM ACTUAL SURFACE

DRESSING FIELD TRIALS

Samples of the retained binder were analysed for their % Redicote N422 content₁ (Table I). These results indicated that the binders had been doped with anti-stripping agent prior to the surface dressing field trials.

TABLE I

Binder Sample	% Redicote N422
CBIOO + 0.2% N422 (1.9.89)	0.16
CBIOO + 0.5%N422	0.45
CBIOO + 1.0%N422	0.95
CBIOO + 0.2%N422 (7.9.89)	0.11

Actual stone samples were analysed for their % Redicote(R) N422 content, (Table II).

TABLE II

Stone Sample	% Redicote(R) N422	
	Doped	Detected
3	0.5	<0.05
4	1.0	<0.05
5	0.2	<0.05

The results indicate that only very low levels of free residual Redicote N422 were detected. Several explanations can be given for these results:-

- i) All the Redicote N422 has degraded or oxidised.
- ii) The Redicote N422 has converted into a reaction product, which is still highly active as an anti-stripping agent, but can not be detected using the present glc analytical method.
- iii) The Redicote N422 remains bonded to the aggregate, after the binder has been removed from the stone samples.

It is considered that all these factors play an important part in determining the fate of an anti-stripping agent in surface dressing.

These initial studies are being continued, to enable a better explanation of the role of anti-stripping agents in surface dressing to be found.

CONCLUSIONS

The most important findings relating to the performance of the Adhesion Agent sections are as follows:

1. Chippings with greater than 2 percent dust may be tolerated if at least 0.5 percent adhesion agent (Redicote N422) is added to the bitumen.
2. The two sections on which adhesion agent concentrations were 0.5 percent and 1.0 percent performed very well. Even though binder application rates were below target and the chipping dust contents were greater than 2 percent, only a maximum of 15 percent chipping loss was recorded by the AASHO method.
3. The authors consider that the performance of surface dressing is a complex function of numerous variables, the most important of which are; binder application rate, chipping dust content, binder type, adhesion agent concentration, chipping shape, binder

viscosity as well as the environmental factors of old road conditions, shading, weather conditions, and traffic volume and speed.

These trials have helped to evaluate the effects of these factors on the performance of the various sections. However the findings are limited in that they relate only to the specific conditions that prevailed at this site, but the trials have indicated that the development of a strong initial bond is essential to ensure longer design life, and thus provide more effective use of financial resources.

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