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THE USE OF THERMOGRAVIMETRY TO DETECT AND IDENTIFY ADHESION AGENTS IN BITUMEN

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ABSTRACT

Thermogravimetry and derivative thermogravimetry are used to analyse a number of samples of bitumen containing different adhesion agents. It was found that adhesion agents could be detected and identified because of the unique thermal breakdown pattern produced by each bitumen/adhesion agent mixture. This study was extended to the examination of bituminous binders that were removed from a number of chip-sealed roads. Adhesion agents were successfully detected and identified in all samples.

INTRODUCTION

Adhesion agents are added to roading bitumen to prevent binder-to-aggregate bond separation in wet conditions. If this bond is broken, water will displace the bitumen film over the aggregate suface [1]; this condition is known as stripping. The adhesion agents generally used are based on organic amine surface active agents, such as alkyl propylene diamine, alkyl amidoamine and alkyl imidazoline.

The detection of these agents in bitumen is important for quality control purposes.

The most frequently used antistripping additives in New Zealand roads are based on alkyl propylene diamines (APD). Agents based on this surfactant are available in various forms. The physical properties may be altered by varying the length or degree of unsaturation of the alkyl chain.

It has been found [2] that altering the physical properties of APD, as described above, affects their properties as adhesion agents. Thus, it is necessary to be able to identify the particular type of APD in the bituminous mixtures.

Due to the complexity of bituminous materials and the small quantities of adhesion agents added, the detection of these agents in bitumen is not a straightforward analytical procedure, and only a small number of methods are mentioned in the literature [3,4]. These methods were developed to

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analyse the bitumen sealing and are not suitable for testing bituminous binders once they are in service.

This paper describes how thermogravimetry (TG) and derivative thermogravimetry (DTG) may be used to analyse bituminous materials to detect the presence of, and distinguish between, various alkyl propylene diamines with different alkyl chains. Standard samples of bitumen containing adhesion agents based on APD were prepared and examined on the thermobalance. Following this initial evaluation, thermogravimetry was used to analyse small amounts of bituminous mixtures taken from a number of chip-sealed roads.

EXPERIMENTAL

Materials

Bitumen

The bitumen used was 180/200 penetration grade obtained from Marsden Point refinery.

Adhesion agents

Duomeen T (in paste and flake form) obtained from Polychem (NZ) Ltd. Diamin HBG and Diamin OLB obtained from Hardie Trading Ltd.

PROCEDURE

Addition of adhesion agents to bitumen [5]

Warmed portions (100 g) of 180/200 penetration grade bitumen were poured into 0.5-l containers and an adhesion agent was added to each in the proportion recommended by the manufacturers (Table 1). The mixtures were stirred for 1 min and heated to 140 °C for 15 min, then cooled and analysed on the thermobalance.

TABLE 1

Adhesion agents/bitumen ratio in standard prepared samples

Sample number	Adhesion agent	Ratio ($\times 10^2$)	Manufacturer's recommended ratio ($\times 10^2$)
1	Duomeen T (paste)	0.71	0.70
2	Duomeen T (flake)	0.70	0.70
3	Diamin HBG	0.73	0.70
4	Diamin OLB	1.04	1.00

TABLE 2

Manufacturers details of adhesion agents

Brand	Type	Melting range	Iodine number	Chain length comp. (%)					
				C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Diamine HBG	hydrogenated tallow–1, 3-propylene diamine	50–70	< 5	–	5	30	65	–	–
Diamine OLB	oleic–1, 3-propylene diamine	3–7	65–72	–	1	12	78	5	4
Duomeen T (paste)	tallow–1, 3-propylene diamine	44–48	32–45	1	4	30	65	–	–
Duomeen T (flake)	hydrogenated tallow–1, 3-propylene diamine	50–70	< 5	1	4	30	65	–	–

The details of the different adhesion agents are shown in Table 2. It can be seen from this table that the alkyl chains for Diamin HBG and Duomeen T (paste and flake) are derived from tallow, and Diamin OLB from oleic fatty acids. The iodine numbers of the unprocessed and hydrogenated tallow–1,3-propylene diamine are in the range 32–45 and < 5, respectively. The agent Diamin OLB has the greatest degree of unsaturation, indicated by the iodine number of > 65; this would account for its relatively low melting point. The chain lengths are about the same for all four agents.

Collection of road samples

Samples were removed from the road by levering aggregate coated with binder from the chip seal. Approximately six chips were necessary to yield the required amount of bitumen needed for each thermal analysis.

These samples were placed into an airtight plastic bag until ready for testing. The weather conditions were chosen so that the surface of the road was unlikely to contain any moisture at the time of collection.

Thermal analysis

The thermal analyses (TG and DTG) were performed on a Mettler Thermoanalyser II thermobalance. A silica crucible with a shallow bowl was used to facilitate the introduction of the bituminous materials. The temperature of each sample was raised to 163°C at 10°C min^{-1} and held at this temperature for 3 h to remove any bitumen diluents, as described elsewhere

[6]. The temperature was then raised from 163 °C at 6 °C min^{-1} to 700 °C. An air flow of 500 ml min^{-1} was used throughout each analysis.

RESULTS AND DISCUSSIONS

Thermal analysis of standard samples

The thermal decomposition parameters of bitumen, and bitumen mixed with various adhesion agents, are shown in Figs. 1–4. The bitumen without adhesion agents degrades in four steps.

It can be seen immediately that the presence of adhesion agents alters the thermal breakdown characteristics significantly.

From the TG and DTG curves of the prepared bitumen/adhesion agent mixtures (Figs. 2–4), it can be seen that each of the mixtures tested produced a unique thermal breakdown pattern, except for the samples containing Diamin HBG and Duomeen T (flake), which yielded almost identical TG and DTG curves. The IR spectra of Diamin HBG and Duomeen T (flake) were also found to be identical. This evidence and the manufacturers data shown in Table 2 strongly suggest that both agents contain the same ingredients.

Thermal analysis of road samples

Samples of aggregate coated with bituminous binders were removed from a number of chip-sealed roads. The brand and proportion of adhesion agent

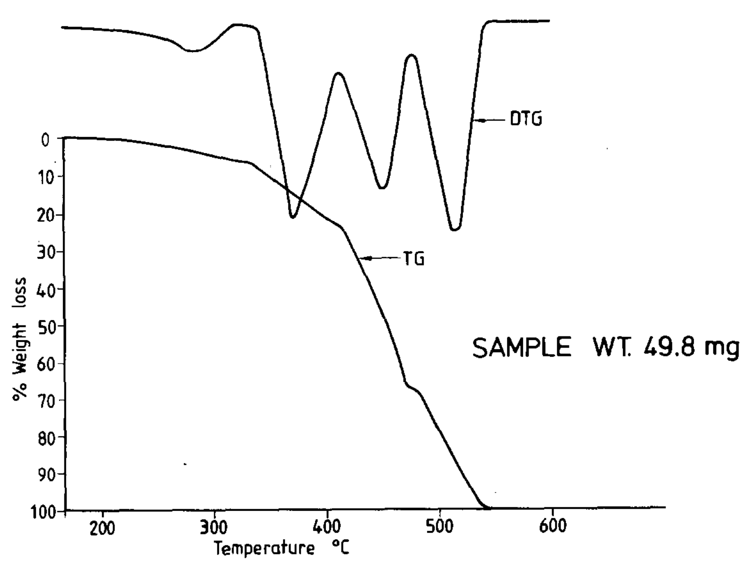

Fig. 1. TG and DTG of 180/200 penetration grade bitumen.

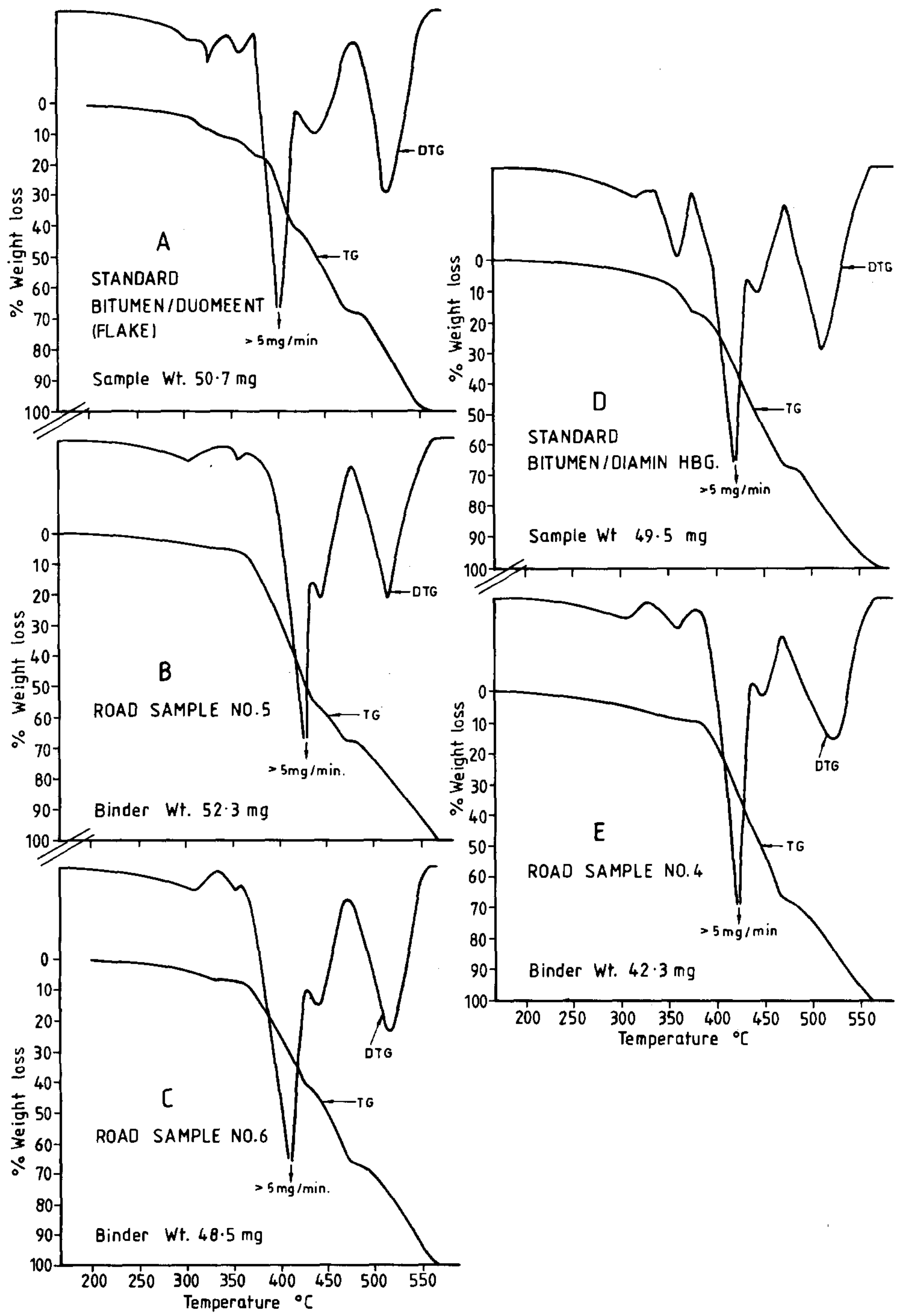

Fig. 2. TG and DTG of standard bitumen/Duomeen T (flake), bitumen/Diamin HBG and road sample Nos. 4, 5 and 6.

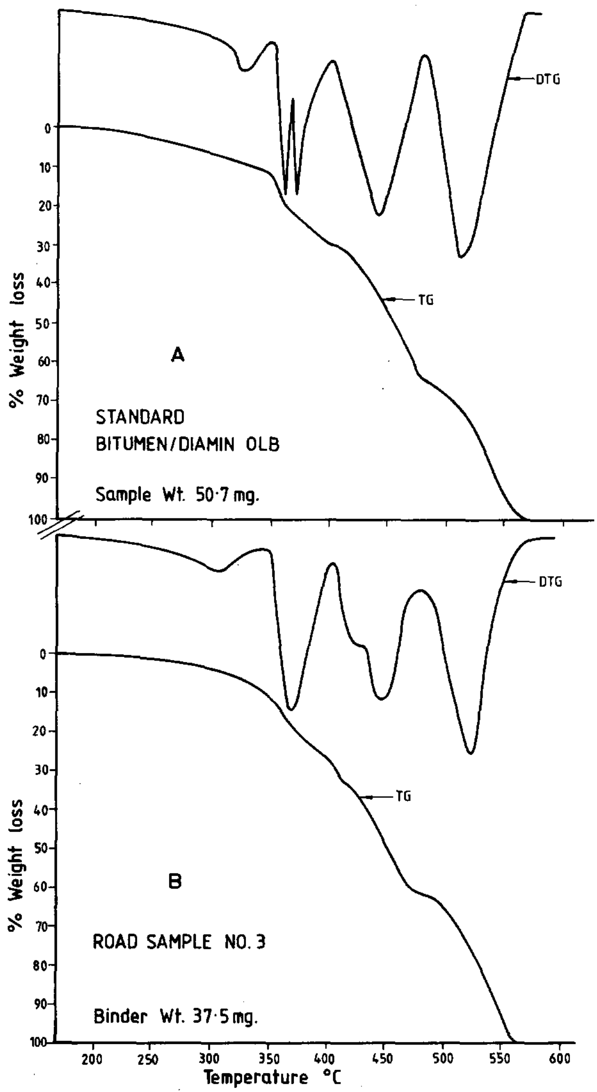

Fig. 3. TG and DTG of standard bitumen/Diamin OLB and road sample No. 3.

in the binder, and the number of months the seals had been in service are shown in Table 3.

The results from the thermal analysis of the road samples are shown in Figs. 2–4. For comparison purposes, the thermal curves of the laboratory prepared bitumen/adhesion agent samples containing the same adhesion agent are shown above those of the road samples.

Small amounts of stone chippings were inevitably introduced into the crucible with the binder, but these stone chippings are thermally inert over the temperature range used for the analysis. The binder weight was calcu-

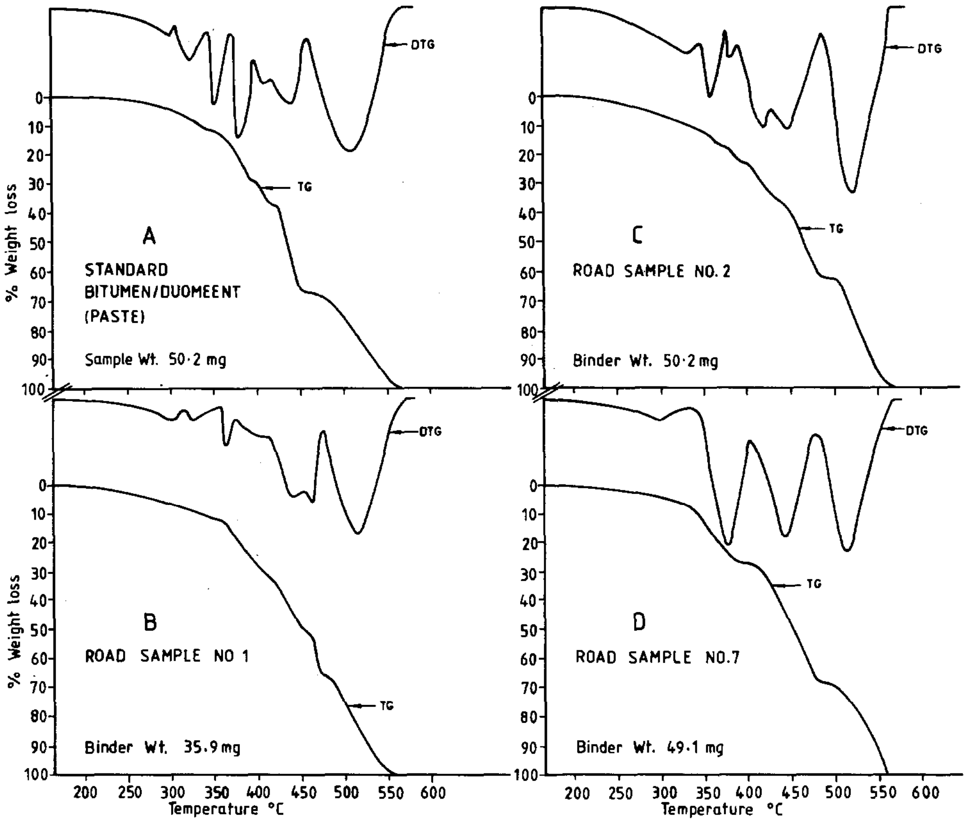

Fig. 4. TG and DTG of standard bitumen/Duomeen T (paste) and road sample Nos. 1, 2 and 7.

lated by subtracting the residue from the sample weight.

It can be seen from these results that the presence of adhesion agents can be detected in all the road samples by the marked effect on the thermal breakdown characteristics of the binder. The TG and DTG curves for the road samples containing Diamin HBG and Duomeen T (flake) are shown in

TABLE 3

Details of road samples

Experiment number	Adhesion agent	Adhesion agent/ bitumen ratio ($\times 10^2$)	Period in service (months)
1	Duomeen T (paste)	0.7	4
2	Duomeen T (paste)	0.7	8
3	Diamin OLB	1.0	8
4	Diamin HBG	0.7	20
5	Duomeen T (flake)	1.0	36
6	Duomeen T (flake)	1.0	49
7	Duomeen T (paste)	1.0	61

Fig. 2B, C, E. As expected from the results obtained from the laboratory prepared samples, these binders produce very similar thermal curves.

All the road samples containing Diamin HBG or Duomeen T (flake) yielded very similar thermal analysis curves to those of the laboratory prepared sample. Each of these samples produced a characteristic large maximum rate of weight loss (> 5 mg min^{-1}).

The results for the road sample (No. 3) containing Diamin OLB as the adhesion agent are shown in Fig. 3B; it can be seen that this sample yields TG and DTG curves similar to those of the laboratory prepared sample and so it would be possible to identify the agent in binders which yield curves such as Diamin OLB.

The samples, Nos. 1, 2 and 7 all contain Duomeen T (paste). They have been in service on the road for 4, 8 and 61 months, respectively. The thermal analysis curves for these samples are shown in Fig. 4B–D. The binders from samples 1 and 2 produce TG and DTG curves which are similar to those of the prepared sample. However, sample 7 produces quite a different thermal breakdown pattern from that of the two roading binders and standard sample. This difference could be due to the bitumen/Duomeen T (paste) mixture oxidising slowly while on the road. It is interesting to note that the TG and DTG curves produced by the bitumen containing Duomeen T (flake) did not change significantly after 49 months in service. This is possibly due to its shorter exposure time or the bitumen/Duomeen T (flake) could be less susceptible to oxidation.

CONCLUSION

Thermogravimetry and derivative thermogravimetry may be used to detect the presence of adhesion agents based on alkyl propylene diamine in bitumen. The particular adhesion agent may also be identified by the unique thermal degradation pattern of the bitumen/adhesion agent mix.

It is found that ageing may affect the thermal characteristics of bituminous binders, but if this ageing effect is taken into account it may still be possible to identify the adhesion agent in old binders.

The use of thermal analysis to examine bituminous binders eliminates the necessity for expensive extraction of large quantities of binder from the road, and the time-consuming pretreatment of samples.

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