NON-VOLATILE FLUX
FOR CHIPSEALING:
LABORATORY STUDY
INTERIM REPORT

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NON-VOLATILE FLUX FOR CHIPSEALING : LABORATORY STUDY INTERIM REPORT

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ACKNOWLEDGEMENTS

EXECUTIVE SUMMARY

A number of materials have been examined as potential alternatives to the automotive gas oil (AGO) presently used as a flux to produce a softer residual bitumen. Much of the AGO initially added is known to be lost through evaporation during sealing and over subsequent years. Two petroleum based materials, waste oil distillation bottoms (WODB) and a rejuvenating oil (RO), were considered along with a tall oil pitch (TOP) product from the pulp and paper industry as alternatives to AGO. The fluxed binders were compared on the basis of 0.5, 5, 15°C penetrations and 70°C and 135°C viscosities. High levels (~10%) of WODB and TOP were required to achieve binder properties equivalent to 1-3% AGO, about 3% RO gave results similar to 1% AGO.

A long term (3.3 year) weight loss study carried out at 43°C showed no volatile loss from WODB and TOP fluxed binders. These behaved in a similar fashion to a control 180/200 (small weight gain due to autoxidation). The RO fluxed binder showed an increased (relative to the control) rate of weight gain, indicating more rapid oxidation; the reason for this is not clear. The AGO fluxed binder showed a rapid weight loss as expected under these experimental conditions. The rate of hardening for all the binders was measured in terms of the moduli and viscosity ratio (after/before). The rate of hardening increased in the order WODB < RO < TOP ~ control 180/200 < AGO. Significantly, AGO demonstrated no fluxing effect after 3.3 years at 43°C. The TOP and RO fluxed binders also demonstrated a desirable high temperature (50°C) elasticity (large tan δ) relative to the control.

In practice, heated tanks would be required for handling the TOP and WODB, and larger quantities of all the materials studied are needed to achieve comparable fluxing to a given AGO concentration. However, no major alterations to sealing practice are foreseen. The high flash points of the alternative fluxes (compared to AGO) would be a considerable advantage from the point of view of safety. The drawback with the use of RO (and similar processes) was the cost which would be 2-3 times that of AGO. The economics of the use of TOP and WODB were more difficult to define. The manufacturers quoted ex factory prices marginally lower than that of AGO. As both these products were semi-waste, the ultimate cost would reflect the ease and expense of dumping which seemed quite variable.

ABSTRACT

Alternatives to automotive gas oil (AGO) used to flux (soften) bitumen used in chipsealing have been investigated. AGO is known to rapidly evaporate from the seal, which is both uneconomic and environmentally unsound. Non-volatile, tall oil pitch (TOP), waste motor oil distillation bottoms (WODB), and a commercial rejuvenating oil (RO) were investigated as alternatives. TOP, WODB and RO were effective as fluxes. Approximately 10 times the concentration of WODB and TOP and three times the concentration of RO were needed to give the fluxing effect of a given AGO concentration. All the alternatives showed no weight loss after storage as 3.0 mm films at 43°C. The rate of hardening, as measured by the rate of viscosity at 25°C before and after the test, was compared to that of a control 180/200 bitumen. The AGO fluxed binder hardened faster than the control, whereas the alternative fluxes showed a slower rate. The order of hardening was AGO > 180/200 ~ TOP > RO > WODB. The AGO fluxed binder had reached the same viscosity as the control after 3.3 years, i.e. there was no softening effect apparent. The other fluxed binders had viscosities considerably lower than that of the control. These findings were confirmed by moduli measurements over the temperature range 5-50°C. Apart from requiring heated tanks, no major alterations are foreseen necessary to sealing practices if any of the alternative fluxes are adopted.

1. INTRODUCTION

Current New Zealand practice is to add automotive gas oil (AGO), commonly called diesel, to bitumen used in chipsealing. This process is called fluxing and is used to obtain a softer residual bitumen.

It was assumed that AGO was non-volatile and had a permanent softening effect. However, recent research in New Zealand and Australia has shown that the majority of the AGO is lost within the first few years of the surfacing's life. The implications of these findings are:

(a)   even if the residual AGO in the seal is sufficient to modify the bitumen to obtain a satisfactory life, a large amount of expensive AGO is simply being wasted, and in the process polluting the environment;

(b)   a smaller amount of a non-volatile flux could replace AGO at the current dosage, and obtain a similar working life without hazard to the environment; and

(c)   a non-volatile flux used at the current AGO levels would produce a significantly longer lifetime.

The purpose of the research described in this report was to investigate possible non-volatile fluxes which could be used as an alternative to AGO. The work was to comprise two parts; the first of which was a laboratory investigation to identify possible alternatives and the behaviour of bitumen fluxed with these materials. Depending on the outcome of the laboratory work, a field trial to verify the performance of a selected non-volatile flux material was to be carried out. This report describes the laboratory phase of the project.

2. MATERIALS

Three different materials were selected for investigation as possible fluxes. The first two were waste/byproducts of New Zealand industries. These were chosen because they were chemically compatible with petroleum bitumen. Supply of these products was also assured, and their chemical and physical properties known to be relatively consistent. The other flux was a commercially available rejuvenating oil. This is an aromatic heavy petroleum oil. It was chosen as being reasonably representative of various similar heavy process oils. A description of these materials is given below with available physical data.

2.1 Waste Oil Distillation Bottoms (WODB)

These are the vacuum distillation bottoms (370°C, 3-6 mbar) remaining after the rerefining of waste automotive oils. They are black, adhesive, viscous solids at room temperature similar in appearance to petroleum bitumen. Waste oil distillation bottoms have been studied previously as potential bitumen extenders (Herrington 1991, Herrington 1992, Dravitzki et al 1993). The physical properties of a typical WODB sample are given in Table 1. Although the WODB are of much lower viscosity than bitumen at 25°C, the viscosities are comparable at 70°C and 135°C. For safe handling at application temperatures, bitumens are normally

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required to have flash points of greater than ~220°C; typically they are of the order of 300-350°C (Ball 1992). Flash points of a number of WODB batches have been found to be greater than 320°C (Herrington 1991).

The rate of evaporation of WODB has been studied by thermogravimetry and found to be negligible below 200°C (Herrington 1991). Although WODB are known to contain high levels of engine wear metals, the possibility of these metals leaching into the environment has been shown to be negligible (Dravitzki et al 1993).

An analysis of carcinogenic polycyclic aromatic hydrocarbons (PAH) shows low levels (generally an order of magnitude lower) compared to those found in bitumen. For example, the highly carcinogenic benzo[a]pyrene (often used as a reference compound in carcinogenicity studies) is present at around 0.011 $\mu g/g$ as opposed to 0.15 $\mu g/g$ in bitumen.

The sulphur content of the WODB is around 2.5%, comparable to that of bitumen. No problems (such as hydrogen sulphide formation) additional to those already experienced with sulphur in bitumen are to be expected.

In general, the use of bitumen/WODB blends for road construction does not appear to pose any significantly increased health, safety or environmental risk compared to bitumen.

The WODB are currently available at ~$350/tonne. About 10^3 tonnes are produced annually, much of which is dumped in landfill. At present only the British Petroleum owned Dominion Oil Refining Company, situated in Auckland, is producing WODB. Another plant (owned by Shell Oil) is "mothballed" in Wellington.

Discussions with the WODB suppliers revealed that in order to supply a product of more consistent viscosity than the crude WODB, variable small amounts of a lubricating oil fraction (also from waste motor oil) would be blended in (this was a virgin rerefined base oil with no additives). To simulate this, the WODB sample used here was modified with 5% of the lubricating oil fraction. Properties of this oil are given in Table 2.

2.2 Tall Oil Pitch (TOP)

Tall oil pitch is the residual material left after distillation of crude tall oil to yield tall oil rosins, tall oil fatty acids, and distilled tall oils (light fractions). The pitch constitutes approximately 30% of the crude tall oil (Peltonen 1989a). New Zealand crude tall oil annual production stands at 13,500 tonnes, with the current plant of Eka-Nobel Ltd at Mt Maunganui able to process up to 15,000 tonnes. Consequently approximately 4000 tonnes of pitch is produced.

Tall oil pitch at room temperature is a very dark brown, tarry solid. When heated, it turns into a viscously running liquid. Properties of the Eka-Nobel product, Pinechem 450, are listed in Table 3.

Tall oil pitch has been studied previously as a bitumen extender and, although being chemically quite different (high in organic acids, low in aromatics), has been shown to blend easily and

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form stable mixtures with petroleum bitumens (Ball 1992, Peltonen 1989b). Weight loss through evaporation is negligible below ~180°C (Ball 1992). Detailed toxicology data on TOP is lacking, however no danger to health associated with exposure to the material is known (Eka-Nobel 1992). Tall oil pitch is presently available at ~$450/tonne.

2.3 Hydrolene Oil 110T (RO)

This is a dark brown oil at room temperature, manufactured by the Sun Refining Company in the United States. Physical data are given in Table 4. This material is typical of a variety of "process oils" produced by the major oil companies. These oils are generally highly aromatic and thus likely to be more carcinogenic than petroleum bitumen. However, they are routinely used in a wide range of industries without major difficulties. The non-polar aromatic character of these oils assures their compatibility with petroleum bitumens, and the rolling thin oven data in Table 4 show a negligible weight loss up to at least 163°C. The cost of these types of oils is high compared to bitumen, at $1,000-$2,000/tonne.

2.4 Diesel Oil (AGO)

AGO was included in the study to provide a basis for comparison. Standard AGO conforming to TNZ M/1 (Transit New Zealand 1989) was used. In bulk, AGO is available at ~$400-$500/tonne. Physical data for AGO is given in Table 5.

2.5 Bitumen

The bitumen used in this study was Safaniya 180/200 penetration grade as this is overwhelmingly the grade of binder fluxed in practice.

Table 1.   WODB physical properties (typical values).

Property	ASTM method	
Viscosity at 25°C (Pas)	D3205	1455
Viscosity at 70°C (mPas)	D2170	26000
Viscosity at 135°C (cSt)	D2170	2000
Ash (% wrt)	-*	12.0
Flash point, COC (°C)	D92	>320

* By thermogravimetry - see Herrington (1991)

Table 2.   Lubricating oil fraction physical properties (typical values).

Property	ASTM method	
Viscosity at 40°C (cSt)	D445	16.3
Density 15°C (g cm^{-3})	D1298	0.8705
Flash point, COC (°C)	D92	150
Acid number (mg KOH g^{-1})	D974	0.42

Table 3.   TOP physical properties (typical values).

Property*	
Acid number (mg KOH g^{-1})	45
Colour (Gardener)	Dark
Rosin acid content (%)	9.0
Other oxidised and esterified acids (%)	10.0
Unsaponifiables (%)	81
Saponification number	106
Viscosity at 35°C (cSt)	80000
Flash point, COC (°C)	240
Fire point, COC (°C)	270
Specific gravity (25/25°C)	1.02

* ASTM D803

Table 4.   RO physical properties (typical values).

Property	ASTM method	
Viscosity at 60°C (cSt)	D2170	180
Flash point, COC (°C)	D92	262
Rolling thin film oven test:	D2872	
Viscosity ratio at 60°C		1.10
Weight change (%)		-0.2
Density 15°C (g cm^{-3})	D1298	0.9620
Asphaltenes, mass (%)	D2007	0.0
Polar compounds, mass	D2007	13.6
(%)	D2007	53.5
Aromatics, mass (%)	D2007	27.0
Saturates, mass (%)		

Table 5. AGO physical properties (typical values).

Property	ASTM method	
Viscosity at 40°C (cSt)	D445	1.9-4.1
Distillation; 85% vol recovered to: (°C)	D86	350 max
Acid number (mg KOH g^{-1})	D974	0.5 max
Flash point, COC (%)	D92	>63

3. EXPERIMENTAL METHODS

Viscosity measurements at 70°C and 135°C, cone and plate viscosities and penetration measurements were made according to the usual ASTM Methods D2170, D3205 and D5 respectively. Viscosity-temperature susceptibility (VTS) was calculated according to equation (1) (Puzinauskas 1979):

$$VTS = \frac{\log \log \text{viscosity at } T_2 - \log \log \text{viscosity at } T_1}{\log T_1 - \log T_2} \quad (1)$$

where T_1 and T_2 are absolute temperatures, and viscosities are in mPas.

In this work VTS calculations were made using viscosities at 135°C (T_2) and 70°C (T_1). For use in equation (1), values of viscosity at 135°C in cSt were converted to mPas using densities measured according to ASTM D70 (ASTM 1992) (see Table 10). Densities measured at 25°C were converted to 135°C using the factors given in ASTM D4311 (ASTM 1992). It was considered a reasonable assumption that the temperature dependence of the alternative flux materials studied was similar to that of bitumen. Densities converted to 43°C are also given in Table 10, these were used for the volatile loss study (Section 4.2). Measurements of binder moduli G*, G' (storage modulus) and G" (loss modulus) and related parameters were made using a Carrimed 500 CSL^2 dynamic shear rheometer. Samples of the fluxed binder were annealed at 85°C between 0.8 cm^{-1} parallel plates (525 μ gap) for 10 minutes before the sample was trimmed and the gap closed to 500 μ. Measurements were made at temperatures from 5 to 50°C at a frequency of 10 rad s^{-1} and 2.5% strain.

4. LABORATORY STUDY RESULTS

The laboratory study comprised two parts, a preliminary investigation of the physical properties of bitumen fluxed with the different test materials, and secondly a long term study of weight loss and binder hardening (at 43°C) to simulate long term in situ performance compared to AGO. The results of the first part of the study were used to estimate concentration levels needed to give binders of approximately equivalent initial consistency.

4.1 Physical Properties of Fluxed Bitumens

Blends of 180/200 grade Safaniya bitumen with AGO, WODB and TOP were prepared by hand mixing at 120°C. The final flux (RO) was not available at the time this work was carried out, and so was unable to be included in this part of the study. Results of measurements made on these blends are given in Tables 6, 7, 8 and 9. The results for the unmodified 180/200 base bitumen are presented for comparison. All of the additives gave the desired increase in low temperature penetration, however compared to AGO, relatively high concentrations were required. For example, at 5°C, 20% WODB or TOP were needed to give an increase in penetration equivalent to 2.9% AGO. Whereas a softening of the binder at low temperatures is the primary reason for fluxing and thus desirable, the observed reduction in 70°C and 135°C viscosities for all three fluxes is less so. For binders of about the same low temperature penetration the greatest reduction in high temperature viscosity was observed for the TOP (increased VTS), followed by AGO (little effect on VTS), while the WODB flux had only a small effect (a small improvement in VTS). For ease of comparison, plots of 5°C penetration and 70°C viscosity versus concentration for each of the fluxes were constructed (Figures 1 and 2).

Table 6.   Physical properties of AGO-bitumen blends.

Material and concentration by weight AGO	Penetration			Viscosity at 70°C (cst)	Viscosity at 70°C (mPas)	Viscosity at 135°C (mPas)	VTS
	0.5°C (0.1 mm)	5°C (0.1 mm)	15°C (0.1 mm)				
180/200 bitumen	11	20	60	18893	20253	248	3.38
180/200 + 1.0%	14	24	76	15542	-	211	-
180/200 + 1.9%	18	32	98	11896	-	195	-
180/200 + 2.9%	23	41	118	9729	10313	173	3.36
180/200 + 3.8%	28	48	144	7982	-	158	-
180/200 + 4.8%	35	58	176	6274	-	142	-

Table 7.   Physical properties of WODB-bitumen blends.

Material and concentration by weight WODB	Penetration			Viscosity at 70°C (cst)	Viscosity at 70°C (mPas)	Viscosity at 135°C (mPas)	VTS
	0.5°C (0.1 mm)	5°C (0.1 mm)	15°C (0.1 mm)				
180/200 bitumen	11	20	60	18893	20253	248	3.38
180/200 + 9.1%	17	29	84	16659	17625	238	3.35
180/200 + 20.0%	24	41	111	15200	15474	242	3.25

Table 8.   Physical properties of RO-bitumen blends.

Material and concentration by weight RO	Penetration			Viscosity at 70°C (cst)	Viscosity at 70°C (mPas)	Viscosity at 135°C (mPas)	VTS
	0.5°C (0.1 mm)	5°C (0.1 mm)	15°C (0.1 mm)				
180/200 bitumen	11	20	60	18893	20253	248	3.38
180/200 + 2.7%	19	31	72	15748	16850	209	3.46

4.2   Volatile Loss Study

To determine the behaviour of the trial fluxes in the long term, samples were exposed in the dark in a forced draft convection oven as 3 mm thin films in aluminium pans (20 cm dia) for several years at 43 ± 1°C. This temperature was chosen as near the upper limit of those found in practice.   The weight of the samples was monitored throughout the period, and the rheological properties of the samples determined at the conclusion of the experiment.

The effect of ultraviolet radiation was originally to have been a variable in the experiments as skin formation due to photo-oxidation might have had a retarding effect on flux evaporation from the binder surface.   Recent work by Dickinson (1989), however, suggests that such skin formation may not be significant as little (~ 7%) of the binder in a chipseal is exposed to direct sunlight, and that skins that do form are easily disrupted by water action and thermal expansion and contraction.

The curves in Figure 1 were used to estimate the concentration of trial flux needed to give a binder with the approximately equivalent 5°C penetration to a given AGO concentration. Initial work was carried out with AGO at 3% and with WODB at an equivalent AGO concentration of 3%.   The 3% figure was chosen as typical of those used in practice.

However, high concentrations of WODB were needed to achieve a 3% AGO equivalent blend, and in any case in the field much of the AGO will actually be lost through evaporation. It was thus decided to carry out the TOP experiment at an AGO equivalent concentration of 1%. The 1% figure was considered closer to the actual level likely to remain in the binder in the long term.

Table 9.   Physical properties of TOP-bitumen blends.

Material and concentration by weight TOP	Penetration			Viscosity at 70°C (cst)	Viscosity at 135°C (mPas)	VTS
	0.5°C (0.1 mm)	5°C (0.1 mm)	15°C (0.1 mm)			
180/200 bitumen	11	20	60	18893	248	3.41
180/200 + 10%	nd	28	nd	12200	182	3.47
180/200 + 15%	16	30	105	9730	161	nd
180/200 + 20%	nd	37	nd	7830	143	nd

nd = not determined

Table 10.   Densities of fluxed bitumens used in long term oven experiment.

Blend	Density (g/cm^3)		
	25°C	43°C	135°C
180/200 bitumen	1.020	1.009	0.9409
180/200 + 3% AGO	1.008	1.001	0.9440
180/200 + 10% WODB	1.006	0.9947	0.9275
180/200 + 20% WODB	0.9680	0.9571	0.9026
180/200 + 10% TOP	1.019	1.008	0.9502
180/200 + 2.7% RO	1.018	1.007	0.9493

In addition to the WODB and TOP already discussed, another material (RO) became available late in the study and was included in the volatile loss study. There was insufficient time to carry out a full study on the physical properties of RO bitumen blends. Instead the concentration needed to give a 1% AGO equivalent concentration was calculated using equation (2):

$$\log \log V_{a+b} = \alpha \log \log V_a = (1 - \alpha) \log \log V_b \qquad (2)$$

where V_{a+b} = viscosity of the blend of components a and b at temperature T
V_a, V_b = viscosity of component a,b at temperature T
α = fraction of component a in the blend
$1 - \alpha$ = fraction of component b in the blend

This is an empirical relationship found to hold true for bitumen and related materials (ASTM D4887 1992). In this case, components `a' and `b' are RO and bitumen respectively. The concentration α of RO required was calculated using 60°C viscosity as this was the only data available for RO.

Blends of each flux were prepared and the densities measured (Table 10). Using the data in Table 10, sufficient binder to give a 3 mm thick film at 43°C was added to an aluminium pan; 3-4 replicate pans were used for each flux. The initial weight (cold) of each pan was recorded and the pans placed in an oven maintained at 43°C ±1°C. As a control, an unfluxed 180/200 bitumen was included in the experiment.

At intervals the pans were removed, allowed to cool to room temperature, and weighed. A plot of weight change as a percentage of initial binder weight versus time for each fluxed binder is shown in Figure 3. With the exception of the AGO, all of the fluxed binders and the control show a small increase in weight over the period of the experiment. In the case of the TOP and WODB, the weight increase was about equivalent to that of the control, whereas the RO (despite some scatter of results) clearly gained weight at a faster rate.

The weight gain is probably due to thermally induced oxidation reactions giving rise to products such as ketones and carboxylic acids, i.e. the weight increase is due to the incorporation of atmospheric oxygen. The reason for the greater rate of weight gain for the RO fluxed binder is not clear.

The AGO binder also probably gained weight through oxidation, but this was offset by a greater rate of loss of AGO. If it is assumed all the weight loss was due to AGO evaporation, and if the weight gain shown by the control was allowed for, then about 55% of the AGO would be lost after 165 days (~5½ months) and 80% after 1200 days (3.3 years) under these conditions. These results are consistent with previous work by Patrick (1984) who measured a 72% weight loss after 132 days at 43°C from 3.18 mm films of Safaniya 180/200 fluxed with 5 pph AGO. In that paper the increase in weight due to oxidation was not allowed for.

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Figure 1.   Penetration at 5°C. (a) AGO, (b) WODB, (c) TOP
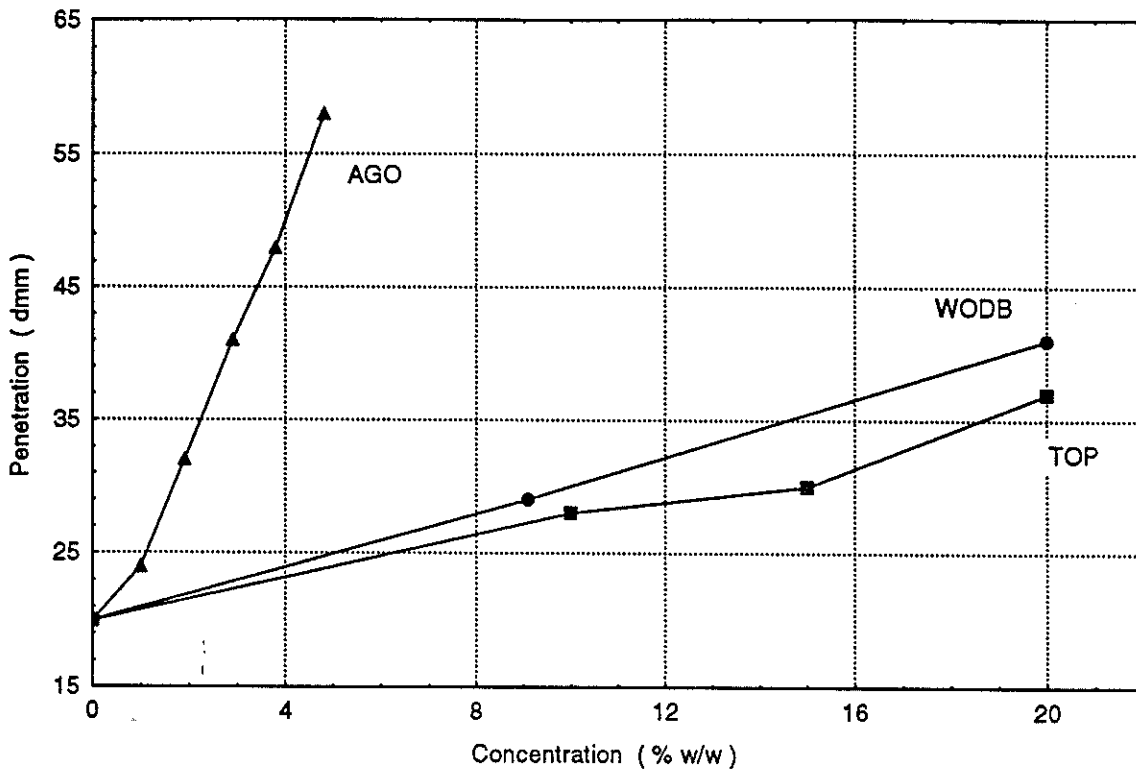

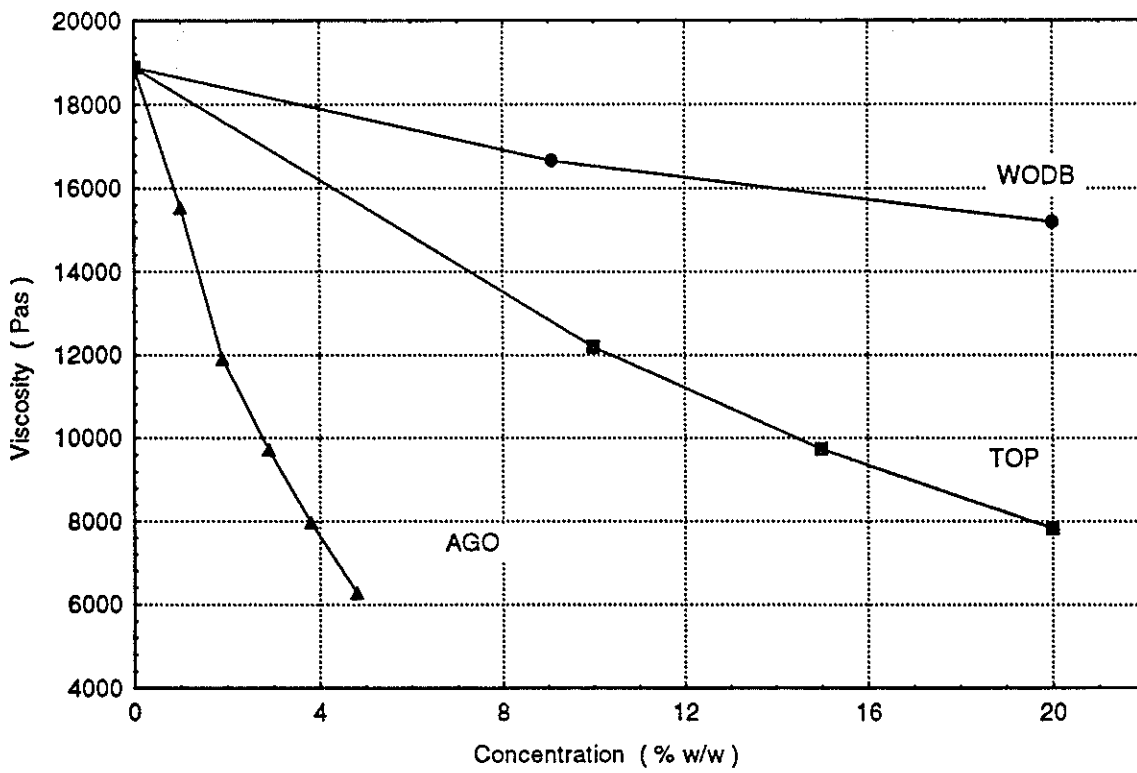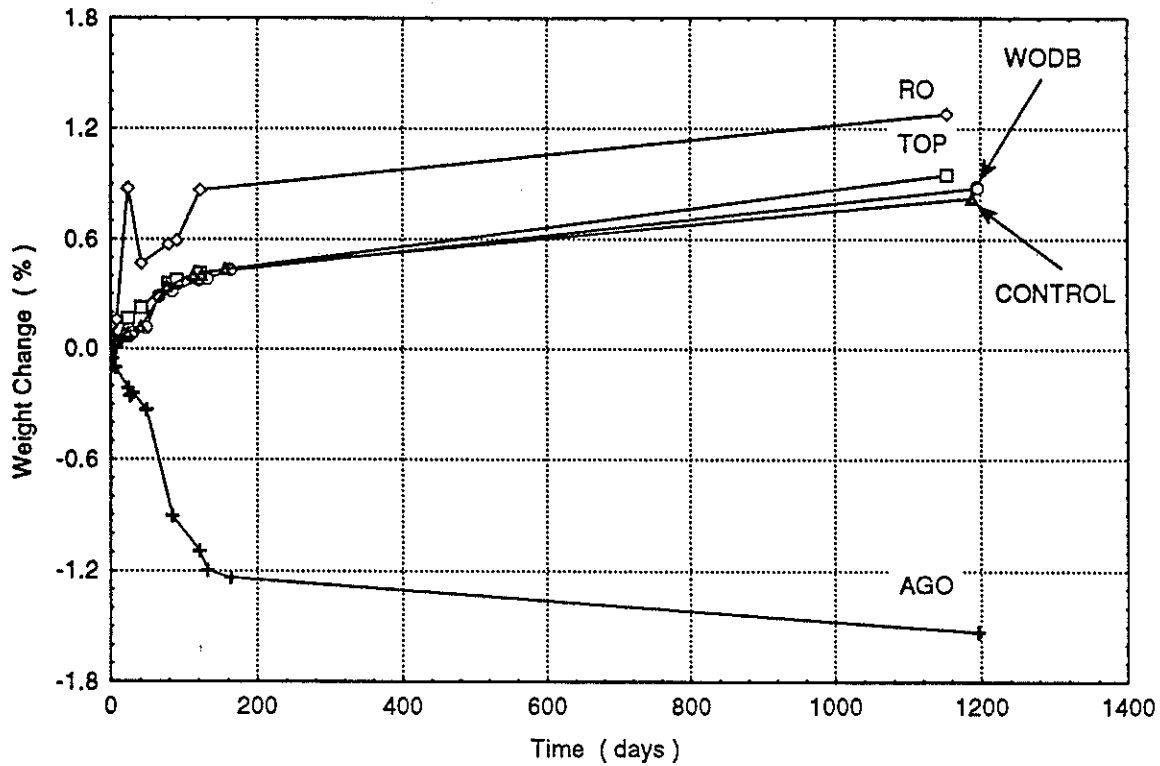Figure 2.   Viscosity at 70°C. (a) AGO, (b) WODB, (c) TOP

Figure 3.   Weight loss of 3.0 mm films of fluxed binders held at 43°C.

4.3   Effect of Oven Aging on Physical Properties

4.3.1   Viscosity

After 122 days (~4 months) and 1200 days (3.3 years) the viscosity of each fluxed binder was measured (by cone and plate viscometer) at 25°C. These results, together with the initial values, are presented in Table 11. The largest increase in viscosity was observed for the AGO sample which was almost twice that of the control. The viscosity after 3.3 years was close to that of the control, indicating that the fluxing effect of the AGO had been lost. The WODB and TOP samples showed less hardening than the control even though the measured weight increased was similar. The RO sample, which showed the greatest weight increase, also demonstrated the smallest increase in viscosity.

These results illustrate the complexity of the interaction between the flux, bitumen and oxidation products of both. From a practical point of view, the experiment demonstrates that the alternative fluxes are both retained in the bitumen and actually reduce the rate of binder hardening compared to the control.

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Table 11.   Viscosities of fluxed binders.

Binder	Viscosity (Pas) at 25°C and 0.02 s⁻¹ (±14%)			Viscosity ratio	
	Initial	After 4 months (165 days)	After 3.3 years (1200 days)	4 months/ initial	3.3 years/ initial
180/200	2.12×10^4	1.48×10^5	1.48×10^6	7.0	70
180/200 + 3% AGO	8.93×10^3	7.32×10^4	1.19×10^6	8.2	133
180/200 + 10% WODB[1]	1.63×10^4	8.68×10^4	7.06×10^5	5.3	43
180/200 + 10% TOP[2]	1.34×10^4	8.73×10^4	9.69×10^5	6.5	73
180/200 + 2.7% RO[2]	1.61×10^4	8.04×10^4	9.45×10^5	5.0	59

[1]   Approximately equivalent to 3% AGO-bitumen (based on 5°C penetration).
[2]   Approximately equivalent to 1% AGO (based on 5°C penetration).

4.3.2   Rheological Properties

Figures 4 to 7 show the moduli (G*, G', G") and tan δ (δ = phase angle) for each fluxed binder after 3.3 years as a function of temperature (values at 5, 25 and 50°C are also given in Table 12).

G* is a measure of the overall hardness of the binder, whereas G' and G" are respective measures of the elastic and viscous nature of the material. Tan δ is the ratio G'/G", a high tan δ value indicates a more elastic material.

Figure 4 shows the fluxed binders to have similar temperature sensitivities (slope of the G*-temperature curve) compared to the control bitumen. Temperature sensitivities were calculated and are presented in Table 13. The G* values at 25°C are lower for the fluxed materials and are consistent with the viscosity data in Table 12. At higher temperatures a high G' is generally desirable to provide adequate cohesion; conversely at low temperatures a binder more viscous than elastic in nature (high G" relative to G') is able to dissipate applied stresses and avoid brittle fracture which occurs if the elastic limit is exceeded.

Elastic and viscous moduli are presented in Figures 5 and 6. It is particularly interesting to note that G', G" (and G*) for the AGO fluxed binder is essentially indistinguishable from that of the control. It is instructive to compare the G'/G" (tan δ) ratio for each binder shown in Figure 7 and Table 12. Tan δ values (as a function of temperature) for the control, AGO and WODB fluxed binders are very similar. The RO and TOP fluxes, however, have considerably higher tan δ values than the control at temperatures above 25°C. Whereas the absolute magnitude of G*, G' and G" are arbitrary in the sense that they are a function of the amount of flux present, tan δ is directly related to the way in which the flux and bitumen components interact. Thus although larger quantities of TOP should give rise to G* values as low as those obtained with WODB (Figure 5), any amount of WODB is unlikely to give rise to tan δ curves as desirable as those of the TOP fluxed binder (Figure 7).

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Table 12.   Rheological properties of fluxed binders after 3.3 years oven treatment at 43°C.

Temperature (°C)	180/200 (control)	180/200 + 3% AGO	180/200 + 10% WODB	180/200 + 10% TOP	180/200 + 2.7% RO
	G* (Pa) ±10%				
5	1.224×10^7	1.151×10^7	7.657×10^6	1.215×10^7	1.013×10^7
25	1.225×10^6	1.246×10^6	0.7717×10^6	1.184×10^6	1.025×10^6
50	4.793×10^4	4.428×10^4	3.019×10^4	4.2904×10^4	3.204×10^4
	G' (Pa) Elastic				
5	9.716×10^6	9.108×10^6	5.919×10^6	9.484×10^6	7.972×10^6
25	7.599×10^5	7.727×10^5	4.720×10^5	6.857×10^5	6.212×10^5
50	1.859×10^4	1.678×10^4	1.151×10^4	1.353×10^4	1.116×10^4
	G" (pa) Viscous				
5	7.440×10^6	7.034×10^6	4.858×10^6	7.600×10^6	6.243×10^6
25	9.615×10^5	9.774×10^5	6.105×10^5	9.663×10^5	8.153×10^5
50	4.418×10^4	4.098×10^4	2.792×10^4	4.071×10^4	3.004×10^4
	Tan δ				
5	0.766	0.773	0.821	0.786	0.783
25	1.278	1.265	1.293	1.409	1.313
50	2.378	2.442	2.427	3.008	2.692

Table 13.   Temperature sensitivities[1], G* (50°C) / G* (5°C).

180/200 (control)	260 ±51
180/200 + 3% AGO	260 ±52
180/200 + 10% WODB	250 ±51
180/200 + 10% TOP	280 ±57
180/200 + 2.7% RO	320 ±60

[1]Larger values indicate a more temperature sensitive material.

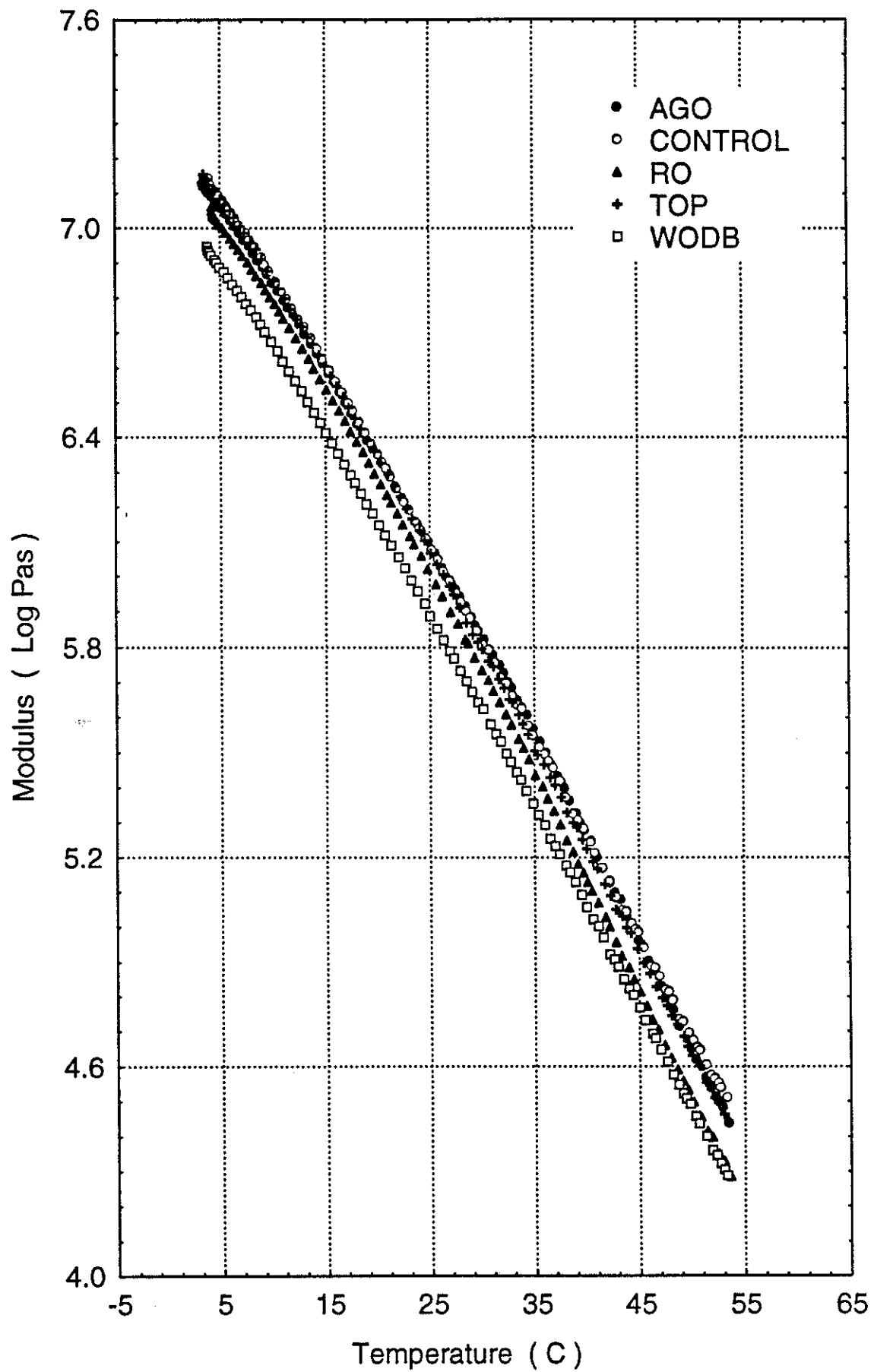Figure 4.   Moduli (G*) of fluxed binders maintained at 43°C for 3.3 years.

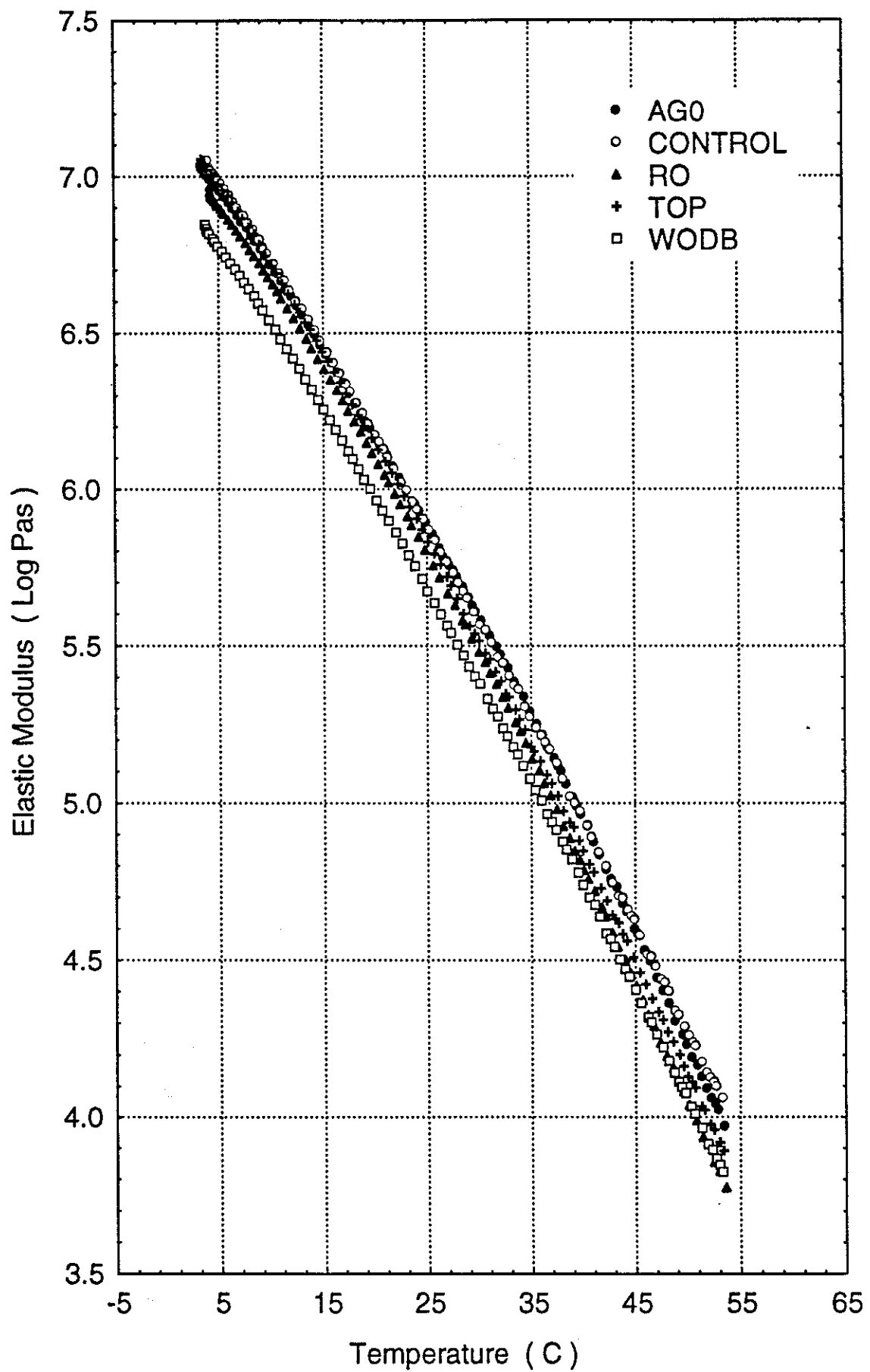Figure 5.   Elastic moduli (G') of fluxed binders maintained at 43°C for 3.3 years.

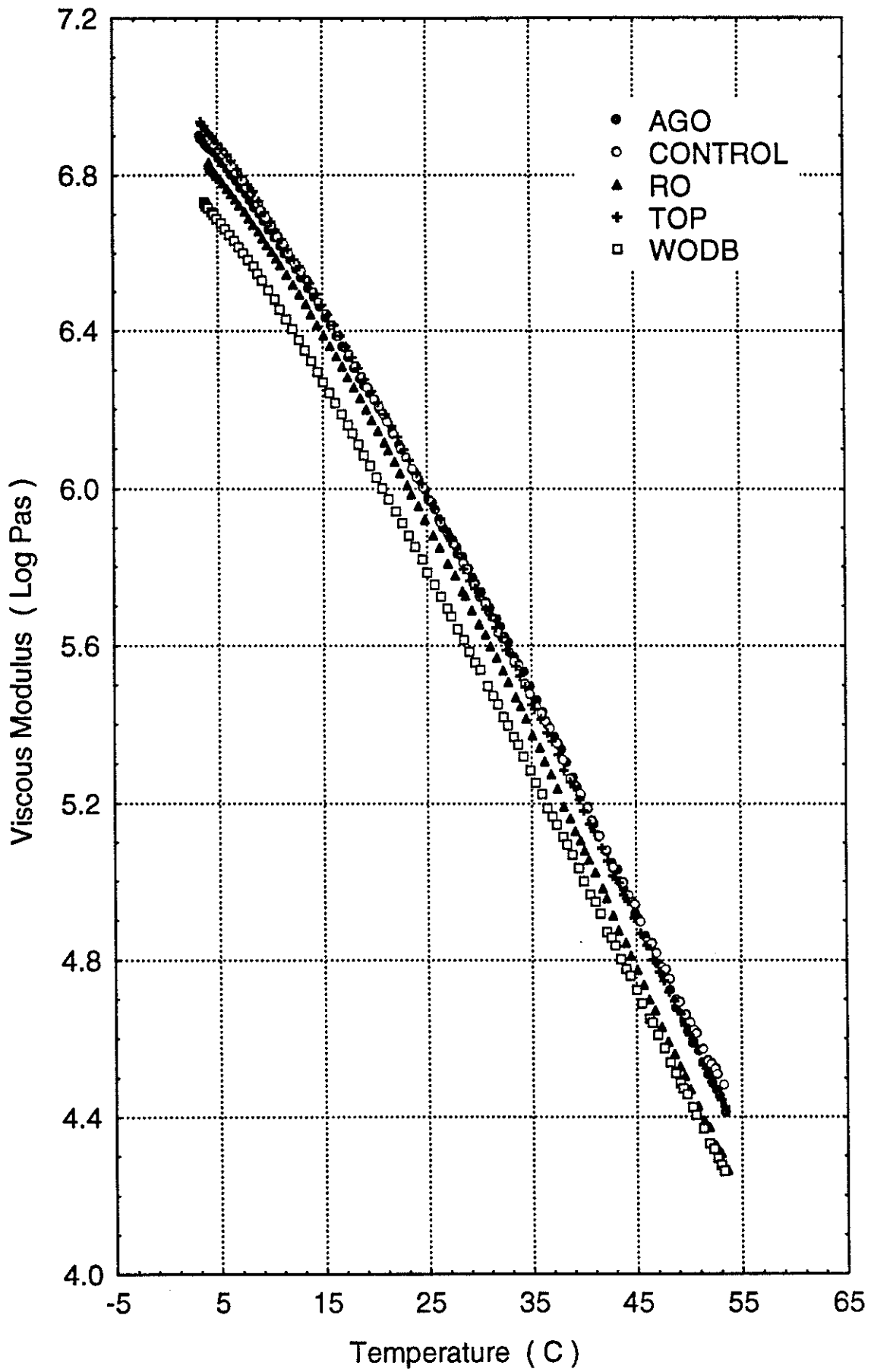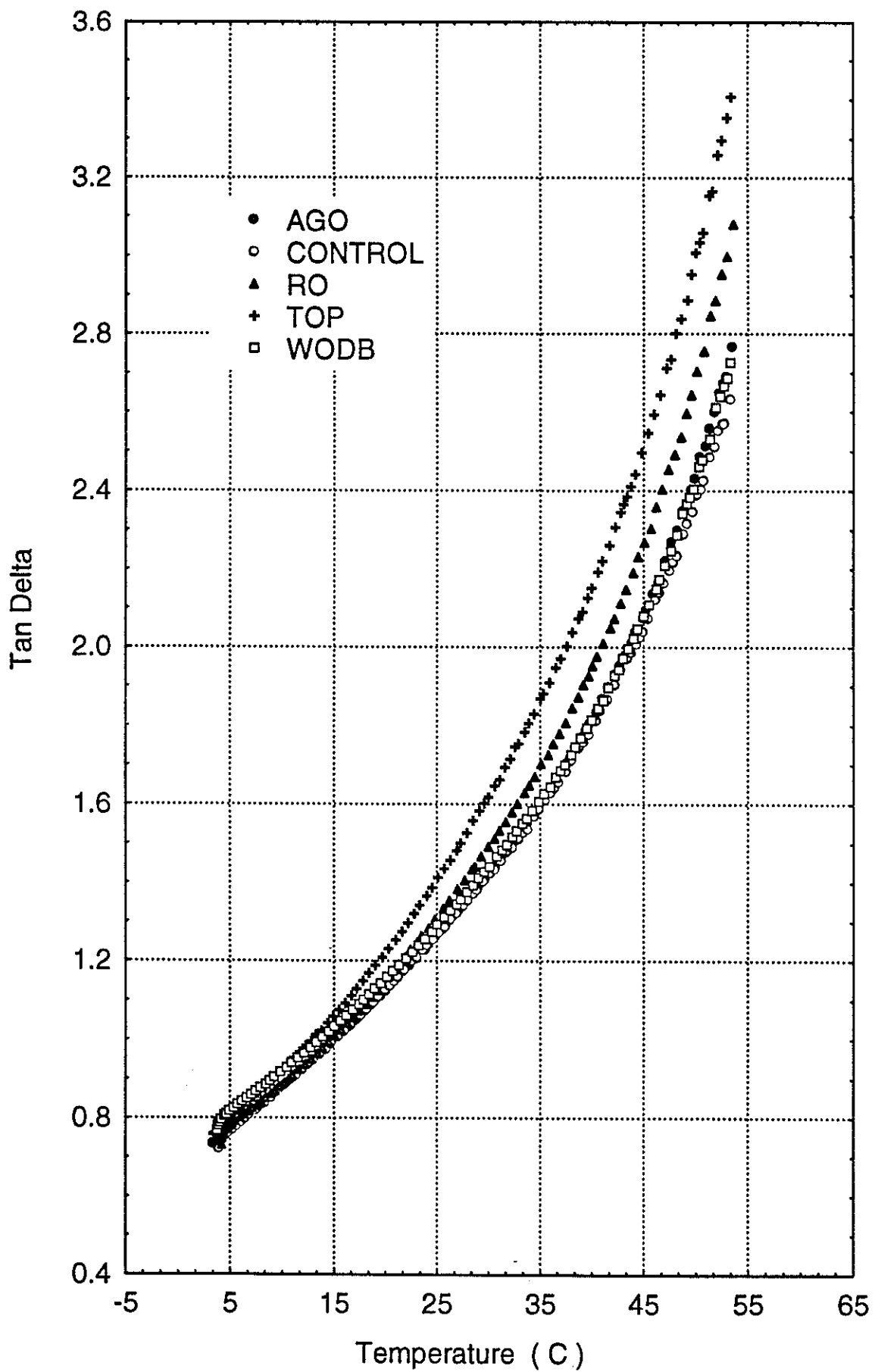Figure 6.   Viscous moduli (G") of fluxed binders maintained at 43°C for 3.3 years.

Figure 7.   Tan δ of fluxed binders maintained at 43°C for 3.3 years.

5.   EFFECT ON SEALING PRACTICE

5.1   AGO

In theory, the determination of the required AGO content for chipseal fluxing has traditionally been made by inspection of aged seals in a particular area. However, there is insufficient data on the level of binder hardness at which distress occurs or the rate of bitumen hardening under different climatic conditions for conclusions to be made on the manner or effectiveness of AGO in extending seal life.

It is commonly perceived that if chipseal life is under eight years and binder hardening is assessed as the predominant cause of distress, then use of an AGO flux in this situation would be appropriate. The amount of AGO used in practice is typically 1-3 pph.

The weight loss measurements made in the present study indicated that about two thirds of the added AGO was lost after 3.3 years from a 3 mm film at 43°C, and physical measurements showed no fluxing effect remained. In the field, only limited work on AGO loss has been reported. Table 14 and Figure 8 show percentage AGO loss from a range of Dunedin chipseals (Patrick 1987) measured using thermogravimetry (Donbavand 1984, Herrington 1988). The data show considerable scatter due to the difficult nature of the analysis (many possible interferences) and also probably due to the assumption that the nominal, initial AGO content was accurate. Nevertheless the data indicated that after 7-8 years percentage losses of 70-80% had occurred, consistent with the extent of loss found in the present study with the lower (than 43°C) temperature of seals in Dunedin obviously accounting for slower overall rate of loss. Limited data from an artificial fluxed binder chipseal exposed to the weather in Gracefield (as part of Transit New Zealand Research Project PR3-0105) is also available (Table 15 and Figure 9). Approximately 40% of the 5 pph AGO added had been lost after 500 days (February 1989 to June 1990). In the present oven experiment, 63% of the AGO had been lost after 500 days. The weight loss results reported here are thus not exceptional or unrealistic compared to the limited field data available.

It has been assumed that although small quantities of AGO may be lost in the field, the residual solvent would still give rise to a significant fluxing effect. An important finding of this work is that this assumption is not valid. Although after 3.3 years 0.6% AGO remained, the measured physical properties of the binder were nearly equal to those of the control.

The conclusion to be drawn is that AGO is ineffective as a fluxing agent and there is little value in using it if long term softening is required.

Table 14.   AGO loss from Dunedin seals (from Patrick 1987).

Year laid	Street	AGO content		
		Original[1] (pph)	Measured[2] (pph)	% loss
1976	Arthur Street	12	3.16	73.7
1976	Gladstone Road	12	2.20	81.7
1978	Balemacewen Road	8	2.43	69.6
1978	Roberts Street	8	1.82	77.3
1979	Sidey Street	8	6.00	25.0
1979	Connongate	8	1.62	79.8
1980	Arthur Street	8	2.61	67.4
1980	Ashmore Street	8	3.39	57.6
1982	Serpentine Avenue	8	2.21	72.4
1984	Harrow Street	2.2	0.53	75.9
1985	Roseberry Street	2.2	1.71	22.3

[1]Nominal value.
[2]By thermogravimetry (Donbavand 1984, Herrington 1988).
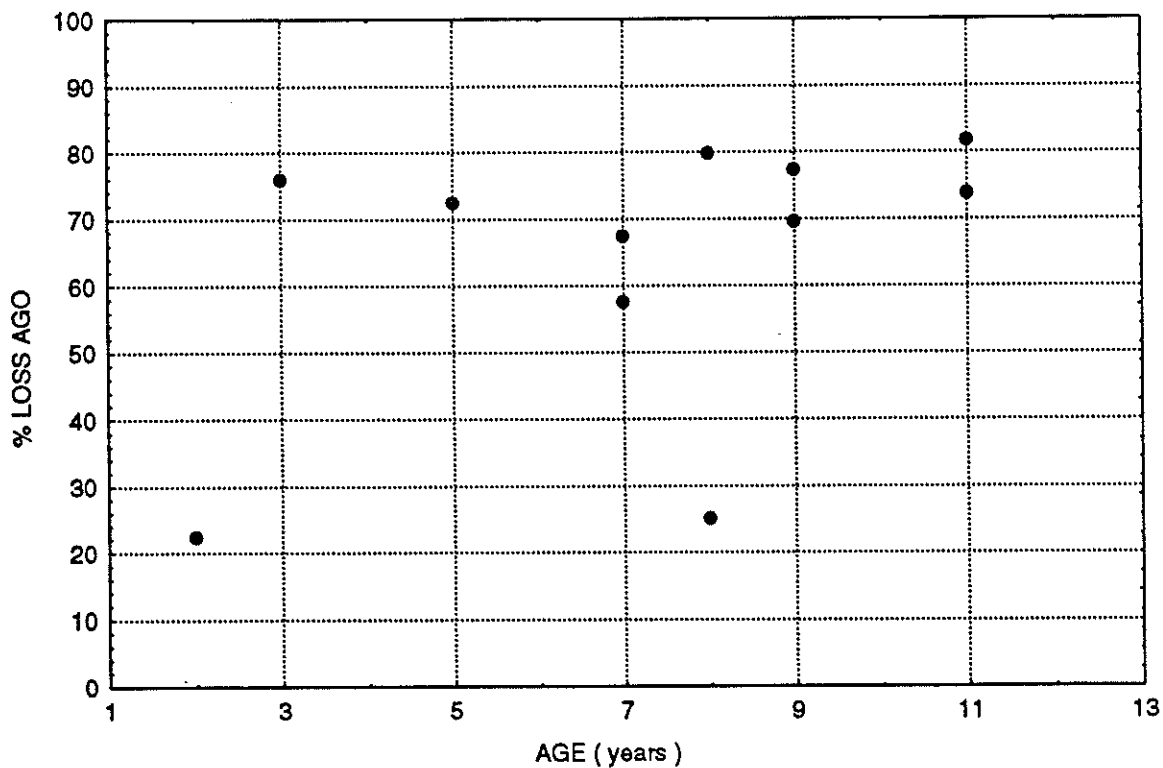
Figure 8.   Loss of AGO from Dunedin chipseals.

Table 15.   AGO loss from fluxed 180/200 artificial seal at Gracefield (Wellington).

Date	Time (days)	Concentration[1] (pph)	% loss
4 February 1989	0	5.0	0
1 June 1989	117	3.9	21.7
14 June 1989	130	4.1	17.3
5 July 1989	151	4.0	19.3
4 September 1989	212	3.4	31.9
26 October 1989	264	4.0	19.3
9 February 1990	370	3.2	34.5
13 February 1990	374	3.1	37.5
7 March 1990	396	2.3	53.5
9 May 1990	459	3.1	36.5
16 July 1990	527	2.7	45.9
29 November 1990	663	3.5	28.9
11 February 1991	737	3.0	39.9

[1]Corrected for average of 0.42 pph "apparent" diluent loss from equivalent control (non-fluxed) seal.

Figure 9.   Loss of AGO from artificial chipseals at Gracefield.
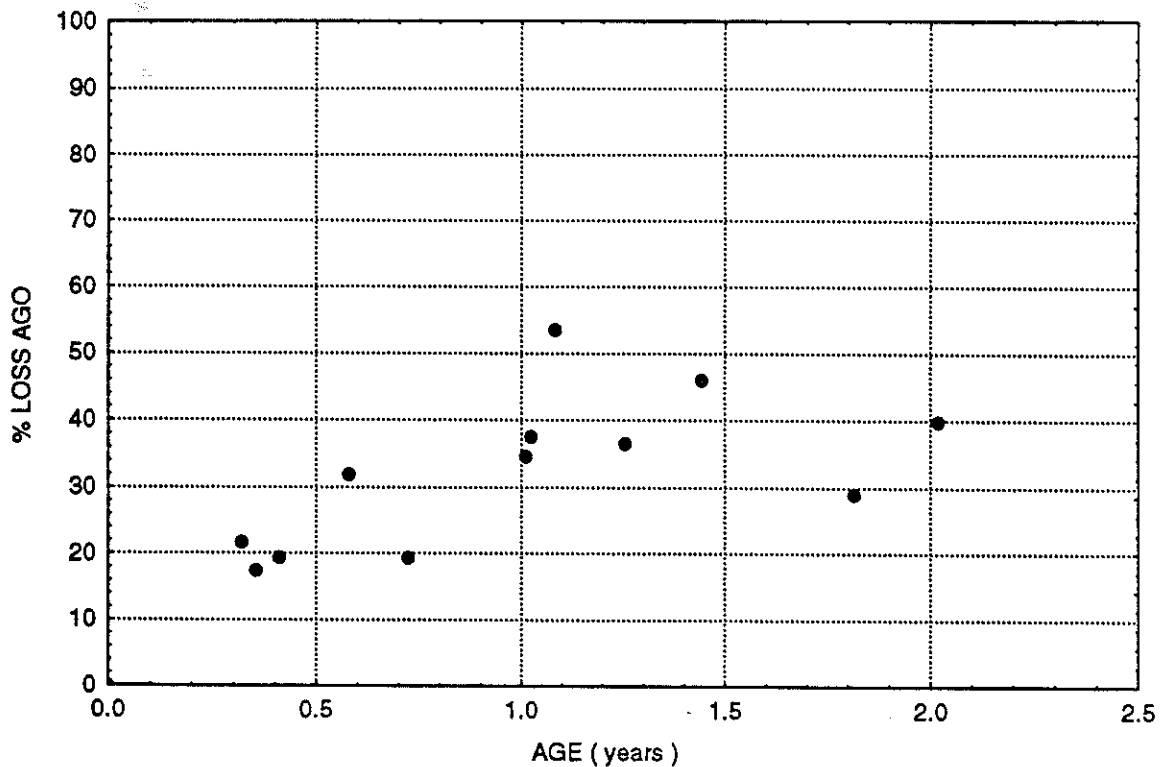
5.2 WODB TOP and RO

The WODB TOP and RO additives all continued to provide a fluxing effect after 3.3 years. Further, the rate of hardening of bitumen fluxed with these materials was considerably lower than that of the unfluxed control bitumen. Speculation on the reason for the reduced hardening rates are beyond the scope of the present work.

From the practical point of view, however, the use of WODB, TOP or RO would present few problems. The handling and storage of these materials would be similar to the handling of bitumen itself. The high flash point of these materials compared to AGO is an advantage from the point of view of safety. The high aromatic content of the RO suggests it may be more carcinogenic than bitumen, and this aspect would benefit from further investigation. However, similar oils have been used for many years in the United States as rejuvenating agents without serious problems. The handling and use of RO would require precautions to minimise skin contact by operators, but this would not be difficult. Both WODB and RO are essentially crude oil fractions and no problems in chip adhesion are expected; however, the high acid content of the TOP (Table 3) may present problems in this respect. Fatty amine-based "adhesion agents" are routinely added to chipsealing binders to promote binder-stone chipping adhesion. As a result, carboxylic acid salts could be formed when TOP acids were present. Although the salts would be still active as adhesion promoters, at binder storage and application temperatures (130-180°C) dehydration of the salt to give an inactive amide could occur. Overseas work indicated that any such effects may be negligible as TOP-modified bitumens had been found to actually improve adhesion properties.

The chief impact on sealing practice of the alternative fluxes considered in this work would be an economic one. At the time of writing, the cost (per tonne) of WODB, TOP and RO were given as approximately $350, $450 and $1,000 respectively. These figures did not include the cost of transportation around New Zealand. AGO was probably available in bulk for $400-$500 per tonne. On this basis, RO and TOP were clearly uneconomic given the dosages required. In this study WODB was added at the equivalent of 3% AGO, in practice residual AGO levels were likely to be only of the order of 1%. To obtain this degree of fluxing, only ~4% WODB would be required (based on 5°C pen, see Figure 1), but the cost would still be considerably greater than AGO. Both Dominion Oil and Eka-Nobel face problems due to the cost of disposal of WODB and TOP, as a ready market for either product is lacking. Thus the costs mentioned above are probably negotiable. The above comparisons of course assume that the residue AGO is still acting as a flux. The findings of the present research, however, indicate that this is not in fact the case.

It is considered that further research into alternative fluxing agents should be performed as part of the programme to extend chipseal life (Transit New Zealand Research Project PR3-0126), of which the use of a flux could form an integral part.

6.   CONCLUSION

The evaporation of AGO from fluxed bitumens is both wasteful and environmentally damaging as a contributor to the greenhouse effect. A number of non-volatile alternative materials to AGO were examined from the point of view of cost, safety and effectiveness as a flux. The materials evaluated were:

(a)   Rerefined and distillation bottoms produced by Dominion Oil Refining Ltd. These had a small amount of a non-volatile oil fraction added to give a product of consistent quality. This material showed no volatile loss and showed a reduced rate of hardening compared to 180/200 bitumen in a three year oven test.

It would have to be transported from its point of manufacture in Auckland to the South Island, and heated to liquefy it before adding to the bitumen. This may add considerably to the final cost of the material. Approximately 4% of the product is equivalent to 1% AGO in initial fluxing effect. The toxicity and environmental threat posed by this material is similar to bitumen except for the presence of engine wear metals and oil and petrol additive residues. Further information on the ultimate fate of these contaminants in the field would be desirable, though they are likely to be tightly bound in the matrix.

(b)   Tall oil pitch (Pinechem 450) from Eka-Nobel, Mt Maunganui. This material is a byproduct of the kraft paper manufacturing process. Its cost is similar to that of AGO ($450/tonne) but about 10% dosage is equivalent to 1% AGO. The transport and heating requirements are similar to those for the Dominion Oil material in (a), and raise the same economic difficulties. In addition, Pinechem 450 is an acidic product, and it could neutralise the effect of the mildly alkaline amine anti-stripping agents routinely used in chipsealing. This product, however, also performed well in the three year oven test and showed no volatile loss and a reduced rate of hardening. Of all the fluxes studied, tall oil pitch appears to have the lowest toxicity with the least potential for environmental damage.

(c)   A rejuvenating oil (Sun Hydrolene 110T). This material became available in the course of the current seal and friction course rejuvenation project, and is typical of a range of "heavy fuel" and "process oils" available from the major oil companies. A dosage of 2-3% would be needed to reproduce the effect of around 1% AGO. The three year oven tests showed a surprisingly high increase in binder mass with time; this, however, was not reflected in the rate of hardening, which was the lowest of all materials tested. At approximately $1 per litre, this makes Hydrolene 110T uneconomic compared to AGO. In addition, its high aromatics content, typical for a rejuvenating agent, makes it potentially carcinogenic. However, recent information from the suppliers indicates that fumes from hydrolene oil-bitumen operations are no more hazardous than those from bitumen alone. The manufacturers of bitumen polymer modifiers are used to dealing with such products as SBS rubber solvents, but additional training of staff would be needed if it was to be used more generally by the roading industry.

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In summary, the fluxing products tested are environmentally more acceptable than AGO in that they are not expected to evaporate and are adequate fluxes. The use of AGO is still in theory considerably cheaper than the rejuvenating oil. In the case of the distillation bottoms and tall oil pitch, a comparison of the cost to that of AGO is more difficult as they are waste products without an established market. It seems likely that they would cost about the same as AGO. The fact remains, however, that AGO fails to demonstrate any softening effect after 3.3 years, and so using it has little real value in the long term.

The long term economic benefits of fluxing in general are in any case unknown. The practice of fluxing appears to be based on anecdotal evidence and intuition. Objective evidence of increased seal life through use of fluxes is lacking. That is not to say it does not exist; rather that research on the long term effects of the practice is urgently needed.

Physical Properties

All the AGO alternatives studied gave rise to a fluxing effect, the extent of which depended on the amount of material added. In order to compare the fluxes, it was necessary to compare the 3.3 year viscosity ratios. These are recorded in Table 11 which shows the ratio for AGO as greater than that of the control, indicating that the fluxing effect has been lost. The ratio for TOP is equal to that of the control, showing that the original fluxing effect has been maintained. The WODB and RO fluxes gave ratios lower than that of the control, meaning that the binder after 3.3 years is softer relative to the control than it was originally - the effect of age hardening has been reduced.

The dynamic shear rheometer was not available at the beginning of the project so that moduli ratios are not available. However, the moduli results indicate no adverse increase in temperature susceptibility due to fluxing by WODB, TOP or RO. Additionally, the large tan δ values at high temperatures for the RO and TOP fluxed binders indicate a greater cohesiveness than the other binders, which would be beneficial in reducing chip rollover and loss during summer.

Preferred Alternative Flux

Of the three alternatives to AGO studied, none demonstrated a marked overall superiority to the others, however differences may be more apparent after field trials are carried out. In terms of low toxicity and potential environment damage (through spillage, etc), the tall oil pitch is preferred. In terms of low initial cost, the waste and distillation bottoms are preferred (given the relatively low dosages required), but in terms of future continuity of supply then a rejuvenating oil is the best choice. Rejuvenating oils also offer the advantage of having been used widely overseas for many years as bitumen additives, and thus the potential for unforeseen problems is reduced. In terms of purely physical benefits, then RO is also the preferred option for the reasons discussed above.

Reduced Age Hardening of the Fluxed Materials

Both WODB and RO fluxed binders showed markedly reduced hardening rates compared to the control, TOP and AGO fluxed binders. Thus not only are WODB and RO softening the bitumen initially, but are either reducing the rate of oxidation or more likely acting to minimise the structure building effects of oxidation products. This finding is of great potential significance and suggests the possibility that such additives could be used in a general fashion to reduce seal age hardening, even where fluxing is not the primary objective. This would be easily achieved by using a slightly harder grade of bitumen initially (e.g. 130/50 pen) and blending RO or WODB to give a 180/200 pen final product.

7. RECOMMENDATIONS

(1)   Confirmation of the ineffectiveness of AGO as a flux should be sought immediately by investigating seals where it has been used. It may be feasible to use dynamic shear rheometry (wide gap, parallel plate geometry) to measure the properties of binders from chipseals without the need for solvent recovery methods. Such an approach would avoid potential errors due to loss of residual AGO during solvent removal.

(2)   Actual lifetime trends for AGO fluxed seals compared to equivalent non-fluxed seals should be investigated by extracting the relevant data from the findings of the Transit New Zealand Research Project PR3-0126, End of Life Chipseal Conditions.

(3)   The laboratory study has demonstrated that all three AGO alternatives studied are satisfactory fluxes (without any being markedly superior overall in terms of cost, toxicity or physical properties). Field trials should therefore be constructed using all the materials used in this study (or variants of them) in conjunction with their suppliers.

(4)   The slower hardening rates of the WODB and RO fluxed binders is highly significant and should be further investigated. Laboratory aging studies using these additives (and a range of other rejuvenating agents) should be carried out to confirm and better understand this phenomenon.

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8. REFERENCES

ASTM 1992. *Annual Book of ASTM Standards*, Section 4, construction. Vol. 04.03, Road and Paving Materials. American Society for Testing and Materials.

Ball, G.F.A. 1992. Wood byproduct extenders for roading bitumen. Works Consultancy Services Ltd, *Central Laboratories Report 92-26102*.

Dickinson, E.J. 1989. The rate of evaporation of volatile diluent (cutter) from cutback bitumen sprayed seal. *Australian Road Research Board Report No. 157*.

Donbavand, J. 1984. An investigation into the use of thermogravimetry and derivative thermogravimetry for the analysis of bituminous materials. *Proceedings 12th ARRB Conference 12(2)*: 71-81.

Dravitzki, V.K., Wood, C.W.B. and Herrington, P.R. 1993. Investigation into the release of heavy metal components from waste oil distillate bottom/bitumen blends. Works Consultancy Services Ltd, *Central Laboratories Report 93-27351*.

Eka-Nobel 1992. Private communication, Eka-Nobel Ltd, Mt Maunganui, New Zealand.

Herrington, P.R. 1988. Diluent content of bituminous binders by thermogravimetry. *Central Laboratories Report 88-B6414A*.

Herrington, P.R. 1991. The use of rerefined oil distillation bottoms as extenders for roading bitumens. Works Consultancy Services Ltd, *Central Laboratories Report 91-26221*.

Herrington, P.R. 1992. Use of rerefined oil distillation bottoms as extenders for roading bitumens. *Journal of Materials Science, 27*: 6615-6626.

Patrick, J.E. 1987. Private communication to R Mair, Dunedin City Council.

Patrick, J.E. 1984. Diluent Loss from Chipseals. *Proceedings of the 12th ARRB Conference 12(2)*: 223-232.

Peltonen, P.V. 1989a. Finnish experience in tall oil pitch as asphalt substitute. *Naval Stores Review, No. 5*: 10-12.

Peltonen, P.V. 1989b. Research into the physico-chemistry of tall oil pitch modified asphalt composites. *TAPPI Proceedings, International Symposium on Wood and Pulping Chemistry*, North Carolina State University, Raleigh, North Carolina, USA: 391-398.

Puzinauskas, V.P. 1979. Properties of asphalt cements. *Proceedings of the Association of Asphalt Paving Technologists, 48*: 646-710.

Transit New Zealand 1989. Specification for asphaltic bitumens. *TNZ M/1*, Transit New Zealand.