TALL OIL PITCH AS BITUMEN EXTENDER

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(Received for publication 21 May 1993; revision 21 August 1993)

ABSTRACT

Blends of tall oil pitch (TOP) and petroleum bitumen were studied as potential binders for road surfacings. The physical properties (viscosity, penetration, softening point) of TOP/bitumen blends (up to 30% w/w TOP) were similar to those of petroleum bitumen alone. Resistance to oxidative hardening likely to occur in asphalt concrete manufacture was examined using the standard rolling thin film oven test. The blended binders showed a drop in 25°C penetration value equivalent to that found with petroleum bitumen of the same initial penetration. No separation of the TOP/bitumen blends was observed even after 3 days' storage at 135°C. Thermogravimetric analyses in air showed the onset temperature for weight loss to be lower (~170°C) than that for bitumen (~210°C). However, the flash point of blends up to 30% w/w TOP remained well above the lower limit allowed for petroleum bitumens.

Keywords: tall oil pitch; bitumen; binders, road surfacings.

INTRODUCTION

The distillation of crude tall oil from the kraft process results in a tarry residue known as tall oil pitch (TOP). New Zealand crude tall oil annual production stands at 13 500 tonnes with current plant able to process up to 15 000 tonnes. Consequently, 4000 tonnes of pitch is produced annually, most of which is used as furnace fuel. Research in Finland (Peltonen 1989a, b, 1992) has recently demonstrated the feasibility of using TOP in conjunction with petroleum bitumen as a binder in the manufacture of roading asphalt. The TOPs examined were completely compatible with bitumen, mixtures remaining homogeneous after 20 days' static storage. The blends were considered somewhat more temperature-sensitive than the original bitumens (Peltonen 1989b) although a close examination of the data presented does not support this contention, at least up to 20% pitch content. TOP also improved both the bitumen's resistance to oven hardening and adhesion to mineral aggregates (Peltonen 1992).

The composition of the petroleum bitumen used in New Zealand and that of the pitch derived from New Zealand *Pinus radiata* D.Don is significantly different from that used in the Finnish work. The purpose of the present research was to investigate the basic properties of New Zealand TOP/bitumen blends and establish their suitability as binders in road construction in this country.

EXPERIMENTAL

Viscosities, penetrations, softening points, flash points, ductilities, and solubilities were determined according to ASTM D2170, D5, D36, D92, D113, and D2042 respectively.

Infrared spectra were measured on a Digilab FTS-7 spectrometer. Spectra were obtained using thin films of sample supported on single KBR disks, or as 4% w/v solutions in tetrachloroethane in a 1.0-mm KBr cell. All spectra are the result of adding 150 scans at 2 cm^{-1} resolution.

Thermogravimetric analyses were carried out on a Mettler TG50 thermobalance/TC10A processor. The following conditions were employed: sample size 10–11 mg, open platinum crucible, heating programme 35°–650°C @ 5°C/min, dry air purge 200 cm^3/mm.

The compatibility of bitumen and TOP was investigated by storing a 15% TOP blend undisturbed at 135°C in an airtight brass cylinder (50 mm i.d. × 150 mm) fitted with taps 15 mm from both top and bottom. After 72 hours, samples were removed first from the upper outlet and then from the bottom; in each sampling the first few millilitres were discarded to purge the dead volume of the taps. A final sample from about the middle of the cylinder was also taken from the lower tap.

RESULTS AND DISCUSSION

Properties of TOP and Bitumen

Tall oil pitch is a dark-brown viscous material at room temperature. Properties of the pitch used here are listed in Table 1. Data on the pitches used in the Finnish work (Peltonen 1992) are included for comparison. Properties of the Safaniyah bitumen used are presented in Tables 2 and 3. The infrared spectra of TOP and a standard 180/200 penetration grade bitumen are shown in Fig. 1.

The strong absorptions in both spectra at ~1460 and ~1380 cm^{-1} were due to the C–H stretching modes in methylene and methyl groups respectively. The aromatic character of the bitumen sample was evident from the absorption at 1600 cm^{-1} and the substitution bands between 800 and 900 cm^{-1}. These bands were absent or of low intensity in the TOP sample. Both spectra showed a band at ~725 cm^{-1} due to methylene chains with four or more carbons. The major differences between the two spectra were the strong TOP absorptions at 1735 and

TABLE 1–Tall oil pitch properties

	TOP	Finnish hard pitch	Finnish soft pitch
Acid number (mg KOH/g)	45	32–42	25–35
Rosin acid content (%)	9.0	5–15	10–30
Other oxidised and esterified acids (%)	10.0	–	–
Unsaponifiables (%)	40.0	25–45	25–35
Saponification number	106	45–80	90–110
Specific gravity (25/25°C)	1.02	0.95–1.05	0.95–1.05
Viscosity (35°C), Pa.s	80.0	–	–
Flash point (Cleveland open cup) (°C)	240	–	–
Fire point (Cleveland open cup) (°C)	270	–	–

Source: Eka-Nobel, Mt Maunganui, pers. comm.

TABLE 2–180/200 binders with TOP

Test	Specification limits*	Representative bitumen (Safaniyah)	15% TOP 85% pen. 94 bitumen	31.5% TOP 68.5% pen. 52 bitumen
Penetration 5°C, 100 g, 5 s	–	20	19	19
Penetration 25°C, 100 g, 5 s	180–200	184	186	185
Viscosity 70°C (mm^2/s)	14 000+	18 100	24 300	20 900
Viscosity 135°C (mm^2/s)	140–350	233	278	253
Softening point (°C)	37–43	40.6	41.9	41.8
Flash point (°C)	218+	302	296	282
Solubility in trichloroethylene (%)	99.5+	99.80	99.91	99.83
Ductility 25°C (m)	1.00+	1.00+	1.00+	–

* Transit New Zealand (1989)

TABLE 3–80/100 binder with TOP

Test	Specification limits*	Representative bitumen (Safaniyah)	12.1% TOP 87.9% pen. 52 bitumen
Penetration 5°C, 100 g, 5 s	–	16	16
Penetration 25°C, 100 g, 5 s	80–100	94	87
Viscosity 70°C (mm^2/s)	40 000+	55 600	64 500
Viscosity 135°C (mm^2/s)	300–650	426	478
Softening point (°C)	45–52	47.8	48.9
Flash point (°C)	218+	290+	300
Solubility in trichloroethylene (%)	99.5+	99.85	99.71
Rolling thin film oven residue			
Retained penetration (%)	50+	58.5	58.2
Ductility 25°C (m)	0.60+	1.00+	1.00+

* Transit New Zealand (1989)

1697 cm^{-1} and the broad peaks between 1100 and 1300 cm^{-1} which were absent in the bitumen specimen. The peaks at 1735 and 1697 cm^{-1} were due to the C=O stretch in esters and carboxylic acids respectively; the C–O stretch in these functional groups gives rise to the broad 1100 to 1300 cm^{-1} absorptions.

The peaks at 1697 and 1735 cm^{-1} in the TOP spectrum provided a straightforward means of quantifying this material in a bitumen mixture. They were strong and did not overlap the bitumen spectrum significantly.

In order to establish possible problems at handling and application temperatures (130°–180°C), the weight loss characteristics of the TOP were examined by thermogravimetry.

The first differential of the thermogravimetric weight loss curve is shown in Fig. 2, along with one for a standard 180/200 Safaniyah bitumen as used in New Zealand. Although the TOP had a higher proportion of material volatilising in the range 170°–370°C, its weight loss curve was not dissimilar in form to a bitumen curve; weight loss commenced around 170°C (cf. around 200°C for Safaniyah bitumen) and was complete at approximately 520°C.

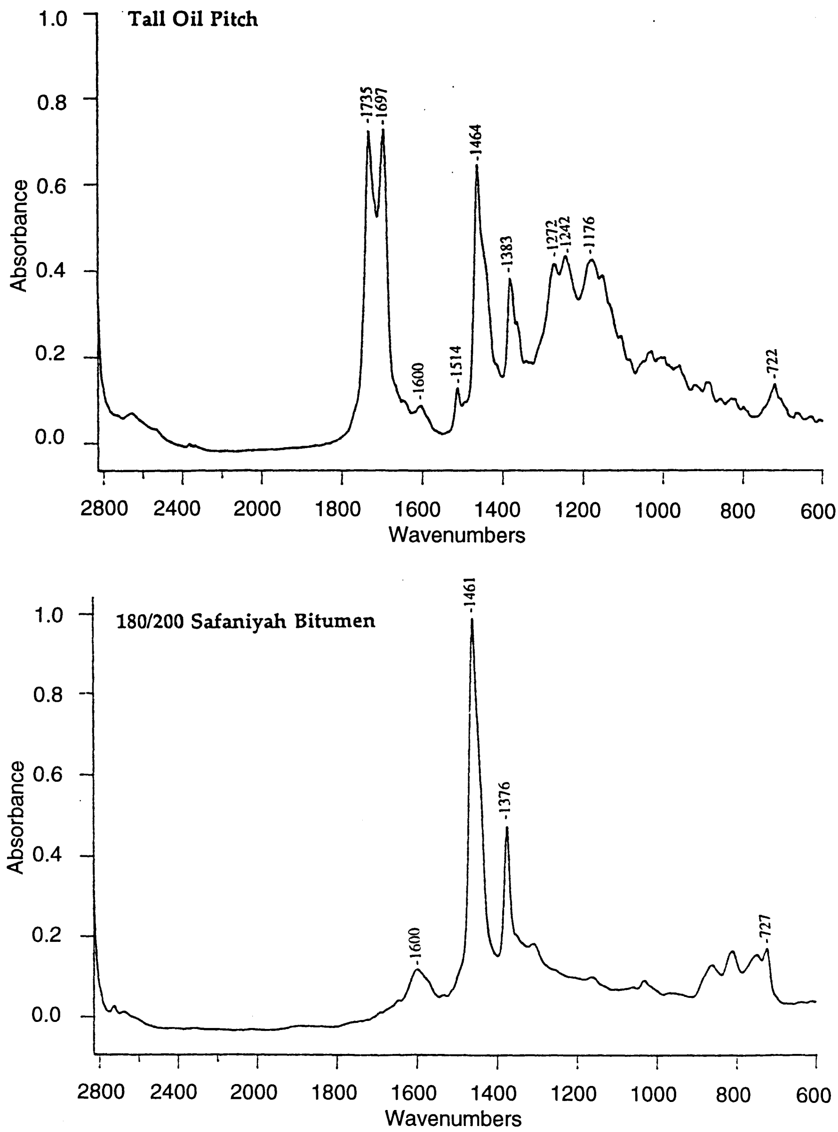

FIG. 1–Infrared spectra of tall oil pitch and 180/200 Safaniyah bitumen.

Tall oil pitch should thus be satisfactorily stable in the temperature range likely to be experienced in sealing and asphaltic concrete manufacture (up to ~180°C but normally in the range 130°–160°C).

TOP-Bitumen Blends

All grades of bitumen have very similar densities of ~1.02 g/cm^2 (25°C). This value is very close to that of TOP. Although phase separation is thus unlikely, the compatibility of

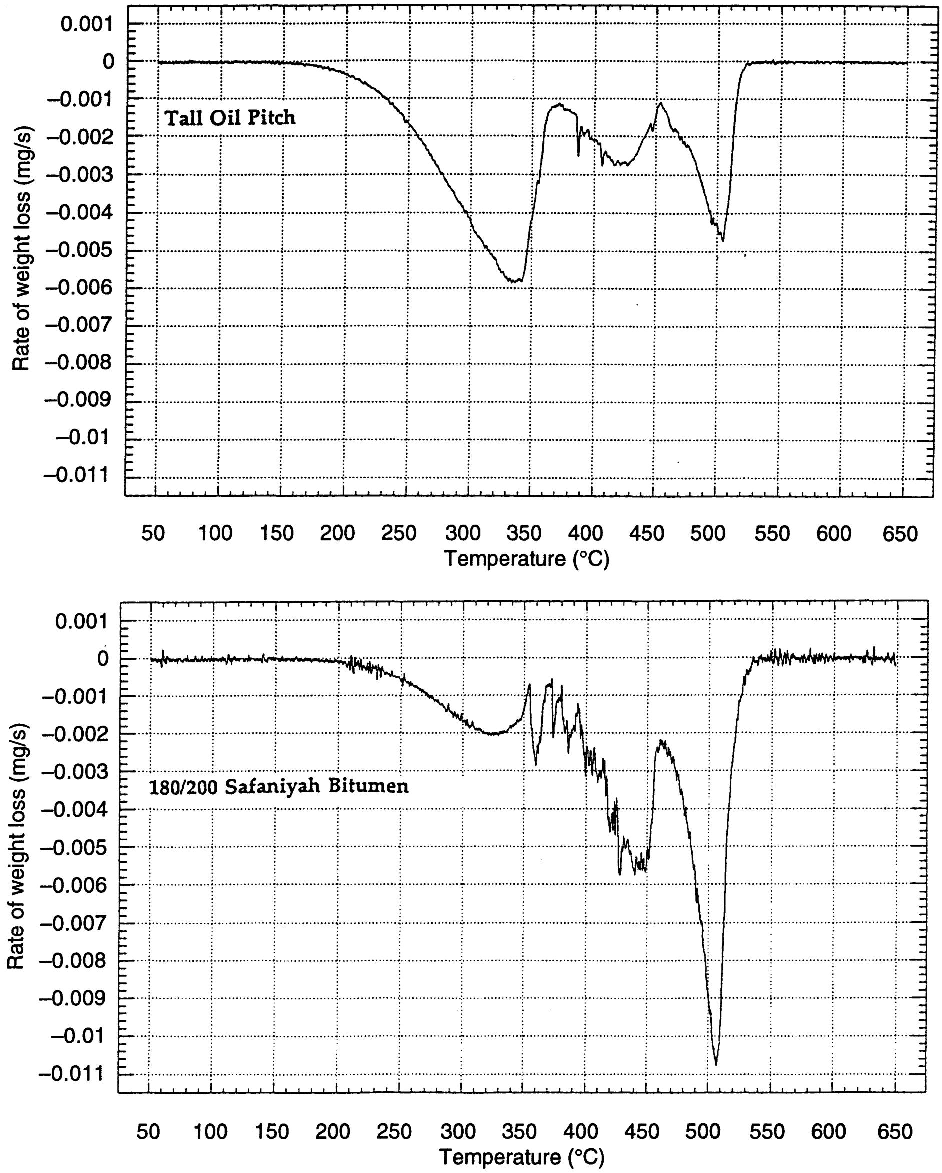

FIG. 2–First differentials of thermogravimetric curves for TOP and 180/200 Safaniyah bitumen.

a blend of 85% bitumen (94 penetration) and TOP (15%) was investigated by hot storage for 72 hours as described above; storage for longer than this is unlikely in practice. Infrared spectra (in duplicate) of the samples were compared using the ratio of peak heights at 1697 cm^{-1} and 1376 cm^{-1} as a measure of TOP concentration (Table 4). The ratios were indistinguishable within error, and indicated no separation of bitumen and TOP had occurred.

TABLE 4–Storage stability of TOP-bitumen blends

Sample (15% TOP, 85% pen. 94 bitumen)	Ratio 1697/1376 cm^{-1}		Mean
Bottom	2.713	2.719	2.72 ±0.04*
Middle	2.797	2.706	2.75 ±0.04
Top	2.761	2.740	2.75 ±0.04

* 95% confidence limits based on the pooled standard deviation of the replicates

All roading bitumen used in New Zealand is graded according to penetration value at 25°C (ASTM D5). The grades, as specified by Transit New Zealand, are 60/70 (penetration from 60 to 70 dmm), 80/100, and 180/200. A 45/55 bitumen is also supplied for blending with the softer 180/200 to produce the harder standard grades.

An 80/100 compound binder was produced by mixing TOP with a 45/55 bitumen and two 180/200 grade products were made by mixing TOP in different proportions with a 45/55 and an 80/100 bitumen.

The properties of the resulting blended binders were compared to standard bitumens of the same grade (Tables 2 and 3) using the specifications set out in Transit New Zealand Standard M/1 (1989). The rolling thin film oven procedure involves heating a thin film of binder @ 163°C for 85 minutes in an air stream, and approximately duplicates the hardening of the binder during asphalt manufacture. The procedure was carried out only on the 80/100 binders as 180/200 grade materials are not used in asphalt in New Zealand, and all products had no difficulty meeting the specification requirements.

For the 180/200 products the materials containing TOP had slightly higher viscosities than for the pure petroleum bitumen material. This result may be due as much to the temperature dependence of the viscosity of the bitumen components in the mixture (these bitumens, unlike the 180/200, contain air-blown material) as to that of the TOP.

The physical properties of the 80/100 petroleum bitumen and those of the TOP mixture showed close agreement. The retained oven penetration of the 80/100 mixture was almost identical to that of the standard 80/100 bitumen. TOP mixtures should thus be satisfactory for asphalt manufacture.

CONCLUSIONS

The tall oil pitch product blends satisfactorily with New Zealand petroleum bitumens in proportions of up to at least 31.5% by weight, to give products that meet the standard Transit New Zealand specifications. The pitch and bitumen do not separate with time, and the mixtures respond satisfactorily to the temperatures experienced in hot mix asphaltic concrete manufacture and in chipsealing with hot binders. TOP is presently approximately 28% cheaper per tonne than petroleum bitumen and would thus appear to have considerable potential as a bitumen extender. Further work is needed, however, to examine the effect of the pitch on the long-term age-hardening properties of bitumen. The high acid content of the pitch may also present problems when used in chipsealing. Fatty-amine-based "adhesion agents" are routinely added to chipsealing binders to promote binder stone chipping adhesion. As a result, carboxylic acid salts are likely to be formed when TOP acids are present. Although the salts are still active as adhesion promoters, at binder storage and application temperatures (130°–180°C) dehydration of the salt to give an inactive amide can occur. This effect would not be a problem in asphaltic concrete manufacture as, in New Zealand, amine-based adhesion agents are rarely used.

REFERENCES

ASTM 1992: "Annual Book of ASTM STandards, Section 4—Construction. Vol.04.03, Road and Paving Materials". American Society for Testing and Materials.

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

———1989b: Research into the physico-chemistry of tall oil pitch modified asphalt composites. Pp.391–8 *in* TAPPI Proceedings, International Symposium on Wood and Pulping Chemistry, North Carolina State University, Raleigh, North Carolina, United States.

———1992: Road aggregate choice based on silicate quality and bitumen adhesion. *Journal of Transportation Engineering 118(1)*: 50–61.

TRANSIT NEW ZEALAND 1989: "Specification for Asphalt Bitumens". Transit New Zealand Specification TNZ M/1 : 1989.