# RECYCLING OF WASTE OIL DISTILLATION BOTTOMS IN ASPHALT

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# RECYCLING OF WASTE OIL DISTILLATION BOTTOMS IN ASPHALT

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# EXECUTIVE SUMMARY

A field trial of hot mix asphalt using distillation residues was undertaken to investigate the potential for use, as bitumen extenders, of the vacuum distillation residues (called "waste oil distillation bottoms" or WODB), produced during the re-refining of waste lubricating oils.

In New Zealand WODB have little or no use and the problem of disposal affects the economics of the whole re-refining process. Dumping is wasteful and environmentally unsound and the high levels of lead and other metals in the residues prohibits their use as a fuel, because on combustion they release these pollutants to the atmosphere.

Roading bitumens in New Zealand are manufactured exclusively from imported crude oils. Partial substitution with WODB presents the prospect of financial benefits and in addition helps to eliminate a potential source of pollution.

The construction of the field trial is described. Three sections of hot mix asphalt pavement were laid at a site on a roundabout in Hamilton, New Zealand, in May 1991. The trial consisted of hot mix asphalt manufactured using 80/100 grade bitumen on a control section, and using blends of 180/200 bitumen with 9% and 20% of WODB respectively, air-blown to a nominal 80/100 grade penetration, on two sections. The physical and age-hardening properties of these binders were examined and found to be comparable to those of the control 80/100 bitumen.

The Marshall stability and flow of bitumen-WODB asphalt mixes were also satisfactory. Manufacture and construction of the trial was carried out using all three trial materials with conventional techniques without noticeable differences in handling and laying properties between control and WODB-blended mixes.

After 14 months (1.3 years) and again after 57 months (4.7 years) the three sections were compared. The hot mix asphalt in all three sections appeared to be performing well, with no evidence of surface deterioration, cracking or rutting. Cores were taken and the percentage air voids measured. These results showed considerable scatter, but provided no evidence for systematic differences in compaction. The binder from the cores was extracted, its viscosity measured and compared to that of the initial binders.

All the binders used showed the expected hardening caused by the pugmill. This hardening appeared to be somewhat greater for WODB-blended binders than that for the control, but the variability introduced by the recovery procedure casts doubt on this finding.

Because of the problems associated with the extraction and recovery of the blended binders and the imprecision of the results, binder viscosity is not considered worthwhile using in future studies on the condition of these trial asphalts. Tensile strength or resilient modulus measurements on the hot mix asphalt as a whole would be more appropriate.

The WODB were known to contain lead (from petrol additives) and metals from engine wear. After 57 months, analysis of lead, chromium and zinc contents of the hot mix asphalt in the trial sections showed that up to 25% of the zinc had been lost, while lead and chromium levels were similar (95% confidence level) to those initially present in the asphalt.

## ABSTRACT

A field trial of hot mix asphalt using distillation residues was undertaken to investigate the potential as bitumen extenders for use of the vacuum distillation residues (called "waste oil distillation bottoms" or WODB), produced during the re-refining of waste lubricating oils.

The construction of the field trial is described. Three sections of hot mix asphalt pavement were laid at a site on a roundabout in Hamilton, New Zealand, in May 1991. The trial consisted of hot mix asphalt manufactured using 80/100 grade bitumen on a control section, and using blends of 180/200 bitumen with 9% and 20% of WODB respectively, air-blown to a nominal 80/100 grade penetration, on two sections.

The physical properties of the mixers were monitored at 14 months (1.3 years) and after 57 months (4.7 years). The WODB-blended mixes did not show greater levels of surface deterioration, cracking or rutting compared to the control.

The WODB were known to contain lead (from petrol additives) and metals from engine wear. After 57 months, analysis of lead, chromium and zinc contents of the hot mix asphalt in the trial sections showed that up to 25% of the zinc had been lost, while lead and chromium levels were similar (95% confidence level) to those initially present in the asphalt.

# 1. INTRODUCTION

The trial evaluated in this report was constructed in May 1991 by Bitumix Ltd in conjunction with Works Central Laboratories (now Opus International Consultants Ltd). It was undertaken to investigate the potential, as bitumen extenders in road pavements, of the distillation residues or "bottoms" produced during the re-refining of waste motor-lubricating oils.

The re-refining process is by high temperature vacuum distillation (which is outlined in Appendix 1) and is carried out by the Dominion Oil Refining Co Ltd, Auckland. In New Zealand waste oil distillation bottoms (WODB) have little or no use and the problem of their disposal affects the economics of the whole re-refining process. Dumping is wasteful and environmentally unsound, and the high levels of lead and other metals in the residues prohibits their use as a fuel, because on combustion they release these pollutants to the atmosphere (J.O'Connor, pers.comm.).

Roading bitumens in New Zealand are manufactured exclusively from imported crude oils. Partial substitution with WODB presents the prospect of financial benefits and in addition helps to eliminate a potential source of pollution.

In the USA considerable quantities of distillation bottoms from re-refining operations are used as extenders of roofing bitumens. The equivalent application in roading is not widespread or at least has not been widely reported (Mohammed et al. 1984, Kim 1985, Swain 1980). Mohammed et al. (1984) have reported that paving grade bitumen (of 40/50 penetration grade) may be produced by blending high temperature (575°C and 550°C) vacuum-distillation residues from waste motor-lubricating oils, at 10% concentration with a 6 pen. base bitumen. This observation is, however, based only on softening point and penetration data.

A full laboratory study (Herrington 1991, 1992) has already been completed on the properties of simple and air-blown blends of the residues and 180/200 and 80/100 Safaniya bitumen. That research covered three main areas:

1. The physical and oxidative hardening properties of simple bitumen-WODB blends at low concentrations.

2. Simple blends at higher concentrations and the potential for converting 45/55 grade bitumen to 80/100, and 80/100 to 180/200 grades.

3. The use of an air-blowing process to eliminate problems associated with variability in the WODB and to produce an 80/100 grade binder.

The most promising line of investigation was the air-blowing of blends to produce 80/100 binders for use in asphalt manufacture.

That research also showed that 10% and, in some cases, 20% blends of 180/200 bitumen and WODB could be air-blown to give an 80/100 penetration binder that meets the physical requirements of the TNZ M/1:1995 *Specification for Asphaltic Bitumens* (Transit New Zealand 1995). The variation in initial viscosity found between batches of WODB is not removed however as, at the blowing temperature (240°C), the rate of oxidative hardening of the batches was also found to differ considerably. The blown blends had lower temperature susceptibilities than 80/100 bitumen at low temperatures but similar values between 70°C and 135°C.

As for the simple blends, the blown materials demonstrated conflicting durability characteristics. The rolling thin film oven (RTFO) residue ductility was, in most cases, below that specified in TNZ M/1:1995, but the retained penetrations were similar to 80/100 bitumen and within this standard specification.

Other data (retained penetration after RTFO, viscosity ratios, shear susceptibilities) also showed no significant difference in ageing properties between blended binders and the base bitumen. The durability characteristics of the trial binders are discussed in Section 2 of this report.

# 2. CONSTRUCTION OF TRIAL & INITIAL PROPERTIES OF MATERIALS

The trial was constructed in Hamilton, New Zealand, in May 1991. The only available site was a roundabout at the intersection of four streets: Peachgrove Road, Clarkin Road, Hukanui Road and Snell Drive (Figure 2.1). Although in many respects a roundabout and its approaches is not the ideal position for such a trial site, it does at least have the virtue of exposing the trial asphalts to high levels of stress, and possibly allowing the trial to be concluded more rapidly. Three sections of hot mix asphalt were laid for the trial, one as control and two with blends of bitumen and WODB.

WODB was blended at two concentrations, 9% and 20%, with 180/200 bitumen, and air-blown in an industrial still to produce a nominal 80/100 binder. Properties of the materials are given in Table 2.1.

Table 2.1 Physical properties of the initial materials and the blended binders.

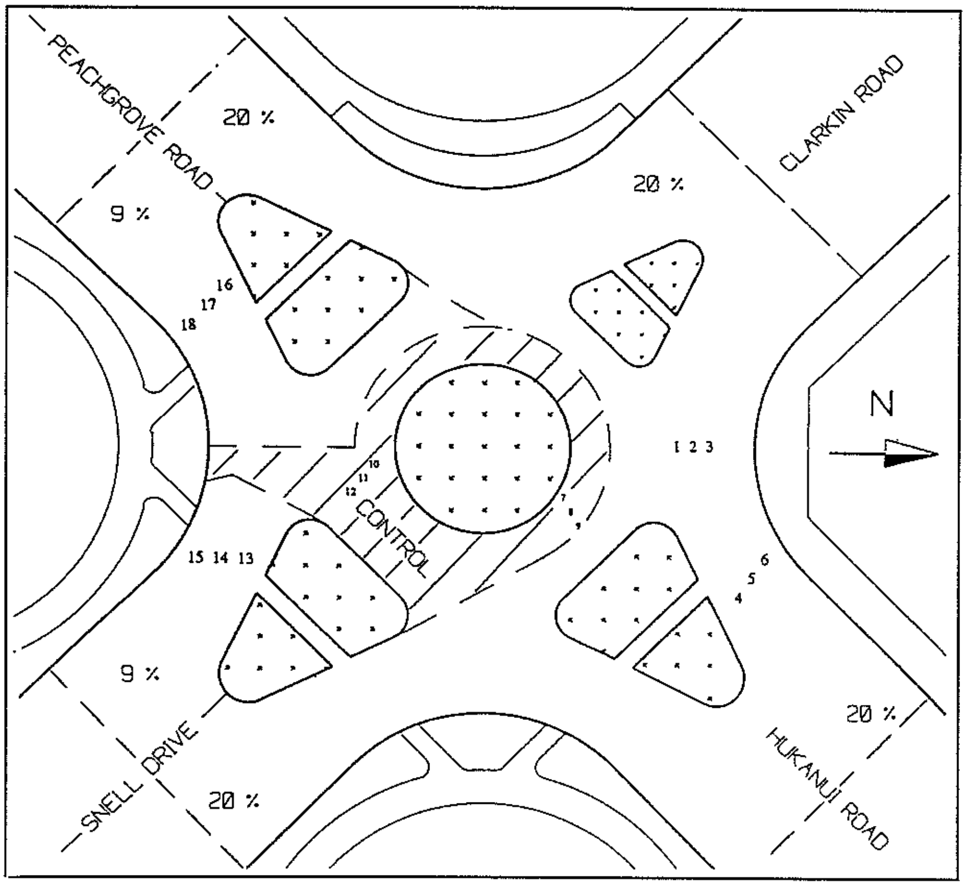
| **Material (% concentration by weight)** | **Penetration at 5°C (0.1 mm)** | **Penetration at 25°C (0.1 mm)** | **Softening point (°C)** | **Viscosity at 70°C (mPa.s)** | **Viscosity at 135°C (cSt)** | **Penetration index** |
|---|---|---|---|---|---|---|
| TNZ M/1 Specification for 80/100 grade | – | 80-100 | 45-52 | 40,000 minimum | 300-650 | – |
| WODB | – | – | – | 11,500 | 1,870 | – |
| 180/200* | 21 | 195 | 40.7 | 17,400 | 226 | –1.2 |
| 80/100** | 15 | 98 | 47.7 | 57,300 | 425 | –0.1 |
| 80/100-9% WODB | 23 | 100 | 49.8 | 86,200 | 575 | 1.6 |
| 80/100-20% WODB | 29 | 113 | 49.1 | 75,500 | 558 | 2.1 |

* This bitumen was blended with WODB and air-blown to nominal 80/100 grade

** This standard 80/100 bitumen was used as control

Conventional techniques and equipment were used. Mixing was carried out in a continuous pugmill at 163°C. The total mix laid was: 31 tonnes of Mix 10 (hot mix asphalt) complying with TNZ M/10:1975 *Specification for Asphaltic Concrete* (TNZ 1975) laid as a control; and the two trial mixes of 34 tonnes of 80/100 bitumen-9% WODB and 85 tonnes of 80/100 bitumen-20% WODB; all at a nominal thickness of 25 mm. Temperatures at laying were ~120°-140°C. No differences were observed between any of the three treatments with the exception of the 20% blend which was considered "lively" during compaction.

Figure 2.1 Trial site showing the three sections of different mixes (control, 9% and 20% WODB concentrations of asphalt mix binders), and locations of the sample cores (No. 1-18). Cores were taken for analysis at 14 months and at 57 months after construction of the trial.



However, examination of the data in Table 2.1 shows that, although the 20% blend has a high 25°C penetration, the 70°C and 135°C viscosities of the two blended binders are similar to one another. Apart from the 25°C penetration of the 20% blend, the other properties of the blended binders are within the relevant TNZ M/1 Specification. The measured flash point of the 20% blend was at 332°C.

From the Bitumen Test Data Chart in Figure 2.2 it is clear that, as was the case with laboratory scale air-blowing, the blends have a slightly lower temperature sensitivity than the 80/100 control bitumen in the low temperature region, but similar susceptibility (parallel slopes) in the 70°-135°C region.

Results of measurements made on the RTFO residues of the three trial binders are presented in Table 2.2. As found with laboratory-blended binders, the penetration of the residues retained are high, but the ductilities are low. Cone and plate viscosity measurements at 25°C of the same binders are presented in Table 2.3. The ratio of before and after viscosities ($\eta_R/\eta_O$) show that the relative increase in viscosity of the blended binders is apparently less than that of the 80/100 control. Given the error inherent in the measurement, it is perhaps safer to say that the increases in blend viscosity are, at least, not greater than the increase in viscosity of the control.

Figure 2.2 Bitumen test data chart for binders used in the field trial.

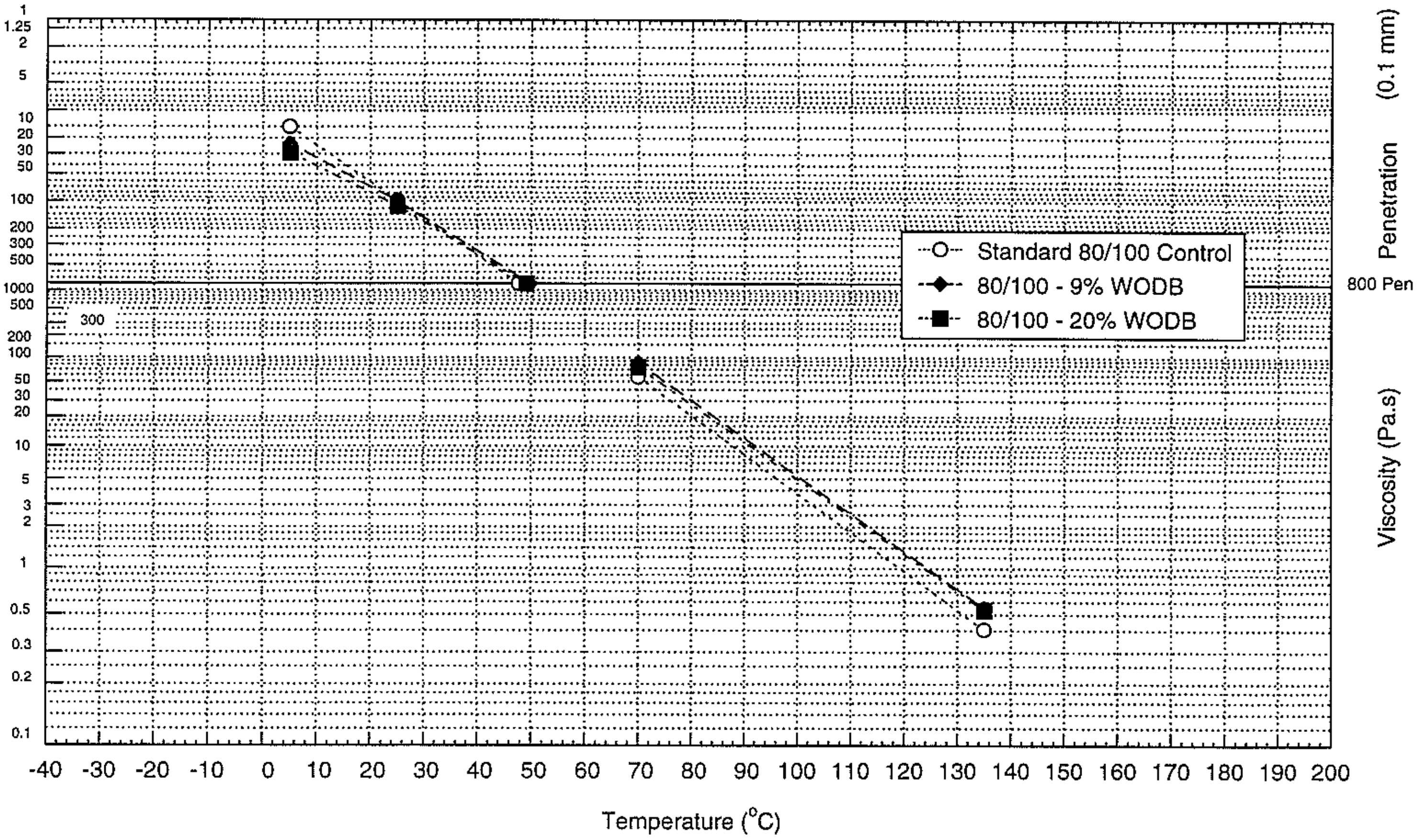


Table 2.2 Penetration and ductility properties of field trial binders after RTFO treatment.

| **Material (% concentration by weight)** | **Ductility (m)** | **Penetration at 5°C (0.1 mm)** | **Penetration at 25°C (0.1 mm)** | **% Pretreatment penetration (at 25°C) retained** | **Penetration index** |
|---|---|---|---|---|---|
| TNZ M/1 for 80/100 grade | 1.0+ | – | – | 50 minimum | – |
| 80/100 | 1.0+ | 11 | 55 | 56 | 0.9 |
| 80/100-9% WODB | 0.25 | 19 | 68 | 68 | 2.6 |
| 80/100-20% WODB | 0.29 | 22 | 85 | 71 | 2.2 |

Table 2.3 Viscosities of field trial binders after RTFO treatment.

| **Material (% concentration by weight)** | **Viscosity (η) at 25°C* (Pa.s)** | | **$\eta_R/\eta_O$**** |
|---|---|---|---|
| | **Before RTFO ($\eta_O$)** | **After RTFO ($\eta_R$)** | |
| 80/100 | 118,100 | 706,000 | 6.1 ±2 |
| 80/100-9% WODB | 216,900 | 419,800 | 1.9 ±2 |
| 80/100-20% WODB | 152,200 | 381,500 | 2.5 ±2 |

* By cone and plate viscometer, shear rate = 0.02 $s^{-1}$

** See Appendix 2 for explanation of errors

However, recent findings from research carried out for the project on non-volatile fluxes for chipsealing (Herrington et al. 1977) are consistent with the lower hardening rates observed in this trial. In that project, 3.0 mm films of simple blends of 10% WODB–180/200 Safaniya bitumen showed significantly reduced hardening rates compared to control samples after 3.3 years' oven ageing at 43 °C.

The observed low ductilities thus contradict the viscosity and retained penetration results. Ductilities can be affected by the presence of particulate matter which can cause premature breaking of the bitumen threads (Barth 1962). The presence of fine particulates (graphite-like dust) observed during solubility studies of bitumen-WODB blends (Herrington 1991) suggests that this mechanism may be operating. The WODB batch used in this trial, for example, had an ash (particulate) content of 14.4% w/w which is typical of WODB material.

Other circumstantial evidence casting doubt on the validity of the ductility results comes from the relationship established by Heukelom (1966) who found ductility to be inversely proportional to stiffness modulus for a large number of bitumens. Stiffness moduli were calculated for the 9% and 20% blends using the penetration index, and van der Poel's nomograph as modified by Heukelom (1966). The loading times used in the calculation were taken as the time of break in the ductility test. (Unfortunately it was not possible to carry out the calculation for 80/100 bitumen which had a ductility beyond the range of the instrument.) Using Figure 5 in Heukelom (1966), the expected ductility can however be estimated for a given stiffness modulus.

The stiffness modulus of the 9% and 20% blends at the time of break of the ductility are 0.02 MPa and 0.07 MPa respectively, giving expected ductilities of approximately 0.6 m and 0.9 m. These are considerably higher than the experimental values of 0.25 m and 0.29 m respectively. Thus there is some reason to suspect that the low ductilities that were measured may be anomalous.

Results of Marshall tests carried out on hot mix asphalt samples taken at the time of trial construction are presented in Table 2.4, and sieve analyses of the aggregates in the hot mix are given in Table 2.5. The results show all three mixes to be comparable, the only difference being a trend to slightly higher stabilities for the mixes with blended binders.

The trial showed that the manufacture and laying of hot mix asphalt using bitumen-WODB blends is perfectly feasible and requires no specialised techniques or equipment. However, as with the laboratory-blended materials, the low RTFO residue ductilities of the trial binders appears to be the major difficulty in meeting the requirements of TNZ M/1:1995.

Table 2. 4 Marshall test results* on field trial asphalts.

| Material (% concentration by weight) | Stability (kN) | Flow (mm) | Density (kg/m$^3$) | Theoretical maximum specific gravity | Air voids (%) | Bitumen content (% w/w) |
|---|---|---|---|---|---|---|
| 80/100 | 12.3 | 6.1 | 2371 | 2.418 | 1.7 | 6.5 |
| 80/100-9% WODB | 13.6 | 6.0 | 2371 | 2.415 | 1.5 | 6.3 |
| 80/100-20% WODB | 14.4 | 5.9 | 2347 | 2.409 | 2.3 | 6.4 |

* Each value given is the mean of three replicates

Table 2.5 Sieve analysis of aggregates used in field trial asphalts.

| Material (% concentration by weight) | Cumulative % passing specified sieve size (mm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 13.2 | 9.5 | 4.75 | 2.36 | 1.18 | 0.600 | 0.300 | 0.150 | 0.075 |
| 80/100 | 100 | 100 | 76 | 53 | 40 | 29 | 19 | 13 | 8.5 |
| 80/100-9% WODB | 100 | 99 | 78 | 57 | 42 | 30 | 20 | 13 | 8.6 |
| 80/100-20% WODB | 100 | 100 | 77 | 58 | 41 | 28 | 18 | 13 | 9.3 |

# 3. STATE OF THE TRIAL SECTIONS AFTER 14 MONTHS

Approximately 14 months (1.3 years) after construction, in June 1992, the site was inspected by walkover survey (Figures 3.1-3.3, p.19) and cores were taken from each of the three trial sections to measure air voids and viscosities.

## 3.1 Surface Condition

A walkover survey of the site revealed that the pavement surface was in good condition, with no variation apparent between the different mixes. The main irregularities in the pavement surface were in the joints. These were visible adjacent to service covers but not faulty (Figure 3.1). Some rutting is apparent in the 9% section, where rut depths of up to 4 mm were measured. Rutting in the other sections was minimal (1-2 mm depth). The absence of rutting may, in part, be related to the large size of the roundabout which enables traffic to deviate from well-defined wheel paths.

## 3.2 Air Voids

Six cores (100 mm diameter) were taken from each section, at the locations noted in Figure 2.1. The percentage air voids (voids in total mix) were determined according to *ASTM D3203-94* (ASTM 1997) using the theoretical maximum specific gravities given in Table 2.4. The results (Table 3.1) show considerable scatter. The 20% site shows particularly wide scatter, which is consistent with the "lively" character of the mix observed during compaction. Thickness of the cores ranged from 25-30 mm.

Table 3.1 Air voids (%) of cores from trial sections.

| **Trial Section** | | | | | |
|---|---|---|---|---|---|
| **80/100** | | **80/100 - 9% WODB** | | **80/100 - 20% WODB** | |
| **Core no.** | **% air voids** | **Core no.** | **% air voids** | **Core no.** | **% air voids** |
| 7 | 5.7 | 13 | 2.9 | 1 | 3.2 |
| 8 | 3.2 | 14 | 7.2 | 2 | 2.4 |
| 9 | 3.5 | 15 | 4.3 | 3 | 3.9 |
| 10 | 4.6 | 16 | 7.6 | 4 | 9.3 |
| 11 | 4.3 | 17 | 6.7 | 5 | 3.7 |
| 12 | 4.4 | 18 | 4.8 | 6 | 3.7 |
| *x* | 4.3 | *x* | 5.6 | *x* | 4.4 |
| *s* | 0.9 | *s* | 1.9 | *s* | 2.5 |

x mean

s standard deviation (see Appendix 2 for explanation of errors)

## 3.3 Binder Viscosities

A portion (~50 g) of three cores from each site were extracted with AR grade toluene, and the viscosities were measured according to the procedure given in Appendix 2 of this report. Figure 2.1 shows trial sections and locations of core samples.

The centrifugation step of the extraction procedure showed that large quantities of fine coke were present in the binders containing WODB: 1.8% w/w and 2.8% w/w of binder in the 9% and 20% WODB-bitumen blend sections respectively. As the process of recovery may have affected the viscosity of the binders, measurements were made on the original binders (not from the cores) before and after recovery. The results are presented in Table 3.2.

Table 3.2 Effect of the recovery process on binder viscosity at 25 °C (shear rate 0.1 $s^{-1}$).

| Viscosity Pa.s | | | | | |
|---|---|---|---|---|---|
| **80/100** | | **80/100 - 9% WODB** | | **80/100 - 20% WODB** | |
| **Before** | **After** | **Before** | **After** | **Before** | **After** |
| 112,761 | 229,874 | 133,257 | 172,616 | 96,962 | 95,433 |
| 101,214 | 157,885 | 151,126 | 121,523 | 109,348 | 100,110 |
| 129,363 | 177,791 | | | 91,340 | |
| 122,290 | | | | | |
| *Mean* 112,000 | 189,000 | 142,000 | 147,000 | 99,000 | 98,000 |
| $\eta_{before}$ 1.7 ±0.3* | | 1.0 ±0.3 | | 1.0 ±0.3 | |

* See Appendix 2 for explanation of errors

Unexpectedly the blended binders were relatively unaffected by the recovery process but the control had hardened noticeably. The scatter in the measured viscosities is somewhat larger than desirable, and can be attributed to variations in the amounts of the residual toluene in the sample from the recovery process.

The average viscosities of the extracted core binders after 14 months are compared to those of the binders extracted at the time the trial was laid and listed in Table 3.3.

Table 3.3 Average viscosity of core binders recovered after 14 months compared to initial binders.

| **Trial Section** | **Viscosity at 25°C (0.1 $s^{-1}$) (Pa.s)** | | |
|---|---|---|---|
| | **Initial binder (0 months)** | **Core binder (14 months)** | $\eta_{core}/\eta_{original}$ |
| 80/100 | 189,000 | 286,000 | 1.5 ±0.5* |
| 80/100-9%WODB | 147,000 | 306,000 | 2.1 ±0.5 |
| 80/100-20%WODB | 98,000 | 371,000 | 3.8 ±0.5 |

* See Appendix 2 for explanation of errors

From the values of the $\eta_{core}/\eta_{original}$ ratios in Table 3.3, hardening in the pugmill appears to increase with the concentration of WODB. However, given the variability introduced to the viscosity measurements by the recovery process, the results must be viewed with caution, especially as they tend to contradict the RTFO results in Tables 2.2 and 2.3.

# 4. STATE OF THE TRIAL SECTIONS AFTER 57 MONTHS

In January 1996, 57 months (4.7 years) after construction, the site was again inspected (Figures 4.1-4.3, p.20), and cores were taken from the three trial sections. Results of rutting and sand circle measurements that had been made at the site in June 1994 (38 months later) are also discussed in this Section of the report.

## 4.1 Surface Condition

The walkover inspection of the site in January 1996 showed the asphalt in all three sections (control, 9%, 20%) to be in generally good condition. No significant differences between the three sections were apparent except that the control was slightly lighter in colour. The surface was smooth in appearance, but showed a constant matrix of aggregate. The site and three sections, and locations of the 18 core samples are shown in Figure 2.1.

Rutting depths have not increased markedly compared to those measured in 1994. Wheeltrack rutting measurements made over the course of the trial are compared in Table 4.1.

Table 4.1 Measurements of rut depths in wheeltracks made over the course of the trial.

| **Trial Section** | **Rut depth (mm mean ±2σ) *** | | |
|---|---|---|---|
| | **June 1992 (14 months)** | **June 1994 (38 months)** | **January 1996 (57 months)** |
| 80/100 control | 0.9 ±0.6 | 1.4 ±3.2 | 2.3 ±3.3 |
| 80/100 - 9% WODB | 2.0 ±3.0 | 0.8 ±1.7 | 1.75 ±1.0 |
| 80/100 - 20% WODB | 1.1 ±1.0 | 1.8 ±5.7 | 0.8 ±3.5 |

* See Appendix 2 for explanation of errors

Sand circles measured in June 1994, 38 months after construction (Table 4.2), showed no significant difference in surface texture between the three sites.

Table 4.2 Surface texture measured by sand circle method, in June 1994.

| **Trial Section** | **Sand circle diameter (mm)** | | | | | | **Mean ±2σ *** |
|---|---|---|---|---|---|---|---|
| 80/100 control | 320W | 355W | 315 | | | | 330 ±44 |
| 80/100 - 9% WODB | 335W | 335 | 325W | | | | 332 ±12 |
| 80/100 - 20% WODB | 330W | 335 | 320W | 335 | 310W | 390W | 350 ±63 |

W Wheeltrack

* See Appendix 2 for explanation of errors

Figure 3.1 Centre of roundabout showing 20% WODB section (foreground) and control section adjacent to roundabout hub, at beginning of trial.

Figure 3.2 Detail of surface of 20% WODB section (foreground) and control section (top right corner) at beginning of trial.

Figure 3.3 Detail of surface of 20% WODB section at beginning of trial.

Figure 4.1 Surface texture of the control section after 57 months.

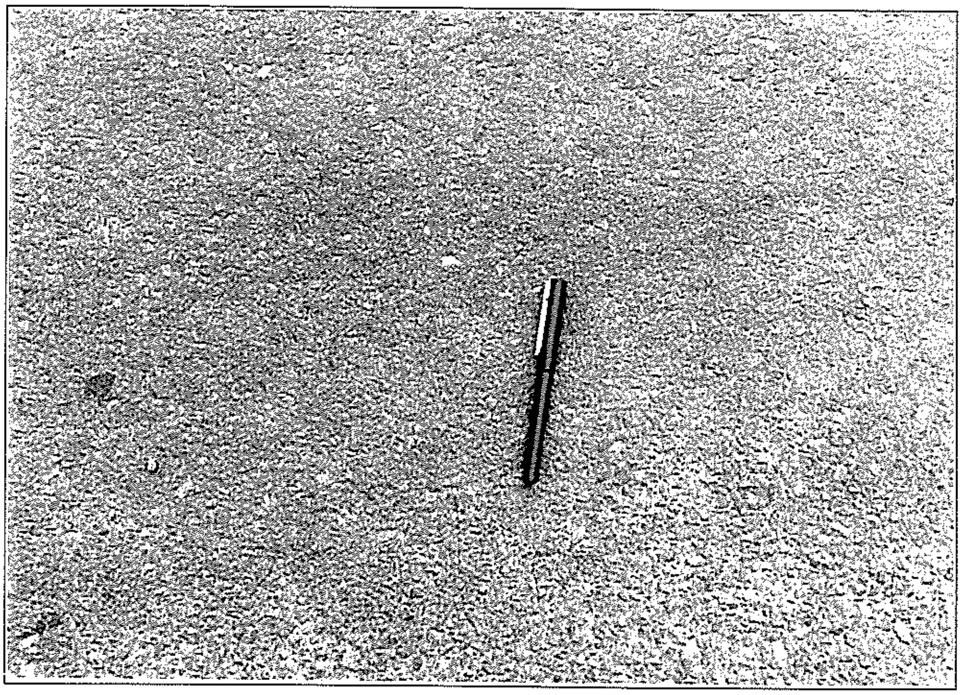


Figure 4.2 Surface texture of 20% WODB section after 57 months.

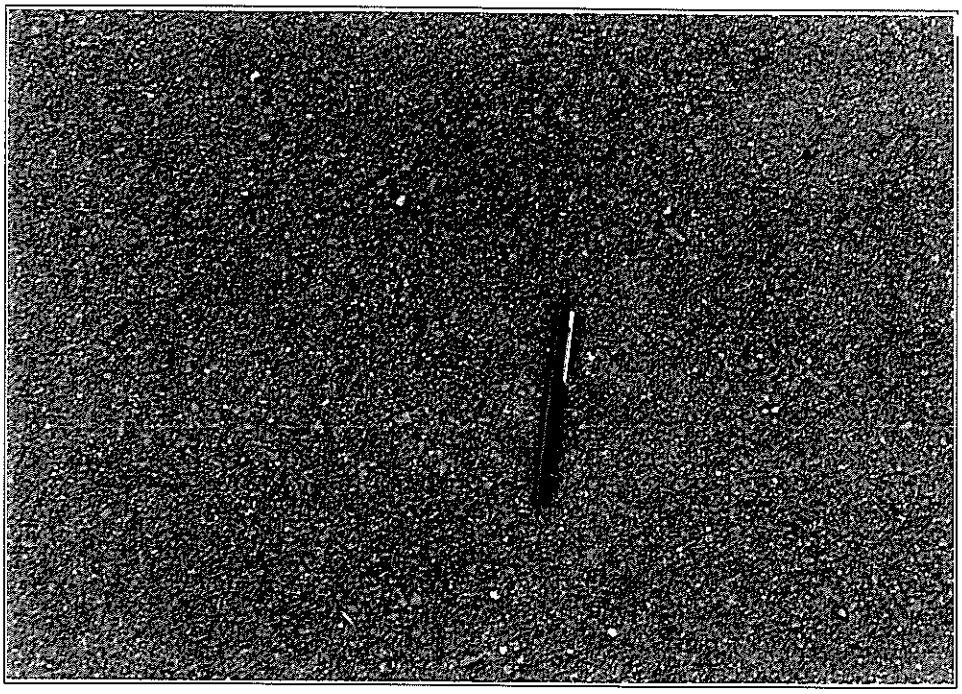
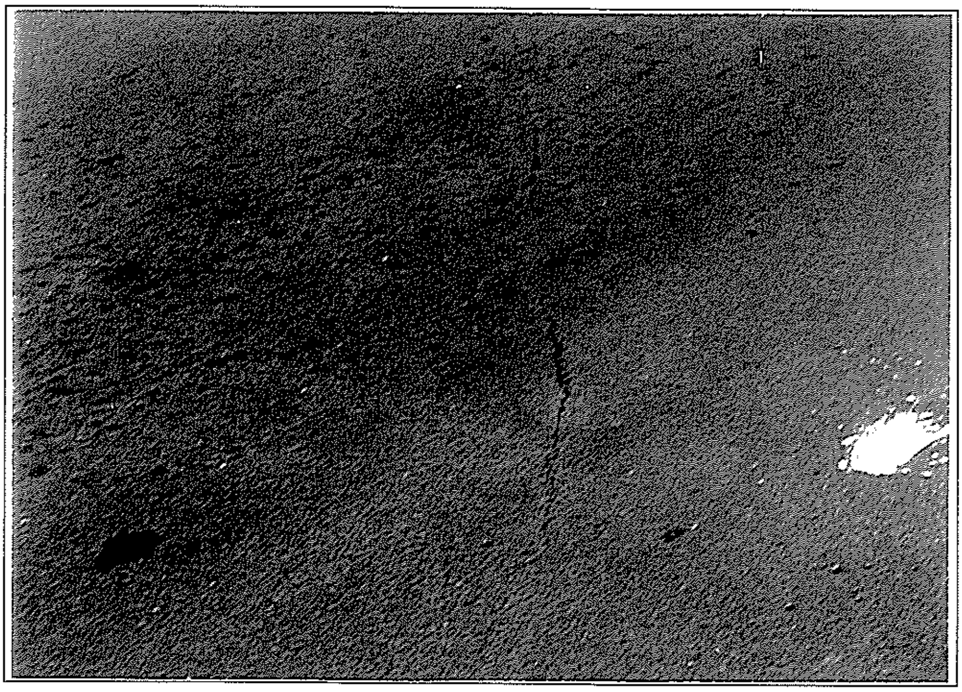


Figure 4.3 Transverse and longitudinal joint between the 9% WODB section (on left) and control section (on right) after 57 months.



## 4.2 Binder Viscosities

Cores were taken from the locations shown in Figure 2.1, and the binder was extracted and recovered as described in Appendix 2 of this report. The binders from the six cores from each trial section were mixed and the viscosities measured (Table 4.3). In 1966 viscosities were measured at 45°C, and not at 25°C which was the temperature used in 1992 at the time of the 14 month inspection (Section 3.3 in this report). The higher temperature was used because a more precise residual toluene correction curve (based on 45°C viscosity data) had been developed at Central Laboratories in late 1992.

Table 4.3 Viscosities of binders in cores recovered after 57 months (to January 1996), compared to viscosities of the initial binder (laid in May 1991).

| **Trial Section** | **Viscosity (0.05 $s^{-1}$) (Pa.s) after 57 months** | | **Relative viscosity** (14 months)†** | **Relative viscosity*** (initial)†** |
|---|---|---|---|---|
| | **Core binder** | **Relative viscosity*†** | | |
| 80/100 | 12,400 | 1.0 ±0.1 | 1.0 ±0.3 | 1.0 ±0.3 |
| 80/100 - 9% WODB | 149,800 | 16 ±1.6 | 1.1 ±0.3 | 0.8 ±0.2 |
| 80/100 - 20% WODB | 32,000 | 2.6 ±0.3 | 1.3 ±0.4 | 0.5 ±0.2 |

* Viscosity relative to control at 45°C

** Viscosity relative to control for binders (measured at 25°C, see Table 3.3 in this report)

*** Viscosity of original binders relative to control (measured at 25°C, see Table 3.3 in this report)

† See Appendix 2 for explanation of errors

The data in Table 4.3 indicate that the WODB-modified binders after 57 months are hardening significantly faster than the control 80/100 binder. However the rates of hardening are inconsistent with the 14 month results. This inconsistency may be due to the relatively small change in viscosity which had taken place in that period. The 57 month results are also inconsistent with the RTFO measurements made on the initial binders (Table 2.2) and, as well, they are not supported by the results of the non-volatile flux for chipsealing project (Herrington et al. 1997) discussed in Section 2 of this report.

An explanation for these apparent contradictions may lie in the differences in the air voids which are apparent between the three sites (Table 3.1). Higher levels of air voids allow greater ingress of oxygen and hence faster oxidation rates. The 9% site has the highest percentage air voids and the fastest hardening rate. The control and 20% sections have similar average air void levels, but the range in voids is much greater for the 20% section with levels as high as 9.3%.

Therefore in order to obtain meaningful binder hardening rates, the effect of air voids must be considered more carefully.

# 5. LEACHING OF CONTAMINANTS

WODB from the re-refining of waste oils contain various levels of lead, chromium, zinc, and other metals arising from engine wear, and from petrol and oil additives (Table 5.1). Earlier work on WODB showed metal levels to be extremely variable, depending on the source of the waste oil. Of particular concern in the early work on the WODB were the high levels of lead present - up to 30,000 mg/kg (3% w/w). The lead was found to be in an insoluble form, being tightly bound to fine coke particles. The possibility of lead and other metals being leached from the asphalt by rainwater was investigated in the laboratory (Dravitzki et al. 1993, Herrington et al. 1993). WODB-bitumen blends (5% and 20% w/w with ~900 and 3600 mg/kg lead respectively) were prepared as thin films and photo-oxidised under UV lamps. Periodic washing and gentle brushing of the surface showed that no significant leaching was occurring.

High levels of lead in the WODB will no longer occur since the removal of leaded petrol from the market. However other metals that are potential pollutants are present in reasonably high concentrations, in particular zinc.

Table 5.1 Levels of metallic contaminants that are typical in WODB (Herrington et al. 1993).

| **Element** | **Concentration (mg/kg)** | **Element** | **Concentration (mg/kg)** |
|---|---|---|---|
| Lead | 29,000 | Aluminium | 120 |
| Sulphur | 22,200 | Chromium | 46 |
| Calcium | 7,300 | Tin | 38 |
| Phosphorus | 5,400 | Manganese | 32 |
| Zinc | 4,300 | Molybdenum | 15 |
| Iron | 1,100 | Nickel | 14 |
| Magnesium | 1,000 | Titanium | 11 |
| Barium | 580 | Cadmium | 5.6 |
| Copper | 190 | Vanadium | 1.1 |
| Silicon | 160 | Silver | 0.7 |
| Boron | 140 | | |

The potential leaching of metals from the trial sections at Hamilton was investigated by the analysis of cores taken from each of the trial sites. As samples of the initial core binders had been retained, a comparison of metal contents present in the initial binder with 57 month-old asphalt was possible. This method was considered superior to the alternative approach of attempting to trap and collect water run-off over a prolonged period. Details of the analysis procedures are given in Appendix 2 of this report.

Results of the metals analysis are given in Table 5.2 and Figures 5.1-5.2. Mean values for each metal at each site were compared to the "true" mean (obtained from the laboratory-prepared mixes) using Students t-test. In all cases except one the metal contents of the cores are not significantly different (95% level) from the expected values. The exception is the level of zinc at the 9% site which is significantly different from that originally present. Examination of Figure 5.2 shows that zinc concentration at the 20% trial section is also low, though the scatter of results is greater than at the 9% trial section.

Table 5.2 Concentrations of lead, chromium and zinc in core samples from field trial sections.

| Trial Section | Core Sample No. | Lead | | Chromium | | Zinc | |
|---|---|---|---|---|---|---|---|
| | | Conc. (mg/kg) | % original level | Conc. (mg/kg) | % original level | Conc. (mg/kg) | % original level |
| 80/100 control | 7 | 21.7 | 118.6 | 30.9 | 97.8 | 53.0 | 103.6 |
| | 8 | 16.4 | 89.3 | 27.2 | 85.0 | 50.1 | 98.0 |
| | 9 | 16.2 | 88.3 | 30.0 | 94.8 | 51.4 | 100.6 |
| | 10 | 18.0 | 98.5 | 30.9 | 97.8 | 51.1 | 100.1 |
| | 11 | 24.4 | 133.5 | 31.9 | 100.8 | 52.1 | 101.9 |
| | 12 | 13.4 | 72.9 | 32.8 | 103.7 | 51.0 | 99.8 |
| *Mean* | *7-12* | *18.3* | *100.2* | *30.6* | *96.8* | *51.4* | *100.7* |
| 80/100-9% WODB | 13 | 136.8 | 93.9 | 32.0 | 112.2 | 82.7 | 72.7 |
| | 14 | 152.6 | 104.7 | 32.0 | 115.5 | 88.2 | 77.5 |
| | 15 | 154.0 | 105.7 | 31.9 | 112.0 | 82.7 | 72.7 |
| | 16 | 138.0 | 94.7 | 30.1 | 105.6 | 84.0 | 73.8 |
| | 17 | 163.1 | 112.0 | 31.9 | 112.0 | 78.0 | 68.6 |
| | 18 | 180.0 | 123.5 | 33.9 | 118.8 | 81.2 | 71.4 |
| *Mean* | *13-18* | *154.1* | *105.8* | *32.0* | *112.7* | *82.8* | *72.8* |
| 80/100-20% WODB | 1 | 165.9 | 107.0 | 32.8 | 104.9 | 93.2 | 78.5 |
| | 2 | 165.5 | 106.8 | 30.0 | 95.9 | 90.1 | 75.9 |
| | 3 | 170.3 | 109.9 | 32.9 | 105.0 | 86.9 | 73.2 |
| | 4 | 160.3 | 103.4 | 31.0 | 99.1 | 88.7 | 74.7 |
| | 5 | 152.6 | 98.5 | 31.0 | 98.9 | 110.3 | 92.9 |
| | 6 | 162.7 | 104.9 | 32.0 | 102.1 | 94.1 | 79.2 |
| *Mean* | *1-6* | *162.9* | *105.1* | *31.6* | *102.0* | *93.9* | *75.9* |

This result contradicts the findings of the earlier leaching study discussed above (Dravitzki et al. 1993, Herrington et al. 1993). A possible explanation is that the rate of the leaching process was too slow to be observed in the laboratory study. Alternatively, factors not allowed for in the laboratory study may be influencing the rate of zinc loss from the field trial. Because of the apparently water-impermeable nature of the binders, the leaching process of metals from the trial has been assumed to be principally mechanical abrasion of the binder surface, but other mechanisms may also be operating.

Figure 5.1 Metal concentrations (mg/kg) of cores from field trial sections.

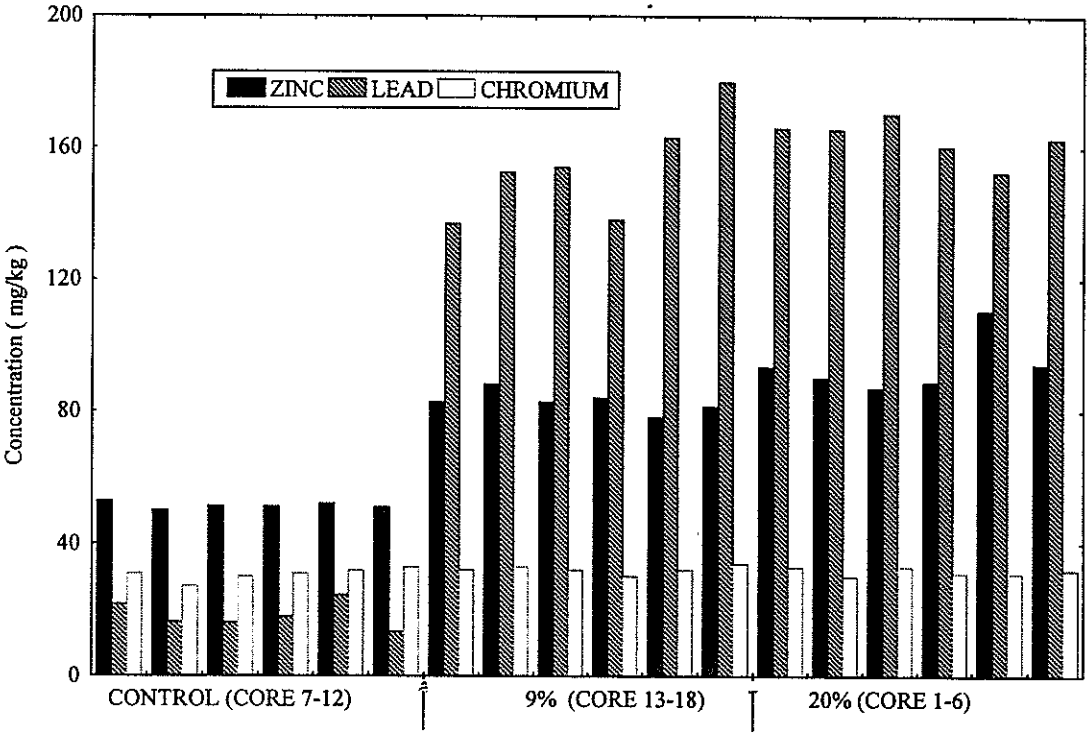
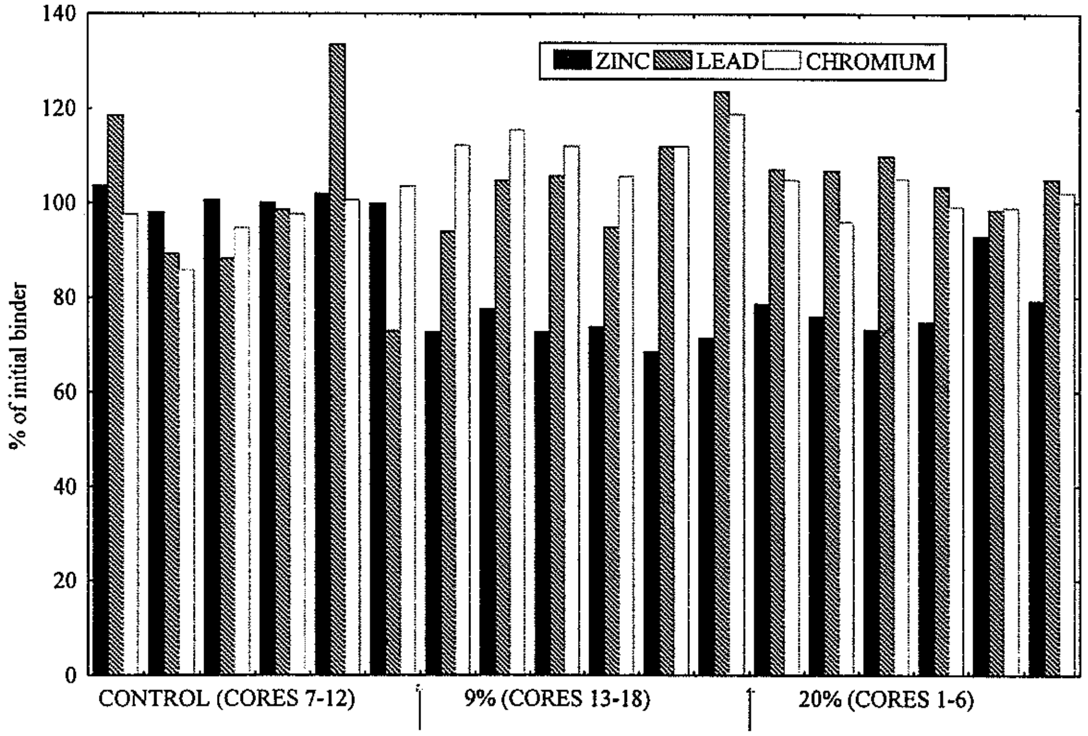


Figure 5.2 Metal concentrations of cores from field trial sections, expressed as % of concentrations present in initial bitumen binder.



# 6. CONCLUSIONS

Both the control and WODB-blended binder sections in the trial were performing well at the conclusion of the trial (1996), and cannot be differentiated visually or by presence of rutting. The viscosity of the binders recovered from the asphalt mix core samples appeared to indicate increased hardening of the binders containing WODB. This contradicts the results of the RTFO experiments (discussed in Section 2 of this report) and independent research findings. It is possible that the WODB behave differently in the presence of aggregates, which may be related to the catalytic effects on the mineral surfaces. The viscosity data should be viewed with caution however, because the recovery process alters the composition of the blended binders (i.e. it removes coke) and also the quantity of residual toluene is variable. The magnitude of the effects of this residual toluene on the viscosity of this type of binder is unknown.

Although some of these problems could well be resolved, the effort involved is probably not warranted. A better, although more time-consuming, approach would be to measure the physical properties of the hot mix asphalt as a whole using, if feasible, resilient modulus or tensile strength measurements.

Measurement of metal concentrations in the trial sections showed that, with the exception of zinc, no significant leaching or mechanical loss had taken place. Up to 25% of the original zinc has been lost from both the 9% and 20% trial sections, which contradicts an earlier laboratory study which showed that no significant leaching occurs. One possible explanation is that the rate of the zinc leaching process was too slow to be observed in the laboratory despite attempting to accelerate the process using photo-oxidation, water washing, and mechanical abrasion. Further monitoring of the trial, including annual walkover surveys, rutting measurements and physical measurements on core samples, is recommended.

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# APPENDIX 1. WASTE OIL RE-REFINING PROCESS.

The re-refining process of waste motor-lubricating oil that is used by the Dominion Oil Refining Company, Auckland, is based on a high-temperature vacuum-distillation as opposed to the older, less efficient, acid-clay type process (Linnard & Henton 1979, Whisman et al. 1974). As some aspects of the plant's operation are proprietary information, only a brief outline of the process can be given here.

The crude waste oil is allowed to settle at ambient temperature in large ($\sim 10^5$ ℓ) storage tanks where heavy insolubles and free (un-emulsified) water separate. Further drying is achieved by heating to 150°C under a slight vacuum (~400 mbar). This step removes any petrol and solvent contamination. After further treatment, an initial distillation at 180°-190°C and 400 mbar removes the "light ends" (fractions) which are collected and used as a fuel. A diesel cut is taken from the waste oil by distillation at 250°C and ~60 mbar vacuum. The final distillation is carried out at 340°-370°C at 3-6 mbar vacuum. The residues from this stage are the "waste oil distillation bottoms" used in the present research and recorded in this report.

# APPENDIX 2. EXPERIMENTAL PROCEDURES

## A2.1 Extraction and Recovery of Core Binders

The core sample to be extracted was dissolved in AR grade toluene. The dissolved bitumen was decanted from the aggregate which was then extracted with two further volumes of toluene. The combined extract (~250 ml) was centrifuged to separate remaining fine aggregates, and filtered through a Whatman grade GF/C glass fibre filter. Finally the bitumen was recovered using a rotary evaporator. The following procedure was used.

The bulk of the solvent was removed at 60°C temperature and >710mm Hg pressure. The remaining solvent was removed at 135°C and >710mm Hg using the sequence: 15 minutes under vacuum, 2 minutes purging of the flask with nitrogen (2 ℓ /min.), 15 minutes under vacuum, 2 minutes purging, and finally 15 minutes under vacuum.

Viscosity ratios are quoted as ± two standard deviations based on a large number of similar measurements made earlier in this laboratory (Central Laboratories).

Rut depth and sand circle data are quoted as ± two standard deviations based on replicate measurements made on the trial sites.

## A2.2 Viscosity Measurement

Binder viscosities in Tables 3.2 and 3.3 were measured using a Cannon Instrument Company cone and plate viscometer according to *ASTM D3205-86* (ASTM 1997). Duplicate (as a minimum) measurements were made and the averages taken. Data were not corrected for residual traces of toluene (extraction solvent) which, as measured by thermogravimetry (see below), lie in the 0-0.5% w/w range. Precision of the viscosity values given is ±15% ($\sigma$).

Viscosity measurements at 45°C (Table 4.3) were performed in 1996, 57 months after construction, on a Carrimed CSL 500 rheometer using a cone and plate geometry. Samples were annealed between the plates at 90°C for 10 minutes before equilibration (30 minutes) at 45°C. Data were corrected for residual toluene content (see A2.3 of this Appendix), and the averages of duplicate measurements were reported. Precision of the viscosity values given is ±5% ($\sigma$).

## A2.3 Toluene Correction

Residual levels of toluene remain in the recovered binders after the procedure described in A2.1 of this Appendix. Levels of toluene are measured using a Mettler TA 3000 thermogravimetric apparatus (Donbavand 1985) with the conditions below:

Crucible: platinum
Sample size: 10-15 mg
Atmosphere: dry air
Temperature programme:

1. 35 °C to 163 °C at rate of temperature increase of 20 °C per minute,
2. Hold at 163 °C for 150 minutes,
3. 163 °C to 650 °C at rate of 20 °C per minute.

Weight loss at step 2 (corrected for buoyancy and ash content from step 3) is reported as % w/w residual toluene. Loss of bitumen volatiles at 163 °C has been found to be negligible (<0.1%).

Measured viscosities are corrected using an empirical calibration equation:

$$\log_{10}\log_{10}\eta_c = \left(1 + \frac{T}{100}\right)\log_{10}\log_{10}\eta_m + 0.028655\ T$$

where $T$ = toluene content (pph)
$\eta_m$ = measured 45 °C viscosity
$\eta_c$ = corrected 45 °C viscosity

## A2.4 Analysis of Asphalt Cores for Chromium, Lead and Zinc

The unavailability of a cryogenic mill to grind the whole cores meant that bitumen and aggregates needed to be analysed separately. The cores were extracted with AR grade toluene using the continuous centrifuge method. Special care was taken during all phases of both the coring and extraction procedures to avoid external contamination or sample losses. Toluene was removed by the process outlined in A2.1 of this Appendix, and binder and aggregate were analysed for lead, chromium and zinc contents by X-ray fluorescence at Spectrachem Analytical Laboratories Ltd (Lower Hutt). Traceable metal-oil standards were used for calibration of the instrument.

To account for any systematic losses or errors in the procedure, artificial asphalt mixtures were prepared using samples retained of the initial trial binders and local aggregate graded similarly to those used in the trial. These mixtures were then extracted and analysed in an identical fashion to the trial cores.

A graded but unmixed aggregate sample was analysed and showed initial levels that were slightly higher than those in the trial control core aggregates. The difference for each metal was subtracted from the measured artificial mix aggregate concentration to arrive at corrected values used in subsequent calculations.

For both the trial core samples and the artificial mixes, the total metal content was calculated using the binder contents.