Development of a Durability Test for Bitumens used on New Zealand Roads

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Contents

List of Figures

List of Tables

Executive Summary

1. Introduction

This report describes the development, between 1997 and 1999, of a test procedure for assessing the long-term durability of bitumen used in chipseals on New Zealand roads. In its final form, the test will be incorporated in the Transit New Zealand Specification TNZ M/1 *Specification for Roading Bitumens*. The test procedure is *Opus International Consultants Central Laboratories Test Method No. B309-99,* and is given in the appendix to the report.

The proposed test is two tiered:

- An **acceptance test** to be used for initial assessment of bitumens not currently approved by Transit New Zealand (Transit). This test would also be applied to approved bitumens if a significant change in a production route occurs. The test would need to be carried out only once, at the time of the introduction of a new bitumen (assuming a consistent crude source and production route). It provides an indication of the durability behaviour of the bitumen at road temperatures.

- A **quality assurance test** for quality control purposes, to be used to monitor consistency of durability. This test is a simplified version of the acceptance test and is much quicker to carry out. It would be carried out at intervals for "batch to batch" quality control, and the results would be compared to the initial test result.

2. Acceptance Test

The essential aspects of this test are as follows:
Thin films (1.0 mm) of the bitumen under investigation are oxidised at 60°C under 2,069 kPa (300 psi) of air. At intervals samples are removed and the shear modulus at 5°C and 9 Hz measured. An equation is fitted to the modulus versus time plot obtained. The test bitumen fails the test if the limiting slope or intercept of the fitted equation is greater than that of Safaniya bitumen of the appropriate grade.

Features of the proposed test are:

- High pressure air is used to accelerate the process.
- A test temperature is used that is close to ambient conditions.
- The extent of oxidation is measured in a way that is relevant to field conditions.
- Durability is assessed on the basis of the long-term rate of oxidation.

To make such a comparison an equation describing the dynamic shear modulus $|G^*|$ as the measure of the extent of oxidation is used:

$$\Delta\,(\log|G^*|) = P\,(1-\exp(-K_f t)) + Kt$$

where: $\Delta\,(\log|G^*|)$ = increase in the log of the modulus
P = constant
K_f, K = constants related to reaction rate

As time increases ($t \rightarrow \infty$), the term $\exp(-K_f t) \rightarrow 0$, and the equation becomes:

$$\Delta\,(\log|G^*|) = P + Kt$$

The suggested pass/fail criteria for the test are that a bitumen would fail unless the fitted constants P and K were less than or equal to those of the appropriate grade of Safaniya bitumen.

3. Quality Assurance Test

The quality assurance test was developed to provide a simple and rapid means of comparing batch to batch consistency of bitumen durability.

The temperature and duration of this test were chosen for convenience and quick turn around, using the same apparatus as the acceptance test. Also the option of using modulus or viscosity to measure extent of oxidation avoids the need to have access to a dynamic shear rheometer.

The method is to oxidise a thin film (1.0 mm) of bitumen at 80°C under 2,069 kPa (300 psi) of air for 48 hours and to measure the modulus at 5°C and 9 Hz. The modulus value is first obtained using the same sample of bitumen as that used in the acceptance test and is then used as a benchmark for future test results. If subsequent tests give a modulus result greater than the benchmark, the bitumen is deemed not to have passed the test. For the greatest utility, provision has been made to allow the conditions of the test to be altered to suit particular circumstances (given in the appendix to the report).

4. Recommendations

The following recommendations are made.

- *Opus CL Test Method No. B309-99* to be specified in *TNZ M/1 Specification* so that the in-service durability performance of a bitumen can be assessed, and thus provide the requirement for such information.

- The method to be used for:
  - assessing the long-term durability of bitumens obtained from new sources or new production routes, and
  - routine checking, for quality assurance, of the durability of different production batches or shipments of bitumen.

- The inter-laboratory reproducibility of the test method should be determined.

- Values of the constants P and K should be determined for 60/70 and 130/150 bitumen grades.

- The practical performance and suitability of the test for its intended purpose should be reviewed after a fixed period (say 2 years).

Abstract

A test procedure to measure the long-term durability of bitumens used in chipseals on New Zealand roads is described. The proposed test *(Opus International Consultants Central Laboratories Test Method No. B309-99)* is two tiered, consisting of an *acceptance test*, used for initial assessment of new bitumens being introduced to the market, and a simpler *quality assurance test* for "batch to batch" quality control testing. In the acceptance test procedure, high pressure air (at 2,069 kPa or 300 psi) at 60°C is used to oxidise 1.0 mm films of bitumen. The modulus $|G^*|$, measured at 5°C and 9 Hz, using a dynamic shear rheometer, is used as a measure of the extent of oxidation. The frequency of 9 Hz was selected as representative of that experienced by bitumens in the field.

An equation is fitted to the modulus data as follows:

$$\Delta (\log |G^*|) = P (1-\exp(-K_f t)) + K t$$

where: $\Delta (\log |G^*|)$ = increase in the log of the modulus
P, K_f, K = constants

To assess durability, the constants P and K are compared to those obtained for standard Safaniya bitumens of the appropriate grade.

The conditions used in the quality assurance test are the same as that used in the acceptance test except that the test temperature is 80°C and the (suggested) test duration is 48 hours. The extent of oxidation is measured by the increase in modulus (or viscosity) and is compared to benchmark data for that bitumen. The test methods are given in the appendix to the report.

1. Introduction

This report describes the development of a test procedure for assessing the long-term durability of bitumen used in chipseals on New Zealand roads. In its final form, the test will be incorporated in the Transit New Zealand (Transit) *TNZ M/1 Specification for roading bitumens.* The research was carried out between 1997 and 1999.

The approach taken in developing the test is discussed in section 2 of this report, the experimental work and analysis used to assess and validate this approach is described in sections 3, 4 and 5. A detailed description of the proposed test *(Opus International Consultants Central Laboratories (Opus CL) Test Method No. B309-99)*, is given in the appendix.

1.1 Need for a Durability Test

Petroleum bitumens oxidise through reaction with atmospheric oxygen. The effect of oxidation is to increase the viscosity of the bitumen, resulting in a greater likelihood that seals will crack or lose chip (scabbing). Oxidation of the bitumen is one of the major factors limiting the lifetime of a well-constructed chipseal. Thus the use of bitumens of poor durability would lead to reduction in average seal lifetimes.

The oxidation susceptibility of bitumens can vary significantly, depending on the crude oil from which they are manufactured and the refinery production route. Test procedures are needed to evaluate the oxidation behaviour (durability) of new bitumens being introduced to New Zealand, or of bitumens obtained by new production routes. Such procedures are also needed as a routine quality control tool for use in ongoing monitoring of all bitumens.

1.2 Current Situation

The previous *TNZ M/1:1995* specified use of the Australian Durability oven test (*AS/NZS 2341.13:1997*). However research showed that the conditions used in this test were not appropriate for assessing bitumen at road temperatures in New Zealand, and the test was dropped from the TNZ M/1 specification. At present TNZ M/1 requires that proposals for approval of new bitumens must include "information on satisfactory in-service durability performance". No clear definition of what constitutes "satisfactory performance" is given however.

2. Test Development Rationale

2.1 Test Format

The proposed test is two tiered:

- An **acceptance test** to be used for initial assessment of bitumens not currently approved by Transit. This test would also be applied to approved bitumens if a significant change in a production route occurs. The test would need to be carried out only once, at the time of the introduction of a new bitumen (assuming the crude source and production route were kept consistent). It provides an indication of the durability behaviour of the bitumen at road temperatures.

- A **quality assurance test**, for quality control purposes, to be used to monitor consistency of durability in a bitumen. This test is a simplified version of the acceptance test and is much quicker to carry out. It would be carried out at intervals for "batch to batch" quality control, and the results would be compared to the initial test result.

The full test procedure *(Opus CL Test Method No. B309-99)* is given in the appendix to the report, and a discussion of the rationale behind the test conditions adopted is presented here. The test procedure is based on extensive research carried out both in New Zealand and overseas, including the US Strategic Highway Planning Program (SHRP). The objective was to develop a test that would give the most accurate prediction of durability possible, given realistic practical constraints. The acceptance test proposed is time-consuming, requiring approximately up to 2 to 3 months for completion. However, given that the test is carried out only once for a given bitumen or production route, this is not considered too unreasonable.

The proposed quality assurance test is necessarily much simpler as it serves merely as a check on the consistency of the product.

2.2 Monitoring the Oxidation Process

To monitor the progress of oxidation, measuring a physical property of bitumen that is relevant to cracking in chipseals (caused by traffic at low temperatures) was considered highly desirable. The temperature sensitivity of bitumens is known to change significantly as oxidation proceeds so that measurement of, for example, viscosity at 60°C may not necessarily correlate in a simple fashion to its behaviour at lower temperatures. Additionally such measurements do not simulate very well the loading rates caused by traffic that are experienced by bitumens in the field. For this reason the dynamic shear modulus at 5°C and 20 Hz was used to measure bitumen oxidation.

2.3 Accelerating the Process

Oxidative hardening of bitumen in the field is a slow long-term process. For a laboratory durability test aimed at comparing different bitumens, some means of accelerating oxidation is needed. Road temperatures rarely exceed 60°C in chipseals in New Zealand (Wood 1998), so the use of high temperatures (e.g. 100°C) was discounted. The reason for this is that, although, for all bitumens the rate of the oxidation reaction increases exponentially with temperature, the exact dependence varies considerably between bitumens (Lau et al. 1992).

This means that the *relative* oxidation rates of two bitumens at, say, 100°C will probably not be the same at 25°C. It is of course the latter temperature that is of more interest. For example Venezuelan (Boscan) 180/200 penetration grade binder oxidises at a rate approximately 4 to 5 times that of Safaniya 180/200 at 100°C (based on viscosity measurements), but the rates have been found to be approximately equivalent in the field (Ball 1999). Although road temperatures vary widely, an approximate reaction-rate-weighted mean temperature can be calculated from available road temperature data (Wood (1998), following Dickinson (1981)). These reaction mean temperatures are shown in table 2.1 which also shows for comparison the values calculated for three Australian sites.

Table 2.1 Reaction mean temperatures (T_E) for chipseal surfaces in New Zealand and Australia.

Site	Relative Reaction Rate	T_E (°C)
Dunedin	0.407	14.4
Cardrona	0.443	15.8
Blenheim	0.505	18.0
Napier	0.685	23.2
Sydney	0.903	28.2
Perth	1.054	31.0
Darwin	1.308	35.0

These data illustrate that, despite short periods of extreme high temperatures in summer, "effective" road temperatures are actually quite low. The need to determine oxidation behaviour at or as near to these temperatures as practicable was a major factor in deciding the temperature used in the acceptance test.

Instead of using high temperatures, rates of reaction were increased by using high (2,069 kPa/ 300 psi) air pressures. The form of the modulus – time curves obtained when oxidising thin films of bitumen under high pressures are the same as those found when oxidising at atmospheric pressure, although the curves at atmospheric pressure must also have a contribution from the finite rate of diffusion of oxygen into the film.

High air pressures are generally believed to have no effect on the bitumen oxidation mechanism (as opposed to the rate), and the available evidence seems to support this assumption (Liu et al.1998, Herrington[1] 1999). The area is still the subject of current research (Glover[2] 1999) and any developments will be monitored.

2.4 Assessing Durability

For approximately the last 15 years the only bitumen used in New Zealand has been manufactured from Safaniya Heavy Arabian crude. A key aspect of the acceptance test is to use the performance of this binder as a baseline for comparison of other bitumens being considered for use in New Zealand.

The approach taken in developing the test was to compare the *overall* hardening behaviour of a test bitumen with that of Safaniya bitumens. An equation describing the modulus – time behaviour was developed for this purpose.

2.5 Outline of the Proposed Test

2.5.1 Acceptance Test

Thin films (1.0 mm) of the bitumen under investigation are oxidised at 60°C under 2,069 kPa (300 psi) of air. At intervals, samples are removed and the shear modulus at 5°C and 9 Hz is measured. An equation is fitted to the modulus versus time plot obtained. The limiting slope and intercept of the fitted equation for the test bitumen are compared to those of Safaniya bitumen of the appropriate grade.

Features of the proposed test are:

- High pressure air is used to accelerate the process.
- A test temperature is used that is close to ambient conditions.
- The extent of oxidation is measured in a way that is relevant to field conditions.
- Durability is assessed on the basis of the long-term rate of oxidation.

2.5.2 Quality Assurance Test

A thin film (1.0 mm) of bitumen is oxidised at 80°C under 2,069 kPa of air for 48 hours and the modulus measured at 5°C and 9 Hz. This value is first obtained during the acceptance test and is used as a benchmark for comparison to future test results.

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[1] Herrington, P.R. 1999. Unpublished data on Safaniya bitumen oxidised at 60C at atmospheric pressure and under 300 psi oxygen.

[2] Glover C. (Professor) (1999) Department of Chemical Engineering, Texas A&M University, USA (private communication).

3. Experimental Methods

3.1 Pressure Vessel

The pressure vessel used in the present work was machined from a single billet of 316 stainless steel. The vessel was cylindrical (245 mm high, 110 mm i.d., 130 mm o.d.). The upper edged was flanged to accept a flat circular lid (200 mm dia, 15 mm thick) held in place by four bolts. An airtight seal was achieved using a viton rubber o-ring which fitted into a machined recess in the flange. The lid was drilled to accept a thermistor, safety valve and fittings for a gas inlet and pressure gauge. The vessel was pressurised from a cylinder of dry air.

3.2 Preparation of Samples for Ageing in the Pressure Vessel

The bitumen to be oxidised was held in a stainless steel holder. The holder was a circular disc (45 mm o.d., 5 mm high), one side of which had been machined to a depth of 1.0 mm to within 2.5 mm of the edge. This provided a cylindrical depression of 40.0 mm diameter with a raised lip to contain the sample.

Sufficient bitumen to form a 1.0±0.05 mm film was weighed into the centre of the sample holder. The holder was heated on a hot plate at about 10 °C until the bitumen had formed a smooth film. This takes about 2 to 5 minutes.

3.3 Ageing of Bitumen in the Pressure Vessel

The sample holders were placed in an aluminium rack and inserted into the pre-heated vessel. The rack was constructed so that it sat flat on the bottom of the vessel. Levelling the vessel in the water bath also ensured that the sample holders were level.

Samples were removed at the required intervals by slowly de-pressurising the vessel over 5 to 10 minutes before removing it from the bath. Sampling and restoration of the test pressure was usually completed in less than 15 minutes to minimise temperature fluctuations. The temperature inside the vessel was logged at 15-minute intervals which showed that the temperature was within 0.5° of the set temperature about 0.5 hours after sampling, but that 2 to 3 hours were needed to reach the set temperature to within ±0.1°C.

After sampling, the bitumen was scraped into glass jars and heated in a vacuum (30 inches Hg) oven at 80-100°C for 15 minutes. This treatment served to homogenise the bitumen and remove air bubbles. Previous studies had shown that the treatment did not result in any measurable changes to the samples.

3.4 Rheological Measurements

The amplitude of the dynamic shear modulus |G*| of the bitumens studied was measured on a Carri-Med CSL^{2}500 rheometer. Measurements were made in the linear viscoelastic region at frequencies between 0.1 and 20 Hz, using 8 mm parallel plates with a 1.0 mm gap. Temperature control was effected by means of a water bath surrounding the measurement geometry. Bitumen samples were annealed at 120°C for 5 to 10 minutes before transfer to the rheometer. The gap was closed to $\approx 1020\ \mu m$ and the sample trimmed before being brought to the measurement temperature.

Viscosity measurements were also made on the Carri-Med rheometer using a 25 mm cone and plate geometry.

3.5 Materials

Three of the binders (S180, S80, V180) studied complied fully with the TNZ M/1 specification for bitumen. Two of these were Safaniya 180/200 and 80/100 penetration grade bitumens (S180 and S80 respectively), manufactured at the Marsden Point refinery. S180 is a straight-run vacuum-distilled binder, S80 is manufactured by air-blowing the 180/200 grade and blending back. Both S180 and S80 are typical of the sealing grade binders that have been used in nearly all New Zealand roading work for the last 15 years. V180 is a straight-run 180/200 grade binder, also manufactured at Marsden Point but is from Venezuelan (Boscan) crude.

To expand the study and help ensure that the findings were generally applicable, a Safaniya 80/100 binder, manufactured using a butane precipitation route, was to have been studied as well. This process was intended to replace air blowing for the manufacture of 80/100 binder at Marsden Point but its use did not eventuate. An American bitumen (approximately 60 pen) was substituted instead. Unfortunately for reasons which are still unclear, modulus measurements made on this binder were highly variable (even before ageing) and were unusable.

Although introduced too late to be included in the full suite of tests, three further bitumens were evaluated using the final test conditions. Two of these bitumens (B1 and B2) were manufactured at Australian refineries and the third (B3) was from a North American crude. These binders were paving bitumens of approximately 60-80 penetration grade and were included simply to help establish the generality of the method.

4. Results

4.1 Comparison with Field Trial Results

Previous pressure vessel work had been carried out using viscosity measurements made at 60°C. It resulted in oxidation – time curves that were similar to those observed from field trial data where viscosity measurements had been made at 25°C and 45°C.

However to further verify that laboratory pressure vessel ageing did simulate field ageing, the 25°C and 45°C viscosities of laboratory-aged samples were measured and the oxidation – time curves were compared to available field data. Bitumens S180, S80 and V180 were oxidised at 40°C and 2,069 kPa (300 psi) air for a range of times and the viscosities were measured. The results are shown in figures 4.1 and 4.2.

For comparison, data from trials conducted with S180 and S80 on Wellington roads (Ball 1999) are presented in figures 4.3 and 4.4. Both laboratory data (figures 4.1 and 4.2) and field-aged (figures 4.3 an 4.4) follow the same pattern of an initial curvature leading to an approximately linear region. The scatter in the 25°C pressure vessel data is related to the fact that the shear rate used (0.1585 s^{-1}) is in the non-Newtonian region of the viscosity – shear rate curve. Hence it is more prone to experimental error. (This unusual shear rate was used in the field trial measurements because of instrumental limitations experienced at the start of the work.)

The absolute values of the viscosities obtained from both the 25° and 45°C pressure vessels after 2000 hours are slightly less than those measured in the field after 7 to 8 years, but do indicate that the vessel samples have been aged to a significant degree.

The results confirm that the pressure vessel experiment duplicates the shape of the viscosity – time ageing curves observed in the field.

4.2 Development of Ageing – Time Relationships

Three of the bitumens (S180, S80, V180) were aged at 40°, 60°, 70° and 80°C, and bitumens B1, B2 and B3 at 60°C only. Moduli were recorded at frequencies from 0.1 to 20 Hz and initially at 0°, 5° and 10°C before deciding on 5°C as the test temperature.

Temperatures lower than 5°C were thought likely to present problems in terms of the torque range of the rheometer, when attempting to measure the moduli of harder oxidised bitumens.

Figure 4.1 **Combined data for viscosities at 25°C, of laboratory-aged bitumens (S180, S80, V180).**

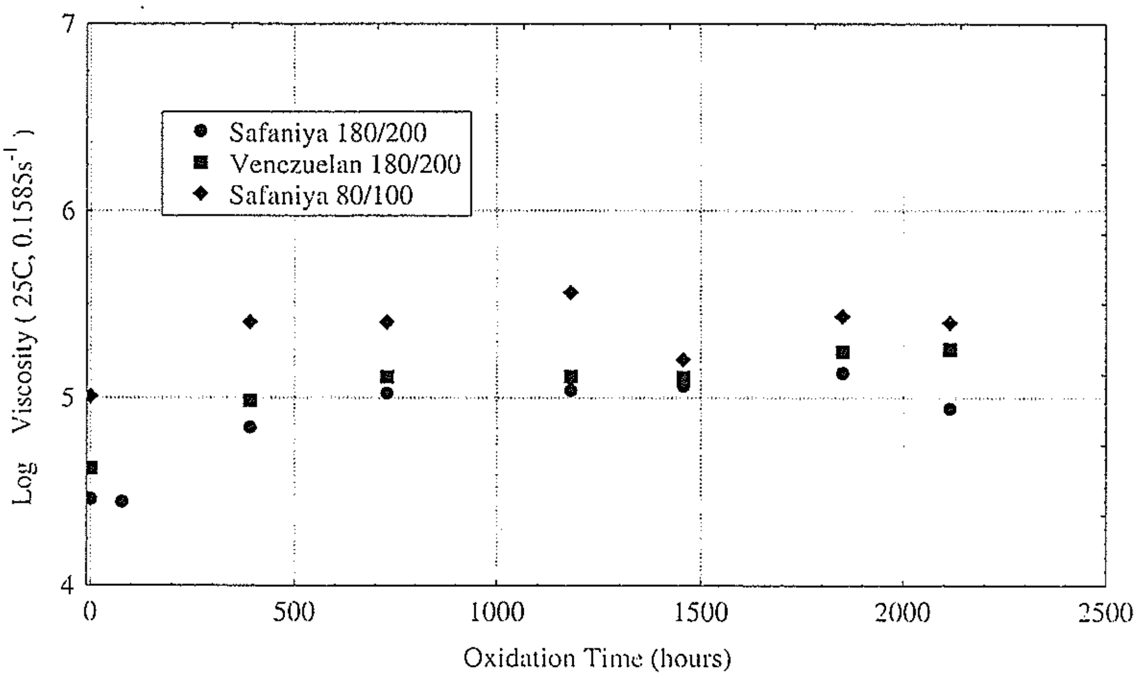


Figure 4.2 **Combined data for viscosities at 45°C, of laboratory-aged bitumens (S180, S80, V180).**

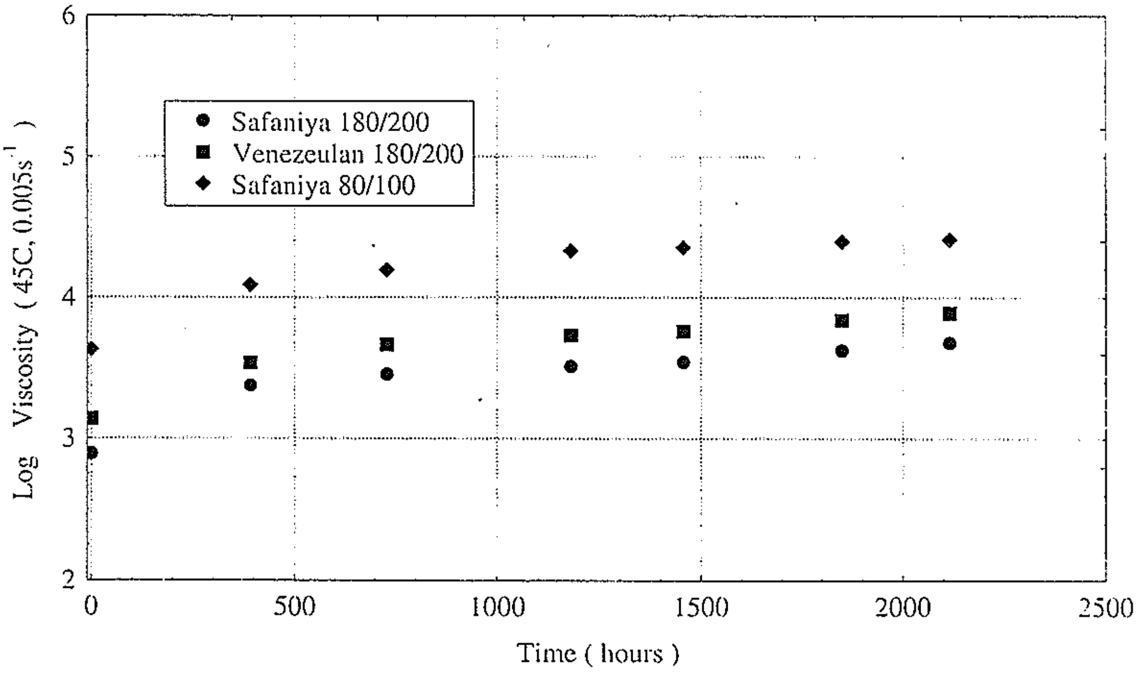


Figure 4.3 Results for viscosities at 25°C, of field trials on S180 and S80 bitumens.

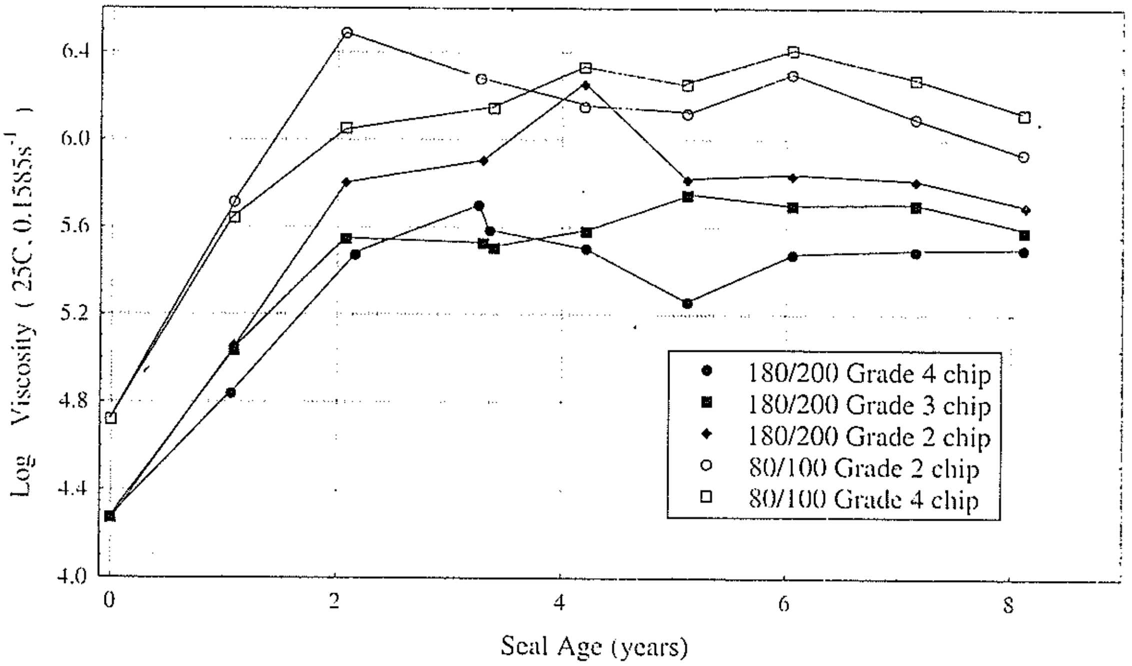
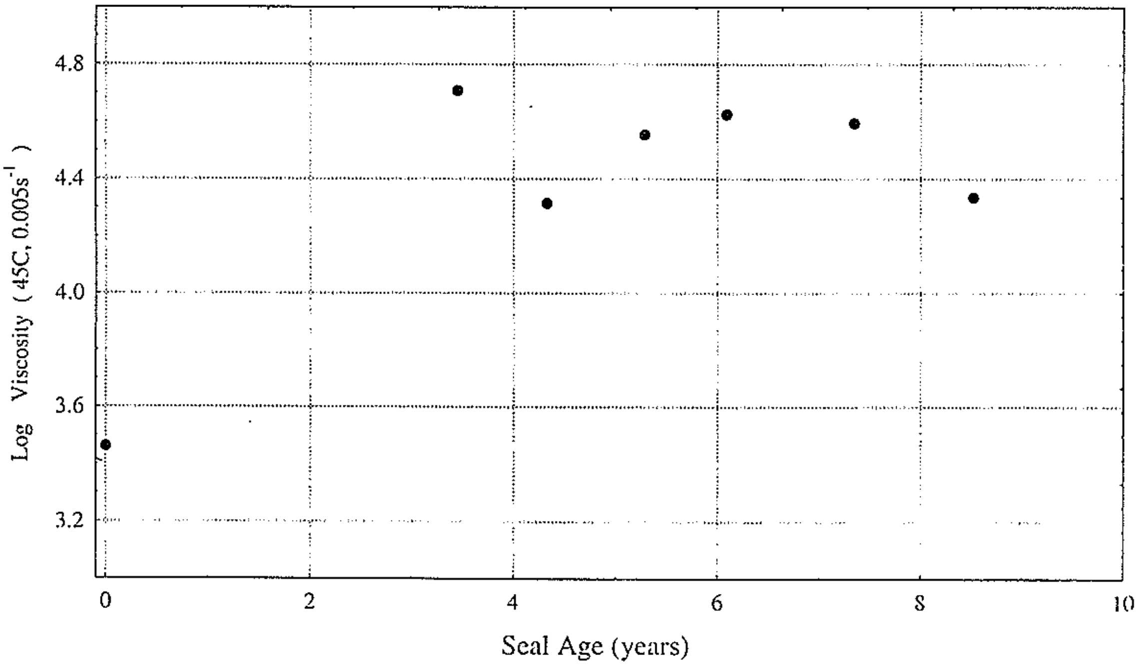


Figure 4.4 Results for viscosities at 45°C, of field trials on S80 bitumen.



The forms of the ageing – time modulus curves obtained at the three temperatures were in any case very similar, and also very similar to those obtained using viscosity as a measure of oxidation (figures 4.1 and 4.2). For example, results for S180 and S80 at a frequency of 9 Hz are shown in figures 4.5 and 4.6.

Figure 4.5 Moduli measured at 9 Hz and at 0°, 5° and 10°C for S180 bitumen.

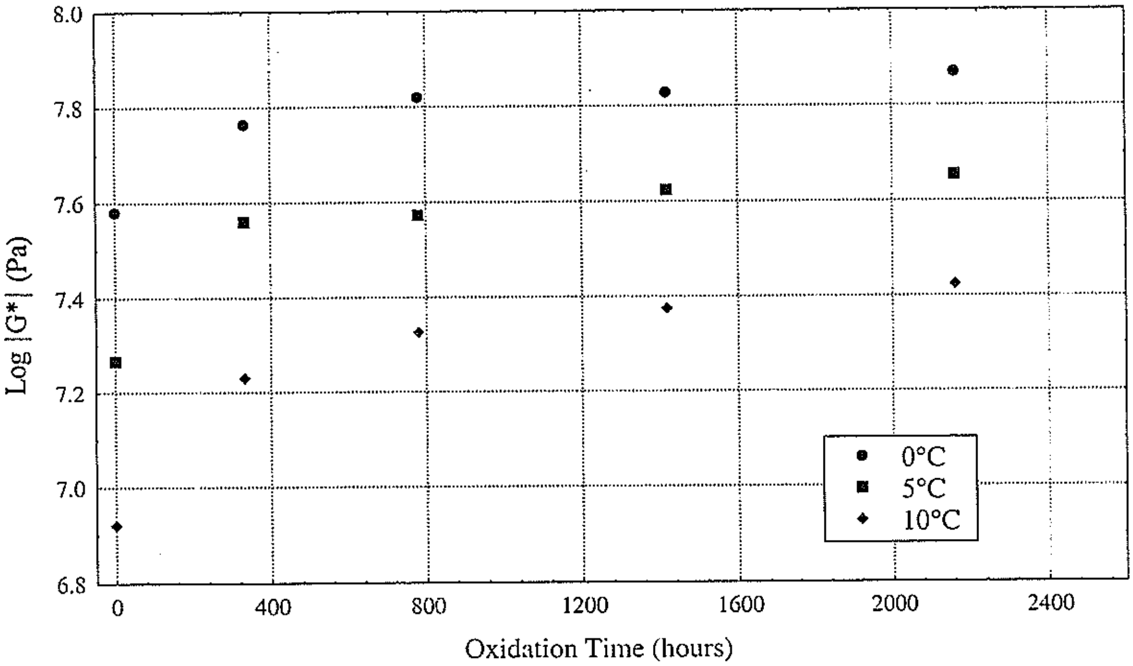
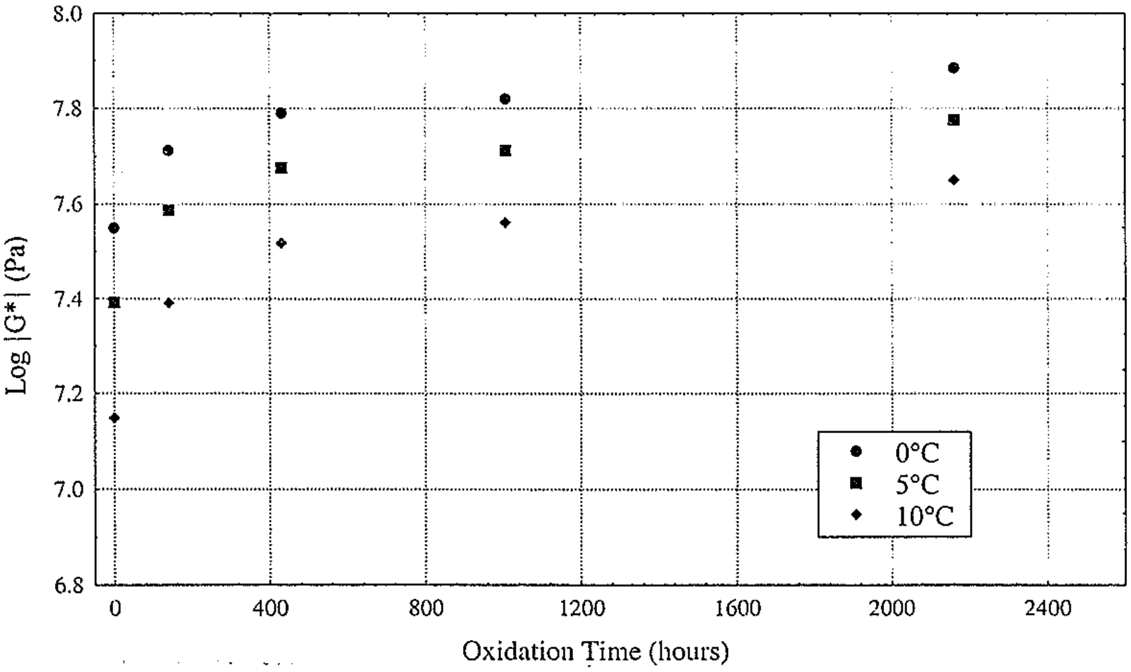


Figure 4.6 Moduli measured at 9 Hz and at 0°, 5° and 10°C for S80 bitumen.



The data do not show any appreciable differences in modulus-frequency dependence as illustrated for S180 and S80 in figures 4.7 and 4.8 respectively.

Figure 4.7 **Moduli measured at 5°C and three frequencies (9, 1.1, 0.1 Hz) for S180 bitumen.**

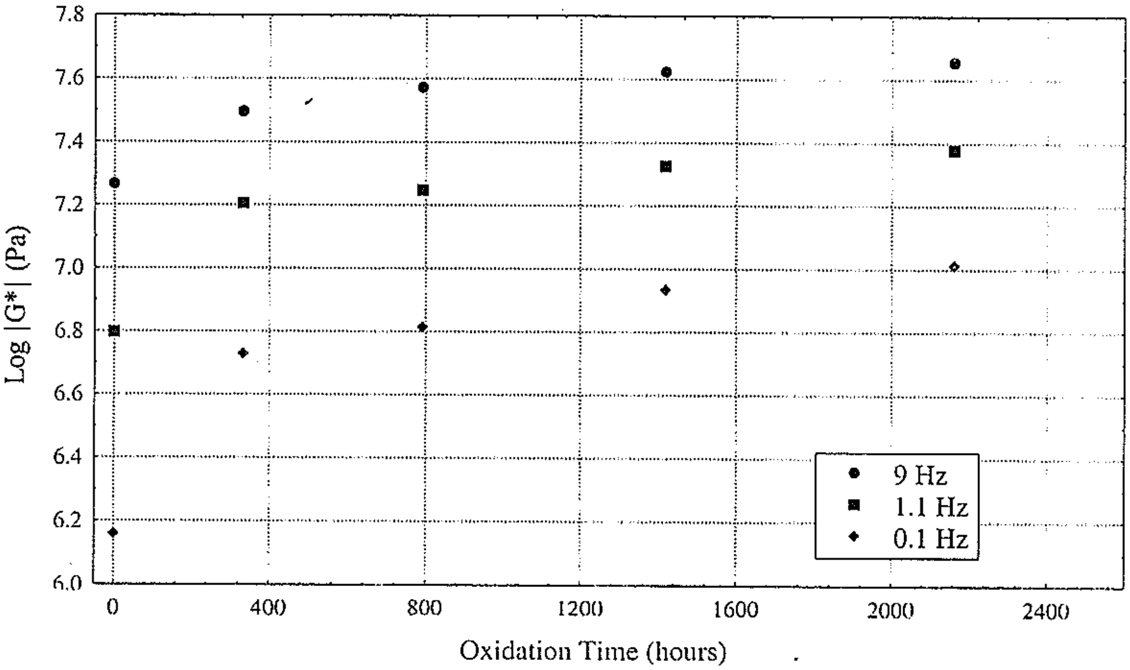
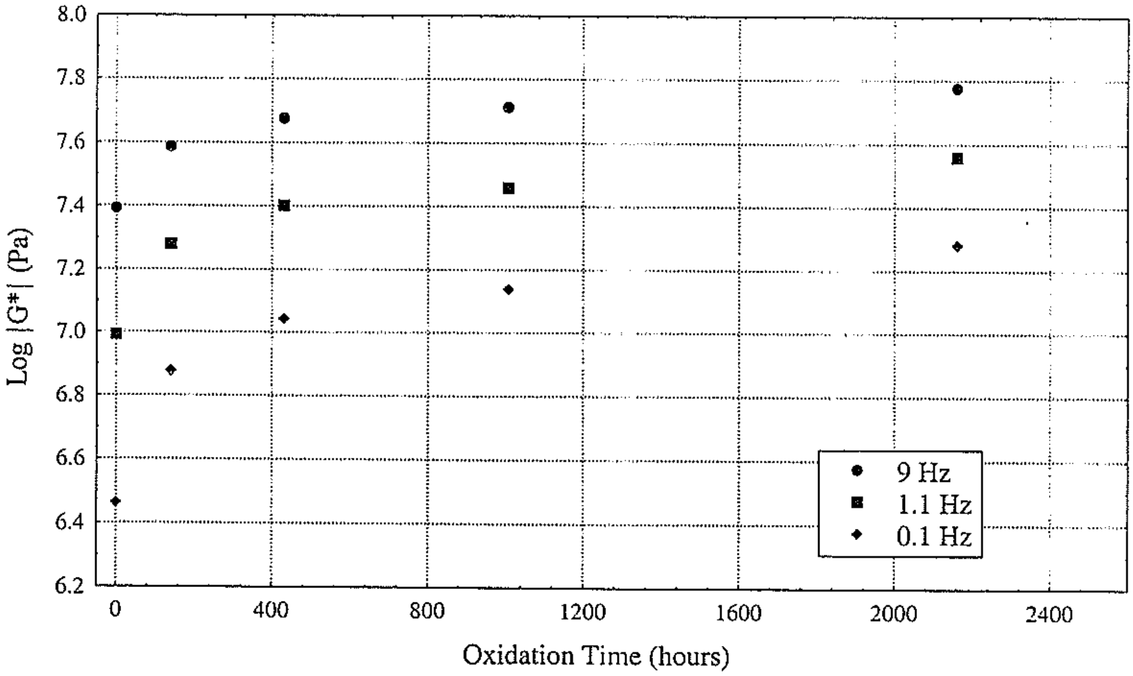


Figure 4.8 **Moduli measured at 5°C and three frequencies (9, 1.1, 0.1 Hz) for S80 bitumen.**



The rate of increase of moduli is however highly dependent on the oxidation temperature, as shown by data (at 5°C and 9 Hz) for bitumens S180 and S80, presented in figures 4.9 and 4.10.

Figure 4.9 Effect of oxidation temperature (40°, 50°, 60°, 80°C) for S180 bitumen.

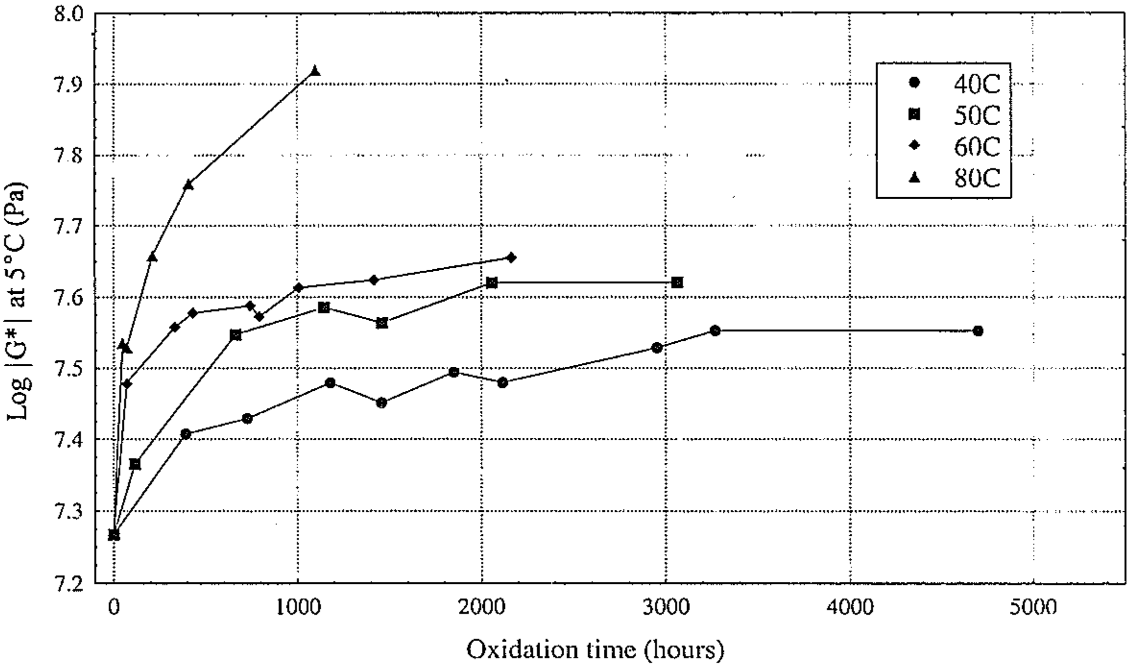
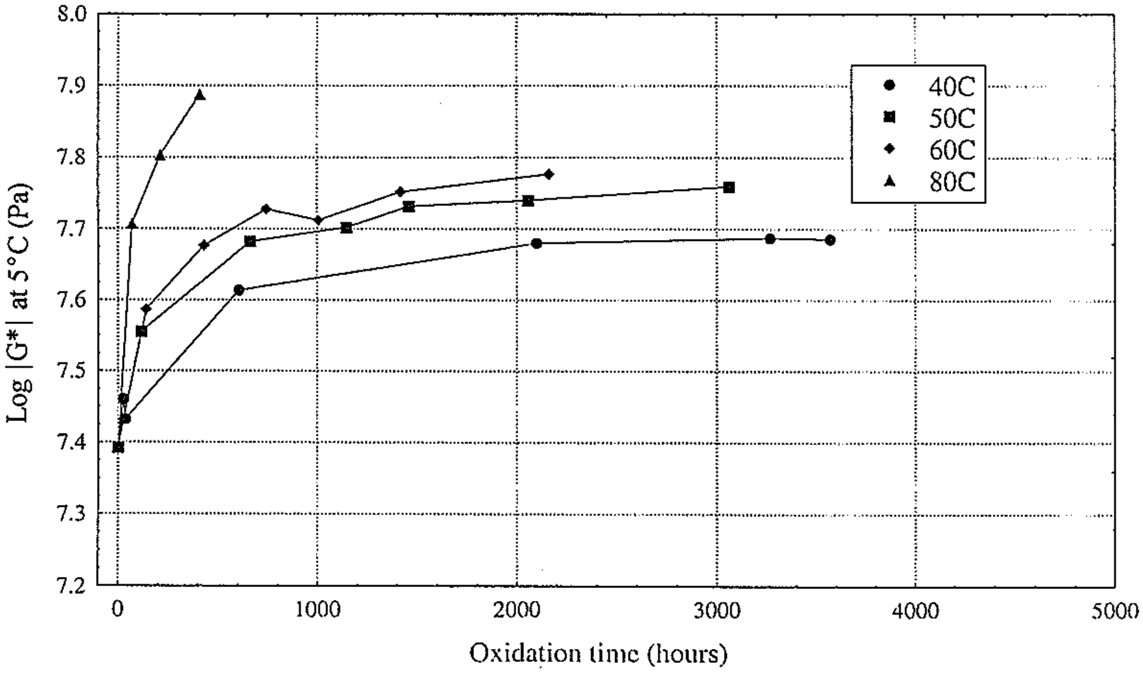
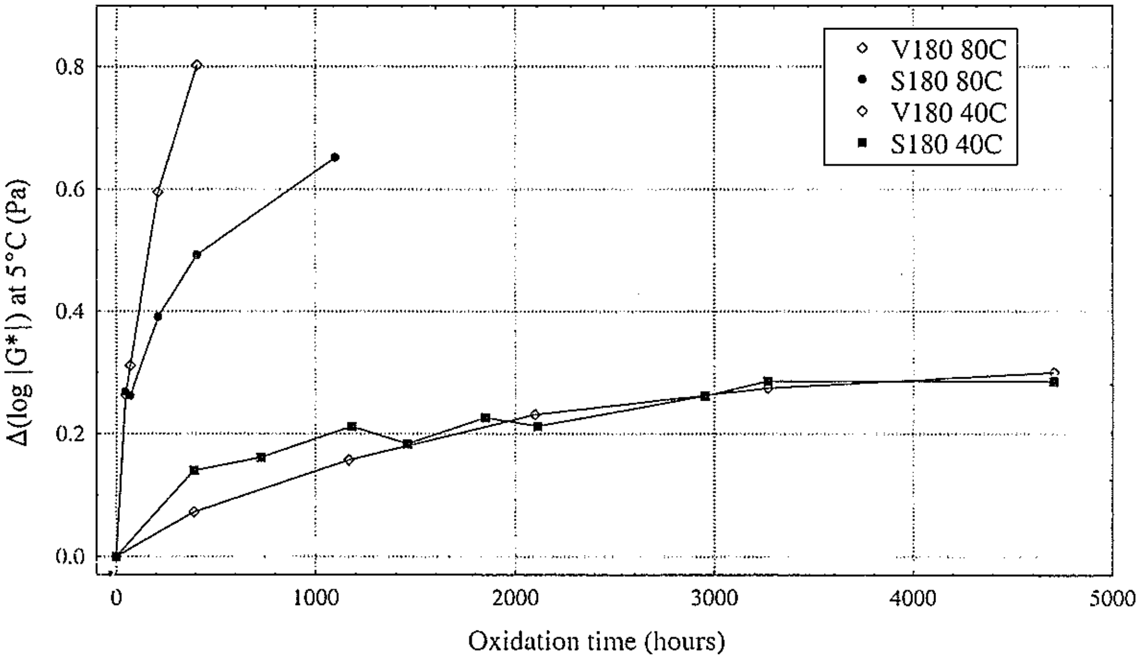


Figure 4.10 Effect of oxidation temperature (40°, 50°, 60°, 80°C) for S80 bitumen.



Moreover, as discussed (in section 2.3 of this report), the bitumen dependence of the rate – temperature relationship is illustrated in figure 4.11. This compares the increase in modulus of V180 and S180 at 40°C and 80°C. The relative rate of increase of modulus (relative durability) is markedly different at the two temperatures.

Figure 4.11 Effect of oxidation temperature (40 °C and 80 °C) on relative oxidation rates for S180 and V180 bitumens.



The data obtained in the oxidation experiments can be described by an equation derived assuming that two simultaneous first order reactions are taking place (Herrington 1998). In the present case where the dynamic shear modulus |G*| is the measure of the extent of oxidation, this equation becomes:

$$\Delta(\log|G^*|) = P(1-\exp(-K_f\,t)) + Kt \qquad (1)$$

where: $\Delta(\log|G^*|)$ = increase in the log of the modulus
P = constant
K_f, K = constants related to reaction rate

As time increases ($t \rightarrow \infty$), the term $\exp(-K_f\,t) \rightarrow 0$, and equation (1) becomes equation (2):

$$\Delta(\log|G^*|) = P + Kt \qquad (2)$$

In other words the equation predicts the observed linear behaviour at long reaction times. The constants reflect the y-intercept, the sharpness of the initial bend, and the slope of the linear portion of the curve respectively.

Moduli data (at 5°C, 9 Hz) fitted with equation (1) for all of the bitumens oxidised at 60°C is presented in figure 4.12 (data points have been omitted for clarity). The fitted parameters are presented in table 4.1. The equation describes the moduli data very well, consistent with earlier work using viscosity as a measure of oxidation (Herrington 1998).

Figure 4.12 Comparative behaviour for test bitumens (S80, S180, V180, B1, B2, B3) oxidised at 60°C.

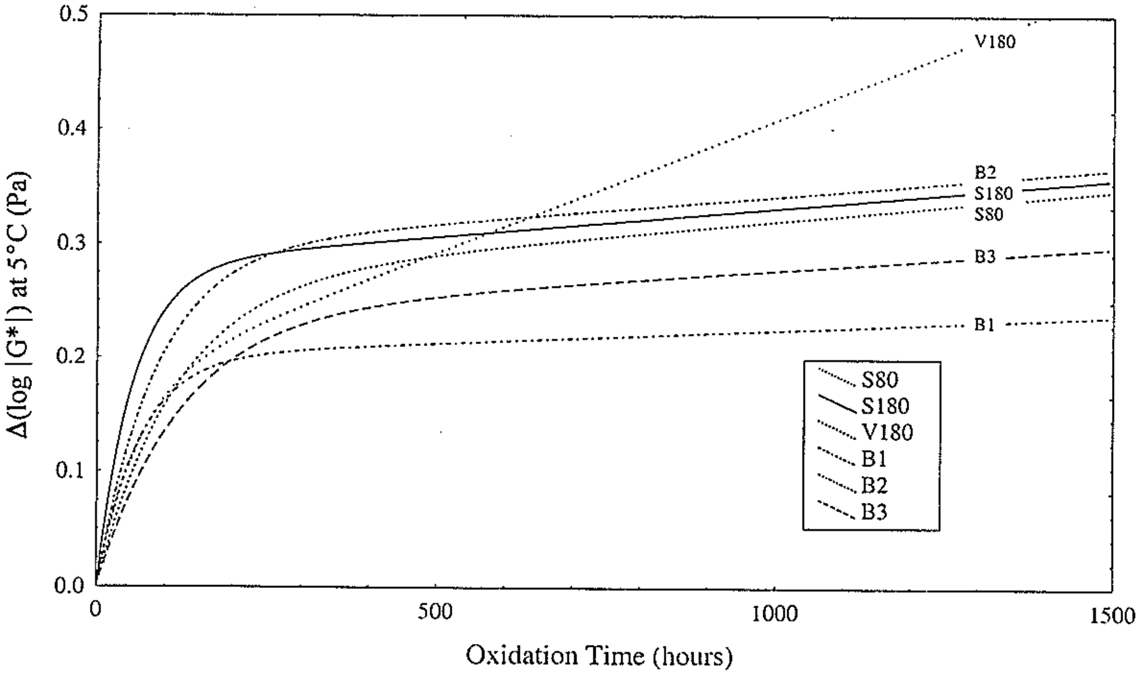


Table 4.1 Fitted parameters for bitumens aged at 60°C.

$$\Delta(\log|G^*|) = P(1-\exp(-K_f t)) + Kt$$

Bitumen	P (x 10^{-1})	K_f (x 10^{-3})	K (x 10^{-5})	R^2 (%)
S80	2.66	8.62	5.4	99.9
S180	2.81	18.60	5.1	99.5
V180	1.76	16.50	23.3	99.6
B1	2.00	16.10	2.5	99.0
B2	2.93	11.60	4.9	99.6
B3	2.37	8.12	4.1	100.0

5. Test Development

5.1 Acceptance Test

5.1.1 Experimental Conditions

5.1.1.1 *Initial Approach Using the Arrhenius Equation*

The rates of most chemical reactions have been found to increase with temperature according to the Arrhenius equation:

$$K = A\exp(-E_a/RT) \qquad (3)$$

where: K = Rate constant
E_a = Activation energy
R = Ideal gas constant
T = Temperature in Kelvins
A = Constant

The equation predicts that a plot of lnK versus 1/T will be linear. The constants, K_f and K in equation (1), are rate constants and should obey the Arrhenius equation. The constant P is related to the concentration of reactive species in the bitumen and should be independent of temperature.

In developing the test, the initial approach involved fitting constants K_f, K to modulus data obtained by oxidising a bitumen at three or four temperatures and extrapolating, using the Arrhenius equation, to the mean road reaction temperature (see section 2.3 of this report). In this way equation (1) would describe hardening behaviour at road temperatures.

Although such plots are indeed linear, the error associated with the necessary extrapolation involved in this procedure was, for practical purposes, too large to warrant the considerable time and effort involved. For example, Arrhenius plots of the fitted constant K for bitumens S180, S80 and V180, aged at 40°, 50°, 60° and 80°C are presented in figure 5.1 (with a "typical" road temperature marked for reference).

The plots show an unsatisfactory scatter especially in the case of S180 and S80. The value of K calculated at 40°C appears particularly suspect which may indicate that the linear part of the curve has not been truly reached, even after 3000 to 4000 hours ageing. The 40°C data for bitumen V180 however is co-linear with the higher temperature data, suggesting that the rate of oxidation has become linear. This is consistent with the overall tendency of this binder to oxidise more rapidly than the other materials (see table 4.1). When the 40°C point is removed, the linearity of the plots is improved considerably. The Arrhenius plots for K_f are shown in figure 5.2. Unfortunately the data are of no use for predictive purposes. The scatter in the results reflects the fact that, at 40°C, the curves are not yet fully developed while at 80°C relatively little data were obtained in the (very short) curved region.

Figure 5.1 Arrhenius plots of constant K for bitumens S180, S80, V180, measured at four temperatures, 80°, 60°, 50°, 40°C (reading left to right).

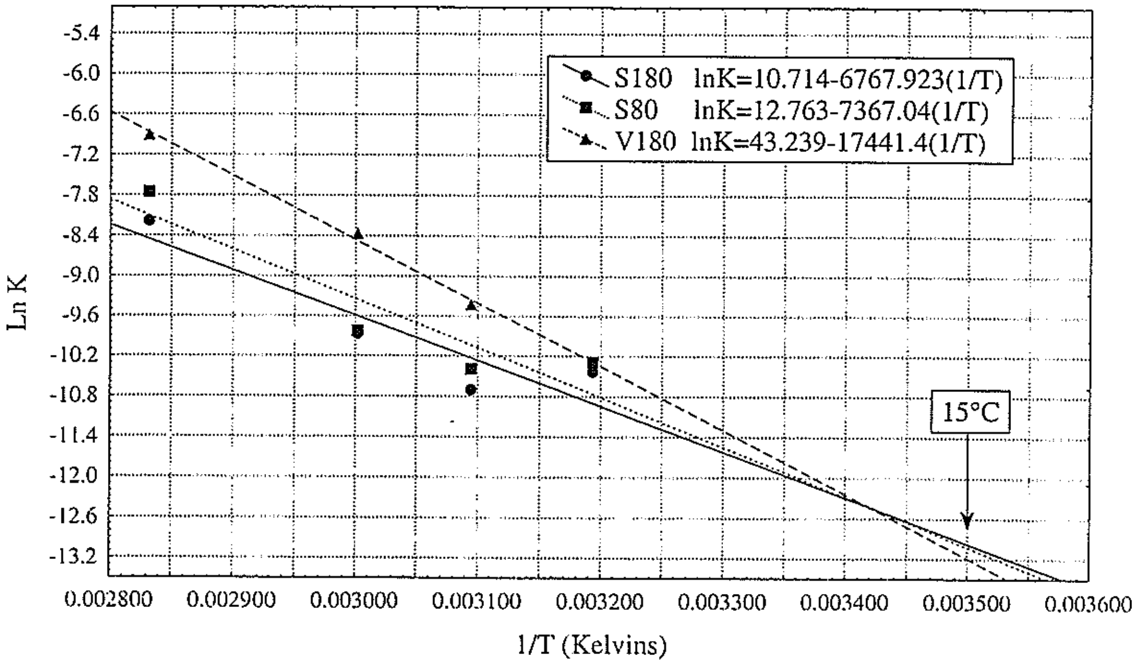
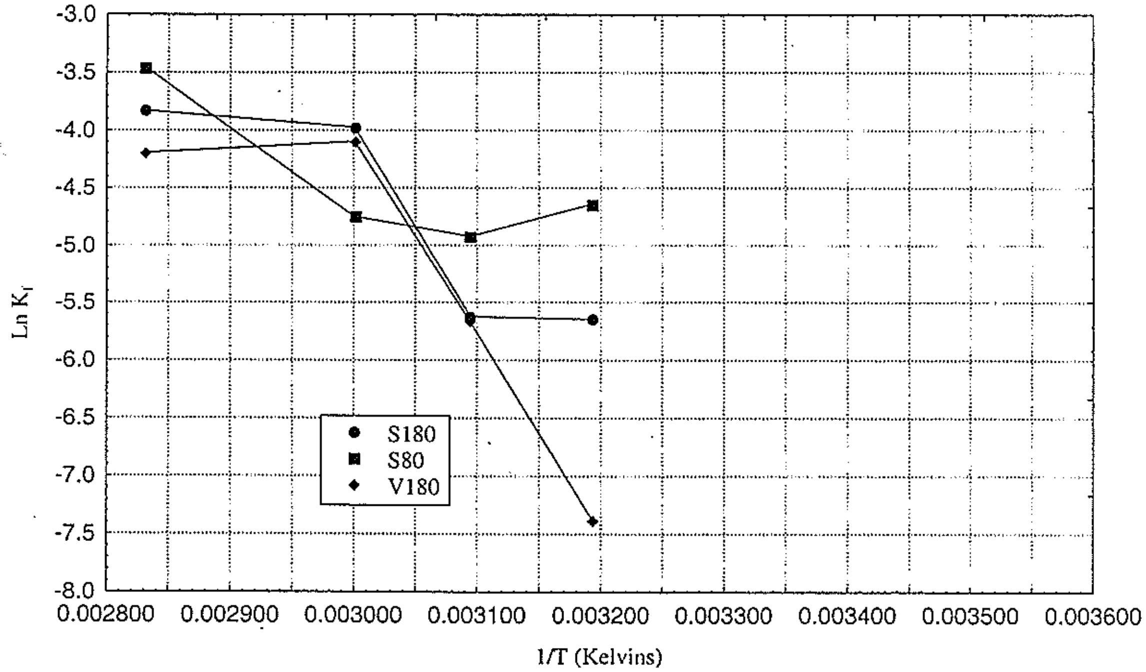


Figure 5.2 Arrhenius plots of constant K_f for bitumens S180, S80, V180, measured at four temperatures, 80°, 60°, 50°, 40°C (reading left to right).



Also the calculated values of K_f are not considered reliable. Collecting data at short time intervals during the 80°C experiments is not possible because of the time required for temperature re-equilibration.

Unfortunately, using this method to predict ageing rates at road temperatures (with any degree of precision), would clearly require experiments to be carried out at perhaps at least 5 or 6 temperatures, which would be impractical due to the time and costs involved.

5.1.1.2 *Final Approach*

The high cost and time required to obtain enough data to enable a sufficiently accurate extrapolation using the Arrhenius method meant that this initial approach was unsatisfactory. As a compromise it was decided to use a single temperature of 60°C. This temperature is as close to typical mean road reaction temperatures (see table 2.1) as possible while still enabling the test to be carried out in a reasonable time and at reasonable cost.

Although the dynamic shear rheometer allows comparison of moduli over a range of frequencies, for the purposes of a practicable test method it was necessary to select a single frequency at which moduli were to be measured.

Calculations assuming a tyre contact patch ratio of 1.5 to 2.0 (length to width), tyre widths of 12-18 cm and vehicle speeds of 10-100 km/h, indicate that appropriate frequencies range from 7 Hz to 455 Hz for the passage of a single tyre (equivalent sinusoidal loadings of 3.5 Hz to 228 Hz). However given that (trip distance-weighted) vehicle speed distributions are unknown, any frequency selected for the test measurement will be somewhat arbitrary and in any case the higher frequencies are outside the range of currently available instrumentation. It was decided, to avoid possible problems with instrument compliance with harder binders, to use a frequency of 9 Hz (equivalent to a speed of about 25 km/h).

Thus the bitumens are to be oxidised at 60°C and the moduli are to be measured at 5°C and 9 Hz.

5.1.2 Assessment of Durability

As illustrated in section 4 of this report, at or near road temperatures (in the absence of diffusion effects), bitumens in general harden with age in the manner expressed by the plot in figure 5.3. The rate of hardening is rapid initially and drops off with time. As shown in figure 5.4 the shape of the curve varies according to bitumen source, both in the sharpness of the bend and the slope of the linear region. As temperature increases the plots become steeper and more linear. The effect of temperature is bitumen-dependent so that the relative behaviour of two bitumens can change with temperature (see section 5.1.1). At a selected temperature the relative durability of two bitumens clearly depends on the oxidation (ageing) time at which measurements are made.

Figure 5.3 Ageing behaviour of bitumens in general.

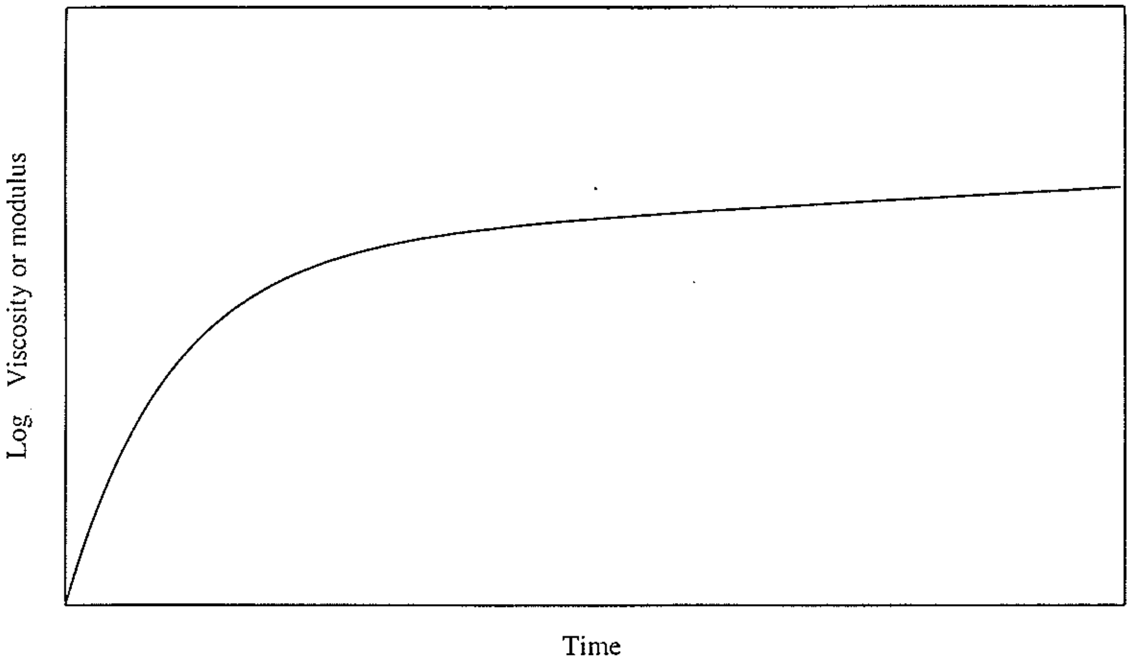
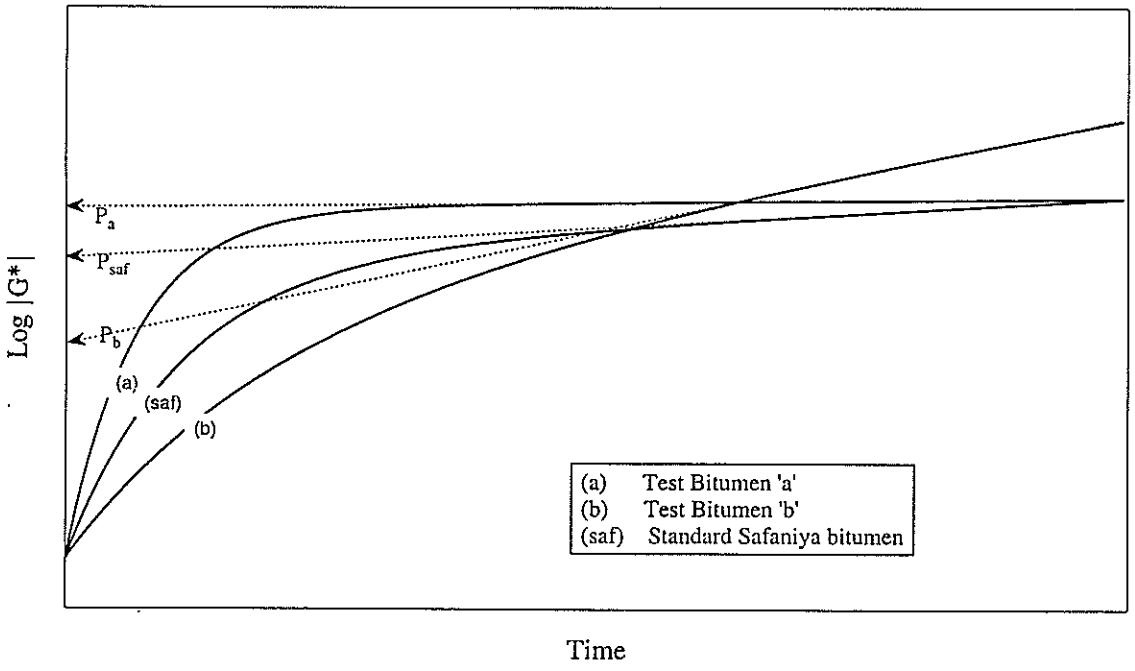


Figure 5.4 Range of ageing behaviours for bitumens, compared to standard Safaniya bitumen.



For approximately the last 15 years the only bitumen used in New Zealand has been manufactured from Safaniya Heavy Arabian crude using a single production route. A key aspect of the acceptance test is to use the performance of this binder as a baseline for comparison of other bitumens being considered for use in New Zealand. In the field (Ball 1998) most hardening occurs in the first three years (the curved region of the plot). After this time the rate of hardening is effectively constant and very low, and in some cases it is negligible. For example in one field site, binder viscosity increased 130% in the first two years of monitoring but only by another 5% over the next five years.

Given that most hardening occurs early on, but failure typically takes 8 to 10 years or longer, the concept of a critical modulus at which sudden failure occurs is probably not valid for New Zealand. Instead failure is likely to be through a fatigue process. Unfortunately, although the subject of current research, the effect of factors such as climate and trafficking on the failure mechanism have not yet been quantified. Fatigue cracking is, however, known to be related to the modulus of the binder, and as bitumens with higher moduli are more prone to cracking, the rate of increase of modulus is a suitable means of measuring durability. In light of the above, the approach taken in developing the test was to compare the *overall* hardening behaviour of a test with that of Safaniya bitumens rather than to pick a specific "critical" modulus value or oxidation time at which to make the comparison. The overall behaviour is characterised and compared using equation (1) (section 4.2 of this report).

The constants P and K are fitted by regression to the moduli data and compared to the constants for the appropriate grade of Safaniya bitumen. (The overall behaviour can be defined without the need to calculate K_f.) The suggested pass/fail criteria for the test are that a bitumen would fail unless the fitted constants were less than or equal to those of the equivalent Safaniya bitumen.

For example, figure 5.4 shows the possible behaviour of two hypothetical bitumens 'a' and 'b' compared with Safaniya ('saf') bitumen. Thus bitumen 'a' in figure 5.4 would be excluded because $P_a > P_{saf}$ even though $K_a < K_{saf}$, and bitumen 'b' would be excluded because $K_a > K_{saf}$.

The criteria suggested would ensure that the hardening behaviours of new bitumens are not significantly worse than those of the currently used (and highly satisfactory) Safaniya binders, but will not restrict the use of bitumens or modified binders with equivalent or improved durability.

5.2 Quality Assurance Test

The quality assurance test was developed to provide a simple and rapid means of comparing batch to batch consistency of bitumen durability. As such, use of a near-ambient test temperature is thus not essential (see section 2.3 of this report).

The temperature and duration (80°C and 48 hours) of this test were chosen for convenience and quick turn around, using the same apparatus as the acceptance test. The option of using modulus or viscosity to measure the extent of oxidation avoids the need to have access to a dynamic shear rheometer.

5.3 Precision

To assess the precision of the acceptance and quality assurance test methods, duplicate or triplicate experiments were carried out for a limited number of ageing times using S180, S80 and V180 bitumens, in which fresh samples of bitumen were aged for the same time but with different start times. The mean coefficient of variation of the resulting moduli measured at 5°C and 9 Hz (effectively the precision of the quality assurance test) was found to be 5% (range 0.2-9.8).

The data were then fitted with equation (1) to give two estimates for the constants P and K and gauge the overall repeatability of the curve (see table 5.1). The fitted equation parameters P and K showed a greater variation than the replicate modulus results, with mean coefficients of variation of 4% (range 0.9-6.6) and 15% (range 6.4 – 23.1) respectively. The inter-laboratory reproducibility of the procedures has still to be determined.

Table 5.1 Precision of fitted parameters P and K for S180, S80, V180 bitumens.

Bitumen	P (x 10^{-1})	K (x 10^{-5})
S180	2.81 2.70	5.15 6.51
S80	2.66 2.70	5.44 7.57
V180	1.76 1.93	2.23 2.12

Replicate and original data are plotted for S80 and S180 bitumens in figures 5.5 and 5.6 respectively.

Figure 5.5 Repeatability of ageing curve for S80 bitumen.

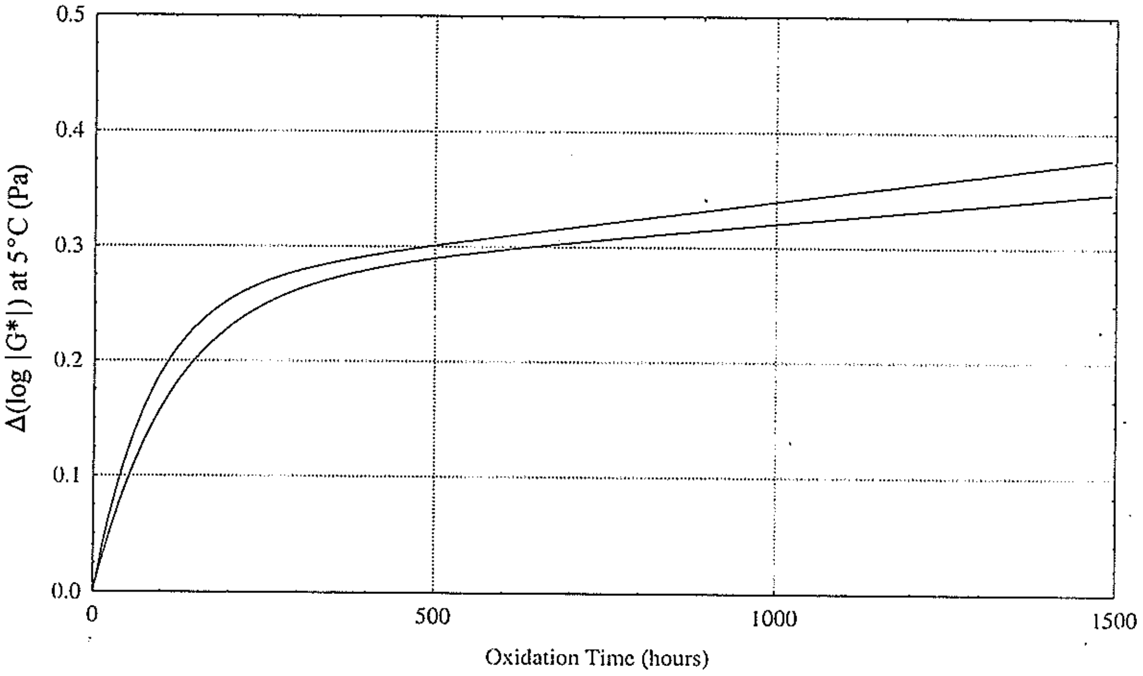
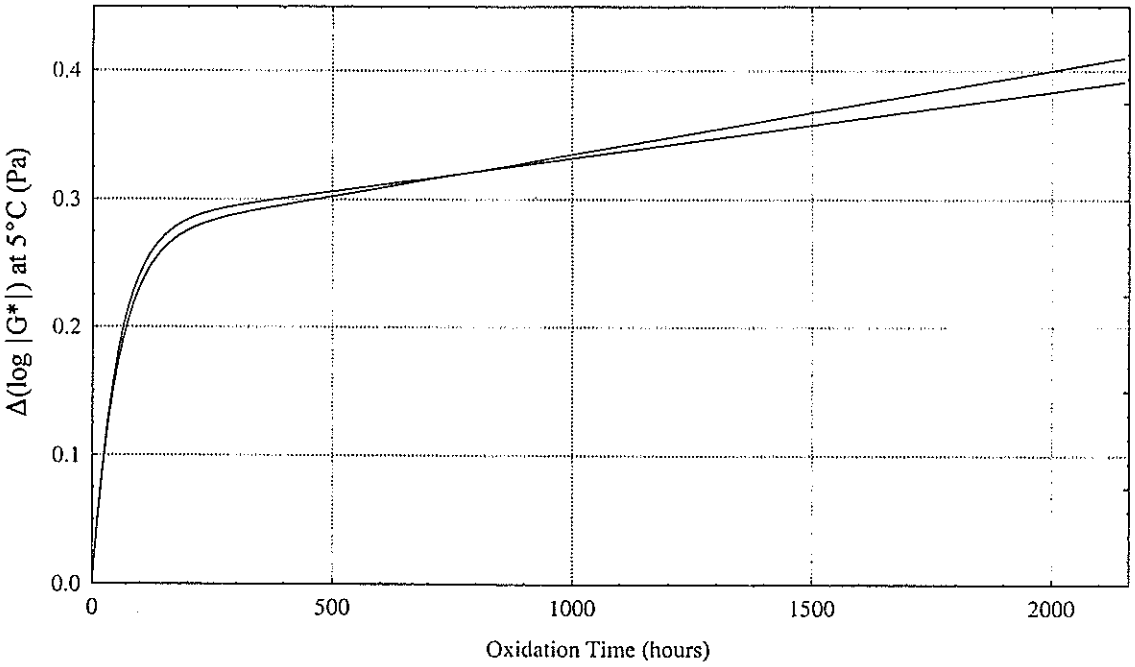


Figure 5.6 Repeatability of ageing curve for S180 bitumen.



6. Recommendations

The following recommendations are made.

- *Opus CL Test Method No. B309-99* to be specified in *TNZ M/1 Specification* so that the in-service durability performance of a bitumen can be assessed, and thus provide the requirement for such information.
- The method to be used for:
  - assessing the long-term durability of bitumens obtained from new sources or new production routes, and
  - routine checking for quality assurance of the durability of different production batches or shipments of bitumen.
- The inter-laboratory reproducibility of the test method should be determined.
- Values of the constants *P* and *K* should be determined for 60/70 and 130/150 bitumen grades.
- The practical performance and suitability of the test for its intended purpose should be reviewed after a fixed period (say 2 years).

7. References

AS/NZS. 1997. Australian durability oven test. Joint Australian & New Zealand Standard *AS/NZS 2341.13:1997.*

Ball, G.F.A. 1999. Chipseal hardening trials in New Zealand. *Transfund New Zealand Report No. 137.*

Dickinson, E. J. 1981. Pavement temperature regimes in Australia. *Australian Road Research Board (ARRB) Special Report No. 23.*

Herrington, P.R. 1998. Oxidation of bitumen in the presence of a constant concentration of oxygen. *Petroleum Science and Technology 16:* 743-765.

Liu, M., Ferry, M.A., Davison, R.R., Glover, C.J., Bullin, J.A. 1998. Oxygen uptake as correlated to carbonyl growth in aged asphalts and asphalt Corbett Fractions. *Industrial and Engineering Chemistry 37(12):* 4669-4764.

Lau, C.K., Lundsford, K.M., Glover, C.J., Davidson, R.R., Bullin, J.A. 1992. Reaction rates and hardening susceptibilities as determined for pressure oxygen vessel ageing of asphalts. *Transportation Research Record 1342:* 50-57.

Transit New Zealand. 1999. Specification for roading bitumens. *TNZ M/1:1999.* Wellington: Transit New Zealand.

Wood, J. H. 1998. Pavement temperature models. *Transfund New Zealand Research Report No. 101.*

APPENDIX

Opus International Consultants Central Laboratories Test Method No. B309-99

BITUMEN DURABILITY TEST

Bitumen Durability Test

1. Scope

The following describes the *Opus International Consultants Central Laboratories (Opus CL) Test Method No. B309-99*, for the accelerated ageing of bitumen to determine its durability, relative to that of a standard Safaniya bitumen. The test is suitable for predicting the hardening of bitumen in chipseal and air-permeable asphalt surfacings.

2. Principle

The test comprises two parts, an **acceptance test** and a **quality assurance test**.

The **acceptance test** is to be used for new bitumens, either being introduced to New Zealand or where significant changes have occurred in the manufacturing process. For the acceptance test 1.0 mm-thick films of the test bitumen are aged at 60°C under 2,069 kPa (300 psi) of air. Samples are removed periodically and the shear modulus is measured at 5°C and 9 Hz. Modulus – time plots are prepared and fitted to an equation. Constants in the equation are compared to standard values. The test bitumen is also separately aged in 1.0 mm films at 80°C for 20 hours and the 5°C, 9 Hz modulus or viscosity (see below) is measured.

In the **quality assurance test** 1.0 mm films of the test bitumen are aged at 80°C for 20 hours and the modulus or viscosity (see below) is measured and compared to that obtained for the bitumen in the acceptance test.

3. Acceptance Test

3.1 Referenced Documents

The following documents are referred to in this method:

TNZ M/1:1999 Specification for roading bitumens.

ASTM D4311-96 Standard practice for determining asphalt volume correction to a base temperature.

ASTM D70-97 Test method for specific gravity and density of semi-solid bituminous materials.

3.2 Apparatus and Materials

3.2.1 Cylinder of industrial-grade compressed dry air, fittings and hose for connection to pressure vessel.

3.2.2 Pressure vessel system comprising:

- Pressure vessel certified for operation at 2,069 kPa (300 psi) and 60°C.
- Thermocouple, thermistor or platinum resistance thermometer, and temperature logging device accurate to ±0.1°C, to measure the temperature inside the vessel.
- Pressure release valve that prevents the pressure inside the vessel exceeding the maximum design pressure.
- Pressure regulator capable of controlling the pressure inside the vessel at 2,069 kPa (300±5 psi).
- Pressure gauge readable to 5 psi and calibrated at 2,069 kPa (300 psi).
- Slow release bleed valve to allow de-pressurisation of the vessel from the test pressure to atmospheric pressure over 15 minutes.

3.2.3 Stainless steel or aluminium sample holders capable of holding at least 1.0 g of bitumen as a uniform, 1.0 mm thick, horizontal film.

3.2.4 A metal rack or holder capable of supporting at least 10 sample holders in a horizontal position so that the bitumen film thickness within the sample holders remains uniform.

3.2.5 A stirred temperature-controlled fluid bath or forced-draft oven capable of maintaining the temperature inside the pressure vessel at 60.0± 0.1°C.

- If a water bath is used it must be fitted with a water inlet and level control device. so that a constant water level is automatically maintained over long periods.
- Both the bath or oven must be sufficiently large to allow air or the bath fluid to freely circulate around the vessel, and contain a shelf or stand to allow the vessel to held in a horizontal (level) position.
- The recommendation is that the position of the vessel relative to the sides of the bath or oven is kept fixed.

3.2.6 Dynamic shear rheometer or similar instrument capable of applying sinusoidal loading and measuring the dynamic shear modulus of bitumen at 9 Hz and 5°C.

3.2.7 Software package for non-linear regression.

3.2.8 Hotplate.

3.2.9 Balance readable and accurate to ±0.001 g.

3.3 Procedure

3.3.1 Calibration of Pressure Vessel Temperature

- Place the pressure vessel in the 60°C water bath or oven to be used in the test, and pressurise to 2,069 kPa (300 ±5 psi).

- The thermocouple should be positioned near the vertical axis of the vessel and at approximately half height.

- After 4 hours, log the temperature inside the vessel at 15 minute intervals for at least 24 hours and adjust if necessary so that a temperature of 60.0 ± 0.1°C is maintained.

3.3.2 Density of Test Bitumen

- Measure the density of the test bitumen at 25°C according to the method given in ASTM D70-97, and calculate the density at 60.0°C using ASTM D4311-96.

3.3.3 Preparation of Sample Bitumen Films

- Weigh a sufficient quantity of bitumen onto the centre of the sample holder to achieve a 1.0 ± 0.5% mm film at 60°C (typically about 1.22-1.23 g).

- Heat the sample holder on a hot plate at 100-120°C for 3-4 minutes to achieve an even film, and allow to cool to room temperature on a level surface.

3.3.4 Ageing the Bitumen Films

- Before the test is begun, ensure that the pressure vessel (containing the sample holder rack) has been maintained at 60.0°C for at least four hours.

- Remove the pressure vessel from the bath or oven and place the sample holders in the vessel.

- Return the vessel to the bath and pressurise the vessel to 2,069 kPa (300±5 psi). The sample loading operation must be completed within 10 minutes and preferably as rapidly as possible to avoid cooling of the vessel.

- After 15-20 minutes, check the pressure in the vessel and re-adjust if necessary.

3.3.5 Sampling the Bitumen

- Remove from the water bath or oven at least 6 samples in total. The modulus of the unaged bitumen is taken as the zero point.

- Sampling should be spaced at approximately 100 hour (4 day) intervals up to 300 hours, and then at approximately 300 hour (12 day) intervals up to 1500 hours (63 days).

- Allow the pressure vessel to de-pressurise slowly over about 15 minutes (to avoid excessive bubbling of the samples), and before removing the vessel from the bath.

- Remove a sample holder and scrape the oxidised film into a small airtight vial and store in a freezer.

- Record the ageing time in hours to the nearest 0.5 hours.

- If necessary extra samples can be added to the pressure vessel at this time to minimise pressure and temperature changes to the remaining samples.

3.3.6 Modulus Measurement

- Exact analysis details will vary according to the type of rheometer used but analysis must be consistent from sample to sample.

- The modulus measurement is carried out using an 8 mm parallel geometry with a 1.0 mm gap. Larger diameter plates can be used if it can be demonstrated that the compliance of the instrument is not significantly affecting the measured modulus.

- A preliminary stress sweep may be necessary to ensure that the strain used lies within the linear viscoelastic region.

- Samples are annealed in an oven at 120°C for 10 minutes and gently stirred.

- A sub-sample is placed on the base plate and allowed to cool to about 60°C.

- The sample is compressed to the 1.0 mm gap and trimmed.

- To ensure proper wetting of the plates, the sample should not be compressed if it is below 45°C.

- The sample is brought to the test temperature of 5.0±0.1°C and the modulus measured at 9 Hz.

3.4 Calculations

Modulus – Time Plots

The modulus results are plotted against time. A smooth curve should be obtained. Given the length of the test it is essential to plot results as they are measured. In this way samples that appear to give suspect results can be repeated or extra data obtained.

The following equation is fitted to the results:

$$(\log |G^*|) - (\log |G_o^*|) = P\ (\ 1\text{-}\exp\ (-K_f t\ ) + Kt \qquad (1)$$

where: $|G^*|$ = modulus at 5°C of aged specimens (kPa)
$|G_o^*|$ = modulus at 5°C of unaged specimens (kPa)
P, K_f, K = constants to be fitted
t = time (hours)

The values of P, K_f and K are determined by non-linear regression. Suitable non-linear regression software packages are readily available from commercial suppliers.

3.5 Reporting

The following information is to be reported:

- Sample identification.
- Total time during the test that the temperature was outside the specified limits (nearest 15 minutes).
- Calculated value of constants P and K.

3.6 Precision

Based on the replicate measurements made on three different bitumens, the coefficient of variation of the calculated values of P and K are ±3% and 15% respectively.

4. Quality Assurance Test

4.1 Referenced Documents

The following documents are referred to in this method:

TNZ M/1:1999 Specification for roading bitumens.

ASTM D4311-96 Standard practice for determining asphalt volume correction to a base temperature.

ASTM D70-97 Test method for specific gravity and density of semi-solid bituminous materials.

4.2 Apparatus and Materials

4.2.1 Cylinder of industrial-grade compressed dry air, fittings and hose for connection to pressure vessel.

4.2.2 Pressure vessel system comprising:

- Pressure vessel certified for operation at 2,069 kPa (300 psi) and 60°C.
- Thermocouple, thermistor or platinum resistance thermometer, and temperature logging device accurate to ±0.1°C, to measure the temperature inside the vessel.
- Pressure release valve that prevents the pressure inside the vessel exceeding the maximum design pressure.
- Pressure regulator capable of controlling the pressure inside the vessel at 2,069 kPa (300±5 psi).
- Pressure gauge readable to 5 psi and calibrated at 2,069 kPa (300 psi).
- Slow release bleed valve to allow de-pressurisation of the vessel from the test pressure to atmospheric pressure over 15 minutes.

4.2.3 Stainless steel or aluminium sample holders capable of holding at least 1.0 g of bitumen as a uniform, 1.0 mm thick, horizontal film.

4.2.4 A metal rack or holder capable of supporting at least 10 sample holders in a horizontal position so that the bitumen film thickness within the sample holders remains uniform.

4.2.5 A stirred temperature-controlled fluid bath or forced-draft oven capable of maintaining the temperature inside the pressure vessel at 60.0± 0.1°C.

- If a water bath is used it must be fitted with a water inlet and level control device, so that a constant water level is automatically maintained over long periods.

- Both the bath or oven must be sufficiently large to allow air or the bath fluid to freely circulate around the vessel, and contain a shelf or stand to allow the vessel to be held in a horizontal (level) position.

- The recommendation is that the position of the vessel relative to the sides of the bath or oven is kept fixed.

4.2.6 Dynamic shear rheometer or similar instrument capable of applying sinusoidal loading and measuring the dynamic shear modulus of bitumen at 9 Hz and 5°C.

4.2.7 Software package for non-linear regression.

4.2.8 Hotplate.

4.2.9 Balance readable and accurate to ±0.001 g.

4.3 Procedure

4.3.1 Calibration of Pressure Vessel Temperature

- Place the pressure vessel in the 80°C water bath to be used in the test and pressurise to 2,069 kPa (300±5 psi).

- The thermocouple should be positioned near the vertical axis of the vessel and at approximately half height.

- After 4 hours, log the temperature inside the vessel at 15-minute intervals for at least 24 hours, and adjust if necessary so that a temperature of 80.0±0.1 °C is maintained.

4.3.2 Density of Test Bitumen

- Measure the density of the test bitumen at 25°C or some other convenient temperature according to the method given in ASTM D70-97.

- Calculate the density at 80.0°C using ASTM D4311-96.

4.3.3 Preparation of Sample Films

- Weigh a sufficient quantity of bitumen onto the centre of the sample holder to achieve a 1.0±0.5%-mm film (typically about 1.22-1.23 g).

- Heat the sample holder on a hot plate at 100-120°C for 3-4 minutes to achieve an even film, and allow to cool on a level surface.

4.3.4 Ageing the Bitumen Films

- Before the test is begun, ensure that the pressure vessel (containing the sample holder rack) has been maintained at 80.0°C for at least 4 hours.

- Remove the pressure vessel from the bath and place the sample holders in the vessel.

- Return the vessel to the bath and pressurise to 2,069 kPa (300±5 psi). The sample loading operation must be completed within 10 minutes and preferably as rapidly as possible to avoid cooling of the vessel.

- After 15-20 minutes, check the pressure in the vessel and re-adjust if necessary.

Note 1. A different ageing temperature can be used if it can be demonstrated to the satisfaction of the Transit New Zealand Engineering Policy Manager that sufficient oxidation has taken place to enable valid comparisons.

4.3.5 Sampling the Bitumen

- Remove the sample after 48.0±0.5 hours, scrape the bitumen into an airtight vial and store in a freezer.

Note 2. A different sampling time can be used if it can be demonstrated to the satisfaction of the Transit New Zealand Engineering Policy Manager that sufficient oxidation has taken place to enable valid comparisons.

4.3.6 Modulus Measurement

- Exact analysis details will vary according to the type of rheometer used but analysis must be consistent from sample to sample.

- The modulus measurement is carried out using an 8 mm parallel geometry with a 1.0 mm gap.

- A preliminary stress sweep may be necessary to ensure that the modulus is measured in the linear viscoelastic region.

- Samples are annealed in an oven at 120°C for 10 minutes and gently stirred.

- A sub-sample is placed onto the base plate and allowed to cool to about 60°C.

- The sample is compressed to the 1.0 mm gap and trimmed.
- To ensure proper wetting of the plates, the sample should not be compressed if its temperature is below 45°C.
- The sample is brought to the test temperature of 5.0±0.1°C and the modulus is measured at 9 Hz.

4.4 Reporting

The following information is to be reported:

- Sample identification.
- Ageing test temperature (nearest 0.1°C).
- Ageing test time (nearest 0.5 hours).
- Total time during the test that the temperature was outside the specified limits (nearest 15 minutes).
- Modulus of the aged bitumen (Pa).
- Benchmark modulus value (Pa).

Note 3. The benchmark modulus may be a single measured value, the average of several repeat tests, or the average of tests carried out on different shipments or production batches of bitumen. A suitable benchmark value and acceptance or rejection limits must be agreed on by the Transit New Zealand Engineering Policy Manager.

4.5 Precision

Based on measurements made on four different bitumens ranging from 64 to 186 penetration at 25°C, the precision of the measured modulus is ±7%.

5. References

ASTM. 1996. Standard practice for determining asphalt volume correction to a base temperature. *ASTM D4311-96.* Pennsylvania, USA: American Society for Testing & Materials.

ASTM. 1997. Test method for specific gravity and density of semi-solid bituminous materials. *ASTM D70-97.* Pennsylvania, USA: American Society for Testing & Materials.

Transit New Zealand. 1999. Specification for roading bitumens. *TNZ M/1:1999.* Wellington: Transit New Zealand.