Field Trials of a Lead-Based Asphalt Antioxidant

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Sprayed seal road trials were laid at two sites in Australia to evaluate the effectiveness of the antioxidant lead diamyldithiocarbamate (LDADC) in reducing the rate of asphalt hardening. Sections containing no antioxidant (control) and sections containing between 1 and 6 percent LDADC in asphalt were placed. Testing of samples taken during construction showed that little or no degradation of the LDADC had occurred during mixing with asphalt or during the spraying operation. Environmental and occupational health monitoring was performed at one of the trials. Both trials were sampled 2 yr after construction and the asphalt recovered for testing. For all three of the asphalts used, it was found that asphalt hardening had proceeded more slowly in those sections containing antioxidant than in the control sections. Increasing LDADC concentration in the asphalt was correlated with a reduced binder hardening rate. The trials will continue to be monitored to determine whether the early improvements in asphalt hardening rate continue in the long term.

The asphalt binder in asphaltic concrete or sprayed seal surfacings hardens with time. If the pavement structure has been properly designed and constructed for the traffic it carries and a durable aggregate has been used, the rate at which the binder hardens can be the critical factor in determining the life of the surfacing. The binder hardens to a level at which brittle fracture takes place under the forces produced by traffic stressing and thermal contraction. Cracking of the surfacing then occurs, and aggregate particles are eroded from its surface.

The main hardening mechanism is thermal oxidation of the asphalt. The faster photochemical reaction, which is catalyzed by sunlight, takes places only in the top 5 or 10 mm of an exposed binder film (*1*). Loss of volatile material can also contribute to asphalt hardening, but ideally an asphalt should contain a low concentration of volatiles.

The addition of antioxidants to asphalt has been shown to be effective in reducing the rate of asphalt hardening. Martin (*2*) studied 33 antioxidants belonging to four major classifications and found that zinc diethyldithiocarbamate (ZDC) was the most promising of those tested. This material belongs to the chemical class known as "peroxide decomposers."

This antioxidant was evaluated under actual pavement conditions by following the asphalt hardening rate in sprayed seal road trials (*3*). Low concentrations of ZDC were effective in reducing the asphalt hardening rate in the first 2 yr of pavement service. For periods in excess of about 2 yr, however, the effect of the antioxidant was reduced and there was evidence that most of the antioxidant had decomposed. After about 6 yr, road trial sections with and without the antioxidant had similar levels of asphalt viscosity. It was concluded that ZDC had no permanent effect on the rate of hardening of the asphalt in the seal.

Work by Haxo and White (*4*) on the effect of a series of lead and zinc antioxidants on asphalt hardening identified lead diamyldithiocarbamate (LDADC) as being particularly effective in reducing the rate of hardening. The good solubility of LDADC in asphalt was considered an important factor. ZDC, used in the road trials reported previously, is a powder with limited solubility in asphalt.

LDADC-modified binder was used in an asphaltic concrete road trial laid in Toronto, Canada, in 1982 (*5*) and this trial is still being monitored. It was considered that additional road trials were needed in hot climate areas, where asphalt hardening proceeds at a rapid rate. Australia was chosen to host a series of trials because of its availability of suitable sites and the experience of the Australian Road Research Board (ARRB) in conducting road trials to study asphalt hardening (*6*).

PREVIOUS WORK ON ASPHALT HARDENING IN AUSTRALIA

The greatest proportion of Australia's road network is surfaced with sprayed seals that normally are placed over light, unbound granular pavements. The term "sprayed seal" is used to describe a surfacing that consists of a thin film of asphalt cement (asphalt) that is sprayed hot from an asphalt distributor and covered with a single layer of approximately single-sized stone chippings. Design and construction procedures (*7*) have been refined by Australian State Road Authorities so that lives of 10 yr or so are common for seals with 10-mm chippings (aggregate).

In these circumstances seal life is very dependent on the durability of the binder, and specifications for asphalt durability have been introduced in most states. The specification is based on the ARRB Durability Test, which is fully described in Australian Standard 2341 (*8*). The test consists of a rolling thin film oven (RTFO) pretreatment followed by exposure of a 20-mm-thick film of asphalt in an oven at 100°C. Further information on the test is given in a paper by Oliver (*7*).

To confirm that the Durability Test correctly ranked asphalts in the order of their resistance to hardening in the field, road trials were laid at sites around Australia. These were followed for periods of up to 10 yr, and a correlation was established between the Durability Test result and asphalt hardening in the road trials (*6*). Further analysis of the data resulted in the

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development of a simple mathematical model for asphalt hardening in sprayed seals (*7*) that took the form:

$$\log \eta = .0476\ T\ Y^{0.5} - .0227\ D\ Y^{0.5} + 3.59 \quad (1)$$

where

- η = the viscosity of the asphalt recovered from the seal (Pa.s),
- T = the average temperature of the site calculated from Equation 2,
- D = the ARRB Durability Test result (days), and
- Y = the number of years since the seal was constructed.

$$T = (TMAX + TMIN)/2 \quad (2)$$

where *TMAX* equals the yearly mean of the daily maximum air temperature and *TMIN* equals the yearly mean of the daily minimum air temperature. The variables *TMAX* and *TMIN* are obtained from published tables of climatic data.

It was possible to develop an asphalt hardening model because the asphalt exposure conditions (in terms of film thickness and access to oxygen) in a correctly designed and constructed sprayed seal are normally reproducible and results obtained at different sites can be compared. This is in contrast to the situation with asphaltic concrete (ac), where the asphalt hardening rate depends on the binder film thickness, the percentage of air voids in the surfacing, and their degree of interconnection, as well as on the intrinsic resistance of the asphalt to hardening. In addition, ac surfacings are commonly subject to traffic compaction in the first few seasons after placement. This compaction results in changes in air void content and does not occur evenly across the pavement.

CONSTRUCTION OF THE TRIAL SECTIONS

Location of the Trials

In view of the complexity of the asphalt hardening situation with asphaltic concrete, it was decided to evaluate LDADC in sprayed seal road trials. A trial was placed near Townsville, northern Queensland, in 1986 and a second trial near Hopetoun, Victoria, the following year (see Figure 1). A third trial is planned for the Alice Springs area in central Australia.

Supply of Antioxidant

LDADC is a thick viscous liquid. So that it could easily be pumped or poured for addition to the asphalt, the material was dedrummed and diluted, at a central depot, with mineral turpentine in the mass ratio of 90 parts of LDADC to 10 parts of turpentine. The material was then packed in 20-l pails for delivery to the site.

Townsville Trial

The Townsville trial site was located in a tropical region 100 km inland from the coast. Twelve experimental sections were sprayed, each approximately 450 m long by 6.0 m wide. Dupli-

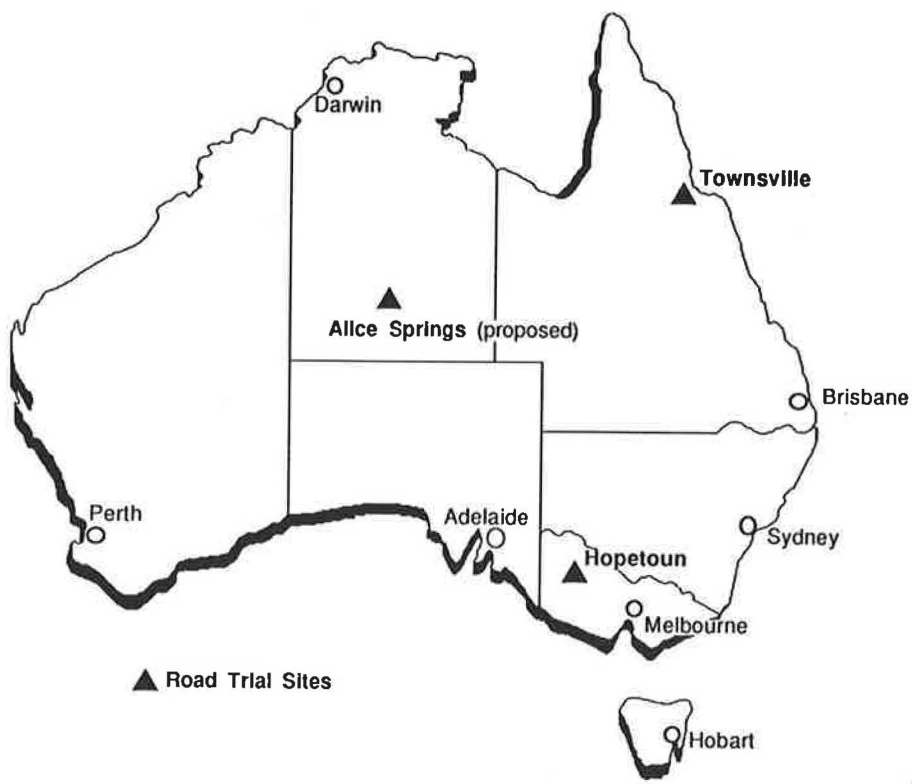

FIGURE 1 Location of current and proposed LDADC road trials.

cate sections containing 0 (control), 1, 2, and 3 percent by mass LDADC were placed. In addition there were single sections with 4 and 5 percent LDADC. No cutter or flux was added to the binder. The binder was applied at a rate of 1.6 l/sq m, and it was placed over a 230-mm-thick unbound, soil aggregate base. The base had been primed with a cutback binder 2 weeks before sealing took place. The sealing aggregate was 16 mm nominal size.

The sections at each end of the trial contained no LDADC and can be used in the future as extra control sections if necessary. Full information on the placement of the experimental sections is given in a construction report (*9*).

Hopetoun Trial

In the Hopetoun trial, two asphalts of different durability were used, and sections containing between 0 percent (control) and 6 percent antioxidant were placed. There were 11 sections in all, each approximately 400 m long by 6.1 m wide. Because of cold conditions at the time of laying, the binder was cut back with 8 parts by volume of kerosene.

The sealing aggregate had a nominal size of 10 mm, and the binder was applied at a rate of 1.3 l/sq m. The base consisted of limestone rubble 300 mm thick that had been ripped in the pit and broken up on the roadbed with a flat drawn steel roller and Bofors compactor. It was primed before spraying with two applications of a tar prime. Further information on the trial is given in a construction report (*10*).

Sampling at Both Trials

The sprayed binder was sampled by placing tared collection trays in the path of the distributor. These trays were removed after the distributor had passed and before the aggregate trucks reached the sampling positions. Four trays were used for each section in the Townsville trial and three in the Hopetoun trial. The trays were spaced at equal intervals along the sprayed length. This permitted the binder application rates to be measured accurately as well as providing samples of the binder "as sprayed." Samples of the asphalts, without antioxidant, were obtained from the asphalt supply tankers.

LABORATORY TESTING OF SAMPLES TAKEN DURING CONSTRUCTION

Asphalt Properties

The three asphalts used in the trials conformed to the requirements of Australian Standard 2008 (*11*) and belonged to Class 170, the normal Australian sealing grade. The class number is the asphalt viscosity measured in Pa.s at 60°C (170 Pa.s = 1,700 poises).

Asphalt 391 was used in the Townsville trial and was supplied from the Townsville depot. It was manufactured from a Kuwait crude that was first processed at a refinery in Victoria by blending a propane-precipitated asphalt with vacuum tower residue. This material was then cut with a gas oil fraction and transported to Townsville where the gas oil was removed by distillation.

Two asphalts were used in the Hopetoun trial. Asphalt 395 was supplied from a South Australian refinery. It was straight run, vacuum reduced from a Light Arabian crude with the addition of 25 percent by mass of propane-precipitated asphalt (PPA) derived from a Light Arabian crude. Asphalt 396 was manufactured in Victoria by air blowing the distillation residue of a Heavy Arabian crude.

The characteristics of the three asphalts are summarized in Table 1. Durability testing was done according to Australian Standard 2341. For a Durability Test result, the number of days represents the time taken for the asphalt to harden during laboratory oxidation to a level associated with distress in sprayed seals (*8*). The greater the number of days, the more durable the asphalt.

Testing of Sprayed Binder

The contents of the collection trays were assayed for LDADC content using an infrared spectrometric procedure (*12*) and for lead content, by atomic absorption spectroscopy. The latter determination was performed by an analytical laboratory. The lead, determined by atomic absorption, was used to calculate the concentration of LDADC added to the binder in each section. If degradation of the antioxidant were to occur during the construction process, the lead concentration would be unchanged. However, the infrared procedure, which is based on measurement of the diamyldithiocarbamate entity, would record a drop in concentration. The difference between the two measurements would thus indicate the degree of degradation of the antioxidant.

The results for the Townsville trial are shown in Table 2 and for the Hopetoun trial, in Table 3. LDADC concentration is expressed as the percentage by mass of LDADC in the binder (asphalt plus LDADC).

To determine if the antioxidant had been uniformly dispersed in the binder, samples from all four collection trays in sections 7, 9, and 10 of the Townsville trial were tested using the infrared procedure. The results (see Table 2) indicated that the level of antioxidant was uniform along the length of the section and that satisfactory dispersion of the LDADC had been obtained.

A comparison of the percentages of LDADC added with those measured in the sprayed binder (see Tables 2 and 3) indicates that little or no degradation of the LDADC occurred during antioxidant mixing or binder spraying. In the case of ZDC, it was estimated that 25 percent of the antioxidant degraded during this operation.

TABLE 1 DESCRIPTION OF ASPHALTS

Asphalt No.	Trial	Production Method	Durability (days)
391	Townsville	Kuwait crude, blend of PPA and vacuum tower residue	10.4
395	Hopetoun	Light Arabian crude, straight run blended with 25% PPA	12.6
396	Hopetoun	Air blown Heavy Arabian	7.0

TABLE 2 RESULTS OF TESTING COLLECTION TRAYS FROM TOWNSVILLE TRIAL

Section No.	% LDADC added (lead analysis)	% LDADC present (by infra-red)			
1	0	-			
2	0.9	0.8	0.8		
3	1.8	2.1	2.0		
4	2.4	2.5	2.7		
5	4.1	4.1	4.0		
6	0	-			
7	0.8	1.0	0.8	0.8	0.8
8	1.6	1.7	1.6		
9	2.8	2.4	2.5	2.5	2.6
10	5.3	4.7	4.7	4.8	4.8

TABLE 3 RESULTS OF TESTING COLLECTION TRAYS FROM HOPETOUN TRIAL

Asphalt	Section No.	% LDADC added (lead analysis)	% LDADC present (by infra-red)	
395	2	0	-	
395	4	1.0	0.9	0.9
395	6	2.0	1.8	1.9
395	8	3.9	3.7	3.8
396	11	0	-	
396	7	1.0	1.1	1.1
396	5	2.1	2.3	2.5
396	10	2.0	1.7	1.7
396	3	3.8	3.8	3.7
396	9	5.8	5.6	5.5

Durability Testing

To determine the effect of the antioxidant on the laboratory measured durability of the binders, samples were subjected to the ARRB Durability Test. Testing was conducted according to Australian Standard 2341 (*8*) except that the rolling thin film oven treatment procedure was omitted, because the samples had already been subject to elevated temperature during transport to the site and storage in the delivery tanker.

For each of the three asphalts, samples taken from the tanker that delivered the material to the site were tested in the "as received" condition (no antioxidant) and with measured amounts of LDADC added. The results are shown in Figure 2. Generally high concentrations of LDADC in the asphalt are correlated with high durability. For bitumens 391 and 395, however, the addition of 1 percent LDADC results in a small reduction in durability compared with the unmodified asphalt.

Environmental and Occupational Health Monitoring

The Australian Mineral Development Laboratories (AMDEL) performed lead analysis of soil samples at the Hopetoun site before and after the experiment and also arranged for monitoring of the lead exposure of construction workers. Analysis of soil samples collected in the area of the experiment 13 months after the construction gave a range of values that were similar to the normal lead concentration of the earth's crust and showed no significant increase compared with samples collected just before the road trial (*13*).

The construction workers were monitored for lead exposure during the trial, and sampling units were attached to the asphalt distributors. On the basis of results obtained, Hamilton and

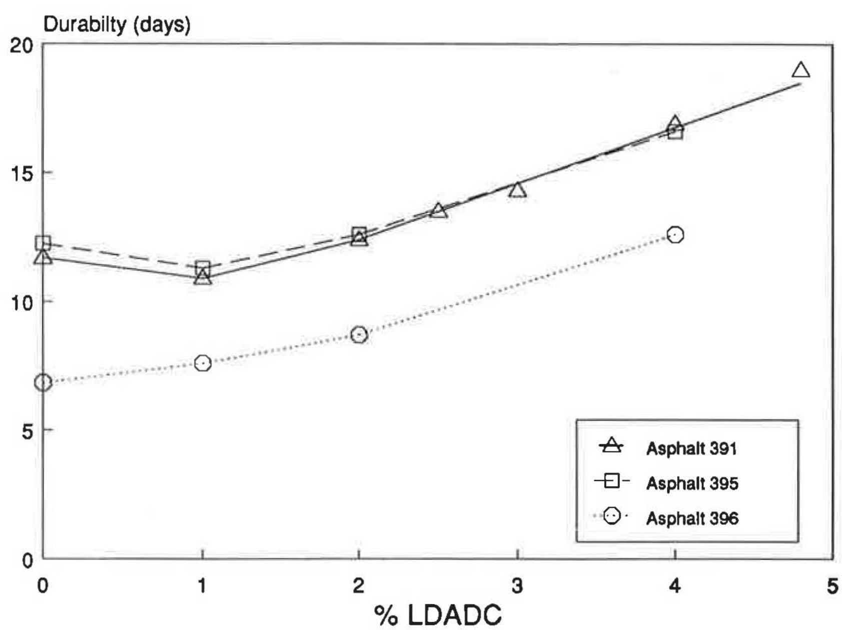

FIGURE 2 Durability test results for road trial asphalts.

Tate (*14*) reported that road worker exposure to airborne lead would be unlikely to present a hazard if LDADC were widely used as an additive to the asphalt used in road making. The highest exposure was calculated to be 0.4 percent of the Threshold Limit Value-Time Weighted Average (TLV-WA) value of 0.15 mg/cu m, recommended by the American Conference of Government Industrial Hygienists (*14*). The blood lead data showed that lead uptake via both ingestion and inhalation during the trial was negligible (*14*).

SAMPLING AND TESTING OF THE TRIAL SECTIONS 2 YR AFTER CONSTRUCTION

Procedure for Sampling and Recovery of Asphalt

The method for monitoring the degree of asphalt hardening in sprayed seals involves first cutting samples, approximately 200 mm square, from the seal with a motor-powered Carborundum cutting disc. Sampling is normally performed in the wheeltrack closest to the seal edge. The samples are returned to the laboratory and individual seal stones plucked from the surface after a sample has been warmed. The asphalt adhering to the undersides of these stones is recovered by solution in toluene, centrifuging and decanting the solution and then removing the solvent by evaporation.

Sampling is normally first performed 2 yr after construction when volatile diluents, such as kerosene, will mostly have evaporated. Any remaining diluent is removed during the solvent evaporation stage of the recovery treatment. The degree of hardening of the recovered asphalt is determined by measuring the apparent viscosity at 45°C and a shear rate of $5 \times 10^{-3}\ s^{-1}$ in exactly the same way as the asphalt recovered from the Durability Test treatment (*8*).

Sampling of the Trials

The results of testing asphalt recovered from the Townsville trial samples showed poor reproducibility of viscosity measurements for duplicate samples. The samples were carefully examined, and the trial was inspected a second time. This revealed that asphalt absorption into the underlying granular base material was occurring. The degree of absorption was not uniform either along the length of the road or transversely. Where substantial absorption occurred, the asphalt film had thinned and oxidation was occurring more rapidly than in other areas.

The trial was therefore resampled, with samples taken in this case from areas where visual inspection of the surface beneath the seal stones indicated that no asphalt absorption had occurred. The results of the first sampling exercise were discarded.

The Hopetoun trial was sampled in the normal manner.

Results and Discussion

Figure 3 shows the viscosity of the asphalt recovered from the trial samples plotted against the percentage of LDADC originally added to the binder in each section. The results for both trials show a trend for viscosity to decrease with increasing antioxidant concentration, and the regression lines for the three asphalts have been plotted. In all cases, the sections with antioxidant have hardened more slowly than the control sections, and the effect becomes more marked with increased concentration of the antioxidant.

Asphalt 391, used in the Townsville trial, has approximately the same durability (intrinsic resistance to hardening) as Asphalt 395, placed at Hopetoun. The higher ambient temperature at the Townsville site has resulted in much more rapid hardening of the asphalt there, compared with the asphalt of similar durability at Hopetoun.

The effect of asphalt durability on hardening rate can be seen by comparing the degree of hardening of the two Hopetoun trial asphalts. Sections containing Asphalt 396, which has a low durability value of 7.5 days, have hardened more than the corresponding sections placed with Asphalt 395 (durability of 12.1 days).

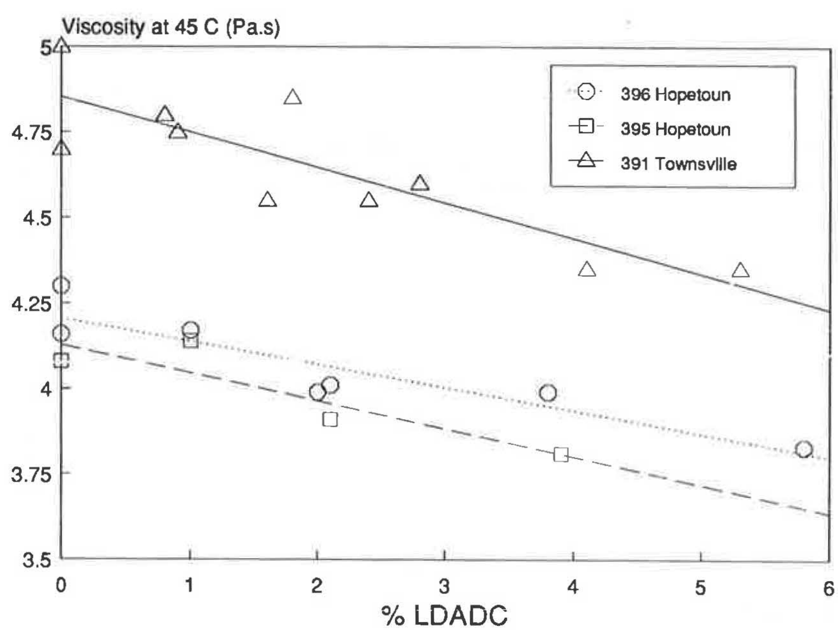

FIGURE 3 Viscosity of asphalt samples extracted from 2-yr-old trials.

Asphalt viscosity at laydown was approximately 3.5 log Pa.s, so only a moderate amount of hardening has occurred so far at Hopetoun. There has been a greater amount of hardening at Townsville, and it is useful to examine the predicted hardening curve for Asphalt 391, which has been calculated for the site using Equation 1.

The asphalt viscosities 2 yr after construction are shown in Figure 4 for the unmodified binder and for binders containing 2.5 and 5 percent LDADC. The values were obtained from Figure 3 by using the regression line for Asphalt 391. The dashed line at the top of Figure 4 is the viscosity level at which distress is considered likely to occur. This is an estimate based on the behavior of the surfacing at a site with minimum winter temperatures similar to those in Townsville (*6*). For the Hopetoun site, the estimated distress viscosity level is 5.7 log Pa.s.

The point for unmodified Asphalt 391 (0 percent LDADC) lies on the prediction curve indicating that the asphalt is hardening at the expected rate. The asphalt hardening model is unlikely to apply to binders containing antioxidant, so no prediction of future behavior can be made by this means. However, if the reduction of 0.5 log Pa.s, produced by the addition of 5 percent LDADC, were to be sustained until distress viscosity was reached, the time to reach distress would be increased from 10.8 yr to 15.0. yr. This situation is shown by the dotted line in the figure. If the reduction in hardening rate were sustained (i.e., the antioxidant curve continued to be flatter than the control, rather than running parallel to it as in the previous case), the improvement in life would be even greater.

Asphalt 391 has a comparatively high durability, so an improvement in durability is not as necessary as it would be in the case of a less durable material.

FUTURE WORK

It is proposed to continue periodically sampling and testing the experimental sections at the two trial sites for a number of years, preferably until distress occurs. Although the early results are more promising than those obtained with ZDC, it is necessary to continue monitoring to ensure that the effect of early improvements is not lost with time, as happened with the zinc antioxidant.

A further trial is proposed in the Alice Springs area because sprayed seals probably experience more severe conditions there than anywhere else in Australia. Alice Springs lies in the geographical center of the continent and experiences very high summer temperatures and cool winter temperatures. Asphalt therefore hardens rapidly by oxidation in the summer and becomes brittle and liable to fracture in the winter. This combination leads to seal lives that appear to be considerably shorter than experienced elsewhere.

Efforts will be made to obtain, for the trial, an asphalt that is not very durable because the major use of LDADC, if it proves successful in the long term, would be to improve low-durability materials.

CONCLUSIONS

1. Little or no LDADC degradation occurred while the antioxidant was being mixed with asphalt or during the spraying operation at two sprayed seal road trials.
2. Tests on samples taken 2 yr after construction of the trial sections showed that incorporation of the antioxidant in asphalt reduced the rate of asphalt hardening for all three asphalts used.
3. The asphalt hardening rate appeared to decrease in a linear manner with increases in LDADC concentration.
4. The road trials should continue to be monitored to determine whether the early improvement in the asphalt hardening rate continues over the long term.

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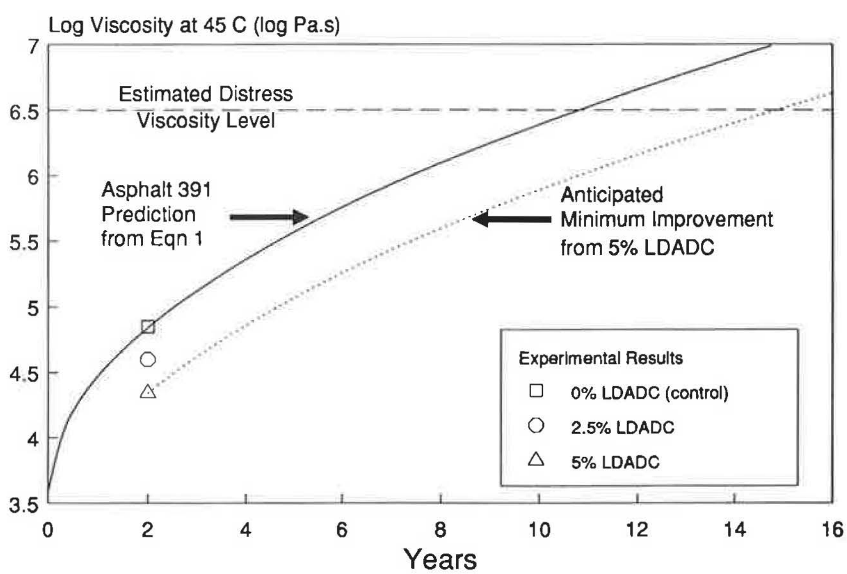

FIGURE 4 Predicted and actual asphalt viscosities at Townsville trial.

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