Results of Road Trials of Two Asphalt Antioxidants

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Laboratory testing indicated that two antioxidants, lead diamyldithiocarbamate (LDADC) and hydrated lime (HL), were effective in reducing the rate of oxidative hardening of asphalt binders. Road trial sections with sprayed seals of of both materials were placed at a number of sites in Australia and were monitored for up to 10 years. Each trial consisted of a number of sections that were identical to each other except for the concentration of antioxidant incorporated into the asphalt. The trials were regularly inspected and sampled. Samples were taken back to the laboratory, the asphalt binder was recovered, and its viscosity was measured. By comparing the viscosities of sections onto which asphalt binders containing antioxidant were laid with control sections (asphalt only, no additive) it was possible to determine how effective the antioxidant was in reducing asphalt hardening. The results suggest that LDADC gives the greatest benefit in pavement situations in which binder hardening is rapid. The addition of more than 2.5 percent LDADC appears to produce substantial reductions in the hardening rate. When binder hardening occurs slowly (a durable asphalt in a temperate climate) the addition of LDADC does not appear to reduce binder hardening rate. Although HL was found to retard the rate of hardening of a range of asphalts under laboratory test conditions, it was shown to have no significant effect under long-term exposure (up to 10 years in a sprayed seal).

Sprayed seals are very important to Australia. Use of this low-cost technology has allowed the establishment of an all-weather road network by a population of 18 million people in a country with a land mass of almost 8 million km^2 (80 percent the size of the United States). When proper design and construction techniques are used, sprayed seals can give satisfactory service on roads carrying in excess of 5,000 vehicles per lane per day.

Of the total Australian road network comprising 800 000 km, approximately 200 000 km is sealed, generally with a single-application sprayed seal. Hot-mixed asphalt is normally used as a thin surfacing only on roads in or close to the major metropolitan centers, but its use is growing. Portland cement concrete roads are very much in the minority, enjoying limited popularity in only one of the six Australian states.

The average seal life before extensive maintenance or a reseal is required is about 10 years in the eastern Australian states and about 16 years in Western Australia, where better road building materials are available. Although Australia is free of the problems associated with freeze-thaw cycles, high ambient temperatures are common and road surface temperatures can exceed 70°C (*1*). Under these conditions the asphalt binder in a surfacing can oxidize rapidly, and binder hardening is thought to be the critical factor in determining the service life of about half of all seals.

The resistance of asphalt binders to hardening is controlled in most Australian states through specification of a minimum durability result in which the binder is tested according to an Australian standard procedure (*2*). The durability test result has been correlated with binder hardening in the field through a number of full-scale road trials (*3*).

A second means of controlling the binder hardening rate in thin surfacings may be through incorporation of an antioxidant in the binder. Two additives that have shown promise in laboratory testing are lead diamyldithiocarbamate (LDADC) and hydrated lime (HL). These antioxidants were evaluated in a series of sprayed seal road trial sections laid in different climatic areas of Australia. The trial sections were regularly inspected and sampled, and binder viscosity was measured in the laboratory. The oldest trial sections are now more than 10 years old, and the monitoring program has been terminated. This paper summarizes the road trial results.

EXPERIMENTAL PROCEDURES

Durability Testing

The Australian Road Research Board Ltd (ARRB) Durability Test (*2*) is a laboratory procedure that measures the intrinsic resistance of an asphalt to thermal oxidation hardening. The test consists of a rolling thin film oven (RTFO) pretreatment (*4*) and then exposure of a 20-μm-thick film of asphalt in an oven at 100°C. This is achieved by depositing a specimen of RTFO-treated asphalt onto the walls of glass bottles that are placed in a rotating rack in a special oven. The bottles are withdrawn periodically, and the asphalt is removed and its viscosity is measured at 45°C. The durability of the asphalt is the time (in days) for it to reach an apparent viscosity of 5.7 log Pa·sec. A high number indicates a durable bitumen that should give a long life.

Sampling and Treatment of Field Samples

Samples from road trial sections were normally taken in the outer (curbside) wheelpath. A motor-powered Carborundum-cutting disk was used to cut a section of seal approximately 200-mm square. The seal sample, with any adhering material, was carefully removed from the surface and was transported to the laboratory for testing.

The seal sample was warmed in an oven, and individual stones were plucked from the surface. The asphalt adhering to the undersides of these stones was recovered by solution in toluene, centrifuging and decanting the solution, and then removing the solvent by evaporation.

The degree of hardening of the recovered asphalt was determined by measuring the apparent viscosity at 45°C and a shear rate of 5×10^{-3} sec^{-1} by using a Shell sliding plate microviscometer.

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LDADC ROAD TRIALS

Previous Studies

The addition of antioxidants to asphalt has been shown to be effective in reducing the rate of asphalt hardening. Martin (*5*) studied 33 antioxidants belonging to four major classifications and identified the chemical class known as "peroxide decomposers" as the most promising of those tested. This class includes zinc and lead dialkylcarbamates.

Work by Haxo and White (*6*) on the effect of a series of lead and zinc antioxidants on asphalt hardening identified LDADC as being particularly effective in reducing the rate of hardening. The good solubility of LDADC in asphalt was considered an important factor.

Laboratory Testing

The ARRB Durability Test (*2*) was used to evaluate the effect of adding LDADC to the eight core asphalts used in the Strategic Highway Research Program (SHRP). Figure 1 shows the results of this experiment, whereas Figure 2 gives the results for the three asphalts used in the Australian road trials. The effect of LDADC on the rate at which an asphalt oxidizes appears to depend on the durability of the original asphalt. For low-durability asphalts the addition of LDADC always produces an increase in durability. For more durable asphalts, however, LDADC concentrations of less than 2 percent can result in a reduction in durability, and this is discussed in a later section.

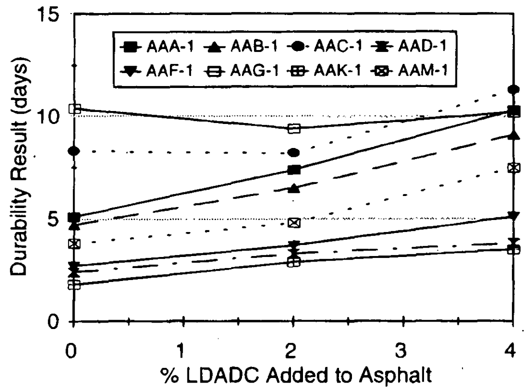

FIGURE 1 Effect of LDADC addition on durability of SHRP asphalts.

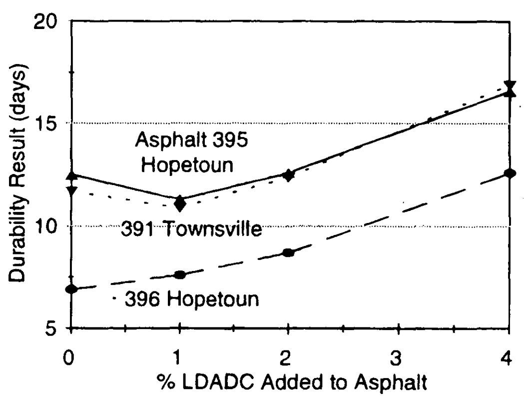

FIGURE 2 Effect of LDADC addition on durability of LDADC trial section asphalts.

Construction of Trial Sections

Two full-scale LDADC road trial sections were laid in Australia. They both comprised sprayed seal surfacings laid over an unbound granular base and used a Class 170 (*7*) (85/100 pen) asphalt. Each trial consisted of a number of sections that were identical to each other except for the concentration of LDADC incorporated into the asphalt. A description of the binders used is given in Table 1. Further information on the construction of Australian sprayed seals is given elsewhere (*8*).

The first trial was laid in a tropical environment 100 km inland from the city of Townsville (yearly average maximum daily air temperature, 28.6°C) in northern Queensland during November 1985. Eleven experimental sections with 16-mm seals were placed by using a single asphalt. The sections had nominal LDADC contents of 0, 1, 2, 3, 4, and 5 percent (by mass), and each concentration, except the highest, was duplicated.

The second trial section, laid in April 1986 at Hopetoun in the more temperate south of Australia, had a 10-mm seal. In this experiment two asphalts were used, and the LDADC concentrations were not duplicated. In both trial sections the sections were between 400 and 500 m in length, and the trial section layouts are shown in Figure 3.

So that LDADC, which is a thick viscous liquid, could be easily pumped or poured for addition to asphalt, the material was dedrummed and diluted with mineral turpentine in the mass ratio of 90 parts of LDADC to 10 parts of mineral turpentine. The material was then pumped into the asphalt distributor on site by using the port normally used for kerosene addition (under cool conditions Australian asphalts are cut back with kerosene on site). Further information on the construction of the trial sections and on early performance is given elsewhere (*9*).

Results

Degradation of Antioxidant

Binder samples were collected by placing trays on the pavement and removing them after the distributor had passed but before application of the cover aggregate. The contents of the collection trays were assayed for LDADC content by using an infrared spectrometric procedure (*10*) and for lead content by atomic absorption spectroscopy. The latter determination was carried out 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 (Figure 3). 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 give an indication of the degree of degradation of the antioxidant.

LDADC is believed to act sacrificially as an antioxidant. That is to say that the LDADC decomposes as it provides protection for the bitumen against oxidation. Infrared spectrometry testing (*10*) indi-

TABLE 1 Asphalt Used in LDADC Trials

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

* Binder sampled after spraying - no RFOT pre-treatment applied before durability testing.

Townsville (Asphalt 391)	Hopetoun (Two Asphalts)
4.8% LDADC	396 + 0%
2.5% LDADC	396 + 2.0%
1.6% LDADC	396 + 5.8%
0.8% LDADC	395 + 3.9%
0% LDADC	396 + 1.0%
4.1% LDADC	395 + 2.0%
2.5% LDADC	396 + 2.1%
2.1% LDADC	395 + 1.0%
0.8% LDADC	396 + 3.8%
0% LDADC	395 + 0%
0% LDADC	396 + 0%

FIGURE 3 Layout of trial sections in two LDADC trials.

cated that for both trial sections only those sections that originally contained about 4 percent or more LDADC had any dithiocarbamate structure remaining after 2 years of pavement service. The concentration of dithiocarbamate in these sections was observed to reduce further, and no material was detected after 6 years.

Viscosity Testing of Samples

The trial sections were inspected and sampled at regular intervals, and the viscosity of the recovered binder was determined.

Figure 4 shows the results for the Townsville LDADC trial. These results indicate that all sections containing LDADC either hardened less than the control section or hardened approximately the same as the control section. For samples initially containing 2.5 percent or more LDADC a substantial reduction in the hardening rate due to LDADC addition was obtained.

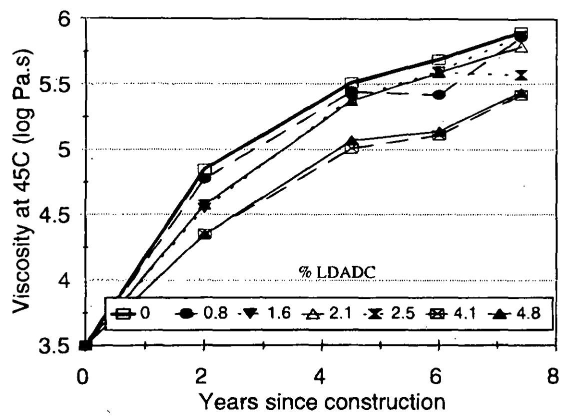

FIGURE 4 Hardening at Townsville site (tropical climate).

Binder hardening at the Hopetoun trial section (Figures 5 and 6) has proceeded more slowly than that at the Townsville trial section because of the lower ambient temperatures at the Hopetoun site. The yearly average maximum daily air temperature at Hopetoun was 23.5°C, compared with 30.1°C at the site near Townsville.

In the case of asphalt 395, sections containing LDADC hardened more slowly than the control section (no LDADC) for the first 2

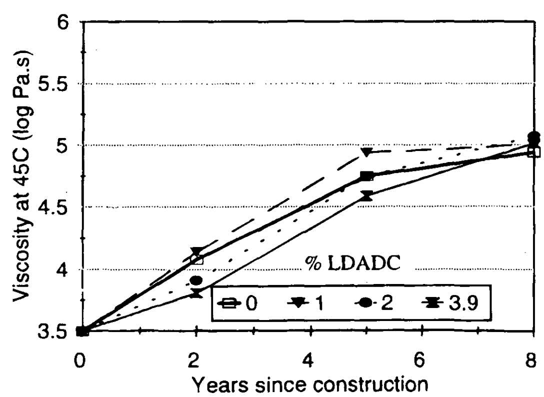

FIGURE 5 Hardening of Asphalt 395 at Hopetoun (temperate climate).

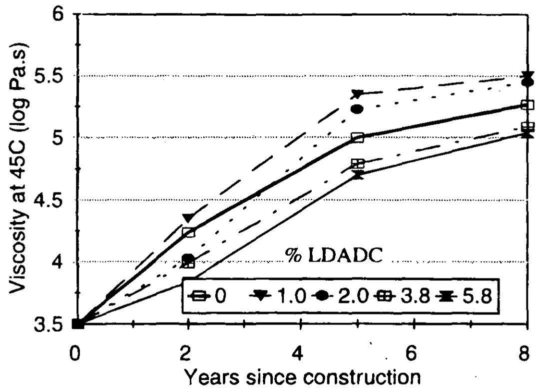

FIGURE 6 Hardening of Asphalt 396 at Hopetoun (temperate climate).

years. After 4 years only the section containing 3.9 percent LDADC had hardened less than the control section. After 8 years none of the LDADC sections had a lower viscosity than the control section.

Asphalt 396 is less durable than Asphalt 395 and has hardened through oxidation more rapidly. After 2 years those sections with more than 2.0 percent LDADC had hardened less than the control section. After 5 years only sections with 3.8 percent or more LDADC had hardened less than the control section, and the situation was unchanged for samples taken 8 years after construction.

Discussion of Results

Results from long-term road exposure of LDADC-modified binders have indicated that when binder hardening occurred slowly (a high-durability asphalt in a temperate climate) LDADC did not provide a significant benefit in the long term. When binder hardening was more rapid a significant reduction in the hardening rate was obtained for LDADC concentrations of 2.5 percent or more.

It is possible that in some asphalts natural antioxidants, perhaps of a phenolic nature, may be present, and these may be antagonistic to the peroxide decomposing carbamates. Part of the carbamate antioxidant reacts with the natural antioxidants and is destroyed, so that small concentrations of LDADC are ineffective.

The road trial results suggest that the most beneficial use of LDADC would be to improve the oxidation resistance of (a) binders used in hot environments, where hardening is likely to occur rapidly, and (b) low-durability binders, that is, those binders most likely to give short service lives. Most North American asphalts appear to fall into this latter category.

Whether the process would be cost-effective depends on the price charged for LDADC. The material used in the trials was manufactured in comparatively small batches, and a considerable reduction in cost might be expected if large-scale manufacture were to be undertaken to supply the road construction industry. No information was available on the future cost of LDADC under these circumstances.

HL ROAD TRIALS

Previous Studies

Plancher et al. (*11*) observed that the rate of hardening of some asphalts by oxidation was reduced when they were first treated with 0.5 to 1.0 percent (by mass) HL. HL is often a constituent of fillers used in hot-mixed asphalt manufacture and is believed to improve the resistance of the mixes to stripping by water action.

Petersen et al. (*12*) later studied the effect of adding between 10 and 30 percent (by mass) HL to asphalt that was then oxidized by a thin film accelerated aging test (113°C, 0.16-mm film for 3 days). The lime was left in the specimens during oven exposure, and a reduction in oxidative hardening was observed for concentrations of up to 20 percent (by mass). This was believed to be due to (a) a reduction in the formation of oxidation products by removal of oxidation catalysts and promoters and (b) reduced sensitivity to the oxidation products through removal of reactive polar molecules that would otherwise interact with the oxidation products to cause an increase in binder viscosity (*11*).

Laboratory Testing

Dickinson (*13*) subjected asphalts with suspensions of HL-containing fillers to the ARRB Durability Test procedure. The asphalts were recovered by solvent extraction after the oven exposure phase. Control tests run in the absence of filler indicated that the solvent recovery procedure did not affect the viscosity of the hardened asphalt. Table 2 gives the results for a number of Class 170 (*7*) (85/100 pen) asphalts manufactured from Middle East crudes. The industrial HL used contained 81 percent calcium hydroxide and 10 percent cement kiln dust (CKD).

Construction of Trial Sections

In all of the chip seal lime trials HL was added to the asphalt by using a transfer box in the line connecting the bulk supply tanker to the distributor. The hot asphalt was sucked by the sprayer pump from the tanker, and the HL was tipped into the transfer box from the bag by hand. Dispersion of the HL in the asphalt was achieved by passing the crude mixture through the distributor pump (either piston or gear type) and subsequent circulation in the sprayer.

Information on the Class 170 (*7*) (85/100 pen) asphalts used in the lime trials is given in Table 3, together with data on the percentage of HL in each section and the period for which each trial section was observed.

Results

Samples from the collection trays (placed in the path of the distributor during placement of the trial) were assayed for lime content. They were also subjected to a shortened form of the Durability Test by measuring the viscosity after 10 days of exposure in the durability oven (rather than determining the days to reach a viscosity of 5.7 log Pa·sec as in the full test). The exception was Manangatang, where a full viscosity test was carried out on two samples. The results are given in Tables 4 and 5.

The results indicate that, in general, the degree of dispersion of the lime in asphalt was satisfactory. For samples from all trials the laboratory Durability Test treatment indicated that increased resistance to oxidative hardening was obtained with the addition of HL.

TABLE 2 Effect of HL-Containing Fillers on Asphalt Durability Test Result

Asphalt Crude Source and Processing	Durability (days)		
	Without Additive	With CKD	With Industrial HL
Additive Concentration 26.6% by mass PPA from Light Arabian distillation residue fluxed with furfural extract of lub. oil stock	4.5	-	7.0
Kuwait blown residue at 300°C to 30/40 pen then fluxed with unblown residue	5.0	7.0	7.0
Kuwait residue blown to grade at 245°C	8.0	11.0	-
Basrah residue blown to grade at 250°C	13.0	18.0	-
PPA from Basrah residue fluxed with that residue	17.0	>23.0	-
Additive Concentration 6.4% by mass Safaniyah (Heavy Arabian) residue blended with PPA from Light Arabian residue	10	-	13

PPA is Propane Precipitated Asphalt - indicates sample not tested

TABLE 3 Details of HL Road Trial Sections

Location	Asphalt	Durability (days)	HL in Sections (% by mass of binder)	Period Observed (years)
Hopetoun (YMMT 23.5°C)	Source uncertain (two asphalts used in the region)	13.2	0, 0, 0, 0, 5.7, 10.7, 15.3	7.7
Lake Boga (YMMT 22.8°C)	Blend of PPA from a Light Arabian crude and a distillation residue from a Heavy Arabian (Safaniyah) crude	8.3	0, 5.7, 10.7, 15.3	9.3
Anna Plains (YMMT 32.4°C)	Imported from Singapore. A blend of a vacuum distillation residue from a Light Arabian crude and a PPA derived from this distillation residue	14.5	0, 3, 6, 9, 12	9.0
Manangatang (YMMT 23.5°C)	Blend of distillation residue from Heavy Arabian (Safaniyah) and a PPA from the vacuum residue of a Light Arabian crude	9.5	0, 1.5, 2.9, 6.1	10.6

PPA = Propane Precipitated Asphalt
YMMT = Yearly average of the maximum daily air temperature

TABLE 4 Testing of Collection Tray Samples: Hopetown and Lake Boga Trial Sections

	Hopetoun Trial		Lake Boga Trial	
HL added (% by mass)	HL in binder sample (% by mass)	Durability Result (10 days exposure) (Log Pa.s)	HL in binder sample (% by mass)	Durability Result (10 days exposure) (Log Pa.s)
0	-	5.27	-	5.78
5.7	4.2	5.11	6.2	5.60
10.3	9.3	5.12	8.2	5.52
15.3	17.3	5.05	15.2	5.45

- indicates sample not tested

TABLE 5 Testing of Collection Tray Samples: Broome and Manangatang Sections

Broome Trial			Manangatang Trial		
HL added (% by mass)	HL in binder sample (% by mass)	Durability Result (10 day exposure) (Log Pa.s)	HL added (% by mass)	HL in binder sample (% by mass)	Durability Test Result (Full Test) (days)
0	-	4.94	0	-	10
3	2.4	-	1.5	1.0	-
6	6.1	4.90	2.9	2.3	-
9	6.4	4.78	6.1	5.5	15
12	10.8	4.79			

- indicates sample not tested

The test sections were sampled and tested by the same procedures used for the LDADC trials. The viscosity of the recovered binder (treated to remove the lime particles) is shown as a function of the added lime content in Figure 7.

The results for Hopetoun trial sections suggest that the addition of lime has caused an increase in the binder hardening rate, whereas the opposite seems to be the case for Lake Boga trial sections. At both the Anna Plains and Manangatang trial sections, sections to which HL was added show little difference in viscosity from the control sections (0 percent HL). Taking all four trials together, it appears that a clear reduction in binder hardening rate with the addition of lime has not been demonstrated.

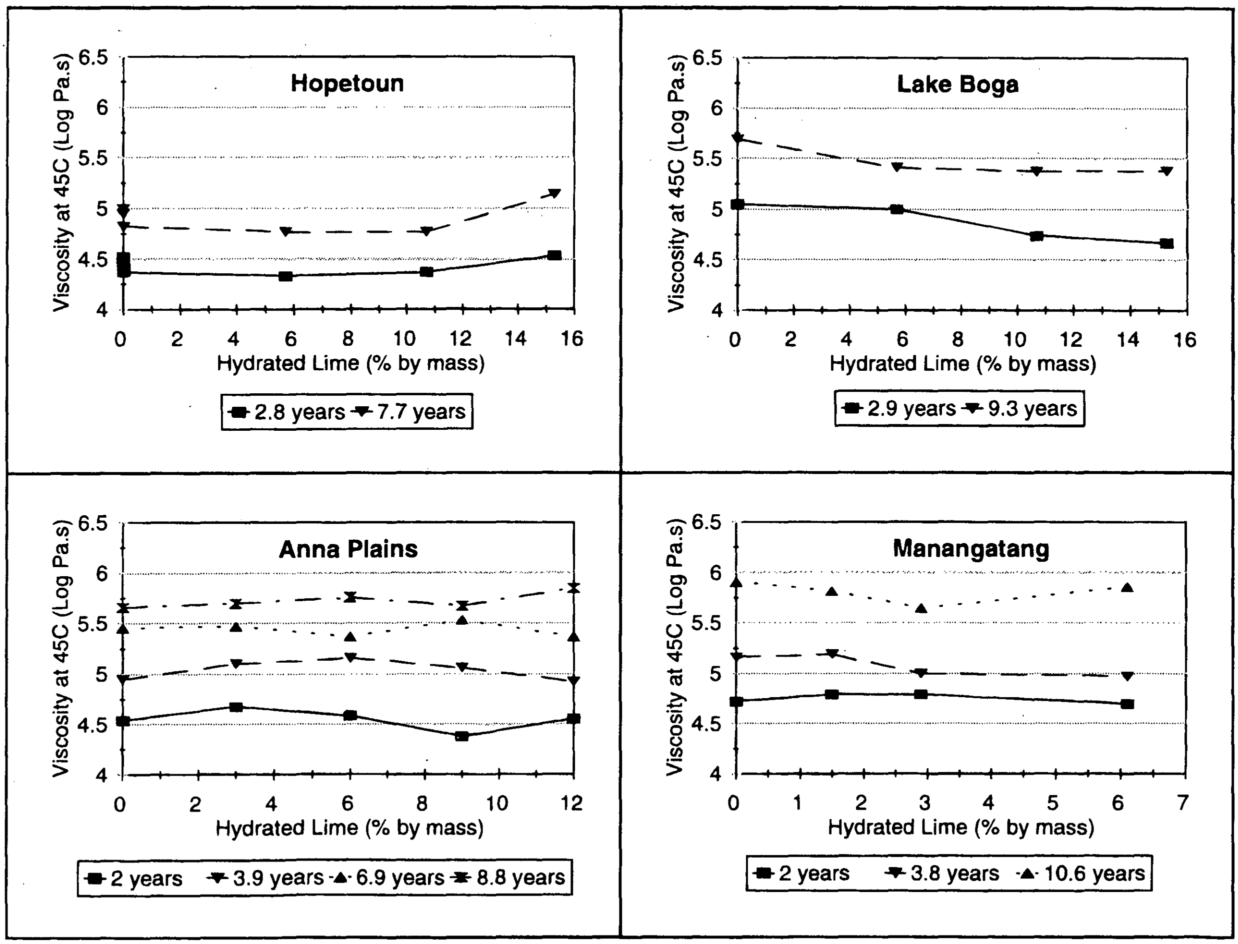

FIGURE 7 Asphalt hardening at HL road trial sections.

Discussion of Results

Although HL was found to retard the rate of hardening of asphalts due to atmospheric oxygen attack under laboratory test conditions (20-μm film at 100°C for 10 days or more), it has now been shown to have no significant effect under long-term exposure (up to 10 years in a sprayed seal).

Finely divided calcium carbonate was found to be ineffective in retarding hardening under the Durability Test conditions (*13*), and carbonation of the surface of the HL particles by atmospheric carbon dioxide early in the life of the seal (converting the HL to calcium carbonate) may have nullified its retarding effect in the pavement.

GENERAL CONCLUSIONS

1. LDADC appears to give the greatest benefit in pavement situations in which binder hardening is rapid. The addition of more than 2.5 percent LDADC appears to produce substantial reductions in binder hardening rate.
2. When binder hardening occurs slowly (a durable asphalt in a temperate climate) the addition of LDADC does not appear to reduce the binder hardening rate.
3. The most beneficial use of LDADC would be to improve the oxidation resistance of binders used in hot environments and low-durability binders. Most North American asphalts appear to fall into this latter category.
4. Although HL was found to retard the rate of hardening of asphalts due to atmospheric oxygen attack under laboratory test conditions, it was shown to have no significant effect under long-term exposure (up to 10 years in a sprayed seal).
5. A possible explanation for the anomalous behavior of HL is that attack by atmospheric carbon dioxide causes carbonation of the surface of the HL particle early in the life of the surfacing.

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