

# Chemical Modifiers To Improve the Strength and Durability of Asphalt Concrete

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The purpose of this paper is to discuss the value of chemical modifiers as a means of improving the physical properties and durability of asphalt concrete. A review of the factors that adversely affect the integrity and durability of asphalt concrete pavements is included. The ability of several different types of chemical modifiers to improve the properties and durability of asphalt concretes is illustrated by test data on laboratory and field specimens with and without chemical modifiers. Liquid chemical modifiers appear to provide a practical means of improving the strength, age-hardening resistance, water resistance, and overall integrity of asphalt concrete pavements.

The United States has the most extensive road system in the world. A vast majority of these roads have been constructed or renewed, or both, with asphalt concrete. Highway departments at all governmental levels are concerned about the quality and integrity of these pavements. Some of the factors that adversely affect the quality and durability of pavements are

- Poor-quality aggregates,
- Poor aggregate gradations,
- Poor-quality asphalts,
- Unstable substrates,
- Unusual and damaging weather,
- Traffic volume and heavily loaded vehicles,
- High temperatures and oxygen,
- Daily temperature cycling,
- Very low temperatures, and
- Water and ice.

In this paper are discussed efforts to improve the strength and durability of asphalt concrete by incorporating chemical additives in hydrocarbon asphalt cements. Chemical additives have been used for many years to improve other hydrocarbon products such as lubricants, fuels, and hydraulic fluids.

## ASPHALT ADDITIVES AND MODIFIERS

A variety of materials has been proposed over the years as modifiers to improve the performance of asphalt concrete. These include fillers and fibers to reinforce the mixture; sulfur as a partial or complete replacement for asphalt; and polymers, elastomers, antistripping agents, and metal complexes to improve the properties of the asphalt cement and ultimately the properties of the asphalt concrete.

The chemical modifiers discussed in this paper are liquid products that readily dissolve in asphalt cements. They do not significantly change the physical properties of the asphalt cements and do not require changes in current road-building procedures. These chemical modifiers are heat stable and remain effective after substantial storage periods in molten asphalt at temperatures in the 250°F-to-350°F range.

Three categories of chemical modifiers will be discussed. Their performance characteristics will be illustrated by test data obtained before and after various aging cycles. Evaluations of (a) asphalt cements, (b) laboratory-prepared asphalt concrete specimens, and (c) cores cut from test roads with and without chemical modifications are presented.

The three types of chemical modifiers are designed to improve the strength of asphalt concrete, improve the resistance of asphalt cements to age hardening, or improve the water resistance of asphalt concrete. The modifiers may be used to obtain a specific improvement, or they may be used in combination to address several problems.

## MANGANESE MODIFICATION TO IMPROVE STRENGTH

Low concentrations of asphalt-soluble manganese compounds improve the strength and stability of asphalt concrete as measured by indirect tensile, Marshall stability, and unconfined compression tests (1-3). The manganese is inactive until the modified asphalt cement becomes a thin coating on aggregate surfaces in the hot-mix plant. Manganese then accelerates oxidation during hot mixing, during transport to the job site, during placement, and for a period of time after placement (4). The rate at which the consistency of the asphalt cement and the strength of the asphalt concrete increase is partly dependent on the ambient temperatures that prevail at a given site. The end result is the production of a high-consistency asphalt cement in the asphalt concrete. It is possible to obtain much higher stabilities with manganese-modified AC-5, AC-10, or AC-20 grade asphalts without the mixing and placement difficulties that would occur if a very high-viscosity asphalt cement (i.e., an AC-70 or AC-80 grade) were used.

The 140°F stabilities in the figures and tables that follow were obtained using the Marshall apparatus. The word Marshall has been omitted because the cylindrical test specimens were not prepared strictly in accordance with ASTM D 1559. The specimens were prepared with an automatic triple mechanical compactor rather than with a hand-operated compaction hammer. In addition, the number of blows to compact, in most

cases, was not 50 per side but the number required to obtain specimens with approximately 7 percent air voids. Specimens compacted to lower densities are important for determining whether adequate stabilities will be obtained immediately after construction and for evaluating the resistance of the pavement to the degrading effects of air and water over extended periods at various temperatures after placement. The method of specimen preparation in a given comparative study is consistent so that effects of chemical modifiers on a given control asphalt cement can be determined without extraneous variables. Three replicates were used for each data point, and the numbers reported are the average of the three.

The effect of temperature on both a control and a manganese-modified asphalt concrete system is shown in Figures 1 and 2. Note that the time required for the modified, softer asphalt to provide increased stability becomes shorter as the curing temperature increases. Oxidation of asphalt is a chemical reaction. As a general rule the rate of chemical reactions doubles for every 10°C (18°F) increase in temperature. Catalysts increase the rate of reaction at any temperature. Manganese is an oxidation catalyst. The curing temperatures are continuous in these laboratory curing cycles. The times to obtain comparable increases in stability in actual service will be longer because peak temperatures on the road are experienced for only a few hours a day and vary with depth. The manganese modifier ultimately becomes inactive as it complexes with oxidized sites in the asphalt cement and the reaction stops. This is indicated by the leveling of the curve in Figure 2. The most effective way to illustrate the effect of manganese modification is to present engineering data on cores taken from highways.

A highway was constructed in West Virginia in 1982. This highway carries a large volume of heavily loaded coal trucks and thus high stability was required. The data given in Table 1 indicate that the modified wearing course had 54 percent higher stability than the control after 4 years and had reached a maximum after 2 years. In the base course the benefit of manganese modification was quite apparent after 2 years: its stability was 82 percent higher than that of the control. The data again indicate that the stability increase induced by the manganese appears to have leveled off after 2 years. Deflection tests run by West Virginia highway personnel after 2 years indicated a 25 percent higher deflection for the control pavement.

A section of Route 97 was placed in the same area of West Virginia in 1984–1985 near Beckley. Data are given in Table 2 that compare the properties of preconstruction laboratory specimens with cores cut from the subsequently placed highway. In this case a 33 percent higher stability was produced in the modified wearing course after 2 years, but the modified base course does not appear to have reached maximum stability. The laboratory results give an indication of the relative stabilities of control and modified systems. The only factor that causes change in the laboratory curing cycle is heat; changes in actual pavements are the result not only of heat but also of water and traffic. The laboratory specimens were all compacted to approximately 7 percent air voids to simulate initial pavement densities and to determine whether the initial stability of the modified asphalt concrete would be adequate to carry initial traffic loads. This proved to be true after placement of this road.

The low-temperature indirect tensile data on road cores from the Beckley, West Virginia, highway also indicate that the

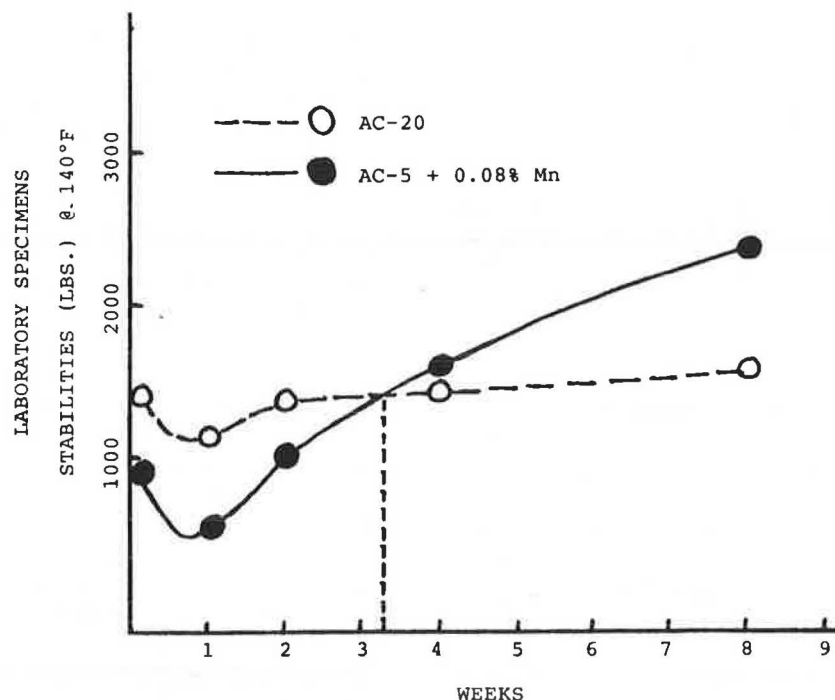


FIGURE 1 Curing rate study, manganese modification, 77°F.

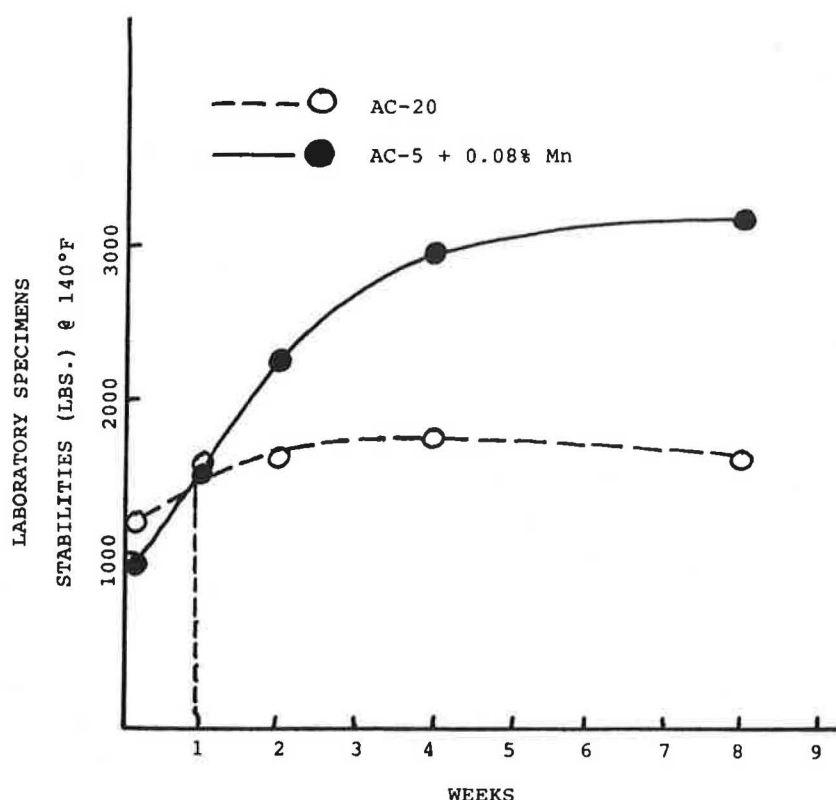


FIGURE 2 Curing rate study, manganese modification, 104°F.

TABLE 1 ROAD CORE PROPERTIES OF ROUTE 97 NEAR PINEVILLE, WEST VIRGINIA (1982 placement)

Core	1984		1986	
	Stability (lb)	Flow (0.01 in.)	Stability (lb)	Flow (0.01 in.)
Wearing course				
Control	2,582	8	2,166	13
Modified	3,738	10	3,325	15
Base course				
Control	1,236	15	1,906	20
Modified	2,247	27	2,432	27

NOTE: There are two 3-in. base courses and one 1-in. wearing course. Control asphalt is AC-20 grade; modified asphalt is AC-10 with 0.125 percent Mn. Cores are 4 in. in diameter. Measurements are at 140°F.

modified asphalt concretes have not reached maximum strength after 2 years. This is indicated by data given in Table 3. The rate of load application for all indirect tensile tests reported in this paper was 0.05 in./min and moduli were computed on the basis of a Poisson's ratio of 0.33.

In general, manganese modification is not recommended for thin overlays. However, in some cases the need for improved stability to prevent excessive rutting and shoving overrides the possibility of cracking caused by having a stiffer surface layer over a lower-strength and more flexible base. The data in Tables 4 and 5 for a modified 1.5-in. overlay put in place in 1985 in Houston, Texas, indicate the potential benefits of low-level manganese treatment to prevent surface rutting and shoving, which are serious problems in that locality. The modified section is currently outperforming the control section.

TABLE 2 PROPERTIES OF LABORATORY SPECIMENS AND ROAD CORES

Specimen	Initial Laboratory		Cured Laboratory		2-Year-Old Road Cores	
	Stability (lb)	Flow (0.01 in.)	Stability (lb)	Flow (0.01 in.)	Stability (lb)	Flow (0.01 in.)
Wearing course						
Control	1,009	15	1,294	7	1,111	15
Modified	680	13	2,003	19	1,478	12
Base course						
Control	1,842	14	1,553	20	1,882	20
Modified	1,186	18	3,270	28	1,617	21

NOTE: Pavement on Route 97 near Beckley, West Virginia, placed 1984-1985. Base courses are 3 in.; wearing courses are 1 in. Control asphalt is AC-20; modified asphalt is AC-10 with 0.125 percent Mn. Laboratory cure = 9 days at 140°F.

TABLE 3 INDIRECT TENSILE PROPERTIES OF 2-YEAR-OLD ROAD CORES FROM BECKLEY, WEST VIRGINIA

Core	Property		
	Strength <sup>a</sup> (psi)	Strain (in./in. $\times 10^{-3}$ )	Modulus (psi $\times 10^{-3}$ )
Wearing course			
Control	121	2.5	110
Modified	103	2.4	119
Base course			
Control	183	3.4	134
Modified	92	3.8	50

<sup>a</sup>At 39.2°F.

Table 6 gives the engineering properties of cores taken in late 1985 and early 1986 from a highway constructed near Carlsbad, New Mexico, in March 1984. The data indicate ideal high-temperature stability, low-temperature flexibility, and water resistance properties for the modified section in comparison with the control. Nevertheless, cracking was observed at the edges of the modified pavement and in some places in the pavement itself after 21 to 24 months. This unexpected cracking may be due to the relatively large day-night temperature changes that occur in this geographic area. Manganese modification can increase asphalt coefficients of expansion and contraction and, in this case, the modified section has not responded to temperature changes as well as the control section.

As a result of studies of many manganese-modified highways, it has been concluded that the major benefits of manganese modification are (a) to improve the strength of full-depth asphalt concrete so that pavements will support heavy loads and (b) to provide an effective means of improving stabilities of local asphalt concrete highways where only poor-quality aggregates are available at a reasonable cost.

For the last 4 years, the performance of manganese-modified highways has been closely monitored and treatment levels have been decreased in accord with field experience. The early experimental manganese-modified roads contained relatively high levels of manganese, and as a result excessive stiffness, which led to cracking, was induced. In general, manganese modification for overlays is no longer recommended because stiffer surface courses do not have the flexibility to accommodate lower stability substrates as the pavement deflects under traffic. Many of the early manganese-modified highways were overlays, and they failed for this reason.

The degree of improvement obtained with manganese modification has steadily increased as the effects of this chemistry have become better understood (Table 7). Since late 1982 much lower levels of manganese have been recommended and, as the data in Tables 4–6 indicate, increased stabilities have been obtained.

### ANTI-AGE-HARDENING AGENTS

Many laboratory studies and documented field experiences have shown that asphalt concrete is subject to cracking and raveling after service exposure. This deterioration has been related to increased hardness and decreased ductility of asphalt cement as it ages in service (5). It is generally recognized that asphalts differ greatly in their resistance to age hardening because they are derived from different crude oils and in some cases produced by different refining processes (6). There is a variety of theories about the mechanism of age hardening of asphalts, but, because of the chemical complexity of these organic materials and their variability from source to source, it has been difficult to identify a completely acceptable mechanism. It is known that oxidation changes the physical and chemical properties of asphalts and that asphalts recovered from deteriorated roads are oxygen rich. Oxidation of asphalt

TABLE 4 COMPARISON OF STABILITY AND FLOW OF LABORATORY SPECIMENS AND FIELD CORES AT 140°F

Asphalt	Laboratory				Road Cores at			
	Initial		Cured <sup>a</sup>		1 Month		7 Months	
	Stability	Flow	Stability	Flow	Stability	Flow	Stability	Flow
AC-20 control	215	7	279	7	515	8	706	9
Modified AC-20 with 0.06% Mn	180	6	1,290	10	570	10	1,018	10

NOTE: 1.5-in. overlay, city of Houston, placed in 1985. Stability is in pounds and flow in 0.01 in.

<sup>a</sup>Laboratory cure = 9 days at 140°F.

TABLE 5 COMPARISON OF INDIRECT TENSILE STRENGTH, STRAIN, AND ELASTIC MODULUS OF LABORATORY SPECIMENS AND CORE SAMPLES AT 39.2°F

Asphalt	Laboratory-Cured <sup>a</sup> Specimen			Road Cores at					
	Strength	Strain	Modulus	1 Month			7 Months		
				Strength	Strain	Modulus	Strength	Strain	Modulus
AC-20 control	171	4.2	82	226	5.9	81	224	4.4	108
Modified AC-20 with 0.06% Mn	171	2.0	169	164	3.1	110	212	1.6	278

NOTE: 1.5-in. overlay, city of Houston, placed in 1985. Strength is given in pounds per square inch, strain in in./in.  $\times 10^{-3}$ , and modulus in psi  $\times 10^{-3}$ .<sup>a</sup>Laboratory cure = 9 days at 140°F.

TABLE 6 PROPERTIES OF FIELD CORES FROM US-62/US-180, CARLSBAD, NEW MEXICO

Property	Field Cores at			
	21 Months		24 Months	
	Control <sup>a</sup>	Modified <sup>b</sup>	Control <sup>a</sup>	Modified <sup>b</sup>
Stability at 140°F (lb)	1,528	1,981	1,761	1,915
Flow at 140°F (0.01 in.)	18	12	20	14
Strength at 39.2°F <sup>c</sup> (psi)			171	174
Strain at 39.2°F (in./in. $\times 10^{-3}$ )			2.2	2.6
Modulus at 39.2°F (psi $\times 10^{-3}$ )			167	133
Voids (%)			9	4
77°F Lottman cycle strength (psi)				
Dry			156	126
Wet			119	114
Wet/dry			0.76	0.91
Voids (%)			5.4	3.6

NOTE: 5-in. construction over a paved base. Aggregate treated with 1.5 percent hydrated lime. Placed March 1984.

<sup>a</sup>Control = 80–100 pen.

<sup>b</sup>Modified = 120–150 pen with 0.06 percent Mn.

<sup>c</sup>Indirect tensile strength.

TABLE 7 FIELD PERFORMANCE RATINGS: MANGANESE-MODIFIED PROJECTS VERSUS CONTROL PAVEMENTS

Year	Average Rating
1980–1982	−1.74
1982	+2.00
1983	+0.16
1984	+0.70
1985	+1.70

NOTE: +3 = modified pavement superior to control, 0 = modified pavement equal to control, and −3 = modified pavement much poorer than control. Intermediate number ratings were assigned, if necessary, on the basis of inspection of the projects.

cements is believed to be, directly or indirectly, a major cause of failure of asphalt concrete pavements.

Thin-film oven tests of asphalt cements are widely used to measure changes in properties when asphalts are exposed, as thin films, to air at elevated temperatures. The ASTM D 1754 procedure exposes a static film of asphalt to heat and air, and the ASTM D 2872 procedure exposes a moving or rolling film. The California Department of Transportation has developed a correlation between an extended rolling thin-film test and long-term aging of asphalt cement in California deserts (7).

The rolling thin-film test procedure has been used to evaluate the effectiveness of a new series of liquid anti-age-hardening agents in a variety of asphalts. These materials vary in chemical functionality and molecular weight. In general they minimize the property changes of asphalts during exposure, as thin films, to air at elevated temperatures. The data given in Table 8 illustrate some of the effects of these anti-age-hardening modifiers in rolling thin-film oven tests. Four tubes, each with 35 g of asphalt, must be used for a given sample in order to have enough aged asphalt to run viscosity, penetration, and ductility tests. Use of an aged asphalt sample in more than one test may give misleading results.

The data in Table 8 illustrate several interesting points regarding age hardening of asphalts without and with chemical modifiers. The proprietary anti-age-hardening asphalt (AAHA) modifiers are identified as M-1 through M-7.

1. Note the property changes within a given asphalt type. Compare Samples 1, 2, and 3; 10 and 11; and 17. Asphalts B and C are much more susceptible to age hardening than is Asphalt A.

2. Anti-age-hardening agents, M-1 through M-7, minimize age hardening of asphalt cements. They prevent consistency increase as indicated by the 140°F viscosities and 77°F penetrations after aging. They also minimize the loss of ductility of asphalt cements.

3. The variability of asphalt cements and their aging tendencies require anti-age-hardening agents of more than one type of chemical functionality. The most effective anti-age-hardening modifier for a given asphalt and the optimum concentration of the modifier must be determined in each case in order to provide the most effective treatment for a given problem asphalt.

The temperature at which extended rolling thin-film oven tests are run is critical. The data given in Table 9 indicate the significantly increased age hardening that occurs when the temperature of the air contacting the rolling thin film of asphalt is increased from 215°F to 235°F. This increase in temperature is sufficient to at least double the rate of the reactions that cause age hardening. The 140°F viscosity values after 7 days at 235°F are as much as seven times higher than those obtained at 215°F. The requirements for the Caltrans durable asphalt specification are based on a temperature of 235°F. To meet this specification a combination of a reasonably stable asphalt and an effective anti-age-hardening additive is required.

The testing of chemically modified asphalt films by exposure to air in thin films at elevated temperatures provides a method of identifying potential anti-age-hardening agents. Their true value, however, can only be assessed in actual asphalt mixtures



TABLE 8 SCREENING OF ANTI-AGE-HARDENING AGENTS IN AN EXTENDED ROLLING THIN-FILM OVEN TEST (properties after 7 days at 215°F)

Sample	Asphalt	Grade	AAHA Modifier	140°F Vis (poises)	77°F Pen (0.01 mm)	77°F Ductility (cm)
1	A	AR1000	None	7 725	20	150+
2	A	AR2000	None	16 660	11	139
3	A	AR4000	None	20 335	10	13
4	A	AR4000	1% M-1	17 300	14	150+
5	A	AR4000	2% M-1	14 045	16	150+
6	A	AR4000	4% M-1	10 170	17	150+
7	A	AR4000	2% M-5	8 698	16	150+
8	A	AR4000	2% M-6	9 864	20	150+
9	A	AR4000	2% M-7	9 076	16	150+
10	B	AC-10	None	56 639	10	6
11	B	AC-20	None	99 500	8	6
12	B	AC-20	2% M-1	85 840	9	6
13	B	AC-20	3% M-1	13 406	17	26
14	B	AC-20	4% M-1	11 905	17	24
15	B	AC-20	6% M-1	11 466	19	37
16	B	AC-20	2% M-5	16 255	17	14
17	C	AR4000	None	87 020	19	9
18	C	AR4000	2% M-1	69 770	17	13
19	C	AR4000	4% M-1	14 963	35	92
20	C	AR4000	2% M-2	21 236	33	52
21	C	AR4000	3% M-2	20 706	32	150+
22	C	AR4000	3% M-2	23 206	27	150+

TABLE 9 CRITICAL TEMPERATURE EFFECTS IN EXTENDED ROLLING THIN-FILM OVEN TESTS

Test Temperature (°F)	Asphalt	AAHA Modifier	140°F Vis (poises)	77°F Pen (0.01 mm)	77°F Ductility (cm)
215	A	None	20 335	10	13
235	A	None	34 123	10	14
215	A	2% M-6	9 864	20	150+
235	A	3% M-6	31 423	12	35
215	A	2% M-5	8 698	16	150+
235	A	2% M-5	28 014	11	35
215	C	None	87 020	19	9
235	C	None	139 092	19	8
215	C	3% M-2	23 206	27	150+
235	C	3% M-2	159 217	19	7
235	Caltrans durable asphalt specification		75 000 max	25 min	30 min

NOTE: Properties are those of grade AR-4000 asphalts after 7 days.

because the aggregate substrate can influence the durability of thin films of asphalt cements. Inorganic aggregate surfaces can adsorb or absorb components of asphalt cement, much like the substrate absorbs specific chemical structures in a chromatographic column. The chemistry of an aggregate surface can influence chemical changes in asphalt cements in the same manner that inorganic catalysts influence cracking and reforming of hydrocarbon crude oil fractions.

The possibility of aggregates influencing the durability of asphalt cement and possibly interfering with the functioning of anti-age-hardening agents led to evaluations of these chemicals in asphalt concrete mixtures. The testing procedures are the same as those described earlier in the paper for evaluating the

physical properties of manganese-modified laboratory specimens and road cores. The following data, however, illustrate the abilities of anti-age-hardening agents to minimize changes in the properties of asphalt concrete specimens during heat-aging cycles.

New, properly designed and constructed asphalt concrete pavements usually have the strength and flexibility to support traffic. Most highways would remain intact if it were not for the degradation of the asphalt cement by the effects of heat, air, and water. The data given in Tables 10 and 11 indicate that these new anti-age-hardening agents, at relatively low levels, will function in asphalt concretes and minimize changes in properties during simulated aging. The choice of the most

TABLE 10 SCREENING OF ANTI-AGE-HARDENING AGENTS IN LABORATORY SPECIMENS: STABILITY AT 140°F

Sample	Asphalt	AAHA Modifier	Initial		Aged		Percent Change
			Stability (lb)	Flow (0.01 in.)	Stability (lb)	Flow (0.01 in.)	
California Granite Aggregate and Mix							
1	A (AR-4000)	None	1,896	12	2,196	14	+16
2	A (AR-4000)	2% M-1	2,129	12	2,146	13	+1
3	C (AR-4000)	None	1,214	12	1,431	16	+18
4	C (AR-4000)	2% M-1	1,162	15	1,246	18	+7
Ohio Limestone Aggregate and Mix							
5	A (AR-4000)	None	559	8	790	8	+41
6	A (AR-4000)	4% M-1	407	8	474	7	+17
7	D (AC-20)	None	687	8	1,244	8	+81
8	D (AC-20)	4% M-1	514	7	711	9	+38
9	C (AR-4000)	None	468	8	1,092	10	+133
10	C (AR-4000)	2% M-2	709	7	1,125	10	+59

effective anti-age-hardening agent and its optimum concentration requires tests on each combination of asphalt and aggregate.

A large area was resurfaced in Wickliffe, Ohio, in the fall of 1985 to determine the effectiveness of anti-age-hardening agent M-1. Cores were taken shortly after placement and again 9 months later in July 1986. The engineering data on these field cores are summarized in Table 12. The high-temperature stability data and the low-temperature strain values obtained on these cores clearly indicate that chemical modifier M-1 minimizes hardening of asphalt concrete under service conditions.

#### ANTI-AGE-HARDENING AGENTS TO MEET ASPHALT SPECIFICATIONS

The new anti-age-hardening agents can also be used in asphalt cements that, as produced, do not meet certain governmental specifications. In particular, ductility requirements after thin-film oven aging are in some cases difficult for an asphalt supplier to meet. Table 13 gives examples of how these chemicals can provide solutions for problems of this type. Note that, after aging, each anti-age-hardening modifier, at the 0.5 percent

level, has enabled the asphalt to maintain higher penetrations, lower 140°F viscosities, and higher 60°F ductilities. In this particular evaluation, both M-2 and M-4 produced an AC-15 grade asphalt that met aged specification requirements of the responsible department of transportation.

#### CHEMICAL MODIFIERS TO IMPROVE WATER RESISTANCE

It is meaningless to discuss the durability of asphalt concrete without considering the damaging effects of water (8). Many aggregate surfaces are hydrophilic in nature and therefore will attract water that can, under certain conditions, saturate asphalt pavements. Water may fill voids and weaken asphalt-aggregate bonds. After the water has run off or evaporated, the asphalt-aggregate bond may not recover. Water, to some extent, is a solvent for most materials, and as it percolates through an asphalt concrete network it extracts components of both the aggregates and the asphalt. The amount of asphalt components extracted could be substantial because some oxidized asphalt components are water soluble. Water as a liquid can degrade the asphalt-aggregate mixture, and as water freezes and expands it can severely stress the pavement structure.

TABLE 11 SCREENING OF ANTI-AGE-HARDENING AGENTS IN LABORATORY SPECIMENS: INDIRECT TENSILE STRENGTH AT 39.2°F

Sample	Asphalt	AAHA Modifier	Indirect Tensile Strength (psi)	Strain (in./in. $\times 10^{-3}$ )	Modulus (psi $\times 10^{-3}$ )
California Granite Aggregate and Mix					
1	A (AR-4000)	None	360	4.4	165.4
2	A (AR-4000)	2% M-1	242	4.2	117.1
Ohio Limestone Aggregate and Mix					
3	A (AR-4000)	None	253	2.2	228.8
4	A (AR-4000)	4% M-1	191	3.9	98.0
5	D (AC-20)	None	166	6.6	50.3
6	D (AC-20)	4% M-1	122	7.4	33.2

NOTE: Measurements made after curing for 9 days at 140°F.

TABLE 12 SCREENING OF ANTI-AGE-HARDENING AGENT IN 1.5-in. OVERLAY

Property	Initial Core		Core at 9 Months		Percentage Change	
	Control	Control + 2% M-1	Control	Control + 2% M-1	Control	Control + 2% M-1
Stability at 140°F (lb)	456	405	872	469	+91	+16
Flow at 140°F (0.01 in.)	9	9	10	9		
Strength at 39.2°F <sup>a</sup> (psi)	111	85	82	110		
Strain at 39.2°F (in./in. × 10 <sup>-3</sup> )	6.7	7.0	2.2	4.2		
Modulus at 39.2°F (psi × 10 <sup>-3</sup> )	34	27	87	56		

NOTE: Placed October 1985 in Wickliffe, Ohio. Ohio aggregate and AC-20 Asphalt D.

<sup>a</sup>Indirect tensile strength.

TABLE 13 ANTI-AGE-HARDENING AGENTS FOR ASPHALT SPECIFICATIONS

Property	Sample			
	1	2	3	4
AAHA modifier	None	0.5% M-1	0.5% M-2	0.5% M-4
Weight loss (%)	0.54	0.59	0.50	0.50
77°F pen				
Initial	48	56	63	64
Aged	31	35	37	38
140°F Vis (poises)				
Initial	1442	1327	1572	1672
Aged	3969	2899	2830	3479
275°F Vis (cSt)				
Initial	322	310	332	318
Aged	430	433	459	440
60°F ductility (cm)				
Initial	150+	150+	150+	150+
Aged	14.6	14.9	20.8	32.3

NOTE: Thin-film oven test (ASTM D 1754-83), 5 hr at 325°F; Test Asphalt E = AC-15.

Antistrip additives have been used for many years to displace water from wet aggregate surfaces in order to enable asphalt cutbacks to bond to aggregate in the field. Heat-stable antistrip compounds have been developed that can be used in asphalt cements to improve the asphalt-aggregate bond in hot mixes and help maintain the bond during periods when pavements are saturated with water. Most antistrip additives are water soluble yet produce stable solutions or dispersions at low concentrations in asphalt.

Hydrated lime is widely used as a treatment for aggregates before they are coated with asphalts in hot-mix plants. This treatment has been found to be effective in improving the water resistance of asphalt pavements, and it appears to be less sensitive to aggregate and asphalt variations than are asphalt dispersible antistrip compounds. The effectiveness of the latter varies widely, although there are commercially available materials the effectiveness of which approaches that of hydrated lime. Hydrated lime is water soluble and not soluble in asphalt, and therefore, to be effective, it must be uniformly distributed over the surface of the aggregate before the aggregate is coated with asphalt cement.

The detrimental effect of water on the strength of an asphalt concrete is shown in Figures 3 and 4. The laboratory specimens were in one case immersed in water at room temperature the sixth day of each week and in the other case held continuously in an oven at the indicated temperatures. Note in Figure 3 that,

at the 77°F cure temperature, periodic water immersion has decreased stability by as much as 45 percent whereas, as indicated in Figure 4, the decrease in stability at the 104°F cure temperature is, at one point, 55 percent.

A liquid modifier, which is much more soluble in asphalt and less soluble in water than are conventional antistrip compounds, has been developed to improve water resistance of asphalt concretes. It is identified as Additive L in the tables and figures that illustrate its performance characteristics.

The Lottman test is gaining increasing acceptance as a means of evaluating the water-resistance properties of asphalt concrete specimens. This test may be too severe for evaluating materials for temperate climates because of its freeze cycle, but it provides a realistic method of comparing the water resistance of asphalt concretes without and with various chemical modifiers.

Table 14 gives an overview of the performance characteristics of Additive L vis-à-vis aggregates, asphalts, and several commercial antistrip compounds.

Figure 5 shows that Additive L provides as much water resistance after seven cycles of Lottman test exposures as does the untreated asphalt concrete after one Lottman cycle.

Figure 6 shows that Additive L does not provide the long-term resistance to water damage that may be obtained by treatment of aggregate with hydrated lime. The relatively small additional improvement is, however, costly in terms of both



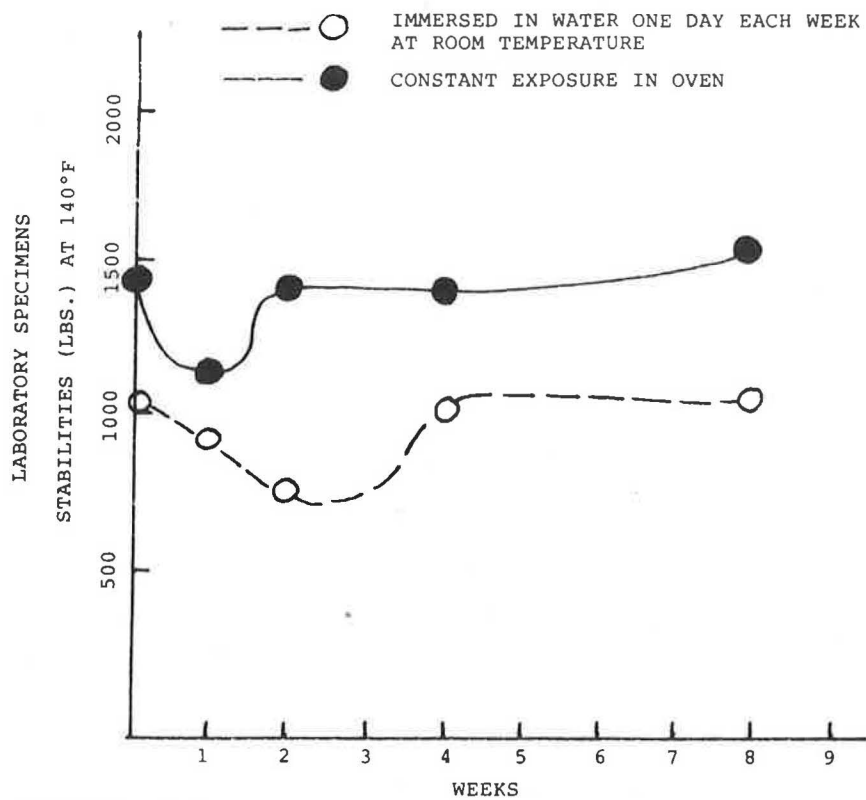


FIGURE 3 Curing rate study with water, 77°F.

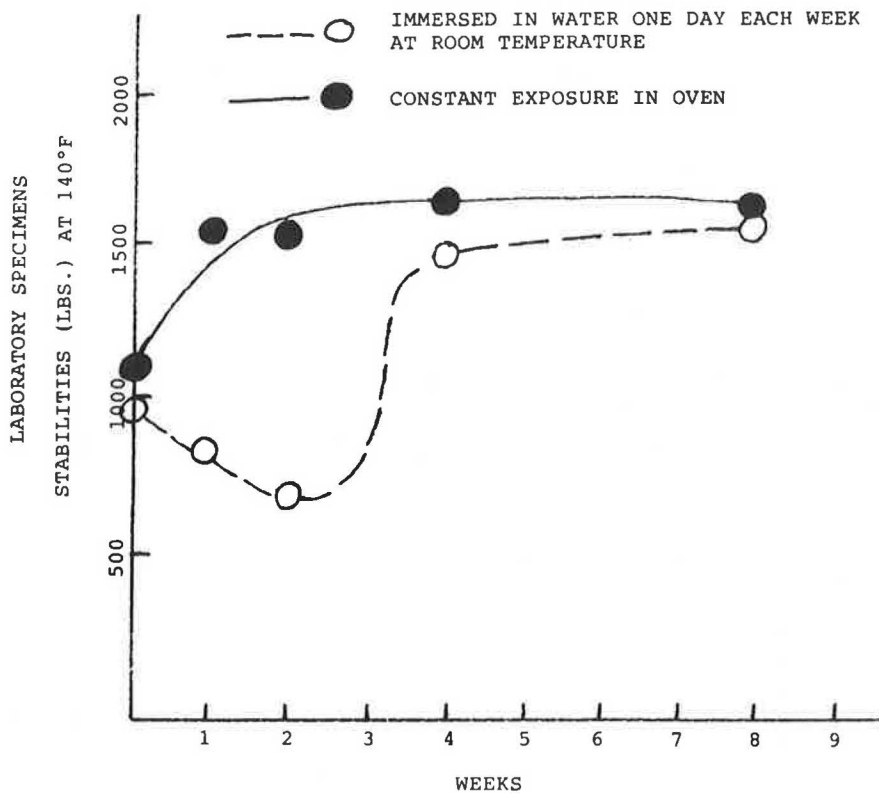


FIGURE 4 Curing rate study with water, 104°F.

TABLE 14 EFFECT OF AGGREGATES, ASPHALTS, AND MODIFIERS ON WATER RESISTANCE

Aggregate	Asphalt	0.5% Additive	Strength (psi)		Wet/Dry Ratio
			Dry	Wet	
Texas pea gravel	I	None	169	70	41
		Commercial A	152	81	54
		Commercial B	167	103	62
		Commercial C	175	127	72
		Additive L	181	132	73
	II	None	129	70	54
		Commercial A	141	110	79
		Commercial B	127	102	80
		Commercial C	122	103	85
		Additive L	117	115	98
Georgia granite	III	None	85	28	33
		Commercial A	87	80	93
		Commercial B	94	82	87
		Commercial C	99	85	86
		Additive L	104	89	86
	IV	None	121	64	53
		Commercial A	145	105	73
		Commercial B	154	134	87
		Commercial C	140	114	82
		Additive L	146	132	91

NOTE: Lottman method; AC-20 asphalt content = 5.2 percent by weight; air voids = 6.5 to 8.5 percent by volume.

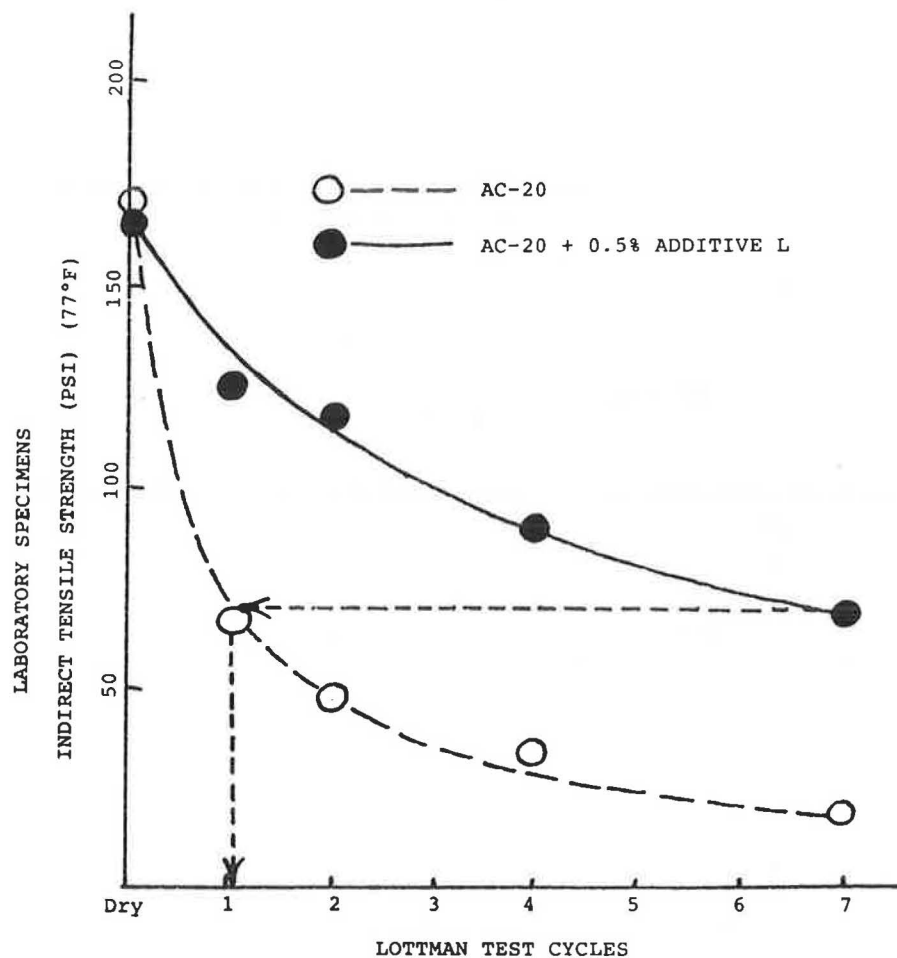


FIGURE 5 Multiple-cycle Lottman testing with and without Additive L.

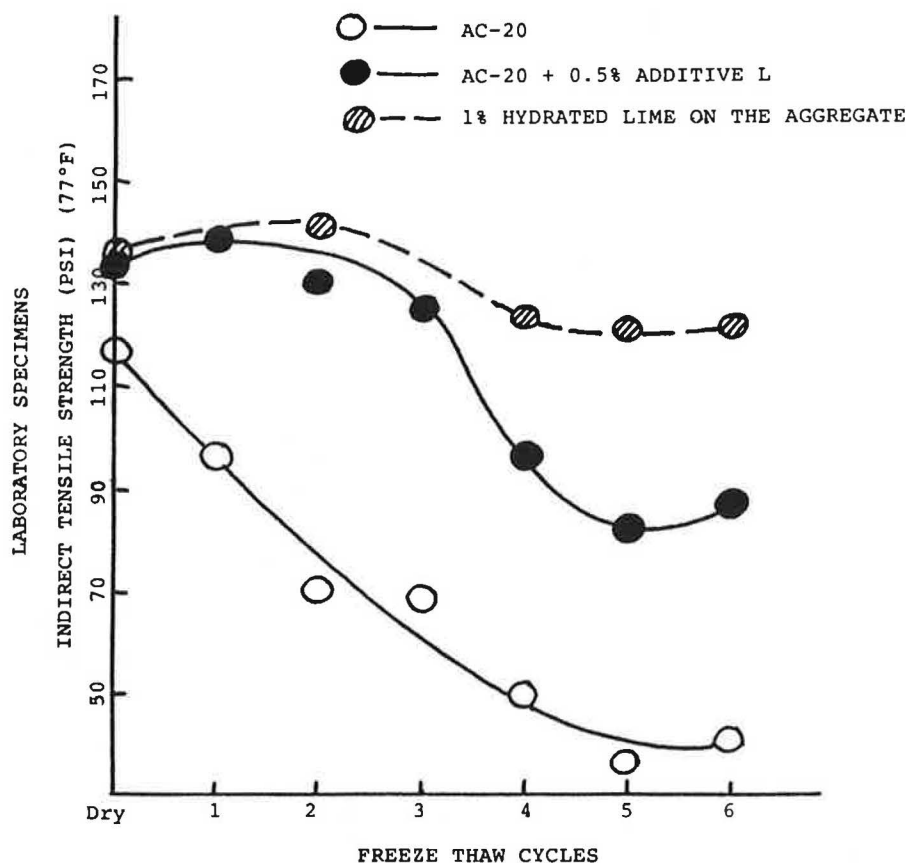


FIGURE 6 Multiple-cycle Lottman testing with and without Additive L and hydrated lime.

materials and plant complexity. Because the multiple-cycle Lottman test is severe, the additional improvement provided by hydrated lime may not be indicative of field performance.

Additive L in combination with other types of functional modifiers may well provide synergistic and beneficial results to enhance the durability of asphalt concrete. An example of potential synergism to provide improvement in both strength and water resistance is given in Table 15. Sample 4 provides an initial strength improvement of 28 percent over Sample 1 and excellent water resistance with only 0.045 percent Mn whereas Samples 2 and 3 provide only 14 and 16 percent strength improvement, respectively, with higher levels of manganese, and little improvement in water resistance. The combination has not only provided significantly improved water resistance,

it has also enhanced the strength improvement of the manganese modifier.

Another interesting example of the efficacy of multifunctional modifiers is given in Table 16 by data obtained after several Lottman cycles. Although these data are not conclusive, a multifunctional treatment with a low level of manganese (0.024 percent) has provided a 66 percent increase in cured stability over the control and, as the multicycle Lottman data indicate, a remarkably stable system as far as water resistance is concerned. The wet/dry indirect tensile strength ratios obtained with the multifunctional additive system in these repeated Lottman cycles are similar to those that can be obtained with hydrated lime.

TABLE 15 MULTIFUNCTIONAL MODIFIER: STRENGTH AND WATER RESISTANCE

Sample	Asphalt Modifier	Indirect Tensile Strength at 77°F (psi)		Wet/Dry Ratio	Relative Binder Cost (\$/ton)
		Dry	Wet		
1	None	129	55	0.43	150
2	0.06% Mn	147	62	0.43	188
3	0.08% Mn	150	66	0.44	201
4	Multifunctional modifier (0.045% Mn)	165	120	0.73	197

NOTE: Lottman method; aggregate is Texas pea gravel; asphalt is AC-20; asphalt content is 4.6 percent.

TABLE 16 MULTIFUNCTIONAL MODIFIER: STRENGTH, WATER RESISTANCE, AND AGE-HARDENING RESISTANCE

Property	Without Modifier		With 0.024% Mn Modifier	
	Initial	Cured	Initial	Cured
Stability at 140°F (lb)	577	1,102	592	1,833
Lottman test wet/dry ratio after cycles				
1	110		95	
2	44		101	
3	55		88	
4	40		89	

## CONCLUSIONS

The data presented in this paper, which are representative of a large amount of data on chemical modification of asphalt cements, lead to several conclusions.

1. Certain liquid, asphalt-soluble chemical modifiers do not require changes in procedures currently used to build asphalt concrete highways.

2. Manganese modifiers may improve the strength and reduce the deflection of full-depth asphalt concrete so that heavy loads may be supported over extended periods.

3. Manganese modifiers make it possible to use poor-quality aggregate to produce asphalt concrete pavements with acceptable stabilities.

4. Certain anti-age-hardening chemicals minimize the decrease in penetration, the increase in viscosity, and the loss of ductility in asphalts exposed to air in thin films at elevated temperature.

5. Anti-age-hardening chemicals may extend the useful life of asphalt concrete pavements.

6. A new asphalt-soluble additive that provides improved water resistance in asphalt concretes has been developed. Its effectiveness approaches that of the hydrated lime treatment of aggregates.

7. Preliminary results indicate that certain multifunctional additives may provide both increased strength and resistance to water in asphalt concretes.

8. Asphalt concrete systems must be evaluated individually to determine the type and concentration of chemical modifier needed to meet performance requirements of specific applications.

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