Chemistry, Rheology, and Engineering Properties of Manganese-Treated Asphalts and Asphalt Mixtures

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Summarized are the results of an experimental program to evaluate the chemistry, rheology, and engineering properties of manganese-treated asphalts and asphalt mixtures. The study was conducted by five universities. The experimental program involved two asphalt sources, three grades of asphalt cement, three levels of manganese treatment, four aggregates, and two air void contents. Static and repeated-load indirect tensile, Marshall stability, Hveem stability, and direct tension tests were performed on mixtures cured for 28 days at 140°F. Resilient moduli were measured at various times during the curing period. Tests were conducted on the asphalt before and after curing on Ottawa sand and in the California tilt-oven durability apparatus. Tests included both chemical and physical tests, including penetration, viscosity, and creep. Based on the findings of the study, it would appear that the modifier is capable of improving the high-temperature stiffness and strength of asphalt concrete. Principal application areas include thick sections of asphalt concrete in new construction and thick overlays. Treated mixtures should not be expected to prevent reflection cracking or to perform in thin lifts over high deflection bases. Laboratory testing programs should be performed to evaluate the effect of crude source, asphalt-concrete grade, and aggregate. Desired mixture properties and hence treatment levels should consider the end use of the asphalt-concrete mixture.

Two major problems affecting the performance of asphalt-concrete pavements are thermal cracking associated with low-temperature service and rutting or other types of permanent deformation associated with high-temperature service. An asphalt additive manufactured and marketed by Chemkrete Technologies, Inc., offers promise for reducing the temperature susceptibility of asphalt cement binders and thereby reducing these distresses. The product is an oil-based, manganese material that, when mixed with asphalt cement and allowed to cure in thin films in the presence of oxygen, modifies the asphalt-cement properties. In most cases, viscosity is increased and the temperature susceptibility is reduced. By using a softer grade of asphalt cement, it is therefore possible to produce a mixture with equal or improved strength and stability at high temperature, and equal or more flexible and less stiff mixtures at low temperatures, compared with the same properties of mixtures containing an untreated harder grade of asphalt cement.

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In mid-1982, the Lubrizol Corporation purchased the U.S. patent rights to produce and market the modifier, and Chemkrete Technologies, Inc., was formed as a wholly owned subsidiary of Lubrizol. The history of the field tests before and after July 1982 has been summarized by Moulthrop and Higgins (*1*).

Lubrizol and Chemkrete Technologies immediately began an evaluation of the product because it was apparent that there was little if any information pertaining to the asphalts, additive, and mixtures used in the previous field projects. In addition, although laboratory information related to engineering properties was available, few if any records of the actual formulation of the additive or the procedure used in conducting the tests were available. Thus in August 1983 a formal university-based research effort was initiated to evaluate the chemistry, rheology, and engineering properties of treated asphalts and treated-asphalt mixtures.

Summarized in this paper are the results of the University Research Program, which are contained in five reports (*2–6*) and a summary report (*7*).

UNIVERSITY RESEARCH PROGRAM

The university-based research program was formulated to address six questions:

1. What chemical reactions occur when manganese is added to the asphalt?
2. Does the reaction stop after a given period of time?
3. What are the rheological characteristics of the treated asphalts?
4. What are the thermal cracking characteristics of manganese-treated asphalt mixtures?
5. What are the engineering characteristics of manganese-treated asphalt mixtures?
6. What are the moisture susceptibility characteristics of manganese-treated mixtures?

Objectives

The objectives of the individual research programs conducted by the five research groups are summarized in the following paragraphs.

The objectives of the investigation conducted at Western Research Institute were to (a) evaluate the kinetics of the cure of manganese-treated asphalt, (b) evaluate the effect of manganese concentration on the properties of the cured treated asphalts, and (c) follow the chemical changes that occur during the curing reaction.

The objective of the study at Pennsylvania State University was to evaluate the consistency, or viscosity, of manganese-treated asphalts that were aged in the laboratory to simulate field conditions, including the effect of treatment level.

The objectives of the study conducted by the University of Waterloo, Canada, were to (a) measure the low-temperature stiffness response of manganese-treated asphalt mixtures and (b) evaluate potential cold-weather cracking performance.

The engineering properties of manganese-treated asphalt mixtures and the effect of curing time on these properties were evaluated at the University of Nevada–Reno and the University of Texas at Austin. In addition, the moisture susceptibility characteristics of manganese-treated asphalt paving mixtures were evaluated at the University of Texas.

Materials

Asphalt Cements

Asphalt cements, representing a range of reactivity with the modifier as well as different refining techniques, were obtained from the American Petrofina (Cosden) refinery at Big Spring, Texas, and from the Shell Oil refinery located at Wood River, Illinois.

The Cosden asphalt cement is produced from a local domestic crude by a solvent refining process. A hard product is produced, which is blended to paving grade by the use of low-viscosity hydrocarbon refinery products. This asphalt has a history of temperature susceptibility and relatively rapid age hardening in service.

The Shell Wood River asphalt is produced in a distillation process to a soft or hard paving grade. These materials are then blended to produce the intermediate grades. Both foreign and domestic crudes are utilized in the refinery.

The three grades of asphalt cements obtained from these sources were AC-2.5, AC-5, and AC-20. Penetration and viscosity data obtained on the original asphalts are given in Table 1. The Cosden AC-2.5 asphalt cement was supplied as an AC-3 to meet Texas specifications.

Modifier

The asphalt modifier was utilized as supplied by the producer from production sources. The physical and chemical properties of this material, which contains soluble manganese, are described by Kennedy and Epps (7). The modifier catalyzes a chemical reaction between the asphalt cement and atmospheric oxygen.

TABLE 1 PHYSICAL PROPERTIES OF TREATED AND UNTREATED ASPHALT CEMENTS

			Penetration, 100 g., 5 sec, 0.1 mm				Viscosity, poises		
Asphalt source	Asphalt grade	% Manganese	39.2 °F	50 °F	77 °F	77[a] °F	140 °F	140[a] °F	275[a] °F
Cosden	AC-2.5	0.00	12	27	200	167	318	375	1.65
		0.08	22	54	>330	277	178	178	1.27
		0.125	30	76	>330	363	130	132	1.26
		0.20	48	138	>330	>400	78	88	0.91
	AC-5	0.00	9	19	128	130	545	451	1.85
		0.08	16	36	252	220	303	259	1.36
		0.125	22	51	>330	289	225	192	1.26
		0.20	37	95	>330	>400	120	120	1.19
	AC-20	0.00	5	11	50	37	2090	2592	3.58
		0.08	9	19	98	71	932	1025	2.80
		0.125	12	23	135	93	575	809	2.30
		0.20	20	44	243	175	305	391	1.74
Shell	AC-2.5	0.00				195		300	1.83
		0.08				331		189	1.37
		0.125				>400		182	1.32
		0.20				>400		155	1.05
	AC-5	0.00	13	22	144	110	553	553	2.24
		0.08	20	44	262	174	308	318	1.71
		0.125	28	60	>330	228	214	229	1.47
		0.20	45	99	>330	360	208	147	1.18
	AC-20	0.00	8	13	66	50	2040	1858	4.02
		0.08	12	21	113	84	1030	952	2.74
		0.125	16	31	153	114	703	630	2.51
		0.20	27	55	272	180	327	366	1.90

[a] Data obtained by Chemkrete Technologies, Inc., on one-year-old stored samples.

TABLE 2 TREATMENT LEVELS

	Cosden Big Spring				Shell Wood River			
% Mn[a]	0[b]	.08	0.125	0.2	0[b]	.08	0.125	0.2
% Modifier[a]	0[b]	4	6.25	10	0[b]	4	6.25	10
AC-2.5	X	X	X	X	-	-	-	-
AC-5	X	X	X	X	X	X	X	X
AC-20	X	X	X	X	X	X	X	X

[a] By weight of asphalt cement
[b] Untreated asphalt cement (control)

A control and three modifier treatment levels were utilized in the studies (Table 2). Treatment levels of 4.0, 6.25, and 10.0 percent modifier by weight of asphalt cement represented 0.08, 0.125, and 0.20 percent manganese by weight of asphalt cement, respectively. Properties of the modified asphalt cements at various treatment levels are also given in Table 1.

Aggregates

Aggregates from four sources were utilized in the asphalt mixture studies. The aggregates were dense graded; actual gradations are given by Kennedy and Epps (*7*).

The Eagle Lake aggregate was a siliceous river gravel and sand from a river deposit near the Texas gulf coast. This aggregate is highly water susceptible and has been utilized extensively at the University of Texas.

The Watsonville granite aggregate is 100 percent crushed material from a quarry located on the central California coast. This aggregate is moderately water susceptible and is utilized as a standard laboratory aggregate at the University of Nevada and the University of California.

The Helms aggregate is a partially crushed subrounded river gravel available near Reno, Nevada. This aggregate is highly water susceptible with a high absorption capacity and is utilized as a laboratory standard aggregate at the University of Nevada.

The Canadian limestone is a crushed material from Ontario, Canada, which was blended with a natural sand. This mixture has been utilized on several other Canadian research studies related to cold temperature characteristics and performance.

Mixture Design

The Hveem mixture design method with Texas gyratory compaction was utilized to establish the asphalt-cement content for the Eagle Lake aggregate. The 50-blow Marshall method was utilized to establish the asphalt-cement content for the other mixes. The resulting asphalt contents were 4.6, 6.3, 7.5, and 6.4 percent by weight of dry aggregates for the Eagle Lake, Watsonville granite, Helm, and Canadian limestone mixtures, respectively. These values were used for all mixtures and defined the binder content (asphalt cement plus modifier).

Specimens were compacted to produce approximately 3 and 7 percent air voids to study curing effects. Samples were compacted by using gyratory compaction, Marshall compaction, and kneading compaction, at Texas, Nevada, and Waterloo, respectively.

TEST RESULTS AND ANALYSIS

Chemistry and Rheology of Binders

Western Research Institute

Previous work at the Western Research Institute indicated that the manganese-containing modifier produced a rapid stiffening of asphalt from the rapid reaction with atmospheric oxygen when a thin film of treated asphalt was exposed to the atmosphere (*8*). Results also suggested that the manganese-induced reaction ceased at the end of the cure by chemical inactivation of the manganese. Research by Petersen et al. in the current study addressed the question of modifier inactivation together with the evaluation of the kinetics of the cure, the effect of manganese concentration on the level of cure, and the chemical changes that occur during the curing reaction (*2*). The chemical and physical tests used are described by Petersen et al. (*2, 8*).

Figures 1 and 2 show the relationships between cure time at 113°F and the reaction with atmospheric oxygen to form ketones and anhydrides in the Cosden and Shell asphalts during exposure of thin asphalt films aged on Ottawa sand. Treated asphalts showed a rapid increase in ketone and anhydride content during the first 8 days of curing, followed by an abrupt cessation of the manganese-induced reaction after about 8 days. Ketone and anhydride formation after the 8-day curing period were typical of the normal aging of untreated asphalts. Shown in Figure 3 is the rapid increase in viscosity corresponding to the rapid increase in ketones and anhydrides during the curing period followed by the cessation of the modifier-induced viscosity increase after cure.

Comparison of data obtained from tests performed on the

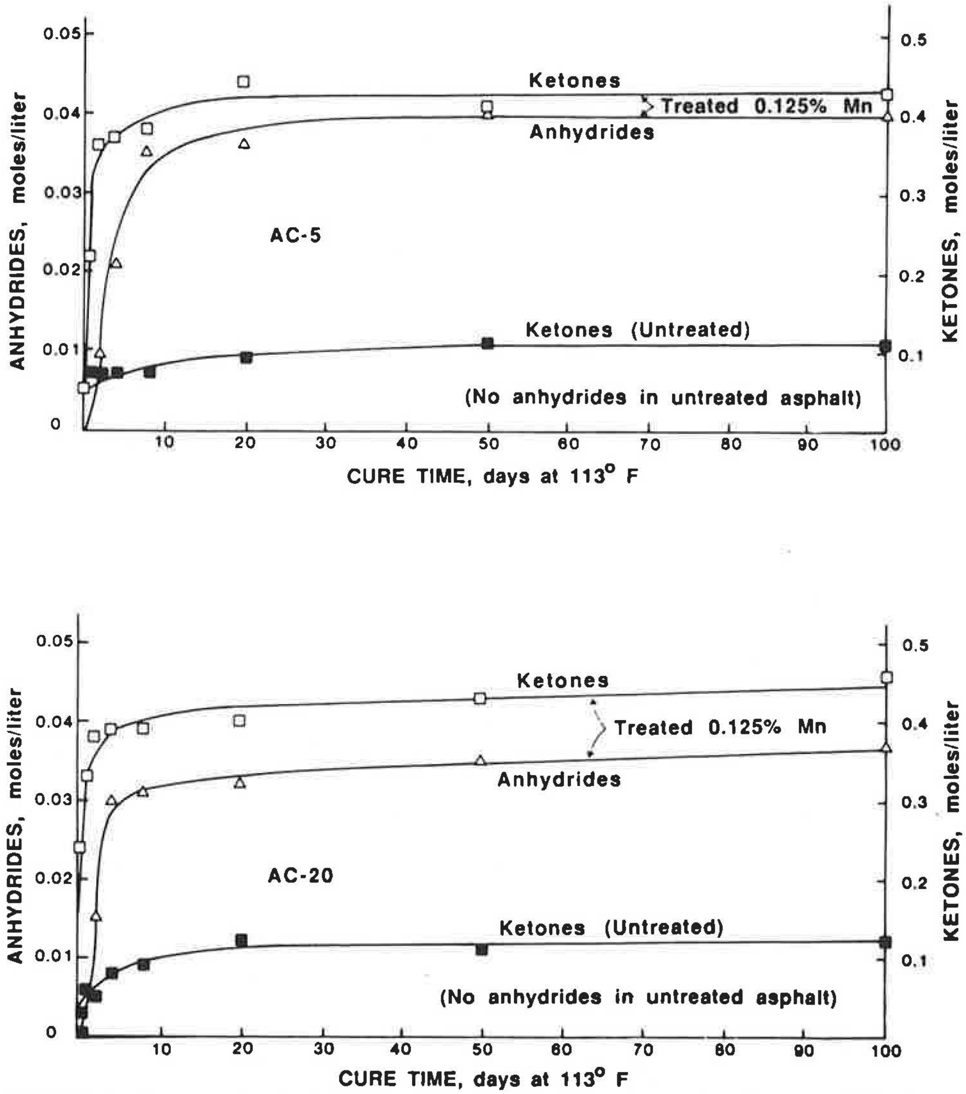
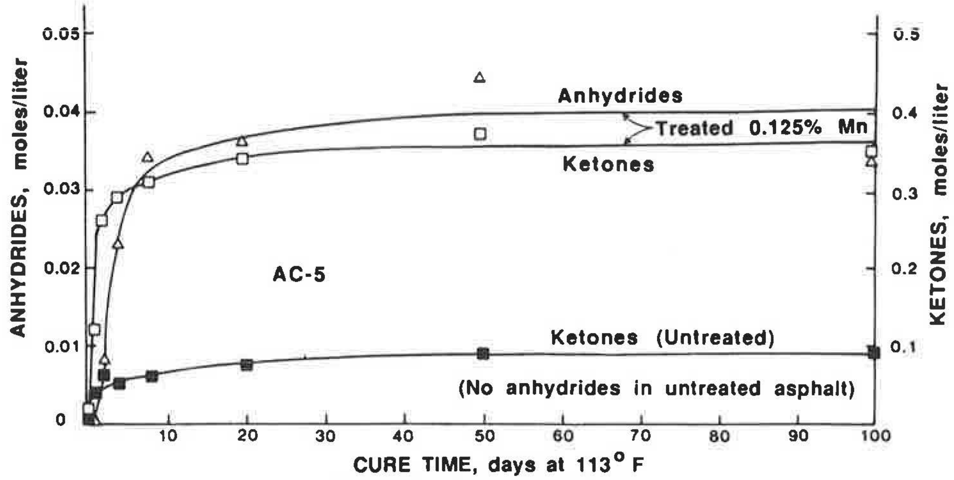


FIGURE 1 Ketone and anhydride formation during curing of treated and untreated Cosden asphalt.

Cosden and Shell asphalts indicated that the manganese-induced reaction and the corresponding viscosity increase were dependent not only on the manganese concentration, but also on the source of the asphalt. This dependency is related to differences in composition between sources, the level of oxidation products produced during cure, the sensitivity of viscosity to the oxidation products formed during the manganese-induced reaction, and possibly some cross-linking associated with the presence of manganese.

The mechanism of action of the manganese modifier, together with the proposed mechanism for manganese inactivation after curing, is summarized as follows. The manganese catalyzes the reaction of asphalt hydrocarbon components with atmospheric oxygen, primarily at the alpha carbon of hydrocarbon side chains attached to aromatic rings, to form ketones by means of a hydroperoxide intermediate. This ketone formation was previously shown in Figures 1 and 2.

According to the mechanism, the manganese is inactivated after curing by formation of a coordinate complex with stereospecific diketones formed by oxidation of adjacent side chains at the bridgehead positions of aromatic ring systems in the asphalt, that is, the 1,8-positions of the naphthalene ring moiety. The proposed transitory precursor of the diketone is a bifunctional oxidation product containing ketone and hydroperoxide functionality, which randomly decomposes to form either a diketone or an anhydride. Because it takes time during random free radical hydrocarbon oxidation to form a significant concentration of the precursor oxidation product, significant concentrations of nonstereospecific ketones, which cannot be differentiated from stereospecific diketones in the functional group analysis, build up before formation of measurable amounts of stereospecific diketones and anhydrides. This induction period is shown in Figure 4, which shows the relationship between ketone and anhydride formation at different levels of oxidation. At the end of the induction period, and the onset of significant stereospecific diketone formation as monitored by anhydride formation, the manganese is inactivated by coordinate complex formation with the diketone. The reaction during the induction period is accompanied by the rapid increase in viscosity of the asphalt cement (Figure 3).



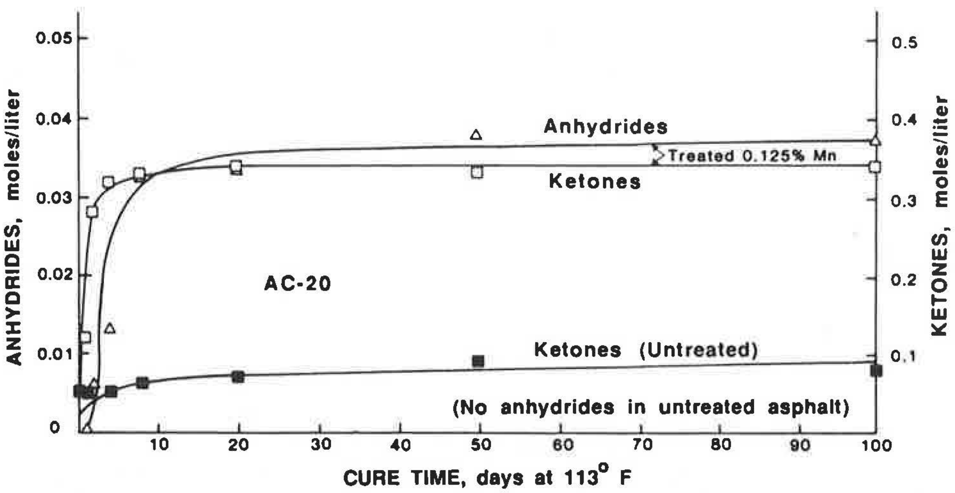


FIGURE 2 Ketone and anhydride formation during curing of treated and untreated Shell asphalt.

Confirming evidence for the mechanism is shown in Figures 4–6. If the stereospecific diketones—which are formed simultaneously with anhydrides—inactivate the manganese, then the amount of anhydrides formed at the end of the manganese-induced cure should be proportional to the amount of manganese present; the relationship should pass through zero, exactly as can be observed in Figure 4. Further, the level of viscosity increase and level of ketone formation at the end of the cure should show a regular dependence on manganese concentration, as shown in Figure 5.

A related and important conclusion can be drawn from Figure 5. If the slope of the relationship between viscosity and manganese content is extended linearly to zero concentration, an estimation of the practical lower limit of viscosity increase that can be obtained for a treated Cosden asphalt is indicated.

Figure 6 shows the most direct evidence for inactivation of the manganese by the stereospecific diketone. During the initial part of the cure (induction period), ketones are formed with no other changes in the monitored chemical functionality. After 24 hr, anhydrides and the proposed diketones begin to form, together with an increase in free carboxylic acids and a decrease in carboxylic acids that were complexed with manganese in the initial modifier formulation.

It is proposed that the carboxylic acids are displaced from the active form of manganese during formation of the coordinate complex of the manganese with the diketone, thus leading to inactivation of the manganese. It is known that significant amounts of carboxylic acids are never formed during low-temperature air oxidation of asphalts. The free acids formed during inactivation of the manganese can be accounted for by the acids liberated from the manganese during diketone complex formation. In the Cosden asphalt, approximately one mole of carboxylic acid per mole of manganese remains associated with the manganese in its inactivated form.

Pennsylvania State University

Anderson evaluated the consistency of asphalt cements aged in the laboratory to simulate approximately 32 months of in-

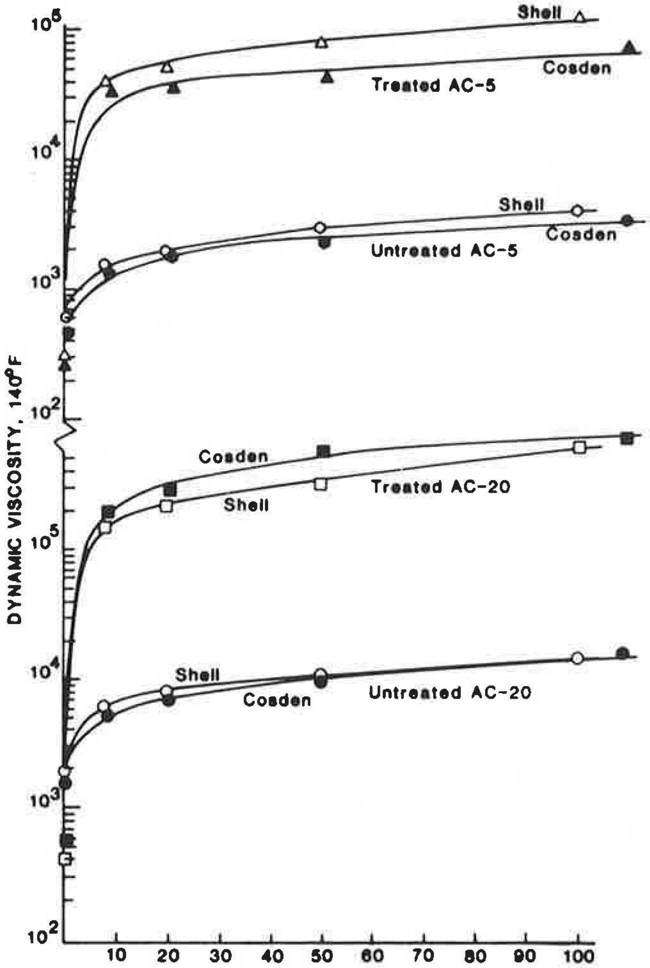


FIGURE 3 Change in viscosity during curing of treated and untreated asphalts.

service hardening as experienced in a very hot, low-elevation, desert climate (*3*). Two asphalt cements with different levels of modifier were aged in the California tilt-oven durability test and tested to define penetration, viscosity, creep, and tensile properties.

Penetration and viscosity measurements were made according to existing ASTM standard test methods. Creep tests were performed in a parallel-plate (three plates) fixture. Test data were utilized to calculate creep compliance, stiffness, and viscosity. Tensile properties were measured by utilizing a modified ductility device. A load cell was installed to measure the load on the sample as the sample of binder was subjected to a constant rate of extension.

Penetration and Viscosity Standard penetration and viscosity test data on treated and untreated asphalt cements before and after aging are given in Tables 1 and 3, respectively. A decrease in viscosity and an increase in penetration associated with increased treatment levels on unaged binders occurred over the range of 39.2°F to 275°F, which is attributed to the relatively low viscosity of the modifier.

Penetration of aged binders over the temperature range of 50°F to 100°F showed little effect of treatment level except for the 0.20 percent treatment, which had a slightly lower penetration at 100°F. Differences between asphalt grades upon aging are evident, and a decrease in penetration occurred with an increase in grade (AC-2.5 to AC-20), as indicated by the data in Table 3.

Capillary viscosity measurements at 140°F and 180°F were made after oven aging. Considerable difficulty was encountered in performing the viscosity measurements at 140°F because of the high viscosity of the aged binders containing the higher treatment level of 0.20 percent. The viscosity values at this high treatment level after aging were two to four times as

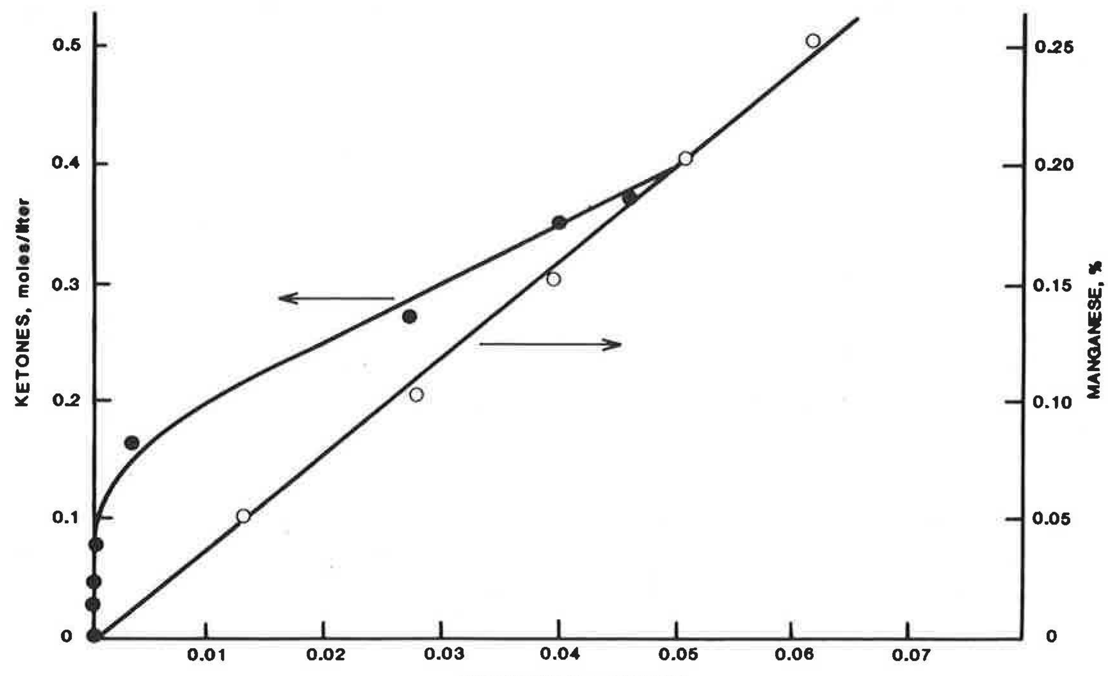


FIGURE 4 Relationships between anhydrides formed in treated Cosden AC-5 asphalt and both manganese content and ketones formed.

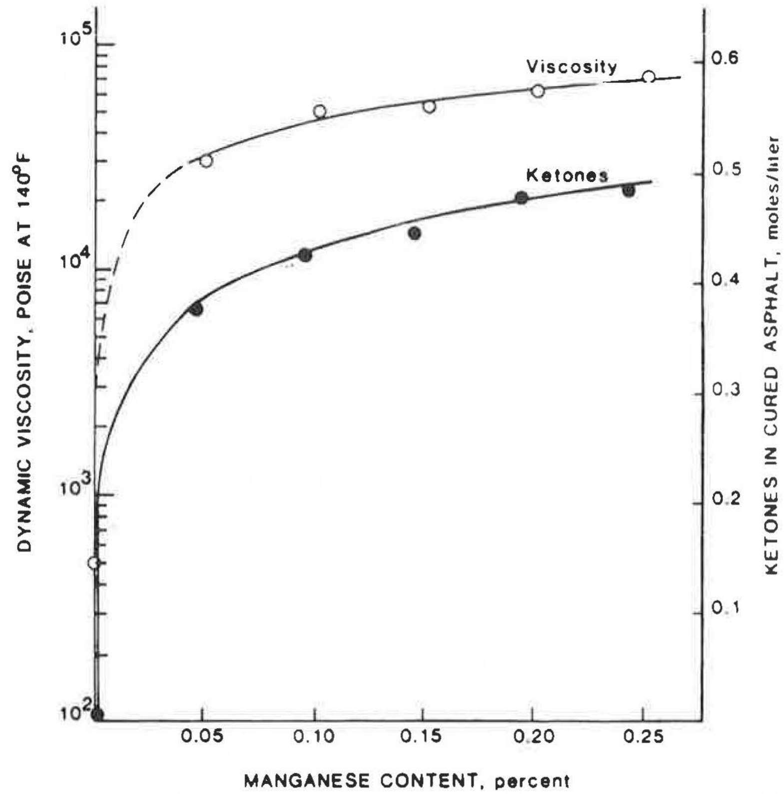


FIGURE 5 Relationship between manganese content and both viscosity and ketone formed in treated Cosden AC-5 asphalt.

high as the viscosities of the untreated samples, depending on the asphalt source and grade. Viscosity increases at lower levels of treatment occurred for certain combinations of asphalt source and grade.

In the case of the Shell material, the treated asphalt exhibited improved temperature susceptibility.

Creep Sliding plate creep tests were performed at 39.2°F, 50°F, 77°F, and 100°F. The effect of treatment level was significant at the longer loading times, with the 0.2 percent treatment producing the stiffest asphalt. In many instances, the stiffness increased as the treatment levels ranged from 0.125 to 0.00 and 0.08 to 0.20 percent. This trend occurred in too many instances

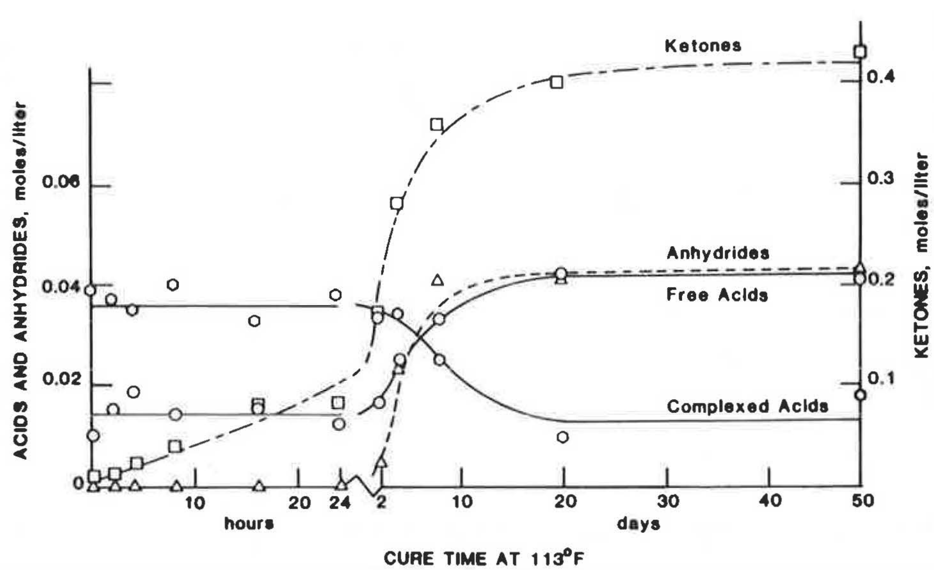


FIGURE 6 Changes in chemical functionality during curing of treated Cosden asphalt.

TABLE 3 ORIGINAL PHYSICAL PROPERTIES OF AGED ASPHALT CEMENTS

			Penetration, 100 g., 5 sec, 0.1 mm			Viscosity, poises x 10³	
Asphalt source	Asphalt grade	% Manganese	50 °F	77 °F	100°F °F	140[a] °F	275[a] °F
Cosden	AC-2.5	0.00	8	19	40	207	3.50
		0.08	8	19	39	250	3.60
		0.125	8	20	42	199	3.00
		0.20	7	17	33	1,550	11.00
	AC-5	0.00	7	15	33		5.48
		0.08	6	16	34		4.30
		0.125	7	16	34		5.12
		0.20	6	17	31		12.76
	AC-20	0.00	5	12	32	126	2.77
		0.08	5	13	26	404	5.90
		0.125	5	13	30	228	3.95
		0.20	5	13	26	894	10.86
Shell	AC-5	0.00	8	17	38		15.35
		0.08	8	20	40		8.23
		0.125	9	18	40		9.86
		0.200	8	20	38		30.80
	AC-20	0.00	7	15	34		12.24
		0.08	9	16	35		12.60
		0.125	7	17	35		19.23
		0.200	7	17	32		47.30

[a] Aged in extended rolling thin film oven test after reference(3).

and with too many other test procedures (including viscosity) to be attributable to experimental error.

Tension The elongation at failure, maximum load, and the energy to failure were determined from direct tension tests performed at 60°F (Table 4). In general, increased treatment levels reduced the elongation at failure. The most noticeable reduction in elongation occurred when the treatment level was increased above 0.125 percent manganese.

The load at failure increased with asphalt grade, but no trend was evident with respect to treatment level. The energy to failure had a behavior pattern similar to the maximum failure load.

Engineering Properties

The engineering properties were evaluated at the University of Texas (Eagle Lake mixture), University of Nevada (Watsonville and Helms mixtures), and the University of Waterloo (limestone mixture). A summary of the work conducted by Kennedy and Epps can be found elsewhere (*9*), and is therefore only briefly included for completeness.

Specimen Preparation

The asphalt cement and Eagle Lake aggregate were mixed at 275°F and the asphalt compacted at 250°F by using the Texas gyratory shear compactor. All specimens were nominally 2 in. high and 4 in. in diameter. Two gyratory shear compaction procedures were utilized to obtain approximately 3 and 7 percent air voids.

The Watsonville and Helms aggregates and asphalt cements were mixed at 300°F and compacted at 280°F. All samples were nominally 2.5 in. high and 4 in. in diameter. The two compaction procedures involved a Marshall compaction hammer using a variable number of blows.

The crushed limestone aggregate and asphalt cements were mixed, then compacted at 230°F into beams using a California kneading compactor (ASTM D 1561-81). The specimens were sawed into beams (1.5 × 1.5 × 4.0 in.) for testing in a constant-rate-of-extension apparatus. Different compactive efforts were utilized to produce 3 and 7 percent air voids for each mixture combination.

Curing and Testing

After compaction, all samples were oven cured at 140°F for 28 days. Air was circulated in the oven throughout the curing period. After 28 days the samples were allowed to cool to room temperature and were then placed in chambers at the appropriate testing temperature for a period of 24 hr.

Specimens were tested by using the static and repeated-load indirect tensile tests, Marshall stability test, and Hveem stability test. Properties measured were tensile strength, resilient modulus, Marshall stability and flow, and Hveem stability. In addition, constant rate of extension (0.00016 in./mm) direct

TABLE 4 TENSILE TEST RESULTS AT 60°F

Asphalt source	Asphalt grade	% Manganese	Elongation at failure cm	Peak load grams	Energy to failure, grams-cm
Cosden	AC-3	0.00	1.4	3000	32
		0.08	1.9	4130	59
		0.125	2.0	3980	58
		0.20	1.0	2330	15
	AC-5	0.00	1.7	4650	54
		0.08	1.8	4880	60
		0.125	1.7	4500	53
		0.20	1.3	4880	38
	AC-20	0.00	2.0	6980	78
		0.08	1.2	6000	41
		0.125	1.6	9000	78
		0.20	1.2	8250	54
Shell	AC-5	0.00	1.8	3980	53
		0.08	2.5	3750	63
		0.125	1.9	3750	48
		0.20	1.5	3750	33
	AC-20	0.00	2.8	5630	99
		0.08	2.6	4880	75
		0.125	2.0	4880	63
		0.20	1.3	4350	33

tension tests were conducted at 0°F to measure the maximum stress, or strength, and the stiffness modulus at failure.

Tensile Strengths and Resilient Moduli

Effect of Temperature and Manganese Content Both tensile strength and resilient modulus decreased with increased temperature and the slope of these relationships varied, generally indicating that the treated-asphalt mixtures were less temperature susceptible (Figures 7 and 8).

In general, there was a crossover in tensile strength–temperature relationships for the treated and untreated (control) asphalt mixtures. The strength and resilient modulus of the mixtures containing the treated asphalt were greater than the strength and modulus of the mixtures containing the untreated asphalt cement at 104°F, whereas the reverse was true at 32°F.

There also appeared to be an optimum manganese or addi-

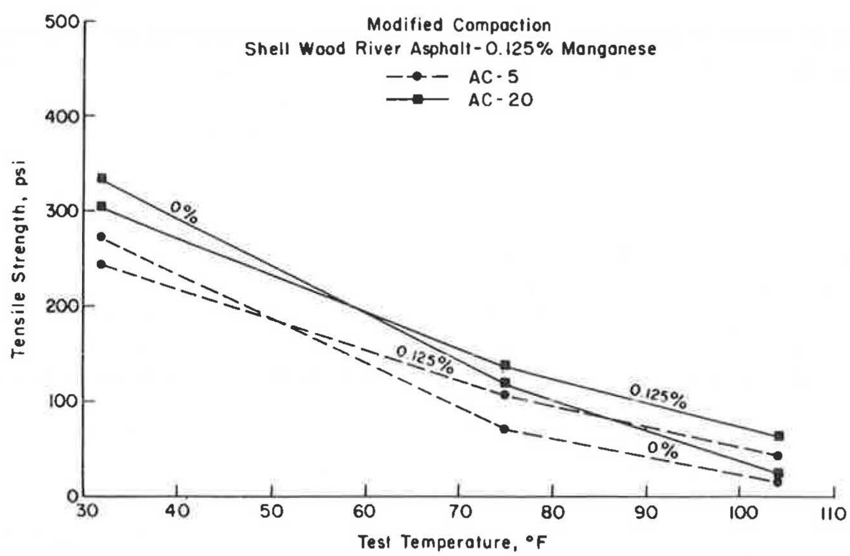


FIGURE 7 Relationships between tensile strength and test temperature for Eagle Lake mixtures with untreated and treated Shell asphalts.

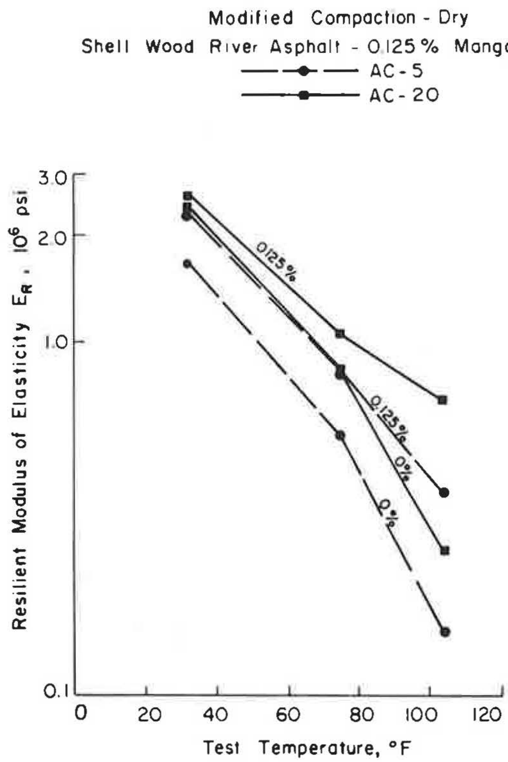


FIGURE 8 Relationships between resilient modulus and test temperature for Eagle Lake mixtures with untreated and treated Shell asphalts.

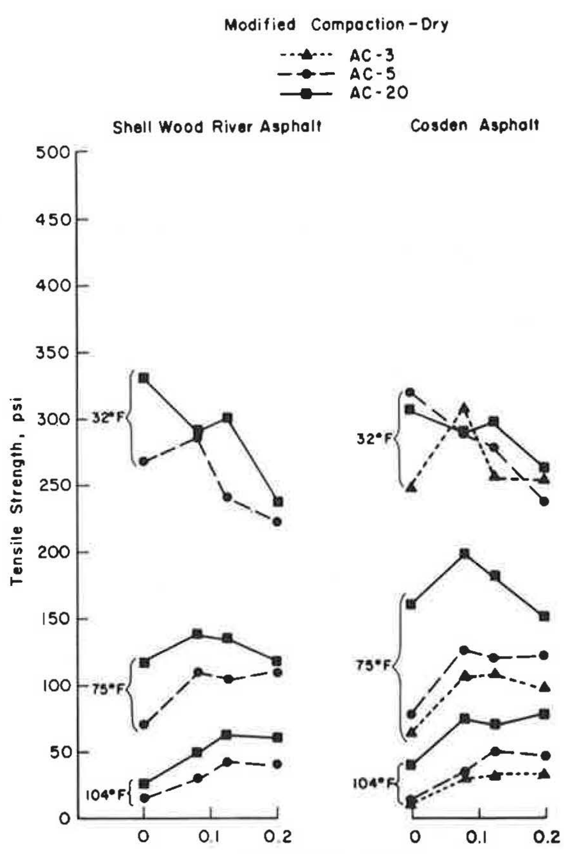


FIGURE 9 Relationships between tensile strength and manganese content for Eagle Lake mixtures.

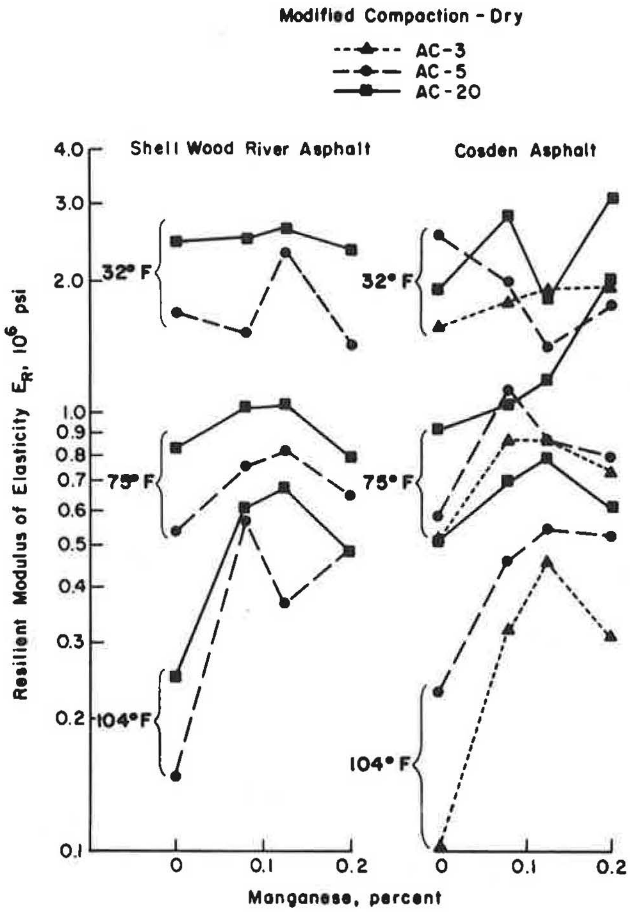


FIGURE 10 Relationships between resilient modulus and manganese content for Eagle Lake mixtures.

tive content for maximum tensile strength and resilient modulus, which was well defined at 75°F (Figures 9 and 10). At 104°F the trend was not as evident, and at 32°F the relationships varied with the suggested possibility that strength decreased with increased manganese or additive content; however, there was no indication that stiffness decreased with increased manganese content.

For the Watsonville and Helms mixtures at 8 percent air voids, the treated-asphalt mixtures had higher strengths than the untreated mixtures at the higher temperatures. At the colder temperatures, the strengths were more nearly equal, indicating a reduced temperature susceptibility. The treated AC-5 mixtures had tensile strengths equal to or greater than the untreated AC-20 at higher temperatures.

Effects of Curing Time and Air Voids At 77°F the treated mixtures initially had lower resilient moduli (stiffness) than the untreated mixtures (Figure 11). After curing, however, the stiffness of the treated mixtures exceeded the stiffness of the untreated mixtures. Although the stiffness of both mixtures continued to increase after 28 days, the rate of increase was relatively small.

Mixtures containing the treated AC-5 asphalts had lower initial resilient moduli than the untreated AC-20 at 77°F (Figure 12). Within 28 days the resilient moduli of the mixtures containing the treated AC-5 asphalts approached or exceeded

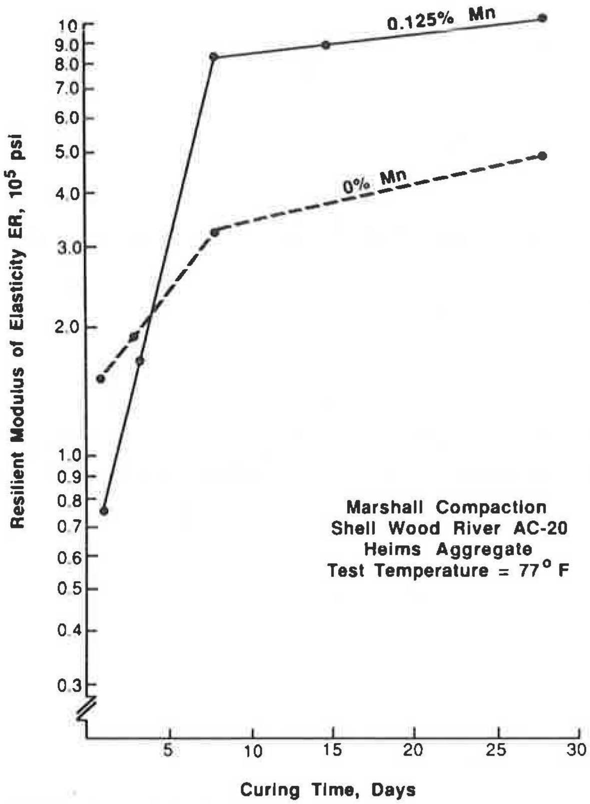


FIGURE 11 Relationships between resilient modulus and curing time for Helms mixtures with untreated and treated Shell asphalts.

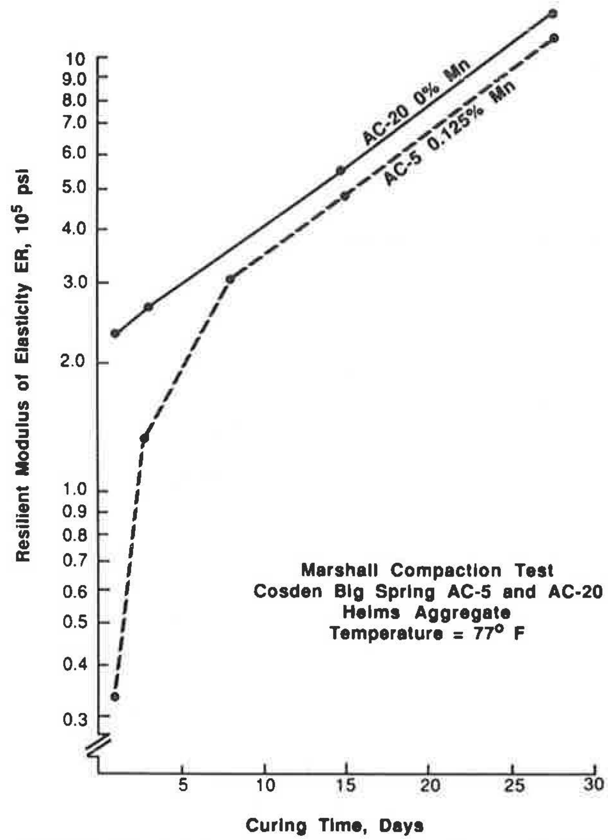


FIGURE 12 Relationships between resilient modulus and curing time for Helms mixtures with untreated AC-5 and untreated AC-20 Cosden asphalts.

the moduli value of mixtures containing the untreated AC-20 asphalt cements (Figure 12).

Treated samples with higher void contents exhibited a higher rate of stiffness increase. For Watsonville mixtures, the crossover between treated and untreated asphalt occurred after approximately 5 to 8 days of curing, whereas for the Helms mixtures, which had approximately 2 percent more voids, the crossover occurred after approximately 3 days (*7*).

Marshall Stability and Flow

Marshall stabilities increased with increased manganese or additive content. In addition, the stabilities of treated asphalt mixtures were equal to or greater than the control (no manganese) asphalt mixtures containing the next grade of asphalt. Flow values did not exhibit consistent relationships, although flow values appeared to increase slightly with increased manganese contents (*7*).

Hveem Stability

For the high void mixtures, Hveem stability increased with increased manganese, or additive, content. Also, the stabilities of the treated asphalt cement mixtures generally were equal to or greater than the stability of the control with no manganese (*7*).

Moisture Susceptibility

The tensile strength ratios and resilient modulus ratios for treated asphalt mixtures with various manganese contents indicated a substantial loss in strength and modulus with exposure to water (*5*). However, increases in the absolute values of strength and modulus were noted in several cases and the results for the Watsonville mixture, while not acceptable, were significantly improved.

Low-Temperature Stiffness and Failure Stress

For the Canadian limestone mixtures, low-temperature stiffness tended to decrease with increased additive level; however, there was a significant amount of scatter in the data. Thus, it is difficult to draw conclusions as to specific effects of the various variables. However, it was concluded that addition of the modifier did not increase low-temperature stiffness and that paving mixtures utilizing treated asphalt cements offer adequate field performance (Tables 5 and 6).

As with stiffness, the maximum failure stress decreased with increased amounts of additive. Increasing the additive level from 0 to 0.125 percent resulted in approximately a 40 percent decrease in the maximum stress.

TABLE 5 CRITERIA FOR ESTIMATING THE LOW-TEMPERATURE CRACKING PERFORMANCE OF AN ASPHALT MIX (*4*)

Measured stiffness modulus of the mix at 0°F. (psi)	Expected performance
< 250,000	Excellent
250,000 to 290,000	Good
290,000 to 470,000	Moderate
> 470,000	Poor

SUMMARY AND SIGNIFICANCE OF RESULTS

Original Properties of Modified Asphalt Cements

A reduction in viscosity and an increase in penetration occurred with the addition of the modifier (see Table 2). These trends observed in asphalt cement properties were confirmed by resilient modulus test results (see Figure 11).

Aged Properties of Modified Asphalt Cements

High Temperature

Viscosity at 140°F or 180°F increased with increased manganese content at the higher treatment levels (see Table 3). A relationship between treatment level and viscosity increase at 140°F and 180°F was not evident in the Anderson study (see Table 3); however, the relationship anticipated was obtained by Petersen (see Figure 5). It should be noted that different curing techniques were used in the Anderson and Petersen studies. The Petersen study was conducted on stationary thin films on Ottawa sand simulating thin films in pavement mixtures.

Penetration data at 100°F show the general trend of a decrease in penetration with increased treatment levels (see Table 3).

Marshall stabilities performed at 140°F generally increased with treatment level. Similar behavior patterns occurred for Hveem stabilities obtained at 140°F. However, the magnitude of the change was small in comparison with that of the Marshall stabilities.

Both resilient moduli and tensile strengths at 104°F generally increased with treatment level (see Figures 9 and 10); however, the rate of increase decreased with increased concentrations.

TABLE 6 APPLICATION OF CRITERIA TO EVALUATING STIFFNESS MODULUS RESULTS (*4*)

Asphalt source	Asphalt grade	% Mn	Stiffness modulus, psi	Expected performance[a]
Cosden	AC-3	0.08	460,000	Moderate
		0.125	340,000	Moderate
		0.20	240,000	Good
	AC-5	0.00	400,000	Moderate
		0.08	260,000	Good
		0.125	380,000	Moderate
		0.20	250,000	Excellent
	AC-20	0.00	360,000	Moderate
Shell	All Grades	0.00	540,000	Poor
		0.08	420,000	Moderate
		0.125	280,000	Good
		0.20	470,000	Moderate

[a] See Table 5.

Intermediate Temperatures

Penetration data obtained by Anderson showed little difference at 50°F and 77°F with the addition of the modifier (see Table 3).

Both resilient moduli and tensile strengths at 77°F substantially increased with the addition of the modifier (see Figures 9 and 10). As the treatment level increased, the moduli and strengths decreased slightly. A similar trend occurred in data developed by Haas.

Low Temperature

Both resilient modulus and tensile strength results performed on mixtures at 32°F decreased with the addition of the modifier (see Figures 9 and 10). A similar trend for stiffness moduli of 0°F and maximum failure stress (strength) was observed by Haas.

Aged, modified asphalt cements, and mixtures tended to be stiffer at high temperatures and less stiff at low temperatures. These observed trends are apparent in studies performed by Kennedy and Epps (see Figures 7 and 8).

Reaction Kinetics

The rate of the modifier-induced reaction in asphalt is controlled primarily by modifier concentration, availability of oxygen (film thickness), and temperature, and to a lesser degree by asphalt source and grade. The data developed by Petersen and Epps indicate that rapid initial reaction occurs, as shown by an increase in viscosity at 140°F (see Figures 3 and 5) and an increase in resilient modulus at 77°F (see Figures 11 and 12).

Reaction rate was tied to the formation of ketones by Petersen. Analytical data showed rapid formation of ketones and rapid increases in viscosity during the first few days of curing at 113°F (see Figure 5). Cessation of the manganese-induced reaction from inactivation of the manganese is evidenced by a reduction in the rate of ketone and anhydride formation to a very low level.

Results of resilient modulus testing indicated differing reaction rates, depending on air void content of the mixtures. Other data also suggested that asphalt source may be important.

Load Distribution Capability

Asphalt-concrete mixtures containing modified asphalt cements generally had higher stiffness (resilient modulus) than mixtures containing untreated asphalt cements of the same source and grade. This observation is more pronounced at the higher temperatures when load distributing capability is most important. Low-temperature stiffness values generally were lower for the treated softer-graded asphalt mixtures than for the untreated harder-graded asphalt (see Figure 8).

Fatigue

Controlled stress fatigue test results are applicable in design and performance considerations of thick asphalt-concrete pavements (greater than 4 to 6 in. of asphalt concrete). In general, mixtures with high stiffness values show improved fatigue performance. As discussed previously, mixtures containing modified asphalt cements have higher stiffness values at the high temperatures at which the fatigue performance of thick sections of pavements is important. Thus it is anticipated, and shown by Kennedy et al. (*10*), that improved fatigue performance can be obtained with the modified mixtures.

In contrast, controlled strain fatigue tests are most applicable to design and performance of thin asphalt-concrete pavements (less than 2 in.). Stiff mixtures are usually associated with poor fatigue life and performance. Thus, the use of modified mixtures for thin pavement or pavements without adequate supporting layers should be approached with caution and/or low treatment levels should be utilized.

Rutting and Permanent Deformation

The high stiffness reported for the treated materials, particularly at high temperatures, suggests improved resistance to rutting and shoving (see Figure 8). High-temperature stiffness was found to be dependent on treatment level and curing. High treatment levels and high temperatures during curing promote very high stiffness. Early cure stiffness values for treated materials are usually lower than untreated materials (see Figures 11 and 12). Thus, caution must be exercised to prevent premature rutting and shoving in mixtures that do not contain good aggregate systems.

Marshall and Hveem stability data also indicated that improved resistance to rutting and shoving can be expected.

Cold-Temperature Cracking

High stiffness values at cold temperatures imply that high stresses will occur in a pavement with the lowering of temperature. In addition, it is possible that mixtures with high stiffness have low flexibility and are more likely to crack. Haas indicated that treated mixtures had equivalent low-temperature cracking resistance compared with those of untreated mixtures (see Tables 5 and 6). Kennedy and Epps found equal or lower values of resilient modulus and tensile strength for treated asphalt mixtures compared with those of untreated mixtures, indicating that cold temperature performance may be equal or better.

Resistance to Moisture Damage

Resistance to moisture damage of treated and untreated mixtures was evaluated by Kennedy (*5*). Indirect tensile strength and resilient modulus were obtained before and after exposure to water. Absolute values of tensile strength and modulus were higher after exposure to water for treated material compared with those of the untreated material. However, in terms of retained tensile strength, the treated mixtures did not attain acceptable levels.

Construction Implications

Reduced viscosity of treated asphalt cements (see Table 2) during construction can result in (a) a tender mixture, which is difficult to compact and will exhibit early rutting, or (b) high-density and low air-void content mixes, which can also lead to early rutting problems. Consideration should be given to reducing mixture temperature at time of placement and to reducing compaction effort if necessary to control air voids. Aggregate characteristics are critical if tenderness is to be minimized.

SUMMARY

Based on the findings of this study, it would appear that the modifier is capable of improving the high-temperature stiffness and strength of asphalt concrete. Principal application areas include thick sections of asphalt concrete in new construction and thick overlays. Treated mixtures should not be expected to prevent reflection cracking or to perform in thin lifts over high deflection bases. A detailed mixture design should be performed for each construction project to adequately consider the effects of asphalt crude source, asphalt chemical and physical properties, and aggregate characteristics. Desired mixture properties and hence treatment levels should consider the end use of the asphalt concrete mixture.

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