

# Coal-Based Synthetic Asphalt: Oxidative Aging and Testing of Compacted Bituminous Mixtures

JAMES A. GUIN, CHRISTINE W. CURTIS, JYH HUEI KANG, SANG J. PARK,  
SAI V. GOLLAKOTA, AND A. RAY TARRER

An asphalt binder material, functionally equivalent to petroleum asphalt, has been produced by catalytic hydroliquefaction of coal. The synthetic coal-based asphalt, with approximately 3 percent polymer additive, meets all ASTM and AASHTO specifications for asphalt paving cements, with the exception of the optional thin-film oven test weight loss specification. Age hardening of the coal-based asphalt is primarily due to air oxidation rather than volatilization or polymerization. Marshall stability and immersion-compression testing show that the polymer-modified, coal-based asphalt produces compacted mixtures with good moisture resistance and high compressive strength compared with those of control samples prepared with petroleum asphalt of the same viscosity grade.

In the United States, highway construction and maintenance consume 25 million to 30 million tons (22.7 million to 27.3 million metric tons) of asphalt each year. In hydrocarbon value, this consumption is approximately equivalent to 400,000 barrels (63 588 m<sup>3</sup>) per day of crude oil. Thus considerable savings in U.S. petroleum consumption could be attained by replacing asphalt with a functionally equivalent substitute. In light of the current oil glut, there is little economic motivation for commercial production of synthetic asphalts. However, considering worldwide political uncertainties, which could quickly affect oil supplies, and the increasing U.S. consumption and declining U.S. production rates, it appears to be useful to continue a limited research effort along these lines and to document findings for future contingencies. Development of such technology also increases the potential value of the vast U.S. coal resources.

Since 1974 many processes for converting coal to liquid and gaseous fuels have been developed. It is possible that similar technology could be used to produce a product functionally equivalent to petroleum-based asphalt (i.e., coal-based asphalt). Thus the overall objective of this project was to investigate, in the laboratory, the application of current liquefaction technology to the production of a synthetic asphalt product from coal. This is a formidable objective because of the inherently differing properties of coal and petroleum. Because asphalt specifications have been developed from petroleum experience, possible

difficulties in producing a material that meets these specifications from a chemically different raw material (i.e., coal) can be expected.

Coal tar pitches and oils derived from carbonization processes have been used to some extent for various road paving and coating applications (1-4). The production of most of these materials did not involve high-temperature, high-pressure, catalytic hydrogenation typical of current direct coal liquefaction technology. However, Calkins and Silver (5) and later Hoffman (6) did use coal liquefaction technology at high severity to produce a coal-based asphalt-type product. In general, this product had higher viscosity temperature susceptibility (VTS) and oxidative hardening rates than did corresponding petroleum asphalt.

Previous work (1) has shown that synthetic asphalt cements with acceptable aging indices and VTS properties can be produced from coal by severe hydrotreatment followed by addition of approximately 3 percent by weight styrene-butadiene copolymer. The purpose of the present paper is to report additional results regarding oxidative hardening of the coal-based asphalt and results of testing compacted bituminous mixtures prepared with the coal-based asphalt for compressive strength and water damage susceptibility.

## EXPERIMENTAL MATERIALS AND PROCEDURES

### Materials

An Illinois No. 6 bituminous coal was catalytically hydrogenated in a batch autoclave in the presence of a heavy coal-derived V1067 recycle solvent and a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The V1067 solvent was produced by the two-stage catalytic coal liquefaction process at Wilsonville, Alabama, in Run 245 and has a viscosity of 97 poises at 60°C. Complete elemental analysis and asphalt testing properties for the V1067 solvent, and analysis of the other materials, are available elsewhere (1). The polymer modifier used throughout was a random, linear copolymer of styrene and butadiene (45 percent styrene, density 0.965 g/cm<sup>3</sup>) purchased from Aldrich Chemical Company.

### Reaction Procedures

The base reaction conditions for the production of the coal-based asphalt are given in Table 1. Liquid and solid reaction products were diluted with trichloroethylene (TCE) and altered

J. A. Guin, C. W. Curtis, J. H. Kang, S. J. Park, and A. R. Tarrer, Chemical Engineering Department, Auburn University, Auburn, Ala. 36849. S. V. Gollakota, Catalytic, Inc., P.O. Drawer 239, Wilsonville, Ala. 35186.

TABLE 1 BASE REACTION CONDITIONS FOR COAL-BASED ASPHALT REACTIONS

Factor	Value
Temperature (°C)	425
Pressure (psig)	2,500
Reaction time (hr)	2
Agitation rate (rpm)	2,000
Catalyst	Shell 324 NiMo/Al <sub>2</sub> O <sub>3</sub> , 1/32-in. extrudates
Coal type	Illinois No. 6 (bituminous)
Solvent	V1067
Solvent-to-coal ratio	2 to 1
Feed-to-catalyst ratio	10 to 1

NOTE: 1 psi = 6.89 kPa, 1 hr = 3,600 sec, 1 in. = 2.54 cm, and psig = pounds per square inch, gauge.

to remove ash and insoluble organic matter (IOM). Sufficient styrene-butadiene copolymer dissolved in TCE was added to the liquid product after filtration to obtain approximately 3 percent by weight polymer in the final asphalt product after distillation. The coal-based asphalt product was then prepared by distillation of the liquid at 1 mm Hg to obtain a specified viscosity-graded asphalt. Complete details of these procedures are available elsewhere (1). No polymer modifier was used in control experiments performed with petroleum-based AC-20.

### Testing Procedures

The properties of the distillation residue were evaluated to assess its potential as a synthetic asphalt. The following procedures were used: absolute viscosity at 60°C (ASTM D 2171), kinematic viscosity at 135°C (ASTM D 2170), penetration at 25°C (ASTM D 5), ductility at 25°C (ASTM D 113), solubility in TCE (ASTM D 2042), and thin-film oven test (TFOT) (ASTM D 1754). Testing of compacted bituminous mixtures was performed using the Marshall testing method (AASHTO T 245) and the immersion-compression (IC) test (AASHTO T 165 and T 167) to assess compressive strength and water damage potential. More specific information on moisture damage could be obtained by AASHTO T 283; however, this test was not used.

## RESULTS AND DISCUSSION

### Aging

Previous results indicated that coal-based asphalt cements tended to age harden faster than their petroleum counterparts (1). In this earlier work the major variable was the (unmeasured) partial pressure of oxygen present during the aging time at elevated temperature in the TFOT. Because the primary difference in the experiments was the amount of oxygen present, this, not simply loss of volatiles or internal polymerization, appeared to be the major factor in the hardening of the coal-derived material in the TFOT, although the absence of the latter two processes was not conclusively shown.

To further examine this hypothesis and explore in more detail the mechanism of age hardening of coal-based asphalt, a series of additional experiments was performed under more closely controlled conditions using a sample of heavy coal-derived V1067 solvent that had been distilled to produce a residue with a viscosity of 2145 poises (215 Pa-sec) at 60°C,

corresponding to an AC-20 grade asphalt. No polymer modifier was added to this material. The purpose of these experiments was to attempt to separate the processes of oxidation, polymerization, and volatiles loss, all of which could contribute to age hardening of the coal-based asphalt.

To facilitate the aging study in a more closely controlled atmosphere, TFOT conditions specified in ASTM D 1754 were slightly modified: The cylindrical flat-bottomed pan containing the asphalt sample was placed in a capped 1-gal stationary vessel inside the TFO. The vessel was equipped with a gas inlet and outlet tube. The vessel contents then were maintained under flowing pure nitrogen or air preheated to the oven temperature of 163°C. This controlled atmosphere flowed over the sample at a rate of 1 standard cubic foot per hour ( $2.83 \times 10^{-2} \text{ m}^3/\text{hr}$ ). The sample was not rotated.

In addition to the flowing air and nitrogen experiments, some experiments were carried out in a closed stainless steel batch reactor (tubing bomb) like that described by Brooks et al. (7). The purpose of these closed tubing bomb experiments was to examine the influence of internal polymerization and condensation reactions, by themselves, on the age-hardening process. Because this was a completely closed system, no loss of volatiles was possible.

As the data given in Table 2 indicate, in a flowing air or nitrogen atmosphere, the viscosity increased with increasing aging time. Generally, two samples were tested under each aging condition. There is some variation in the results; this was most probably due to the formation of a film on the surface of the samples, which made it difficult to obtain a uniform representative sample. However, the large differences among the different aging conditions are significant. For the 5-hr run, the viscosity of the sample aged in air is about 70 times that of the sample aged in nitrogen. These results confirm that oxygen is the major factor in the age hardening of coal-based asphalt.

For control purposes, age hardening of a commercial AC-20 grade petroleum asphalt was also determined under the same conditions. With an initial viscosity of 2209 poises (221 Pa-sec) for the petroleum AC-20, the viscosity after 5 hr under flowing nitrogen and air increased to 2740 poises (274 Pa-sec) and 14 119 poises (1412 Pa-sec), respectively. The petroleum asphalt experienced a weight loss of 0.045 percent in nitrogen and a weight gain of 0.045 percent in air. The age hardening experienced in the flowing nitrogen is primarily a result of volatiles loss for both the AC-20 control and the coal-based asphalt. The results in the batch reactor (tubing bomb) under nitrogen at 163°C (Table 2) indicate that, in the absence of volatiles loss and oxidation, there is no significant age hardening.

The viscosity of coal-based asphalt remained essentially unchanged even after 15 hr at reaction temperature. The viscosity of the AC-20 control was 2161 poises (216 Pa-sec) after 5 hr in the tubing bomb. These tubing bomb results indicate that condensation (polymerization) reactions alone (in the absence of oxygen) are not a significant factor in the short-term aging of coal-based asphalt.

Coal mineral matter is known to have a catalytic effect in various chemical reactions. The specific ash sample used here was not tested for catalytic activity; however, in past work, it was found that essentially all tested coal ashes, especially those containing iron, possess some activity (8). To examine a

TABLE 2 AGE HARDENING OF A COAL-BASED ASPHALT IN CONTROLLED ATMOSPHERE EXPERIMENTS

Aging Time <sup>a</sup> (hr)	Flowing Nitrogen <sup>b</sup>		Flowing Air <sup>b</sup>		Tubing Bomb <sup>c</sup> , Nitrogen Atmosphere, Viscosity (poises)
	Viscosity <sup>c</sup> (poises)	Weight Loss (%)	Viscosity (poises)	Weight Loss (%)	
1	2850	0.85	4889	0.61	1975
	2562	0.58	4641	0.62	2121
3	3992	2.20	32 238	1.74	2077
	3652	1.76	25 998	1.76	2060
5	5308	3.19	422 604 <sup>e</sup>	2.90	1900
	6050	3.11	243 540	2.54	
15	16 941	6.63	— <sup>f</sup>	8.18	2023
	13 245	6.38			2058

NOTE: 1 poise = 0.1 Pa-sec.

<sup>a</sup>Aging conditions: temperature = 163°C, sample amount = 25 g.<sup>b</sup>Flow rate = 1 standard cubic foot per hour ( $8 \times 10^{-6}$  m<sup>3</sup>/sec).<sup>c</sup>Viscosity of sample before aging = 2145  $\pm$  47 poises; all viscosities are measured at 60°C in poises.<sup>d</sup>Agitation rate = 500 cycles/min (52.2 rad/sec) (2 steel balls added); N<sub>2</sub> pressure at room temperature = 100 psi (689 kPa).<sup>e</sup>Large difference in values caused by extreme hardening and film formation on sample surface.<sup>f</sup>Viscosity too high to measure.

possible catalytic effect of coal ash on the aging process, 6.6 percent by weight of coal ash was added to a sample of the coal-based asphalt and it was subjected to flowing air at 163°C. The presence of ash in the coal-based asphalt increased the initial viscosity before the test from 2145 poises (215 Pa-sec) to 2715 poises (272 Pa-sec). After aging 3 hr in air, the viscosity was 27 584 poises (2758 Pa-sec), and a weight loss of 1.38 percent was noted.

Comparison with the corresponding results after 3 hr in air (Table 2) shows no significant catalytic effect of ash on aging. Additional studies conducted with the residue from previous coal liquefaction experiments, which contained coal mineral matter and heavy, highly carbonaceous organic material commonly called insoluble organic matter (IOM), also showed no effect on aging.

To examine the effect of water vapor (present in asphalt hot-mix plants) on the aging process, 3-hr aging experiments were conducted at 163°C using flowing air saturated with water at room temperature. A marginal decrease of approximately 15 percent in aging was observed when the flowing air contained water vapor compared with air without water vapor. It is possible that this effect is caused by the decrease in oxygen partial pressure in the gas mixture due to added moisture.

The use of antioxidant compounds, usually at 1 to 4 percent by weight, has been investigated in an attempt to reduce the age hardening of petroleum asphalts. Oxidative aging is generally thought to proceed by a free radical chain reaction, initiated by light or heat, or both, and propagated by peroxide radicals. The antioxidants are thought to inhibit this process by either (a) terminating the free radicals carrying the chain or (b) reacting with peroxide radical precursors to form inactive species. In particular, lead dialkylthiocarbonate (LDADC) has been thought to function by the second mechanism, depending to some extent on the particular asphalt used (9, 10). LDADC in the form of Vanlube™ 100 (R. T. Vanderbilt Co., Inc., New York) was tested with the same coal-based asphalt (Table 2).

Two percent by weight LDADC was added to two samples of coal-based asphalt, and they were then exposed to flowing air at 163°C. The presence of LDADC decreased the average initial sample viscosity from 2145 poises (215 Pa-sec) to 1747 poises (175 Pa-sec). After aging for 3 hr in air the average viscosity was 4548 poises (455 Pa-sec), and a weight loss of 2.1 percent was noted. Comparison with corresponding results after 3 hr in air without LDADC (Table 2) shows that the antioxidant reduced the amount of hardening, although the weight loss is still high. A similar effect was found by Haxo and White (9), who also made a detailed study of the volatility of the antioxidant and found this effect to be small at 60°C. It should be noted that the reduction in age hardening could have been partly due to a thin film formed on the asphalt surface during this test; however, further testing of this additive, such as in a rolling TFOT where film formation would not be a factor, does appear to be warranted.

A final set of measurements was made to examine chemical changes caused by aging in the coal-based asphalt samples (Table 2). A solvent fractionation technique was used with the following fractions (11):

- Oil—pentane solubles,
- Asphaltenes—pentane insolubles and benzene solubles,
- Preasphaltenes—benzene insolubles and methylene chloride/methanol (90/10) solubles, and
- IOM—methylene chloride/methanol (90/10) insolubles (ash free).

As the data given in Table 3 indicate, the oil and IOM in the original coal-based asphalt are 68.8 and 3.5 percent, respectively. For the sample aged in air for 15 hr, oil decreased to 57.5 percent and IOM increased to 14.0 percent. Thus it appears that, during age hardening of coal-based asphalt, the lighter fractions are oxidized to produce heavier, less soluble fractions. The product distribution of samples aged in nitrogen

TABLE 3 PRODUCT SOLUBILITY ANALYSIS OF COAL-BASED ASPHALT DURING AGING

	Original (unaged)	Aged in Flowing Air for				Aged in N <sub>2</sub> (tubing bomb) for		
		1 hr	3 hr	5 hr	15 hr	1 hr	5 hr	15 hr
Oil	68.8	64.4	65.5	62.4	57.5	69.3	68.2	65.1
Asphaltenes	23.6	23.9	22.2	23.4	20.5	20.8	22.4	25.2
Preasphaltenes	4.1	4.3	4.0	5.1	8.0	6.5	5.6	6.0
IOM	3.5	7.4	8.3	9.1	14.0	3.4	3.8	3.7

NOTE: All values are in percentage by weight.

in the closed tubing bomb was not changed significantly, which again shows reaction with oxygen to be the primary cause of age hardening.

### Testing of Bituminous Mixtures

The properties of bituminous mixtures prepared with the coal-based asphalt binder were evaluated by the Marshall testing method (AASHTO T 245) and by the immersion-compression test (AASHTO T 165 and T 167).

### Marshall Stability Results

To produce sufficient specification-grade, coal-based asphalt for Marshall stability testing, two experiments (Runs CP 30 and 31) were performed in which Illinois No. 6 bituminous coal and V1067 solvent were catalytically hydrogenated in a 1-gal autoclave under the conditions given in Table 1. Experimental methods were the same as those used previously (1). When the temperature in the distillation flask reached 213°C at 1 mm Hg, an AC-20 grade coal-based asphalt was obtained (Table 4). After the two asphalt products from Runs CP 30 and 31 were collected, they were blended with approximately 3 percent by weight of copolymer, and the viscosity of the blended mixture was determined as indicated in Table 4. This blended mixture was used in the following testing.

To compare the resistance to plastic flow of coal-based asphalt mix with that of petroleum-based asphalt mix, both the coal-based asphalt (from Table 4) and Chevron AC-20 were sent to the Bureau of Materials and Testing of the Alabama Highway Department at Montgomery for Marshall stability testing according to AASHTO T 245. The aggregate mix used in this test, from Sharp Sand and Gravel Co., Tuskegee, Alabama, consisted of 15 percent pea gravel, 30 percent shot gravel, 40 percent coarse sand, and 15 percent fine sand. The sieve analysis for the job mix is given in Table 5 and is in accordance with the specification of the Alabama Highway Department. Each compacted mix (i.e., specimen) consisted of 67 g of asphalt and 1100 g of total aggregate; that is, it consisted of 5.74 percent asphalt and 94.26 percent aggregate by weight of total mix. Because of differences in specific gravities, equal weight percentages resulted in different volumes of binder being used in the tests (65.0 cm<sup>3</sup> versus 60.2 cm<sup>3</sup>). As the data in Table 6 indicate, a larger volume percentage was obtained of the AC-20 than of the coal-based binder. Marshall testing was performed only at this single condition, and optimum binder contents were not determined for the two

TABLE 4 CHARACTERISTICS OF COAL-BASED ASPHALT USED IN MARSHALL TESTING

	Run		Blend of CP 30 and 31
	CP 30	CP 31	
Product recovery (%)	97.36	97.37	
Coal conversion, maf (%)	84.59	84.98	
Asphalt/distillate ratio	1.43	1.40	
Distillation end point (°C at 1 mm Hg)	213	213	
Polymer modifier by weight (%)	3.31	3.34	
Asphalt properties			
Absolute viscosity at 60°C (poises)	1830	1897	1875
Kinematic viscosity at 135°C (cSt)	455	470	466
VTs	3.36	3.35	3.35

NOTE: 1 poise = 0.1 Pa-sec, 1 cSt = 10<sup>-6</sup> m<sup>2</sup>/sec; maf = moisture and ash free.

TABLE 5 SIEVE ANALYSIS OF AGGREGATE COMBINATION USED IN MARSHALL STABILITY TESTING

U.S. Sieve Series (square mesh type)	Percentage Passing by Weight	Section 411 Mix A Specification <sup>a</sup>
1/2 in.	100	100
3/8 in.	94	87-100
No. 4	75	60-85
No. 8	61	44-74
No. 50	15	10-32
No. 100	8	3-13
No. 200	4	1-5

NOTE: 1 in. = 2.54 cm. Aggregate mix composition: 15 percent pea gravel, 30 percent shot gravel, 40 percent coarse sand, and 15 percent fine sand.

<sup>a</sup>From *Standard Specifications for Highway Construction*, 1985 ed., State of Alabama Highway Department. This job mix is designed by the Marshall method to produce a minimum of 750-lb (3336-N) stability.

binders. Thus the conclusions obtained from the Marshall tests must be viewed with these limitations in mind.

Table 6 gives a summary of the test results for Marshall stability testing. The average Marshall stability of the three coal-based asphalt specimens (after multiplication by a stability correlation ratio of 1.04) is 1,919 lb (8536 N); the average Marshall flow value of these three specimens is 9.9 (0.25 cm) in units of 1/100 in. (0.25 mm). The average Marshall stability for the three petroleum mix specimens, after multiplication by a stability correlation ratio of 1.04, is 1,389 lb (6178 N), which is lower than that of the coal-based asphalt mix. The average



TABLE 6 SUMMARY OF RESULTS FOR MARSHALL STABILITY TESTING

	Coal-Based Asphalt	Chevron AC-20
<b>Asphalt Properties</b>		
Absolute viscosity at 60°C (poises)	1875	2023
Kinematic viscosity at 135°C (cSt)	466	448
VTS	3.35	3.41
Specific gravity (25/25°C)	1.1127	1.0300
<b>Marshall Test Results of Mixes</b>		
Asphalt content, % by weight of aggregate (% of compacted bulk volume)	6.10 (12.4)	6.10 (13.4)
No. of blows at each end of test specimen	50	50
Mixing temperature (°C)	151.7	151.7
Compaction temperature (°C)	140.6	140.6
Test temperature (°C)	60	60
Bulk specific gravity of compacted mixture	2.257	2.262
Maximum specific gravity of mixture	2.435	2.411
Asphalt absorption (% by weight of aggregate)	0.49	0.47
Effective asphalt content (% by total weight of mixture)	5.29	5.31
Voids in mineral aggregate (% of bulk volume)	18.0	17.8
Air void content (% of total volume)	7.3	6.2
Marshall stability (N)	8536 (1,919 lbf)	6178 (1,389 lbf)
Marshall flow (0.25 mm)	10	8.8

NOTE: 1 N = 0.224 lbf; 1 cm = 0.4 in.;  $^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8$ ; 1 kPa = 0.145 psi.

Marshall flow value for these specimens is 8.8 (0.22 cm), which is also lower than that of the coal-based asphalt mix.

According to Marshall design criteria from the Asphalt Institute Manual Series 2, for medium traffic conditions, the Marshall stability should be at least 750 lb (3336 N), and the Marshall flow should be between 8 and 18 (12). Examination of the results in Table 6 shows that requirements are met by both compacted mixtures. It is notable that the coal-based asphalt mixture shows both greater Marshall stability and Marshall flow values, although the higher flow value for the coal-based asphalt could be viewed as a negative factor. In addition to meeting the previously mentioned criteria, a satisfactory paving mixture should have sufficient voids in the compacted mixture to allow for a slight amount of additional compaction under traffic loading without flushing, bleeding, and loss of stability; however, void content should be low enough to keep out harmful air and moisture.

The data in Table 6 indicate that the coal-based asphalt compacted mixture has slightly higher air voids than the Chevron AC-20 compacted mixture. This results because, as noted earlier, the specific gravity (25/25°C) of the coal-based asphalt is higher than that of Chevron AC-20, which results in less volume of coal-based asphalt in the mixture when equal binder weights are used. The air voids given in Table 6 are within the 3 to 11 percent specified for base or binder courses in Table II-2 of the AASHTO *Interim Guide for Design of Pavement Structures*; however, they are greater than the 5

percent recommended by the Asphalt Institute Marshall design criteria (12). Thus some adjustments in the mix would be necessary to produce a design that had all properties within recommended limits. Because of the limited scope of the present study, this procedure was not performed. However, similar procedures used in compressive strength testing (Tables 7 and 8) show that air voids can be varied by changing the asphalt binder content of the mix. Of course, other properties would need to remain within specifications.

TABLE 7 COMPRESSIVE STRENGTH FOR THE LIMESTONE MIX AT VARIOUS COAL-BASED ASPHALT CONTENTS

	Mixture			
	A	B	C	D
<b>Coal-Based Asphalt Properties</b>				
Absolute viscosity at 60°C (poises)	1805	1768	1856	1856
Kinematic viscosity at 135°C (cSt)	445	447	413	413
VTS	3.37	3.36	3.45	3.45
Specific gravity, 25/25°C	1.1127	1.1127	1.1127	1.1127
Polymer modifier (% by weight)	3.23	3.38	3.13	3.13
<b>Test Results</b>				
Asphalt content, % by weight of total mix (% by bulk volume of compacted mixture)	4.11 (8.60)	6.00 (12.8)	6.91 (14.7)	9.69 (20.4)
Bulk specific gravity of compacted mixture	2.330	2.378	2.368	2.344
Maximum specific gravity of mixture	2.580	2.515	2.464	2.396
Effective asphalt content (% by total weight of mixture)	3.96	5.85	6.76	9.54
Voids in mineral aggregate (VMA), % of bulk volume	17.94	17.91	19.04	22.26
Air void content (% of bulk volume)	9.69	5.45	3.90	2.17
Compressive strength at 25°C (psi)	374 ± 18	549 ± 22	445 ± 26	402 ± 20

NOTE: 1 psi = 6.8948 kPa.

### Compressive Strength Testing

To compare compressive strength of coal-based synthetic asphalt and petroleum asphalt, immersion-compression testing was conducted (AASHTO I 165 and I 167). In these experiments, two aggregate mixtures, which are commonly used for highway construction in Alabama, were tested using synthetic coal-based asphalt and a control petroleum asphalt. One mixture consisted of No. 78 limestone (20 percent), No. 810 limestone (65 percent), and coarse sand (15 percent). The other mixture consisted of 1/2-in. (1.27-cm) crushed gravel (70 percent), 3/8-in. (0.95-cm) to dust limestone (10 percent), and coarse sand (20 percent). The sieve analysis for the limestone aggregate mix and the crushed gravel aggregate mix is given in Table 9. As a baseline, these aggregate mixtures and Chevron AC-20 grade petroleum asphalt, which contained no antistripping agent, were used. The coal-based asphalt used in these tests was prepared at conditions noted previously in Table 1 and included approximately 3 percent of the polymer additive described earlier.

TABLE 8 COMPRESSIVE STRENGTH FOR THE LIMESTONE MIX AT VARIOUS PETROLEUM ASPHALT CONTENTS

	Mixture				
	A	B	C	D	E
Asphalt content, % by weight of total mix (% by bulk volume of compacted mixture)	4.16 (9.40)	5.61 (12.9)	6.48 (14.9)	7.34 (16.8)	9.01 (20.4)
Bulk specific gravity of compacted mixture	2.327	2.369	2.364	2.354	2.337
Maximum specific gravity of compacted mixture	2.560	2.503	2.471	2.439	2.366
Effective asphalt content (% by total weight of mixture)	3.97	5.43	6.30	7.16	8.83
Voids in mineral aggregate (VMA), % of bulk volume	18.06	17.85	18.77	19.86	21.44
Air void content (% of bulk volume)	9.10	5.35	4.33	3.48	1.23
Compressive strength at 25°C (psi)	258 ± 8	318 ± 7	325 ± 12	322 ± 16	255 ± 13

NOTE: 1 psi = 6.8948 kPa. Properties of the petroleum asphalt: absolute viscosity at 60°C = 2023 poises, kinematic viscosity at 135°C = 448 cSt, VTS = 3.41, and specific gravity (25/25°C) = 1.0300.

### Effect of Binder Content

Experiments were performed with both coal-based asphalt and the petroleum AC-20 control asphalt to evaluate the effect of binder content on the compressive strength of a compacted bituminous mixture. The specimens were prepared according to the procedures in ASTM D 1074 (AASHTO T 167) with various asphalt contents using the limestone aggregate described in Table 9. The specimens were cured for 24 hr at 60°C and then maintained at 25°C in an incubator for 24 hr. Testing was done in axial compression at a uniform rate of vertical deformation of 5.08 mm/min (0.2 in./min), and the compressive strengths were obtained at each asphalt content. In this work, all asphalt contents were based on total weight of compacted mixture. Experimental results obtained according to methods specified by the Asphalt Institute (12) are given in Tables 7 and 8. The properties of the coal-based asphalt in Table 8 vary slightly from column to column because it was prepared in individual 1-gal autoclave reactions. For the mix with 6 percent by weight asphalt, the maximum specific gravity was determined by vacuum saturation (ASTM D 2041). To calculate the maximum specific gravity of the other mixtures in Tables 7 and 8, it was assumed that the effective specific gravity was constant at various asphalt contents. Because asphalt absorption does not vary appreciably with variations in asphalt content, this assumption is acceptable (12). As the data in Table 7 indicate, the compacted mixture with 6 percent by weight coal-based asphalt gives the highest compressive strength, 549 psi. For the petroleum asphalt, 6.48 percent by weight asphalt content was near the optimum. The results given in Tables 8 and 9 indicate the existence of an optimum binder content for maximum compressive strength. Additional experiments would be needed to more accurately locate the optimum. For the remaining tests, a coal-based asphalt content of 6 percent by weight was used.

### Effect of Temperature on Compressive Strength

As noted previously, the compressive strength at 25°C of compacted specimens prepared with coal-based asphalt is typically higher than that of the AC-20 control specimens. This trend was examined further at additional temperatures of 40°C and 60°C. To attain the test temperature, the 4- × 4-in. cylindrical specimens were stored in an oven for 4 hr at 40°C or

TABLE 9 AGGREGATES USED IN COMPRESSIVE STRENGTH AND IMMERSION COMPRESSION TESTING

U.S. Sieve	Percentage Passing
Sieve Analysis of Limestone Aggregate Mixture	
3/4 in.	100
1/2 in.	100
3/8 in.	96
No. 4	68
No. 8	46
No. 50	11
No. 100	8
No. 200	5
Sieve Analysis of Crushed Gravel Aggregate Mixture	
3/4 in.	100
1/2 in.	100
3/8 in.	97
No. 4	74
No. 8	57
No. 50	21
No. 100	12
No. 200	8

60°C and then tested immediately upon withdrawal. The coal-based asphalt used at 40°C and 60°C was prepared under the reaction conditions of Table 1 and had an absolute viscosity of 1805 poises at 60°C, a kinematic viscosity of 445 cSt at 135°C, a VTS of 3.37, and a polymer modifier content of 3.23 percent by weight. Equal volumes (105 cm<sup>3</sup>) of the coal-based and petroleum asphalt binders were used. The results given in Table 10 and shown in Figure 1 indicate that the compressive strengths for the coal-based asphalt mix remained higher at the elevated temperatures for both the limestone and the crushed gravel mixes.

### Water Damage Potential

A large problem in pavement durability is the stripping action of water on the asphalt aggregate mixture and the resultant loss of strength and pavement integrity (13). One measure of this susceptibility to water damage can be obtained by the immersion-compression test (AASHTO T 165 and T 167). The retained compressive strength of specimens is measured after

TABLE 10 COMPRESSIVE STRENGTH AT DIFFERENT TEMPERATURES

	Coal-Based Asphalt		Petroleum Asphalt (AC-20)	
	Limestone	Crushed Gravel	Limestone	Crushed Gravel
Binder in total mix (% by weight)	6.00	6.00	5.61	5.61
Volume binder in total mix (cm <sup>3</sup> )	105	105	105	105
Compressive strength at 25°C (psi)	549 ± 22	473 ± 19	318 ± 7	249 ± 15
Compressive strength at 40°C (psi)	273 ± 16	217 ± 15	168 ± 10	140 ± 4
Compressive strength at 60°C (psi)	128 ± 8	116 ± 4	107 ± 6	86 ± 5

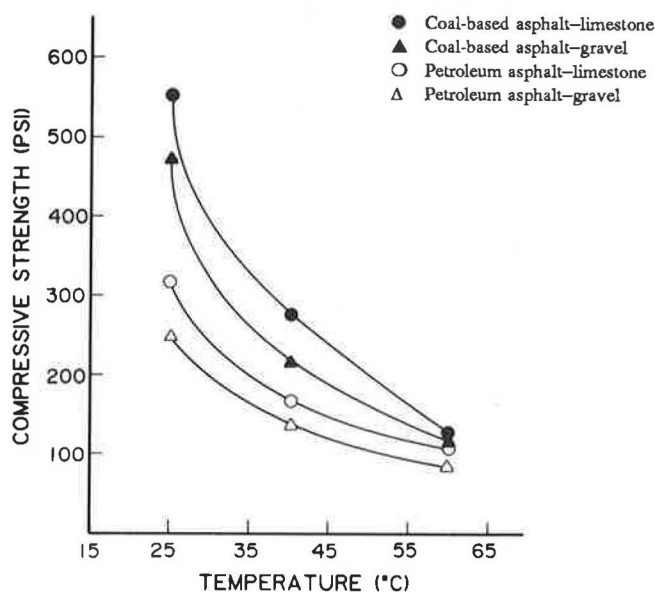


FIGURE 1 Compressive strength as a function of temperature.

immersion in water at 60°C for 24 hr and compared with the initial compressive strength. Tables 11 and 12 give the results of these tests for both the limestone and the gravel mixes with coal-based and petroleum asphalts. These results indicate superior performance of the coal-based asphalts in regard to susceptibility to water damage. For both aggregates, the coal-based mixes have higher percentages of retained strengths after immersion. Although the increased retained strength index of the coal-based asphalt for the limestone aggregate may not be highly significant, the increased retained strength for the gravel is quite significant. Many antistripping additives give less retained strength improvement than is shown by the difference between the coal-based asphalt and the AC-20.

#### Effect of Coal Solids

In commercial production of a coal-based asphalt, it would not be economical to remove the mineral matter and undissolved

TABLE 11 SUMMARY OF RESULTS FOR IMMERSION-COMPARSSION TEST FOR LIMESTONE MIX

	Coal-Based Asphalt Mix	Chevron AC-20 Mix
<b>Asphalt Properties</b>		
Absolute viscosity at 60°C (poises)	1768	2023
Kinematic viscosity at 135°C (cSt)	447	448
VTs	3.36	3.41
Specific gravity (25/25°C)	1.1127	1.0300
Polymer modifier (% by weight)	3.38	0.00
<b>Test Results</b>		
Asphalt content, % by weight of total mix (% by volume of compacted mixture)	6.00 (12.8)	5.61 (12.9)
Bulk specific gravity of compacted mixture	2.378	2.369
Maximum specific gravity of mixture	2.515	2.503
Asphalt adsorption (% by weight of aggregate)	0.161	0.194
Effective asphalt content (% by total weight of mixture)	5.85	5.43
Voids in mineral aggregate (% of bulk volume)	17.91	17.85
Air void content (% of bulk volume)	5.45	5.35
Initial strength at 25°C (psi)	549	318
Retained strength at 25°C (psi)	481	222
Retained index, %	88	70

NOTE: 1 psi = 6.8948 kPa.

TABLE 12 SUMMARY OF RESULTS FOR IMMERSION-COMPRESSION TEST FOR CRUSHED GRAVEL MIX

	Coal-Based Asphalt Mix	Chevron AC-20 Mix
<b>Asphalt content, % by weight of total mix (% by volume of compacted mixture)</b>		
	6.00 (11.9)	5.61 (12.0)
Bulk specific gravity of compacted mixture	2.198	2.205
Maximum specific gravity of mixture	2.374	2.366
Asphalt absorption (% by weight of aggregate)	0.259	0.307
Effective asphalt content (% by total weight of mixture)	5.76	5.32
Voids in mineral aggregate (% of bulk volume)	18.78	18.19
Air void content (% of bulk volume)	7.41	6.80
Initial strength at 25°C (psi)	473	249
Retained strength at 25°C (psi)	397	144
Retained index (%)	84	58

NOTE: The asphalts described in Table 11 were used. 1 psi = 6.8948 kPa.

coal solids (IOM) from the asphalt product. This material most likely would be retained in the binder and would thus act as filler in the binder-aggregate mix. The effect that this type of filler material (i.e., coal mineral matter and insoluble organic matter) would have on the resulting properties of the bituminous concrete is not known, and thus some experiments were performed in this area.

Solids-free, coal-based asphalt in the AC-20 range was produced as usual. To this asphalt, sufficient coal liquefaction residue (67 percent ash, 37 percent IOM) obtained from coal liquefaction runs at the Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama, was added to produce a binder containing 29 percent by weight solids. This

solids-containing binder was then used to prepare compacted specimens for the immersion-compression test. An amount of the -200 mesh solids in the limestone aggregate equal in weight to the coal-derived solids contained in the binder was removed before mixing so that the total weight of solids in the compacted specimens remained the same as in earlier tests. The results of tests with the coal-derived, solids-containing binder are given in Table 13. Comparison with the corresponding data in Table 12 shows that these results are not significantly different. Thus, on the basis of these admittedly limited data, it appears that coal mineral matter and IOM will not be detrimental to the properties of bituminous concrete prepared with coal-derived asphalt binder if the solid material is accounted for as aggregate fines. Although the coal-based asphalt binder contained 29 percent by weight coal-derived solids, because the binder content of a compacted specimen was only 6 percent by weight, the coal-derived solids were only 2.6 percent by weight of the total aggregate.

TABLE 13 IMMERSION-COMPRESSION TEST FOR THE COMPACTED MIXTURE OF LIMESTONE AGGREGATE AND SOLIDS-CONTAINING COAL-BASED ASPHALT

	Value
Properties of Solids-Free Coal-Based Asphalt	
Absolute viscosity at 60°C (poises)	1752
Kinematic viscosity at 135°C (cSt)	397
VTS	3.46
Specific gravity (25/25°C)	1.1127
Polymer modifier (% by weight)	3.13
Test Results	
Asphalt content (solids containing)	
% by weight of total mixture	7.74
% by volume of compacted mixture <sup>a</sup>	14.7
Asphalt content (solids free)	
% by weight of total mixture	6.00
% by volume of compacted mixture	12.14
Bulk specific gravity of compacted mixture	2.251
Maximum specific gravity of mixture	2.435
Asphalt absorption (% by weight of aggregate)	0.161
Effective asphalt content (% by total weight of mixture)	5.85
Voids in mineral aggregate (% of bulk volume)	22.29
Air void content (% of bulk volume)	7.56
Initial strength at 25°C <sup>b</sup> (psi)	583 ± 33
Retained strength at 25°C <sup>b</sup> (psi)	525 ± 24
Retained index (%)	90

NOTE: 1 psi = 6.8948 kPa.

<sup>a</sup>Based on assumed specific gravity of coal solids of 1.5.

<sup>b</sup>Value was obtained from average of the specimens.

## CONCLUSIONS

A polymer-modified coal-based asphalt has been produced that is functionally equivalent to petroleum asphalt according to standard laboratory tests. The coal-based binder is more susceptible to age hardening than are petroleum binders. Age hardening of the coal-based synthetic asphalt binder is caused primarily by oxygen, not internal polymerization or volatilization. Antioxidant compounds indicate some promise for decreasing the age hardening of coal-based asphalt. Bituminous concrete prepared with polymer-modified coal-based asphalt has satisfactory Marshall test values, compressive strength, and moisture resistance, which generally exceed those of the same

viscosity-grade petroleum asphalt. The presence of coal solids (e.g., ash and undissolved coal) has little effect on aging or compacted mixture properties, as long as it is allowed for as filler material in the mix.

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