

HIGHWAY RESEARCH RECORD

Number 231

Physical Factors
Affecting the
Durability of
Asphaltic Pavements

A Symposium

6 Reports

Subject Area

31 Bituminous Materials and Mixes

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Foreword

This RECORD contains six reports covering some aspects of durability measurements and/or evaluation of asphalt cements as used in asphaltic-concrete mixtures. The approaches followed by the authors divide into two general groups. In one group the authors have examined changes in asphaltic concrete exposed to the usual field conditions either by means of generally accepted laboratory tests or by the development of a special test. The other group is developing new laboratory procedures for determining changes in durability by means of measurements on asphaltic materials aged by laboratory process. In these cases it is expected that the procedures will subsequently be correlated with service aging.

The information reported largely involves physical research. However, composition data are provided in most cases.

The number of researchers working in this subject area is impressive and reflects in part the absence of broadly accepted theories that explain the behavior of these materials and to a lesser extent the absence of broad acceptance of a single test procedure to measure durability change. This activity results partly from the need for a suitable and practical measure of asphaltic concrete pavement quality.

Gotolski and co-authors report on six asphalt cements used in the surface mixtures of each of three projects constructed during 1964 and 1965. The asphalts were measured by penetration, standard and micro-ductilities, and absolute viscosity, and their compositions were determined. Time-temperature relationships of the spread and compacted mixtures were measured, and specific gravities, densities, and air voids of the compacted asphaltic concrete determined. Although future study of these projects is expected, the conclusions of the work reported suggest some new concepts and in part confirm conclusions from similar studies.

Lamb and Couper report on the relationship of flow properties of nine paving grade asphalts to chemical composition. Conclusions presented indicate that such relationships exist at one of the three temperatures investigated. At the other two temperatures it appears that factors other than composition have greater effect on flow properties. The work reported is a portion of a continuing study.

Lee's report describes a laboratory method of simulating field-hardening of six paving-grade asphalts by treating the residue from the thin film oven test with oxygen at high pressures. Measurements were made of changes in penetration, softening point, absolute viscosity, asphaltic content, and percent oxygen. The conclusions show differences in the asphalts examined and indicate that agreement of the results with hardening reported by other investigators is good. The present work is to be extended to include correlations with asphalt in field service.

Majidzadeh and Schweyer report on the viscoelastic response of four types of asphalt cements aged and unaged at 32 F. The asphalts were aged at 325 F for 5 hours. The penetration, ductility, and viscosity of the aged asphalt are compared with corresponding properties of the unaged material. Changes in composition are also discussed. Dynamic response data were

calculated from data obtained from the creep test. The conclusions indicate that aging results in an instantaneous elastic response and that dynamic responses are significantly affected by aging. An aging index is discussed.

Sisko reports a procedure for the measurement of tensile stresses on asphalts and its use with asphalt cements in the unaged condition, after the thin film oven test, and in material recovered from pavements with up to 11 years of service. Tensile strengths are reported at 0, 40 and 80 F for all three conditions with 20 and 60 F included for the thin film oven test condition. Several interesting observations are made concerning tensile strength of the asphalts, including some concerning the relation of tensile strength to composition and to pavement cracking.

In his discussion on the rheological aspects of aging, Majidzadeh reports on the rheological response of two sand-asphalt mixtures, in one case where the asphalt is aged at different temperatures prior to mixing and in another case where the asphalt mixture is aged prior to testing. Ottawa sand was used as the mineral aggregate. Creep comparisons are shown at 15, 25, 45 and 60 C. The effects of aging in general on creep are shown as well as the effects of different types of aging.

The information contained in the papers of this RECORD should be of interest to all who follow developments in the theory of the behavior of asphalt cements and asphaltic concrete mixtures. It should be of particular interest to researchers working in the area of the effect of change in durability on measured properties.

— F. M. Willams

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Study of Physical Factors Affecting the Durability of Asphaltic Pavements

W. H. GOTOLSKI, S. K. CIESIELSKI, and R. W. SMITH, Pennsylvania State University, and
J. A. KOFALT, Pennsylvania Department of Highways

This investigation was undertaken to study changes in asphalt and asphaltic mix properties to gain an understanding of the factors affecting the durability of asphalt pavements. In particular, pavements were constructed to determine the penetration-absolute viscosity relationship for the different asphalts used. Several different asphalts were used, varying in penetration and absolute viscosity, but the same aggregate was used for each project. Investigations were confined to the wearing course, due to its exposed position in a pavement. The test pavements were asphaltic-concrete overlays on portland cement concrete. Field data were accumulated during construction and periodically after construction; Abson recovery tests were made on the obtained samples as part of the laboratory investigation. Penetration, standard ductility, microductility, absolute viscosity, and chemical analysis tests were made and the data analyzed.

Results from one project indicate that a common (70-85 penetration, $3,000 \pm 200$ viscosity) asphalt is performing as well as any other asphalt used to date, as indicated by a higher percent retained penetration and ductility and a lower percent original viscosity. No degradation of aggregates is occurring under traffic use. Increasing asphaltenes indicate a hardening but no trend is indicated by the Rostler coefficient. All of the asphalts softened after the first winter cycle, hardened during the summer, and, in some cases, softened again the following winter. Further research is required in this area.

From early test data on two other projects, it appears that a definite hardening of the asphalts occurred during mixing. However, from the time of construction to the early core samples, very little change in test data took place. Some of the core data are erratic in that a slight softening occurs as indicated by decreases of absolute viscosities and increases in penetration and ductility values. This phenomenon is unexplainable at present and requires further research. At this stage of the study, final conclusions are not possible.

•DURING recent years, much research and experimentation has been performed in the asphalt field to gain a better understanding of the physical and chemical changes that occur during the age-hardening of asphalt (1, 2, 3, 4). One goal of this research is to eventually relate the observed physical and chemical changes with the durability of a roadway as measured by its longevity. The Bureau of Materials of the Pennsylvania Department of Highways, through its Bituminous Research and Development Section, is

TABLE 1
DESCRIPTION OF TEST ROADS

County	LR No.	Spec. Gradation	Date of Construction
Clinton	219	ID-2	October 1964
Jefferson	338	FJ-1	September 1965
McKean	101	ID-2	August 1965

now engaged in an intensive effort to determine the effects of physical and chemical factors on the longevity of asphalt pavements. In addition, under the sponsorship and with the cooperation of the U. S. Bureau of Public Roads and the Pennsylvania Department of Highways, the Civil Engineering Laboratories of the Pennsylvania State University have undertaken an investigation of the physical and chemical properties of asphaltic concrete material at in-service projects.

Several projects are included in the overall study; however, this report covers only the data for LR 219—Clinton County, LR 338—Jefferson County, and LR 101—McKean County. The data and findings of the physical and chemical testing of the asphalts recovered from these three projects are presented.

OBJECTIVES

The principal aim of this investigation is to study the physical and chemical changes of the asphalt and asphaltic-concrete mixture that occur with the passage of time, with a view to gaining an understanding of the factors affecting the durability of asphaltic-concrete pavements. In particular, the asphalts in these pavements will be tested for the purpose of arriving at relationships of penetration to absolute viscosity. The objective is to verify the desirability of either complementing or supplementing penetration control with absolute viscosity control as a design specification.

An effort will be made to determine the effects of chemical changes on pavement performance, the effects of traffic on pavement density with time, and whether or not the aggregate used in the pavement is subject to degradation with use.

TEST AREAS

This interim report deals with the laboratory data accumulated from the Clinton, Jefferson, and McKean County projects. Each of these projects possesses a common characteristic in that, on each of the pavements, six different asphalts were used to produce asphaltic concrete. In Clinton County, a crushed limestone aggregate was used; in Jefferson County, a sand mixture was used; and in McKean County, a sand and gravel mixture was used. Table 1 describes the test roads.

The Clinton County project is in the central area of Pennsylvania, the Jefferson County project is in the west-central area, and the McKean County project is in the north-

TABLE 2
DESCRIPTION OF ASPHALTS

Experimental Designation	Absolute Viscosity (poises, 140 F, 30 cm Hg), Reported Values ^a			Penetration (77 F, 100 gm, 5 sec, in mm), Reported Values ^a				
	Specified Ranges	LR 219	LR 338	LR 101	Specified Ranges	I.R 219	I.R 338	I.R 101
Type I	1500 ± 200	1732	1782	1795	50-75	59	67	59
Type II	1500 ± 200	1548	1630	1482	90-100	89	86	91
Type III	1500 ± 200	1440	1527	1701	140-160	146	136	130
Type IV	900 ± 200	949	1048	1090	90-100	110	87	84
Type V	3000 ± 200	2136 ^b	3054	2970	90-100	94	84	85
Type VI	3000 ± 200	2951	3092	3124	70-85	77	74	74

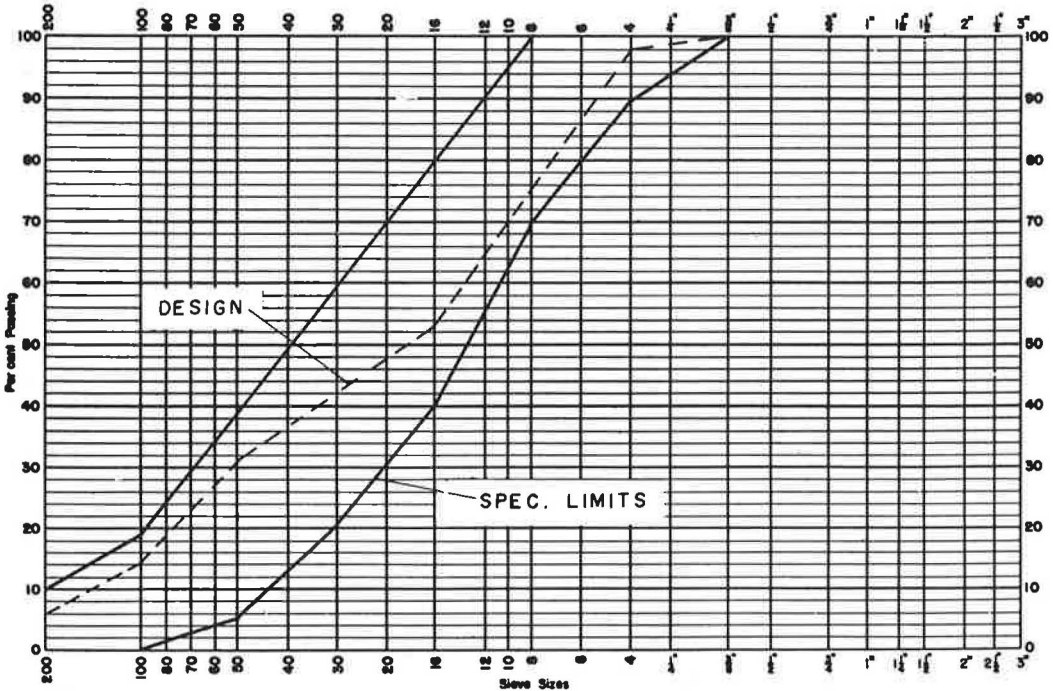
^a Average values.

^b Out of specified range.

PENNSYLVANIA DEPARTMENT OF HIGHWAYS
GRADATION CHART

Specification FJ-1 Course Wearing

District 10-0



BASIC FORMULA A.C. 8.6

JOB IDENTIFICATION

* 70 - 85 Asphalt % _____
 * 85 - 100 Asphalt % _____
 * Minus No. 8 Material % 75.0
 Approved CONTRACTOR'S REP. M.R.
 Approved P.D.H. INSPECTOR _____
 Approved MATERIALS ENGR. HWB
 Approved DISTRICT ENGR. WSS
 * Percent by weight to be Designated by District Engineer

County Jefferson Rt. 308 Section _____
 Contractor or P.O. Interstate Amiesite Corp.
 Plant Reynoldsville, Pa.
 Date 8-25-65
 Date 9-2-65
 Date 9-2-65

Figure 1. Asphalt plant report, Part A (Jefferson County).

central area. Each project contained six different asphalts. Five of the asphalts are considered experimental and the sixth is a standard type for purposes of comparison. The design penetration and absolute viscosity characteristics are given in Table 2.

Each of the experimental wearing courses was constructed in six continuous sections, placed the full width of the pavement. Approximately 8,000 gallons of each experimental type of asphalt cement were supplied for each designated experimental section. Each type of asphalt was furnished in cleaned transports in loads of approximately 4,000 gallons each. The transports were equipped to maintain the temperature of the asphalt cement at its designated mixing temperature. The experimental asphalt cements were introduced directly into the mixer from the transports through approved plant asphalt proportioning facilities and supply lines.

The total completed length of the experimental sections of wearing course was dependent on the size of the loads as delivered and the requirements of the job-mix formula. The remaining portion of paving was completed with the common 70-85 penetration grade asphalt having a 3000 ± 200 poise viscosity.

The individual paving mixtures were designed by the Pennsylvania Department of Highways (PDH) design and control method, and the roadways were constructed under the direct control of the Department using currently approved methods (5).

From previous experience, it is known that the portion of the roadway that is exposed most to environmental conditions exhibits age-hardening and consequently deteriorates first. For this reason, the testing was confined to the asphalts used in the wearing course.

PROCEDURES

Sampling and Construction

Samples of the aggregate for the binder and wearing courses were delivered to the central office of the PDH Materials Testing Laboratory in Harrisburg. Samples of the raw asphalt were also submitted so that hot asphaltic mixes could be designed, tested, and approved. Stability and flow tests were performed on laboratory-compacted test specimens according to Pennsylvania design and control specifications and the test data were recorded. Since the asphalts varied from each producer according to predetermined specifications, individual mix designs were required. Asphalt plant reports were compiled by PDH personnel as they maintained plant inspections and field control of construction. A typical plant report is shown in Figures 1 and 2.

The Pennsylvania method of testing was performed jointly during construction by PDH laboratory technicians and by those provided by the contractor. These tests consisted of compacting asphaltic concrete specimens in the field and plant laboratory, and testing for stability, flow, asphalt content, and aggregate gradation. The results conformed to Pennsylvania specifications.

Normal conditions existed during the mixing, placing, and compaction operations. Temperature measurements were made at various stages in the handling of the hot mix by PDH personnel. Separate temperature measurements were made by technicians of Pennsylvania State University's Civil Engineering Laboratory from the time of spreading to one hour after spreading. This was accomplished through the use of No. 24 gage thermoplastic copper-constantan insulated thermocouple wires placed in the wearing course. These thermocouples were connected to continuous temperature recording devices (Fig. 3) to obtain the changing temperature of the asphaltic concrete during construction. These thermocouples were placed $\frac{1}{4}$ and $\frac{7}{8}$ in. below the compacted surface of the pavement. A typical time-temperature plot of the recorded data is shown in Figure 4; it is considered typical since it was found that the numerous graphical presentations of the data yielded similar results.

The actual construction methods used on these projects were basically similar, being those currently approved by the PDH. The initial or breakdown roller was a 12-ton, 3-steel-wheel roller. This was followed by a pneumatic-tire roller, 9 tires, 15 tons, with 14-ply tires and a tire pressure in the 90-psi range, and a 2-axle tandem wheel finishing roller of a 12-ton capacity.

Stock Gradations

Sieve Sizes	Filler	Lime	Hard Asph.	Fine Agg. No. 1		Fine Agg. No. 2		Sand		Coarse Agg.		Cold Blend		Combined Gradings
				Stock	Spec.	Stock	Spec.	Stock	Spec.	Stock	Spec.	%	%	
200								5.9						
100								14.2						
50								32.0						
30								42.6						
16								52.9						
8								74.8						
4								98.0						
3/8"								100						
1/2"														
3/4"														
1"														
1 1/2"														

Bins Over Mixer

Sieve Sizes	Gradations				% Combination				Gradings		
	Bin 1	Bin 2	Bin 3	Bin 4	Bin 1	Bin 2	Bin 3	Bin 4	Combined	Extraction	Spec. Limits
										A.C. 8.6 %	
200	5.9									6.0	
100	14.2									14.0	
50	32.0									32.0	
30	42.6									43.0	
16	52.9									53.0	
8	74.8									75.0	
4	98.0									98.0	
3/8"	100									100	
1/2"											
3/4"											
1"											
1 1/2"											

Mix Design

Material	A.C.	Hard A.C.	Flux	Naphtha or W.C.	Lime or Filler	Bin				Total	Official Inspections- _____ Inspectors-_____ Checked by-_____	
						1	2	3	4			
Wearing Course												
Binder Course												
Course	8.6					91.4				100		
Lbs.	344					2656				4000		

Remarks -

Figure 2. Asphalt plant report, Part B (Jefferson County).

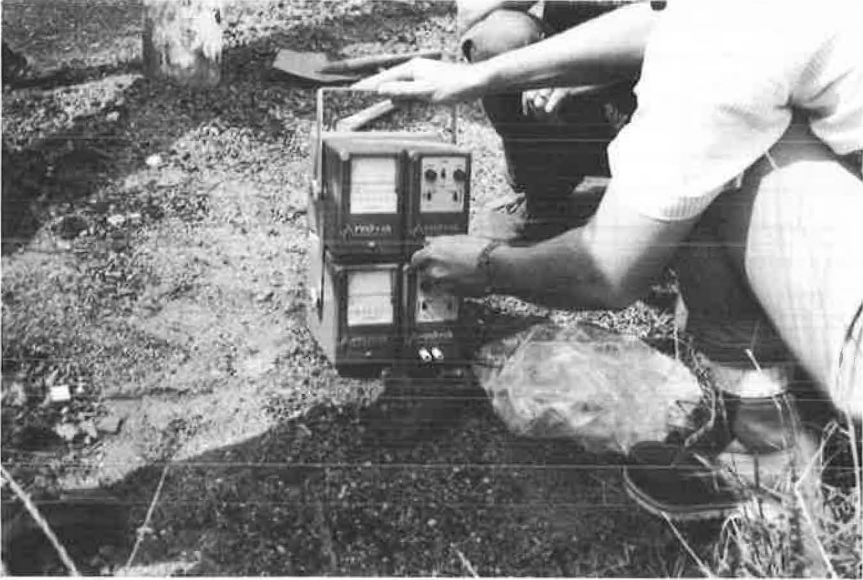


Figure 3. Continuous temperature recording devices.

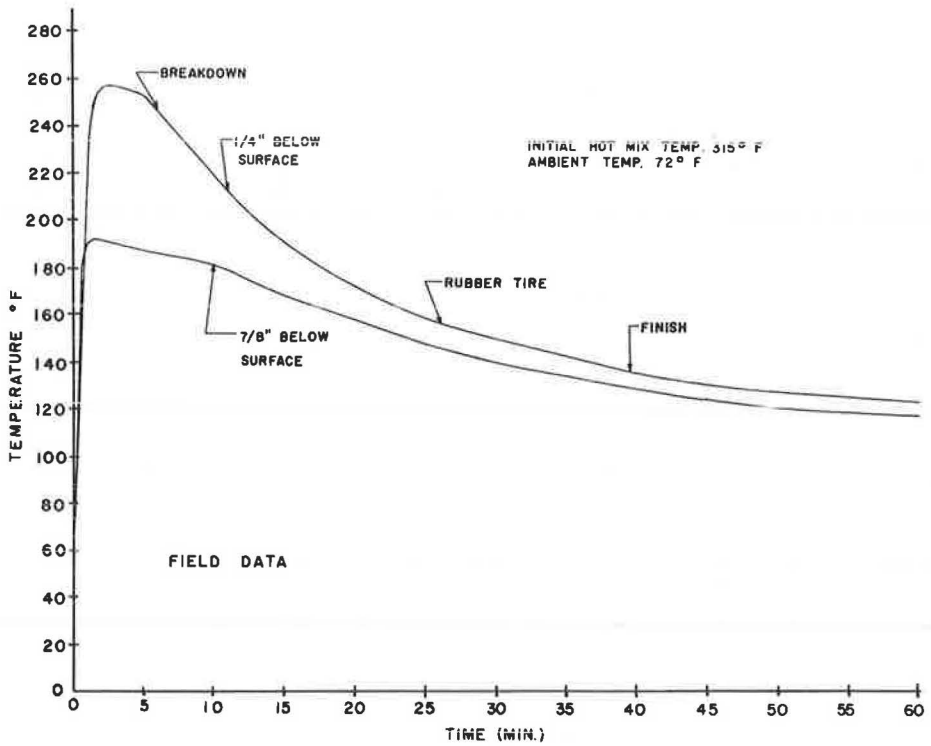


Figure 4. Typical field time-temperature plot.

Sampling procedures were formulated to isolate as completely as possible the various stages of asphalt hardening that could take place. Laboratory samples were taken for analysis by the Department of Highways and by the Pennsylvania State Civil Engineering Laboratory.

Seven 1-gallon test samples of the raw asphalt cement were drawn from the transports at the plant; the test results were used as the basis of comparison with later test data. Test samples of the hot mix were taken during the mixing at the pugmill, directly from the paver during the laydown operation, as cups one or two hours after compaction, and as compacted slabs cut from the roadway within 24 hours after actual construction. The cups were pried from the pavement while the slabs were removed using a power-driven, water-cooled, abrasive circular saw.

The samples were taken in duplicate, i.e., two such sampling operations per test transport. The asphaltic concrete in the first set was taken from a labeled test truck while the second set was taken from a randomly selected batch of the mixture. This procedure was followed for the hot mix produced from each transport of asphalt cement to ascertain the uniformity of the mix, or lack of it, being maintained in production.

Core sampling was performed on each of the test projects. This report deals with 8-month cores of the McKean County project and 7-month cores of the Jefferson County project. The 12- and 18-month cores of the Clinton County project are also discussed. The cores were taken using a rear-mounted core-drilling device. The cores taken were 6 in. in diameter as agreed upon by the participating agencies. This method of sampling should provide a relatively complete picture of the changes that are taking place in the asphalt with age and weathering. The age-hardening process will be followed further by periodically taking core samples from the pavement until complete deterioration of the roadway pavement occurs.

Testing

The testing procedures for an asphalt cement adopted for this investigation may be classified as new and routine. The routine tests include penetration, ASTM D 5-65; standard ductility, ASTM D 113-44; and absolute viscosity, ASTM D 2171-63T. Among the new tests in asphalt technology are microductility and chemical analysis. Microductility tests were performed only on the Clinton County samples.

In addition, sieve analyses were performed on the aggregates resulting from the extraction of the mix samples. The surface area (7) and fineness modulus (8) were calculated for each sieve analysis to determine whether degradation of the aggregate is occurring under handling and in-service conditions.

Specific gravity determinations, using PDH specifications, were made on the mix samples to ascertain degrees of compaction at construction and during service life. Asphalt cement samples were obtained from mix and field core specimens by the immerex (immersion-reflux) method of extraction and the Abson method of recovery, ASTM D 1856-65. Benzene was used as the solvent to minimize any chemical reaction between solvent and asphalt during the contact time of the recovery process. The recovered asphalts were then stored in 3-ounce metal containers for testing.

Penetration—Certain properties of asphalts have been found by experience to be necessary for the construction of a good asphaltic pavement. Early attempts to define the limits of these properties led to the development of the empirical penetration test. Through the years, the penetration test has been accepted as a standardized method for the classification of asphalt grades. In this study, the penetration tests conducted were in accordance with ASTM D 5-65 using test conditions of 77 F, 100 g, 5 sec.

Ductility—Another test that has been standardized to specify a desired characteristic of asphalt is the standard ductility test. The empirical test results at low temperatures appear to be better indicators of cracking occurring in asphaltic concrete pavements (9) than other current scientific means available. Earlier investigators (10, 11) indicated that asphalts with greater ductility loss failed most frequently. In this study, the standard ductility tests were conducted in accordance with ASTM D 113-44 using test conditions of 39.2 F and 1 cm/min.

In addition to standard ductilities, microductility tests of the asphalts were performed at Clinton County to investigate the possible correlation of microductility and standard ductility values. The microductility test used in this research was the one developed by the Phillips Petroleum Company of Oklahoma (12).

Absolute Viscosity—Researchers have established the importance of a more scientific approach for measurement of the consistency of an asphalt. To comply with this need, tests were made to determine the absolute viscosities of an asphalt sample. This test permits measurements of consistency in terms of poises, the unit of absolute viscosity. This fundamental property of an asphalt may be termed the internal friction that gives the material resistance to flow or to a shearing stress. A correlation of flow properties (absolute viscosity) with other physical and chemical properties as well as performance data may lead to a more scientific approach to asphalt technology.

Various types of viscometers used for highly viscous materials have been described by Heithaus (13) and Griffith and Puzinauskas (14). The viscometer used in this investigation was an instrument generally known as the Cannon-Manning vacuum capillary viscometer. The absolute viscosity data reported are based on test conditions of 140 F temperature and 30 cm Hg vacuum (ASTM D 2171-63T).

Chemical Analysis—One of the most important indicators of the consistency of a paving asphalt is its chemical composition. Since recent studies (15, 16) show a relationship between chemical composition and pavement durability, chemical analyses were performed as part of the University's laboratory investigations.

The Rostler precipitation method (16) defines asphalt as consisting of five groups of components that can be isolated and the amounts determined by weight. This method accomplishes a sharp division between resins and oily fractions, and then further subdivides the resinous fractions. The principal feature of this method is that the fractions determined are well-defined groups of like chemical activity. The use of this division process reveals not only the differences between fractions but also what changes occur during aging and in-service exposure in terms of percent change in composition, particularly in percent change of asphaltene content as it relates to durability, i.e., embrittlement or hardening.

The work of Rostler and White defines asphalts as consisting of five basic constituents: asphaltenes, nitrogen bases, first acidaffins, second acidaffins, and saturated hydrocarbons. By precipitation this method isolates these five constituents, the values of which are determined by differential weighing and then reported as percentages of the total sample weight. The samples of original and recovered asphalt cements were analyzed using this method.

Chemical analyses appear to be indicators of change in consistency of the asphalt components in the pavement. The asphaltene content, which is the first fraction in the test, appears to be an adequate predictor of age-hardening of the asphalt. Increases in asphaltene content are generally manifested in physical tests by decreasing penetrations, decreases in ductility, and increases in absolute viscosity. This trend is present, but data are insufficient regarding age to determine true relationships of physical tests to asphaltene content.

In addition to asphaltene content, the prevailing combination of components may be a determining factor. Some investigators (16) have shown that a preponderance of the nitrogen bases (N) will result in an asphalt exhibiting very rapid embrittlement. A high content of first acidaffins (A_1) will result in an asphalt that will undergo the greatest change in composition with time. An asphalt containing a high concentration of second acidaffins (A_2) appears least harmfully affected. Saturated hydrocarbons (SH) in small to moderately large amounts are beneficial. However, saturated hydrocarbons in excessive amounts result in a product that lacks cohesion and ceases to be an asphalt.

The ratio $(N + A_1):(A_2 + SH)$, which is expressive of the concentration of more reactive components to the less reactive, has been proposed by Rostler as indicative of the influence of chemical reactivity on durability. Presupposing that durability, expressed as abrasion resistance and change in abrasion resistance due to embrittlement, must depend on this ratio, Rostler illustrates a definite trend in asphalt behavior based on this ratio. A value of less than 1.14 for this ratio has been reported as being characteristic for asphalts of excellent abrasive resistance. Further work is continuing in

this area to develop a better approximation. Rostler proposes that the parameter $(N + A_1):(A_2 + SH)$ be considered only a first approximation for an expression relating composition to durability.

In using the ratio $(N + A_1):(A_2 + SH)$ to analyze data from previous work (17), inconsistencies were found. Due to these inconsistencies, a modification of the Rostler parameter was developed. The ratio $(A_1 + A_2 + N):(A + SH)$ was computed and found to give data showing a decreasing trend. At the present time, a minimum value for this ratio, that is, when the asphalt is no longer durable, cannot be estimated.

Aggregate Gradations—Sieve analyses were performed on all of the extracted mix samples so that it could be determined whether or not degradation of the aggregate is taking place. After the percentages retained were determined, fineness modulus and surface area data were computed for each sample.

The fineness modulus makes use of the percentages retained on the No. 4 to No. 200 sieves inclusive and presents repeatable data for any gradation of aggregate. Decreases in the fineness modulus indicates a degradation of aggregate. The surface area is another means of determining whether an aggregate is degrading or not. This calculation is based on predetermined coefficients multiplied by the percents retained from the No. 4 through the No. 200 sieves inclusive. Increases in the surface area, measured in pounds per cubic foot, indicate aggregate degradation.

Specific Gravities, Densities, and Air Voids—Determinations of specific gravities were made on all the asphalt roadway samples using the procedures set forth in the PDH manual for bituminous concrete design, compaction, and control (5, pp. 46-80). Asphalt specimens were not coated with paraffin because the chemical analyses of the extracted asphalt would be adversely influenced by paraffin that would have defied removal.

These tests were performed at the time of construction on plant-compacted specimens, cups, and roadway slabs cut from the pavement. Specific gravities were also performed on the in-service core samples. After specific gravities were determined, further computations were performed to determine the density and air voids based on percent of maximum theoretical design specific gravity, and density based on plant-compacted specimen specific gravity.

It is anticipated that the changing densities and air voids will correspond to core location in the pavement and will perhaps, with future research and field investigations, contribute to a better understanding of pavement durability.

Core Locations—Some of the core samples taken from the roadways have exhibited an erratic behavior, that is, the asphalt is softening with age and use. This phenomenon is shown by the results of laboratory tests. Penetration values are increasing, ductility values are increasing, and absolute viscosity values are decreasing. The core location is suspect as a possible explanation for these erratic test data. The method of classifying which zone—namely, transition, load, or center—from which a core was obtained was presented in another report (6).

This classification method shows some promise in gaining a better understanding of the behavior of the asphaltic cement. More research is required to gain a more complete picture of the behavior of asphalt in a roadway pavement.

CLINTON COUNTY, LR 219

The Clinton County test roadway is 4.36 miles in length, located between the towns of Beech Creek and Mill Hall. The original roadway consisted of 18 to 20 ft of 8-in. reinforced concrete constructed in 1929 and 1934. This concrete pavement was in fair condition for its age but had outlived its usefulness as a smooth, high-speed traffic route, without being resurfaced.

In October 1964, the roadway was resurfaced with 1 in. of ID-2 wearing course on 2 in. of ID-2 binder course. The route can be identified as Legislative Route 219 or Traffic Route 220. It has an average daily traffic count of 4,020 to 4,220 vehicles.

Table 3 contains the physical properties of the Clinton County asphalts from the time of construction to the present. Also included are data indicating the percent retained or percent original values for the physical tests conducted, the percent asphaltenes and percent original asphaltenes for the asphalts, and the fineness modulus and surface area

TABLE 3
PHYSICAL PROPERTIES OF ASPHALTS—CLINTON COUNTY, LR 219

Asphalt Type	Line	After Mixing	After Compaction	5 Mo. Core	12 Mo. Core	18 Mo. Core	24 Mo. Core	30 Mo. Core	Asphalt Type	Line	After Mixing	After Compaction	5 Mo. Core	12 Mo. Core	18 Mo. Core	24 Mo. Core	30 Mo. Core	
(a) Penetration Test—0.1 mm at 77 F, 5 sec, 100 gm									(g) Microductilities—cm at 39.2 F and 1 cm per min									
I	59	36	31	37	24	22	18	20	I	8.0	1.8	*	*	*	*	*	*	*
II	89	69	61	67	47	51	42	50	II	3.6	2.4	3.1	2.6	1.4	*	5.4	0.7	
III	146	98	90	91	75	76	63	68	III	42.3	13.0	10.0	10.6	3.9	4.0	2.4	2.5	
IV	110	66	57	70	45	50	45	49	IV	3.4	1.9	1.8	1.9	1.2	1.2	4.1	1.4	
V	94	69	62	65	44	44	45	50	V	12.9	2.9	2.5	3.0	1.4	1.1	1.4	1.8	
VI	77	60	50	58	40	39	33	35	VI	2.5	1.8	3.0	2.1	1.4	1.1	0.7	1.2	
(b) Percent Retained Penetration									(h) Percent Retained Microductility									
I	100	61	53	63	41	37	30	34	I	100	23	0	0	0	0	0	0	
II	100	78	69	75	53	57	47	56	II	100	67	86	72	39	0	150	19	
III	100	67	62	62	51	52	43	47	III	100	31	24	25	9	9	6	6	
IV	100	60	52	64	41	45	41	44	IV	100	56	53	56	35	35	121	41	
V	100	73	66	69	47	47	48	53	V	100	57	51	61	29	22	29	37	
VI	100	78	65	75	52	51	43	45	VI	100	72	120	84	56	44	28	48	
(c) Absolute Viscosity (Cannon-Manning)—poises at 140 F, 30 cm Hg Vacuum									(i) Percent Asphaltenes									
I	1732	3645	3731	3384	6745	8961	13267	10270	I	20.9	22.1	20.7	19.5	24.6	26.4	23.0	25.2	
II	1548	2505	2630	2614	4553	4759	5090	4769	II	19.2	21.2	21.2	21.0	25.1	25.0	21.7	24.8	
III	1440	2971	3028	3250	4868	5581	7021	6512	III	26.8	28.8	31.6	29.8	32.4	32.8	32.4	34.0	
IV	949	2078	2584	2302	4772	4520	4555	5183	IV	19.5	20.7	22.2	22.7	26.0	24.7	20.4	22.7	
V	2136	3463	4035	3797	7910	9674	7901	7043	V	28.2	29.2	30.6	31.1	33.2	34.6	31.0	33.1	
VI	2951	4770	5220	7384	9886	10695	13449	12444	VI	28.2	29.0	29.4	30.2	31.5	31.8	30.7	33.3	
(d) Percent of Original Absolute Viscosity									(j) Percent Original Asphaltenes									
I	100	210	215	195	389	517	766	593	I	100	106	99	93	118	126	110	121	
II	100	162	170	169	294	307	329	308	II	100	110	110	109	131	130	113	129	
III	100	206	210	226	338	388	488	452	III	100	107	118	111	121	122	121	127	
IV	100	219	272	243	503	476	480	546	IV	100	106	114	116	133	127	105	116	
V	100	162	189	178	370	453	370	330	V	100	104	109	110	118	123	110	117	
VI	100	162	177	250	335	362	456	422	VI	100	103	104	107	112	113	109	118	
(e) Standard Ductility—cm at 39.2 F and 1 cm per min									(k) Fineness Modulus of Aggregate									
I	14.0	4.1	4.5	4.0	*	*	*	*	I	—	4.15	4.06	4.04	4.08	4.05	4.00	3.98	
II	53.3	11.9	11.9	15.4	6.4	8.8	5.4	7.2	II	—	4.10	3.99	4.03	4.02	3.95	3.96	3.90	
III	101.0	42.2	43.4	72.1	26.7	23.4	10.7	13.7	III	—	4.17	4.02	3.93	4.05	3.98	4.02	4.00	
IV	23.5	7.5	3.4	7.0	4.6	5.2	4.1	5.4	IV	—	4.16	4.13	4.03	4.07	4.03	4.02	3.96	
V	68.3	24.3	17.6	36.7	15.2	6.6	5.4	7.4	V	—	4.14	4.08	4.02	4.05	3.99	4.03	3.99	
VI	21.9	7.3	3.3	14.1	5.0	5.6	2.0	2.4	VI	—	4.14	4.07	3.99	4.08	3.98	3.98	3.98	
(f) Percent Retained Standard Ductility									(l) Surface Area of Aggregate—ft ² per lb									
I	100	29	32	28	0	0	0	0	I	—	29.0	30.8	33.3	31.1	34.4	32.8	33.9	
II	100	22	22	29	12	17	10	13	II	—	30.3	32.9	34.9	34.7	38.3	36.2	38.0	
III	100	42	40	71	26	23	11	14	III	—	29.8	33.9	37.3	35.1	39.5	34.8	35.8	
IV	100	32	27	30	20	22	17	23	IV	—	30.0	30.4	41.3	36.9	38.9	36.8	39.9	
V	100	35	26	54	22	10	8	11	V	—	30.4	34.2	38.2	35.8	38.5	36.5	38.7	
VI	100	33	38	64	23	26	9	11	VI	—	30.3	31.8	35.3	34.2	38.1	34.8	35.3	

*Brittle fracture.

TABLE 4
AVERAGE CHANGES IN CHEMICAL PROPERTIES—CLINTON COUNTY, LR 219

Description	Line	After Mixing	After Compaction	5 Mo. Core	12 Mo. Core	18 Mo. Core	24 Mo. Core	30 Mo. Core
Asphalt No. I								
Asphaltenes	20.9	22.1	20.7	19.5	24.6	26.4	23.0	25.2
Nitrogen Bases	22.5	21.4	21.6	24.9	22.3	26.6	25.8	20.6
First Acidaffins	16.0	11.4	11.0	12.8	14.5	8.4	12.5	16.8
Second Acidaffins	29.0	32.2	30.6	31.3	27.3	28.5	28.8	27.1
Saturated Hydrocarbons	11.6	12.9	15.9	11.6	11.4	10.2	10.0	10.3
Rostler Coefficient	0.95	0.73	0.70	0.88	0.95	0.90	0.98	1.00
Mod. Rostler Coefficient	2.07	1.86	1.73	2.22	1.78	1.73	2.03	1.82
Asphalt No. II								
Asphaltenes	19.2	21.2	21.2	21.0	25.1	25.0	21.7	24.8
Nitrogen Bases	23.2	22.0	21.7	24.6	19.7	25.7	23.6	19.5
First Acidaffins	13.3	12.9	13.8	12.8	13.3	7.4	13.7	15.9
Second Acidaffins	30.5	30.0	30.5	29.7	28.0	30.1	28.4	27.6
Saturated Hydrocarbons	13.8	13.9	13.0	12.0	13.9	11.9	12.8	12.1
Rostler Coefficient	0.82	0.79	0.82	0.90	0.79	0.79	0.91	0.89
Mod. Rostler Coefficient	2.03	1.85	1.92	2.03	1.56	1.71	1.92	1.71
Asphalt No. III								
Asphaltenes	26.8	28.8	31.6	29.8	32.4	32.8	32.4	34.0
Nitrogen Bases	15.9	16.4	14.6	17.5	15.0	17.0	17.0	13.4
First Acidaffins	14.7	14.8	14.8	15.2	14.6	-2.5	13.6	15.7
Second Acidaffins	30.9	27.8	26.8	27.5	26.5	27.7	26.8	27.1
Saturated Hydrocarbons	11.8	12.2	12.3	10.1	11.5	10.1	10.2	9.7
Rostler Coefficient	0.72	0.78	0.75	0.87	0.78	0.78	0.82	0.80
Mod. Rostler Coefficient	1.59	1.44	1.28	1.51	1.28	1.33	1.46	1.29
Asphalt No. IV								
Asphaltenes	19.5	20.7	22.2	22.7	26.0	24.7	20.4	22.7
Nitrogen Bases	18.9	18.8	19.6	20.6	16.5	23.9	20.5	15.7
First Acidaffins	13.7	14.2	12.8	13.6	12.9	6.5	14.9	19.3
Second Acidaffins	33.7	31.8	31.7	31.1	29.6	31.4	31.6	28.9
Saturated Hydrocarbons	14.3	14.6	13.8	12.2	15.1	13.6	12.6	13.5
Rostler Coefficient	0.68	0.71	0.71	0.79	0.66	0.68	0.80	0.82
Mod. Rostler Coefficient	1.96	1.83	1.78	1.87	1.43	1.61	2.02	1.76
Asphalt No. V								
Asphaltenes	28.2	29.2	30.6	31.1	33.2	34.6	31.0	33.1
Nitrogen Bases	20.6	21.2	22.2	20.7	19.9	24.3	23.1	17.5
First Acidaffins	18.0	17.8	17.1	16.7	17.3	12.3	17.9	22.8
Second Acidaffins	24.3	23.3	22.8	24.0	21.1	22.0	21.2	19.74
Saturated Hydrocarbons	8.7	8.5	7.3	7.5	8.7	7.0	6.8	6.8
Rostler Coefficient	1.16	1.23	1.31	1.19	1.25	1.26	1.46	1.52
Mod. Rostler Coefficient	1.71	1.65	1.64	1.59	1.39	1.40	1.65	1.50
Asphalt No. VI								
Asphaltenes	28.2	29.0	29.4	30.2	31.5	31.8	30.7	33.3
Nitrogen Bases	22.6	21.2	21.4	22.6	19.6	25.2	22.0	16.7
First Acidaffins	17.7	16.3	16.1	16.6	16.0	10.9	14.4	19.9
Second Acidaffins	23.5	24.7	25.5	23.7	23.6	24.5	25.7	23.1
Saturated Hydrocarbons	8.0	8.6	7.7	6.9	9.4	7.7	7.2	7.0
Rostler Coefficient	1.29	1.13	1.3	1.28	1.08	1.12	1.12	1.22
Mod. Rostler Coefficient	1.76	1.66	1.70	1.70	1.44	1.53	1.64	1.48

of the recovered aggregate from the extraction process. Table 4 presents the chemical analyses of the six asphalts.

The results of the physical and chemical testing of the asphalts to date present interesting facts. In general, the test data indicate an overall hardening of the asphalts. However, from the time of compaction to the 5-month core data, a softening trend was observed that was common to all the asphalts. The degree of softening varies in magnitude depending on which test one considers, but it did exist. This 5-month period was during the winter of 1964-65. The asphalts definitely hardened over the summer of 1965, but some further softening occurred the following winter, i.e., in the 12- to 18-

month cores. The softening during the second winter was much less severe and in some asphalts was nonexistent. This fluctuation is continuing but at a less noticeable rate.

In a previous report (18), data were presented to indicate the influence various percents of motor oil have on physical and chemical test data. This was done because in many instances oil drippings were visually observed on the test projects in the area of the coring operation. Every precaution is taken to remove these drippings before extraction, but inevitably some penetration of the oil into the cores occurs. We also know that two principal reasons that an asphalt hardens are volatilization and oxidation. These are quite prevalent during the summer months and decrease in magnitude during the winter since each is a function of temperature. In view of these facts, a possible reason for this supposed seasonal hardening and softening is that, during the summer, the rates of oxidation and volatilization exceed the softening effect of motor oil drippings. In the winter, the rates of oxidation and volatilization decrease to the point that the effects of the motor oil become dominant.

The percent original and percent retained data were included in the tables because they may be better indicators of the true quality of the asphalts. It is perhaps more important to consider the relative characteristics of the asphalts rather than their actual test values. If one asphalt has a higher percent retained penetration than another asphalt, which reflects a rate of change, then the first asphalt may be more desirable.

An example of this hypothesis is the application of a simple rating system to the tabular values. If we consider actual test values, Asphalt II seems superior. However, if we consider the percent age-based data, Asphalt VI appears superior. Asphalt VI is the common 70-85 pen, 3000 \pm 200 viscosity material. Some type of rating system will be developed so that a direct comparison of the asphalts will be possible in order to evaluate their durability.

JEFFERSON COUNTY, LR 338

The Jefferson County test roadway is 3.41 miles in length, located just south of the Borough of Sykesville. The original pavement consisted of 18 ft of 9- by 6- by 9-in. reinforced concrete constructed in 1924 and 1925. In 1954, the original pavement was widened with a 2-ft by 12-in. crushed aggregate base course and overlaid with 22 ft of 2½-in. ID-2 bituminous concrete. In September of 1965, the roadway was resurfaced with 1 in. of FJ-1 wearing course on 2 in. of ID-2 binder course, as shown in Figure 5. The route can be identified as Legislative Route 338 or US 119; it has an average daily traffic count of 2,030 to 2,250 vehicles per day.

A sand aggregate was used to produce the FJ-1 wearing gradation on the entire project. The design variables were the six test asphalts; the limits of work for the different asphalts, as well as the penetration grade of the asphalts supplied, are shown in Figure 6.

Air and water flow rate determinations were made on the test pavement during the construction of this project. The complete test procedure and results have been re-

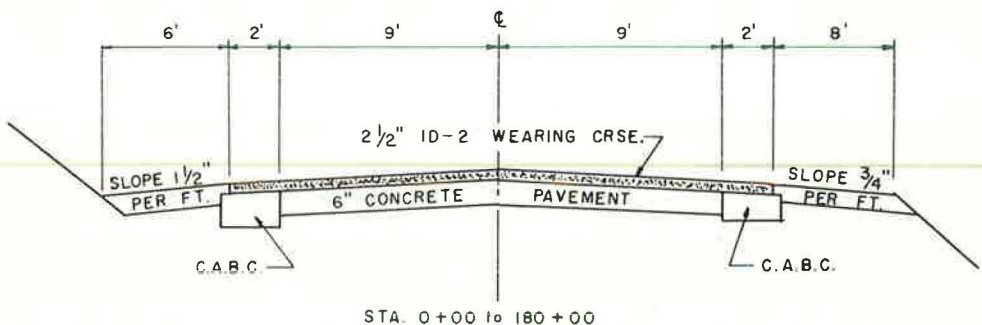


Figure 5. Typical section, LR 338.

STATION	0+00	31+80	65+80	93+75	122+12
DATE	9-14-65	9-15	9-16	9-16 & 17	
LEFT LANE	TYPE NO. 5	TYPE NO. 2	TYPE NO. 4	TYPE NO. 1	
RIGHT LANE	PEN. 90-100	PEN. 90-100	PEN. 90-100	PEN. 50-60	
STATION	0+00	30+75	62+80	93+25	124+50

STATION	122+12	152+12	166+15	180+00
DATE	9-17	9-20	9-20	
LEFT LANE	TYPE NO. 3	TYPE NO. 6	TYPE NO. 5	
RIGHT LANE	PEN. 140-160	PEN. 70-85	PEN. 90-100	
STATION	124+50	151+58	165+55	180+00

Figure 6. Asphalt producer limits, LR 338.

EXPERIMENTAL (VISCOSITY VERSUS PENETRATION)
 L.R. 338 JEFFERSON COUNTY
 F J-1 WEARING COURSE

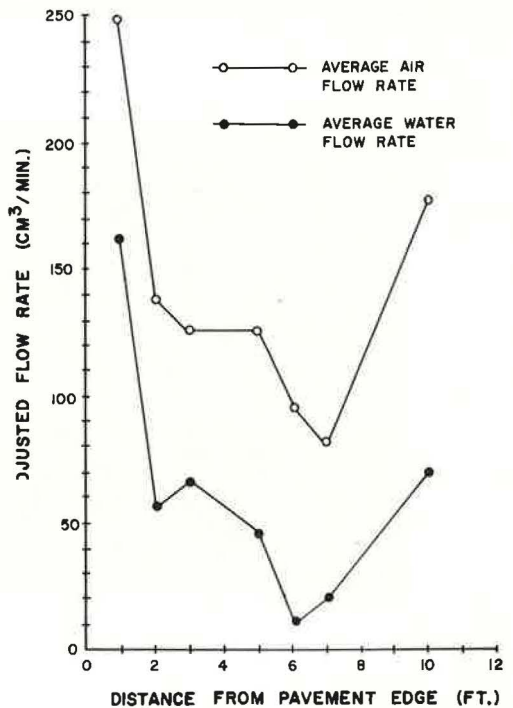


Figure 7. Variation of adjusted flow rates with transverse pavement location.

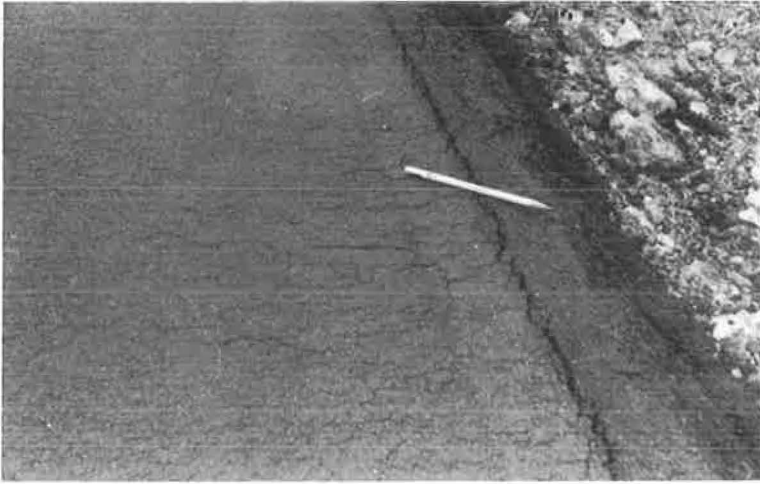


Figure 8. Surface cracking after final compaction.

ported elsewhere (19). The most interesting result of this extra testing is shown in Figure 7, which clearly indicates that more care should have been exercised during the compaction of the asphaltic concrete. It is suspected that early deterioration may begin at the pavement's edge or near the center joint.

In general, the construction of the pavement proceeded smoothly. There were some problems, however, that appeared during construction. Figure 8 shows the pavement containing numerous 3- to 12-in. cracks that opened after the finish roller completed its passes. This condition was quite severe for approximately 400 ft of pavement. Large longitudinal cracking along the edge of the pavement may also be noted. This crack appeared over the edge of the underlying pavement upon which the new surfacing was placed. Sluffing of the edge material was also noted. This phenomenon occurred immediately after the finish roller had completed its passes.

These phenomena were the result of either low temperatures during compaction or overcompaction. Data pertaining to laydown and compaction temperatures and asphalt



Figure 9. Excessive shoving of binder course.

viscosity during construction were as follows: air temperature 69 F; surface temperature 61 F; asphalt mix in truck, temperature 298 F, viscosity 1.8 poises; asphalt mix in hopper, temperature 298 F, viscosity 1.8 poises; mat before breakdown, surface temperature 258 F, viscosity 4.4 poises, interior temperature 278 F, viscosity 2.4 poises; breakdown rolling completed, surface temperature 186 F, viscosity 70 poises, interior temperature 200 F, viscosity 37 poises; pneumatic tire rolling completed, surface temperature 150 F, viscosity 500 poises, interior temperature 164 F, viscosity 210 poises; surface temperature upon completion of finished rolling was 116 F, which corresponded to a viscosity of 6500 poises. The asphalt used was Type IV.

The problem of bleeding did not present itself too often during construction and thus was not a major construction difficulty. Numerous areas of shoving were noted during the construction of the binder course, varying from slight to very severe as shown in Figure 9. The length of this shove was about 18 inches. This phenomenon was most predominant on sections of the roadway which had a grade line in excess of about 5 percent.

This test road will be quite interesting to observe, since it represents the first multi-penetration-viscosity asphalt project using an FJ-1 wearing course. The test data to date, both physical and chemical, are given in Tables 5 and 6. It is still too early to evaluate fully this test pavement or the test asphalts used on this project.

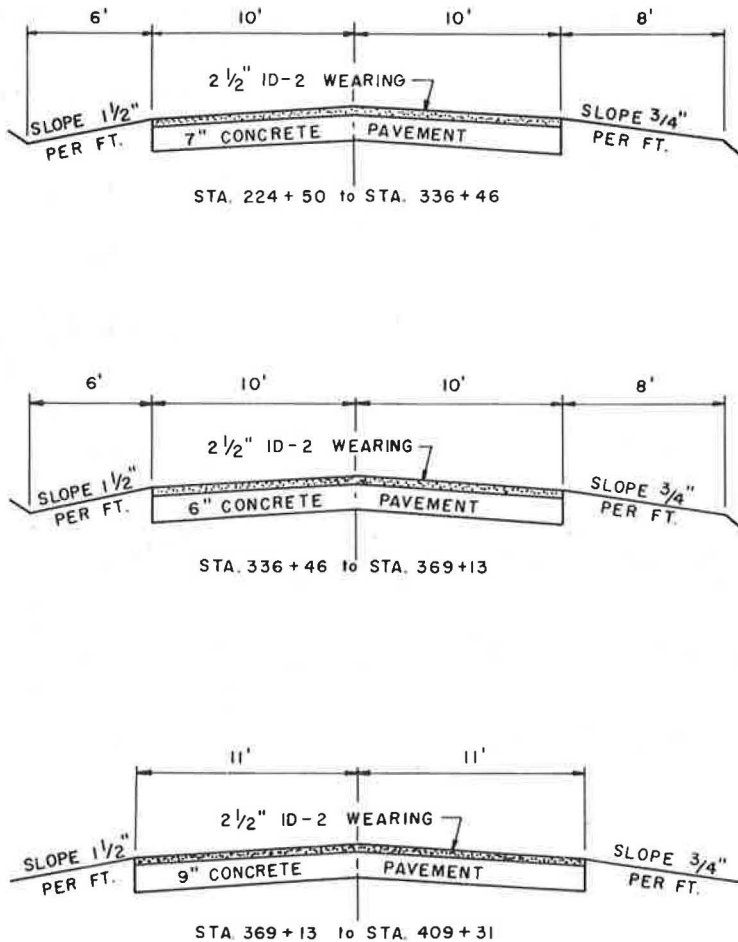


Figure 10. Typical sections, LR 101.

TABLE 5
PHYSICAL PROPERTIES OF ASPHALTS—JEFFERSON COUNTY, LR338

Asphalt Type	Line	After Mixing	After Compaction	7 Mo. Core	19 Mo. Core	Asphalt Type	Line	After Mixing	After Compaction	7 Mo. Core	19 Mo. Core
(a) Penetration Test—0.1 mm at 77 F, 5 sec, 100 gm						(f) Percent Retained Standard Ductility					
I	66	36	32	34	30	I	100	54	49	30	0
II	86	47	46	49	35	II	100	11	10	12	7
III	136	69	68	70	56	III	100	17	30	20	7
IV	87	54	50	47	35	IV	100	30	30	28	0
V	84	45	49	47	37	V	100	11	13	12	9
VI	74	40	48	49	30	VI	100	9	13	13	0
(b) Percent Retained Penetration						(g) Percent Asphaltenes					
I	100	54	48	52	45	I	19.0	20.2	22.3	22.6	19.6
II	100	55	53	57	41	II	22.3	24.2	24.7	24.7	22.0
III	100	51	50	51	41	III	27.8	30.0	32.0	31.2	35.9
IV	100	62	57	54	40	IV	16.8	18.7	19.4	21.0	19.1
V	100	54	58	56	44	V	29.5	32.2	32.1	31.9	31.7
VI	100	54	65	66	40	VI	28.2	31.7	32.4	31.9	36.5
(c) Absolute Viscosity (Cannon-Manning)—poises at 140 F, 30 cm Hg Vacuum						(h) Percent Original Asphaltenes					
I	1782	4952	6506	4925	7953	I	100	106	117	119	103
II	1629	5622	7348	4842	10277	II	100	108	111	111	99
III	1527	6116	6199	7940	9194	III	100	108	115	112	129
IV	1048	2532	2824	2820	5032	IV	100	111	115	125	114
V	3051	13715	11561	11850	19042	V	100	109	109	108	107
VI	3092	13118	8485	7240	17084	VI	100	112	115	113	129
(d) Percent of Original Absolute Viscosity						(i) Fineness Modulus of Aggregate					
I	100	278	365	276	446	I	—	2.80	2.76	2.84	2.80
II	100	345	451	297	631	II	—	2.76	2.80	2.86	2.84
III	100	400	406	520	602	III	—	2.90	2.82	2.78	2.85
IV	100	242	269	269	480	IV	—	2.81	2.78	2.82	2.76
V	100	450	379	388	624	V	—	2.90	2.78	2.82	2.92
VI	100	424	274	234	552	VI	—	2.92	2.91	—	2.92
(e) Standard Ductility—cm at 39.2 F and 1 cm per min						(j) Surface Area of Aggregate—ft ² per lb					
I	7.4	4.0	3.6	2.2	*	I	—	58.0	60.6	62.2	59.2
II	60.5	6.4	5.8	7.3	4.2	II	—	59.4	60.3	67.4	57.5
III	105+	17.4	31.0	20.9	7.2	III	—	57.4	60.2	67.0	58.8
IV	19.6	5.9	5.9	5.4	*	IV	—	57.9	60.2	63.5	59.5
V	51.2	5.6	6.5	6.3	4.4	V	—	55.5	60.9	67.4	56.6
VI	58.5	5.4	7.6	7.8	*	VI	—	55.5	57.1	—	57.5

*Brittle fracture.

TABLE 6
AVERAGE CHANGES IN CHEMICAL PROPERTIES--JEFFERSON COUNTY, LR338

Description	Line	After Mixing	After Compaction	7 Mo. Core	19 Mo. Core	Description	Line	After Mixing	After Compaction	7 Mo. Core	19 Mo. Core
Asphalt No. I						Asphalt No. IV					
Asphaltenes	19.0	20.2	22.3	22.6	19.6	Asphaltenes	16.8	18.7	19.4	21.0	19.1
Nitrogen Bases	23.1	20.8	24.2	25.8	25.0	Nitrogen Bases	23.0	21.4	22.7	25.0	25.2
First Acidaffins	16.8	13.7	11.5	10.7	15.4	First Acidaffins	15.6	13.9	14.6	10.9	12.8
Second Acidaffins	29.5	27.9	29.7	28.6	27.1	Second Acidaffins	31.5	29.3	28.9	29.6	30.1
Saturated Hydrocarbons	11.7	17.3	11.9	12.6	13.0	Saturated Hydrocarbons	13.1	16.7	14.5	13.5	12.8
Rostler Coefficient	0.97	0.76	0.88	0.88	1.00	Rostler Coefficient	0.87	0.77	0.86	0.84	0.88
Mod. Rostler Coefficient	2.26	1.68	1.95	1.85	2.08	Mod. Rostler Coefficient	2.35	1.84	1.95	1.90	2.13
Asphalt No. II						Asphalt No. V					
Asphaltenes	22.3	24.2	24.7	24.7	22.0	Asphaltenes	29.5	32.2	32.1	31.9	12.7
Nitrogen Bases	20.9	19.3	20.2	22.6	22.2	Nitrogen Bases	17.0	14.7	16.9	18.5	12.7
Second Acidaffins	28.6	27.3	28.6	29.4	29.6	First Acidaffins	17.8	13.3	13.6	10.6	17.1
Saturated Hydrocarbons	12.1	16.9	13.6	12.9	12.5	Second Acidaffins	25.8	24.3	25.7	29.2	27.6
Rostler Coefficient	0.90	0.72	0.79	0.78	0.86	Saturated Hydrocarbons	9.9	14.5	12.0	9.8	10.8
Mod. Rostler Coefficient	1.90	1.44	1.62	1.66	1.90	Rostler Coefficient	0.97	0.71	0.81	0.76	0.77
						Mod. Rostler Coefficient	1.54	1.14	1.29	1.40	1.35
Asphalt No. III						Asphalt No. VI					
Asphaltenes	27.8	30.0	32.0	31.2	35.9	Asphaltenes	28.2	31.7	32.4	31.9	36.5
Nitrogen Bases	19.0	16.1	18.7	18.4	18.1	Nitrogen Bases	22.9	19.7	21.6	23.2	20.5
First Acidaffins	17.4	15.0	13.2	13.8	11.2	First Acidaffins	21.5	16.9	17.5	16.4	15.2
Second Acidaffins	27.3	25.7	25.7	27.3	25.2	Second Acidaffins	21.0	19.9	21.2	21.0	21.4
Saturated Hydrocarbons	9.4	13.4	10.6	9.2	9.6	Saturated Hydrocarbons	6.5	11.8	7.4	7.6	6.4
Rostler Coefficient	1.01	0.80	0.88	0.88	0.84	Rostler Coefficient	1.61	1.15	1.37	1.38	1.29
Mod. Rostler Coefficient	1.72	1.32	1.35	1.47	1.20	Mod. Rostler Coefficient	1.88	1.30	1.52	1.53	1.33

McKEAN COUNTY, LR 101

The McKean County test roadway is 3.50 miles in length, located between the towns of East Smethport and Port Allegheny. The original pavement consisted of three different sections. Section one, station 224 + 50 to station 336 + 46, consists of 20 ft of 9 by 7 by 9 in. reinforced concrete pavement that was placed in 1935. Section two, station 336 + 46 to station 369 + 13, consists of 20 ft of 8½ by 6 by 8½ in. reinforced concrete pavement that was placed in 1938. Section three, station 369 + 13 to station 409 + 31, consists of 22 ft of 9-in. reinforced concrete pavement that was placed in 1947. In 1955, section two was overlaid with 20 ft of 2½-in. ID-2 bituminous concrete wearing surface. In August of 1965, the entire test section was resurfaced with 1 in. of ID-2 wearing course on 2 in. of ID-2 binder material. Typical sections for this project are shown in Figure 10. The route can be identified as Legislative Route 101 or US 6.

In general, the construction of this roadway was performed very smoothly. Figure 11 shows the very first section of the job. This area of tender mix was approximately 300 ft in length. Considerable movement was noted as the breakdown roller began making its passes and it was immediately withdrawn. The pneumatic tire roller was then put into operation, but the problem became more severe. Figure 11 was taken at this stage. The pneumatic tire roller was removed, and the mat was left to set up for approximately 60 to 90 minutes. At that time the breakdown and pneumatic rolling was eliminated, and final compaction of this section was achieved with the finish roller at 225 F (viscosity 14 poises).

A sand and gravel aggregate was used to produce the ID-2 wearing gradation on the entire project. At the start of the job the mat temperature was high (315 F) and resulted in a viscosity of 1 poise during initial rolling. This, in combination with moisture in the aggregate, may have been responsible for the results shown in Figure 11. Upon lowering the temperature of the mix to 290 F (viscosity 1.8 poises) in this troublesome section, the mat temperature at start of rolling was 250 F (viscosity 6 poises) and paving and compaction were completed satisfactorily on this section of the project.

The design variables were the six test asphalts, and the limits of work for the different asphalts as well as the penetration grade of the asphalts supplied are shown in Figure 12. The test data to date, both physical and chemical, are given in Tables 7 and 8 of this report. It is too early to evaluate this test pavement or the test asphalts used on this project.

Other than the high-temperature problem at the very start and some low early morning temperatures that prevented early morning pavement laydown, construction proceeded on schedule. This test road will be quite interesting to observe, because it is located in

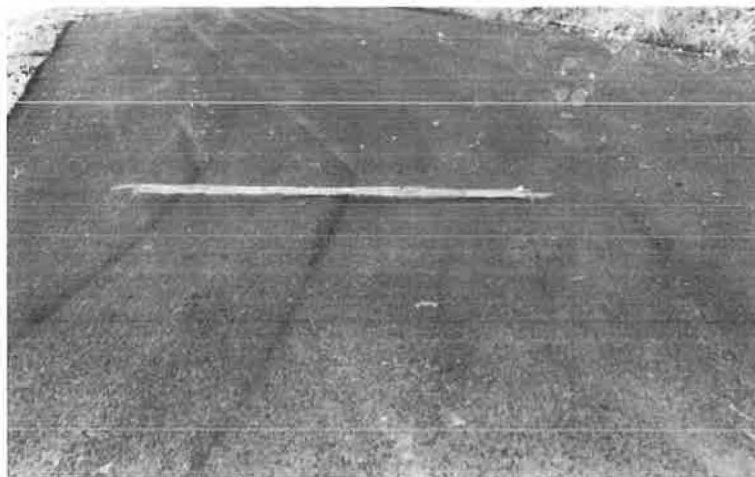


Figure 11. Extremely tender mix resisting compaction.

TABLE 7
PHYSICAL PROPERTIES OF ASPHALTS—McKEAN COUNTY, LR 101

Asphalt Type	Line	After Mixing	After Compaction	8 Mo. Core	20 Mo. Core	Asphalt Type	Line	After Mixing	After Compaction	8 Mo. Core	20 Mo. Core
(a) Penetration Test—0.1 mm at 77 F, 5 sec, 100 gm						(f) Percent Retained Standard Ductility					
I	59	44	40	39	36	I	100	55	0	42	43
II	90	79	78	62	60	II	100	58	51	14	13
III	130	96	84	85	82	III	100	75	41	48	38
IV	84	69	68	59	60	IV	100	33	48	29	41
V	85	68	68	60	52	V	100	37	33	25	14
VI	74	49	48	53	47	VI	100	18	16	20	17
(b) Percent Retained Penetration						(g) Percent Asphaltenes					
I	100	75	68	66	61	I	17.2	18.4	18.9	20.2	19.6
II	100	88	87	69	67	II	20.8	21.4	22.0	23.8	21.8
III	100	74	65	65	63	III	29.6	29.9	31.1	31.2	30.1
IV	100	82	81	70	71	IV	15.2	15.4	16.3	19.1	17.0
V	100	80	80	71	61	V	29.6	30.4	30.5	30.5	31.4
VI	100	66	65	72	64	IV	29.6	31.8	32.2	31.6	31.1
(c) Absolute Viscosity (Cannon-Manning)—poises at 140 F, 30 cm Hg Vacuum						(h) Percent Original Asphaltenes					
I	1794	3246	3269	3882	4629	I	100	107	110	117	114
II	1482	1571	1796	3109	2922	II	100	103	106	114	105
III	1701	3313	3694	4066	3930	III	100	101	105	105	102
IV	1090	1336	1604	2102	1672	IV	100	101	107	126	112
V	2970	5127	5218	6965	8715	V	100	103	103	103	106
VI	3124	8334	7612	7488	8141	VI	100	107	109	107	105
(d) Percent of Original Absolute Viscosity						(i) Fineness Modulus of Aggregate					
I	100	181	182	216	258	I	—	4.07	4.00	3.96	4.08
II	100	106	121	210	197	II	—	4.19	4.17	4.21	4.24
III	100	195	217	239	231	III	—	4.27	4.17	4.18	4.26
IV	100	123	147	193	153	IV	—	4.32	4.32	4.27	4.30
V	100	173	176	234	293	V	—	4.14	4.08	4.05	4.10
VI	100	267	244	240	261	VI	—	4.24	4.13	4.13	4.17
(e) Standard Ductility—at 39.2 F and 1 cm per min						(j) Surface Area of Aggregate—ft ² per lb					
I	6.9	3.8	*	2.9	3.0	I	—	34.2	37.0	43.0	35.0
II	105+	60.9	54.0	14.7	13.8	II	—	36.0	36.1	40.1	33.9
III	105+	79.0	42.6	50.0	40.2	III	—	31.2	33.0	39.7	32.5
IV	26.4	8.8	12.8	7.6	10.8	IV	—	29.9	29.0	35.8	31.0
V	49.7	18.2	16.6	12.4	6.9	V	—	35.0	36.4	42.9	35.8
VI	44.2	7.8	7.1	9.0	7.3	VI	—	31.3	34.2	40.0	34.2

*Brittle fracture.

TABLE 3
AVERAGE CHANGES IN CHEMICAL PROPERTIES—McKEAN COUNTY, LR 101

Description	Line	After Mixing	After Compaction	8 Mo. Core	20 Mo. Core	Description	Line	After Mixing	After Compaction	8 Mo. Core	20 Mo. Core
Asphalt No. I						Asphalt No. IV					
Asphaltenes	17.2	18.4	18.9	20.2	19.6	Asphaltenes	15.2	15.4	16.3	19.1	17.0
Nitrogen Bases	23.1	23.4	23.9	27.6	24.1	Nitrogen Bases	25.6	24.0	23.0	27.0	26.2
First Acidaffins	15.3	15.3	15.2	10.9	15.8	First Acidaffins	16.8	14.2	16.4	9.9	13.7
Second Acidaffins	28.0	30.0	29.4	29.3	28.3	Second Acidaffins	28.4	31.5	31.7	31.8	30.6
Saturated Hydrocarbons	16.4	12.9	12.6	11.1	12.2	Saturated Hydrocarbons	14.0	13.8	13.0	12.3	12.5
Rostler Coefficient	0.76	0.90	0.94	0.96	0.98	Rostler Coefficient	1.00	0.86	0.89	0.84	0.92
Mod. Rostler Coefficient	1.83	2.20	2.18	2.10	2.15	Mod. Rostler Coefficient	2.42	2.42	2.44	2.18	2.40
Asphalt No. II						Asphalt No. V					
Asphaltenes	20.8	21.4	22.0	23.8	21.8	Asphaltenes	29.6	30.4	30.5	30.5	31.4
Nitrogen Bases	22.8	21.4	21.7	25.2	22.6	Nitrogen Bases	15.0	16.7	16.1	22.0	18.6
First Acidaffins	15.2	15.5	15.4	10.8	12.7	First Acidaffins	16.6	16.7	16.2	11.3	12.0
Second Acidaffins	26.6	29.6	28.7	28.6	30.2	Second Acidaffins	25.4	26.6	27.0	27.0	27.4
Saturated Hydrocarbons	14.6	12.0	12.2	11.6	12.7	Saturated Hydrocarbons	13.4	9.6	9.2	9.2	10.6
Rostler Coefficient	0.92	0.89	0.91	0.90	0.82	Rostler Coefficient	0.82	0.92	0.92	0.92	0.80
Mod. Rostler Coefficient	1.84	1.93	1.92	1.82	1.90	Mod. Rostler Coefficient	1.33	1.50	1.52	1.52	1.38
Asphalt No. III						Asphalt No. VI					
Asphaltenes	29.6	29.9	31.1	31.2	30.1	Asphaltenes	29.6	31.8	32.2	31.6	31.1
Nitrogen Bases	14.5	15.6	15.2	19.2	17.0	Nitrogen Bases	20.6	21.2	20.9	25.4	21.2
First Acidaffins	16.8	16.9	15.9	12.8	14.8	First Acidaffins	18.8	19.1	18.9	13.9	20.6
Second Acidaffins	25.2	27.3	26.3	27.0	28.1	Second Acidaffins	19.4	20.6	20.8	21.9	19.5
Saturated Hydrocarbons	14.0	10.2	11.5	9.6	10.0	Saturated Hydrocarbons	11.6	7.2	7.1	7.3	7.6
Rostler Coefficient	0.80	0.87	0.83	0.88	0.84	Rostler Coefficient	1.26	1.45	1.42	1.36	1.54
Mod. Rostler Coefficient	1.30	1.49	1.35	1.45	1.50	Mod. Rostler Coefficient	1.43	1.56	1.54	1.58	1.58

STATION	224+50	260+34	291+91	320+21
DATE	8-25-65	8-26	8-27	
LEFT LANE	TYPE NO. 4	TYPE NO. 2	TYPE NO. 5	
RIGHT LANE	PEN. 90-100	PEN. 90-100	PEN. 90-100	
STATION	224+50	260+37	291+88	320+23
				CONTINUED BELOW
STATION	320+21	350+35	378+16	409+31
DATE	8-30	8-31	9-2	
LEFT LANE	TYPE NO. 3	TYPE NO. 1	TYPE NO. 6	
RIGHT LANE	PEN. 140-160	PEN. 50-60	PEN. 70-85	
STATION	320+23	350+30	378+83	409+31

EXPERIMENTAL (VISCOSITY VERSUS PENETRATION)
L.R. 101 MCKEAN COUNTY
ID-2 WEARING SURFACE

Figure 12. Asphalt producer limits, LR 101.

a northern county. It will probably undergo the severest cold temperature exposure of any of the pavements under evaluation.

SUMMARY

Of all the projects in our overall research programs, the Clinton, Jefferson, and McKean County projects are of the greatest importance. It is still too early to evaluate the quality and aging characteristics of the asphalts used on the Jefferson and McKean roadways. However, on the Clinton County project, using a very basic rating system, the common type asphalt, i.e., 70-85 penetration and 3000 ± 200 viscosity, is as good as, or better than, any of the test asphalts. This statement will be validated if the test project is studied until final deterioration occurs or until portions of the pavement are reclaimed, reconstituted, or resurfaced. It is then that a true evaluation of the asphalts can be made.

From Table 2 it can be seen that some of the asphalt cements used on the projects are somewhat out of specifications. One of the asphalts, Type V on LR 219, was in violation of the viscosity specification. The test value shown was observed at the Penn State laboratory and the value confirmed by the PDH laboratory. Rather than reject the material, it was accepted so as to not impede the progress of construction. It was considered a test asphalt and on this basis accepted. However, this fact will make it impossible to

compare the Clinton County data with the Jefferson and McKean County data for asphalt Type V in the future.

There seemed to be numerous construction problems on the Jefferson and McKean projects, such as improper plant mixing temperatures, insufficient edge and centerline rolling, the introduction of wet aggregates into the pugmill, and the absence of corrective measures for field problems. These two projects were not constructed according to the rigid specification and inspection methods that existed on the Clinton County project. Since it is a foregone conclusion that the inevitable durability of an asphaltic-concrete pavement is greatly influenced by proper construction methods and control, a great need exists in this area. Much improvement can and should be made in the area of quality control of batching operations and more rigid construction techniques.

A recent inspection tour of these projects was made by personnel from the Highway Department, University, and others. The pavements appear to be in excellent physical condition except for some minor base reflection cracking. It was not possible to distinguish visually any test asphalt section from another. Future inspection tours of this nature will be made.

It is difficult to draw any conclusions at the present time concerning all the projects. The following general conclusions are based only on the Clinton County test data:

1. In general, all the asphalts are hardening with time based on physical test data and percent asphaltenes.
2. During the winter months (from compaction to the 5-month cores and from the 12- to 18-month cores) no field age-hardening is indicated. In fact, some softening is indicated during these periods.
3. The percent retained and percent original concept of analyzing data may be a better indicator of the relative merits of the six test asphalts.
4. Some degradation of aggregates is occurring during construction. The breakdown occurs when the hot mixture is being compacted. Very slight changes, if any, are occurring under traffic compaction.
5. The Rostler coefficient is not producing any trend at this time to indicate chemical changes of the asphalts. The modified Rostler coefficient is decreasing somewhat with time, but this may be a reflection of increasing asphaltene contents which are used in the denominator of the ratio.

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Relationships of Flow Properties to Chemical Composition for Paving Asphalts

CHARLES W. LAMB and JAMES R. COUPER, Department of Chemical Engineering,
University of Arkansas

In recent years considerable research has been devoted to the physical and chemical properties of asphalt. Because of the dependency of the physical properties on chemical composition, there is a need for more fundamental knowledge of their interrelationships. This study was conducted to determine relationships between chemical composition and rheological properties of paving-grade asphalts.

Rheological properties and chemical compositions were determined for nine paving-grade asphalts. Flow properties at 45, 77, and 120 F were obtained by means of a sliding-plate microviscometer. A modified Corbett-Swarbrick chromatographic method for chemical composition data was employed.

Multiple-linear-regression analysis yielded equations that related flow properties at 120 F to chemical composition. The coefficient of thermal expansion was found to be a significant quantity for the description of the flow properties at the lower temperatures. Regression equations were obtained for the flow properties at 45 and 77 F, and for the Walther viscosity-temperature slope when the expansion coefficients were included in the regression analysis.

It was concluded that the flow behavior of asphalts in the lower range of service temperature was more dependent on factors such as association and colloidal state than on the relative content of the generic chemical groups used in this study.

•THE characteristics of asphalts of immediate importance in most applications are of a physical nature. However, it has been realized for some time that the physical properties are all dependent on the chemical constitution of the asphalts. Much of the motivation for the large amount of research concerning the chemical composition of asphalts has been the desire to establish relationships between composition and physical properties. However, despite the plethora of literature on the subject, few meaningful relationships have been developed. Most of the studies have yielded only qualitative results that are not generally applicable to different types of asphalts. Insufficient knowledge about the chemical constitution of asphalts and the use of empirical physical tests have been the main impediments to progress in asphalt technology. Recent advances in composition analysis and the measurement of fundamental physical properties promise to provide increased knowledge about the nature of asphalt. However, use of the new techniques in studies relating to rheological behavior has been limited.

It is the object of this paper to present the partial results of a study on the relationships between certain rheological properties and composition of paving-grade asphalts. This study is a cooperative research effort between the Department of Chemical Engineering at the University of Arkansas, the Arkansas State Highway Department, and the

U. S. Bureau of Public Roads. A companion project being conducted by Professor J. R. Bissett, Department of Civil Engineering at the University of Arkansas, is concerned with the investigation of changes in physical properties of asphalt as a function of time and service conditions. It will be approximately two years before the complete results of these two studies are available.

BACKGROUND

Asphalt is a complex heterogeneous mixture composed of a large number of molecular species. Its components are primarily chain and ring hydrocarbons, but as much as 10 percent oxygen, sulfur, and nitrogen may be present. Even with present analytical techniques and instruments, it appears to be virtually impossible to determine completely the chemical composition of asphalts with respect to all the myriad species present. Due to this complexity, composition analyses usually consist of separations of asphalt into generic groups that have similar chemical characteristics.

The use of liquid chromatography to separate asphaltic components has become widespread, and most recent chemical analysis techniques have employed chromatography to various extents. Chromatographic separations are based on the principle of selective adsorption of chemical compounds on the surface of porous, adsorbent solids. Fractionation is achieved by passing different solvents through the column to remove portions of the adsorbed materials. The most popular adsorbent materials are silica gel and alumina, but several others have been used. Likewise, several different solvents have been used as elutants. Traxler (11) gives a history of the application of chromatography to the separation of asphaltic materials, and a few of the recent investigations will be discussed.

Before performing a chromatographic separation of an asphalt, the asphaltenes are usually removed by treatment of the asphalt with a light hydrocarbon. A solution of maltenes is passed through a column filled with adsorbent solids, and the heavier components are selectively drawn to the surface of the adsorbent. Solvents of increasing solvent power are successively added to elute, or desorb, the more strongly held materials. The fractions obtained are arbitrary since they depend on the adsorbent, solvents, and temperatures used. However, the judicious application of chromatography has resulted in the separation of asphalts into useful generic groups with similar characteristics.

Corbett and Swarbrick (1) developed a chromatographic technique for the separation of asphalts that effected relatively clean-cut fractionation and required only a moderate amount of time. The asphaltenes were separated from the maltenes by refluxing the asphalt with n-hexane. The maltenes were fractionated into paraffins plus naphthenes (saturated hydrocarbons) and aromatic oils in a chromatographic column packed with activated bauxite. The saturated hydrocarbons and the aromatic oils were eluted with iso-octane and pyridine, respectively. The overlap between fractions was reported to be small, with the amount of aromatics in the saturate fraction being consistently less than 3 percent.

Various analytical techniques, ultraviolet, infrared, nuclear magnetic resonance, electron paramagnetic resonance, molecular weight, and carbon-hydrogen analyses were used to determine the general characteristics of the fractions. The saturate fraction contained paraffins and cycloparaffins with side chains. The average molecular weight for this fraction was in the C₄₀ to C₅₀ range. The aromatic oils consisted of highly branched aromatic rings connected by aliphatic chains and had molecular weights of 800 to 1100. The asphaltenes had the highest molecular weights and consisted of highly condensed aromatic rings with a few short side chains.

In a subsequent paper, Corbett and Swarbrick (2) modified their technique to yield five asphalt fractions. The asphaltenes and maltenes were separated by refluxing with hexane as before. The paraffin plus naphthene (PN) fraction was eluted with n-heptane. Then, the single-ring aromatic compounds (SRA) were removed with a mixture of heptane and benzene. Benzene was then used to remove the low-molecular-weight multi-ring aromatic compounds (LMA). Heavy multiring aromatic compounds (HMA) were eluted with pyridine.

The PN fraction was a mixture of paraffin and naphthene hydrocarbons with alkyl side chains. The SRA fraction contained single aromatic rings with several long aliphatic side chains. The LMA and HMA contained more aromatic rings per molecule and possessed higher molecular weights. The asphaltenes were multiple-ring aromatics with very short aliphatic side chains and possessed an average molecular weight of about 3000. Essentially, the difference between this technique and the previous one is that the aromatics fraction obtained in the first technique was separated into three relatively distinct fractions.

Tucker and Schweyer (13) used a variation of the Corbett-Swarbrick technique to separate asphalts into five generic groups. The asphaltene (HX) and PN fractions were obtained as by Corbett and Swarbrick (2), i. e., by refluxing with n-hexane and elution with n-heptane. The first aromatic fraction was obtained by using benzene as the elutant and was called the light aromatic fraction (LA). This LA fraction contained both the SRA fraction and the LMA fraction, which Corbett and Swarbrick had separated individually. The column temperature was then increased from 45 to 65 C before the remaining aromatic fractions were removed. The first heavy aromatic fraction (HA₁) was eluted with 1-butanol. Benzene was used to remove the second heavy aromatic fraction (HA₂) from the column. The total of the two heavy aromatic fractions was designated heavy aromatics (HA). This technique was used to separate three asphalts and several products obtained from air-blowing and sulfurizing the three charge stocks. Infrared analyses were used to determine the effect of the various processes on the asphalts.

The various versions of the Corbett-Swarbrick separation method have proved useful in studies concerning the aging and durability of asphalts (1, 2, 5, 13). However, to the authors' knowledge, no studies have been reported where the Corbett-Swarbrick method has been used to relate composition to rheological properties. In 1965, Schweyer (8) reported that such research was being conducted at the University of Florida. At that time, work had not progressed to the stage where composition could be correlated with any type of performance.

Jones (5) used the modified Corbett-Swarbrick method proposed by Tucker and Schweyer (13) to separate asphalts in a study of changes exhibited by asphalts in construction and service as a pavement binder. He found that the HX and HA fractions increased with aging, while LA and PN decreased. Since the viscosity of asphalts usually increases with aging, the ratio (LA + PN)/(HX + HA) appeared to be a parameter that might prove useful in correlation studies.

Simpson, Griffin, and Miles (9) used a chromatographic technique to separate an asphalt into four fractions, namely, asphaltenes, resins, aromatics, and saturates. These fractions were recombined, holding the asphaltene content at 25 percent, to form a series of model asphalts with different compositions. Tests of these model asphalts indicated that viscosity was a direct function of the ratio of resins to saturates.

In a durability study of several commercial paving asphalts, Traxler (12) found fair correlation between composition and oxidative hardening. The asphalts were separated by solvent extraction into asphaltenes, resins, cyclics, and saturates. A coefficient of dispersion was defined as the ratio of resins plus cyclics to the sum of asphaltenes and saturates. The rationale of this ratio was that a well-dispersed asphalt contained an excess of resins and cyclics, and would therefore have a large coefficient of dispersion. In general, the asphalts with the largest coefficients of dispersion exhibited the least hardening.

Exact comparison of the fractions obtained by various separation methods is difficult because of the different techniques used. For example, the HA fraction obtained by the Corbett-Swarbrick method and the resins fraction obtained by the Traxler-Schweyer method (12) are both considered to be highly aromatic materials that tend to peptize the asphaltenes. It is highly probable that if the two fractions were obtained from the same asphalt they would not be identical in either quantity or chemical nature. However, general characteristics of the fractions should be similar.

From the work of Simpson et al (9), viscosity was a function of the ratio of resins to saturates. In terms of the fractions obtained from the modified Corbett-Swarbrick

technique (13), the ratio would be HA/PN. The dispersion coefficient of Traxler (12) should be approximately equivalent to the ratio (LA + HA)/(HX + PN).

EXPERIMENTAL

Flow properties and chemical compositions were determined for nine paving-grade asphalts. Five of the asphalts were from an AC-10 series supplied by the U.S. Bureau of Public Roads. These are designated by a prefix B, e.g., B2975. The AC-10 asphalts chosen varied greatly in flow characteristic from Newtonian to non-Newtonian. The four asphalts without the letter prefix were obtained from Arkansas paving projects. These asphalts were derived from Smackover crude oil.

A sliding-plate microviscometer was used to obtain the flow properties at 45, 77, and 120 F. The instrument and operating procedure were as described by Griffin et al (4). An area-correction technique was used with the microviscometer that allowed plate displacements of over 2500 microns. This technique was described in a previous publication (6). A linear relationship resulted between shear area and plate adjustment.

Chemical compositions were determined by separating the asphalts into five fractions by a modified Corbett-Swarbrick chromatographic method (5). The technique was identical to that described by Tucker and Schweyer (13) except for the method of activating the Porocel adsorbent. Tucker and Schweyer heated the Porocel at 700 F for two hours, while a heating time of three hours at 270 ± 5 F was used in the present study. A detailed description of the apparatus and procedure was given by Jones (5).

RESULTS

The viscosity data for the nine asphalts are given in Table 1. The viscosities shown are the apparent viscosities evaluated at a constant power input of 1000 ergs/sec-cc, as proposed by Romberg and Traxler (7). Also included are viscosities determined at a shear rate of 0.05 sec^{-1} . The power law was found to provide an adequate description of the microviscometer results at the three temperatures. The logarithmic form of the power law is

$$\log F = A + B \log S$$

where

F = shear stress (dynes/cm²);

A = intercept on shear stress axis;

TABLE 1
ASPHALT PROPERTIES

Asphalt	η_c			$\eta_{0.05}$		
	45 F (10 ⁹ poise)	77 F (10 ⁹ poise)	120 F (10 ⁴ poise)	45 F (10 ⁹ poise)	77 F (10 ⁹ poise)	120 F (10 ⁴ poise)
1370	4.051	3.483	2.833	1.373	3.264	3.011
2509	5.180	4.268	3.631	1.680	3.902	3.924
2661	6.906	5.345	4.018	1.567	4.978	4.263
B2963	0.4914	0.4911	0.5954	0.3907	0.4886	0.6705
B2975	30.41	53.49	1.459	1.619	34.06	1.678
B3009	1.892	1.012	1.269	0.7316	0.9896	1.392
B3055	11.53	3.566	1.436	1.842	3.221	1.707
B3602	3.701	1.270	0.9748	3.607	1.269	1.489
4473	5.314	3.767	2.503	1.463	3.701	2.502
Average Variation	7.83 ^a	12.96 ^a	9.71 ^a	12.94 ^a	10.44 ^a	7.79 ^a

^aCoefficient of variation.

B = non-Newtonian index; and
S = shear rate (sec^{-1}).

A least-squares technique and computer program were used for the determination of the power-law parameters, A and B, from microviscometer data (6).

The non-Newtonian index, B, the Walther slope, m, and the coefficient of thermal expansion, α_T , are given for the nine asphalts in Table 2. The non-Newtonian index is a measure of an asphalt's deviation from Newtonian behavior. The closer the value of B is to 1, the more Newtonian the asphalt.

The viscosity-temperature susceptibility is specified by the Walther slope, m, obtained from the relationship (14):

$$m = \frac{\log \log (100\eta_1) - \log \log (100\eta_2)}{\log T_2 - \log T_1}$$

where

η_1 = viscosity at temperature T_1 (poises);
 η_2 = viscosity at temperature T_2 (poises); and
T = temperature (deg K).

Various types of viscosity were plotted on Walther plots. Included were the apparent viscosities at several shear rates and the differential viscosities. However, the linearity of the constant-power-input viscosities was superior. Only the data for asphalt B2975 showed significant curvature on the Walther plots. The values of m in Table 2 were obtained from η_c data in Table 1, since the lines for $\eta_{0.05}$ were curved for most of the asphalts. Two values of m are given for B2975; the first is the slope between the 45 F and 77 F points, and the second is the slope between the 77 F and 120 F points. Also given in Table 2 are the coefficients of thermal expansion calculated from density data.

The composition data are shown in Table 3, as well as the three composition ratios previously discussed.

Examination of the results given in Tables 1, 2, and 3 reveals no simple relationships between composition and rheological properties. The data were analyzed by a multiple-linear-regression computer program and the equations shown in Table 4 were obtained. These equations were the best obtained from numerous combinations of rheological and composition variables. Only variables significant at the 80 percent confidence level were retained in the equations.

TABLE 2
ASPHALT PROPERTIES

Asphalt	B			Walther Slope (m)	$\alpha_T \times 10^4$ (1/deg F)
	45 F	77 F	120 F		
1370	0.6873	0.9401	0.9542	3.6335	3.63
2509	0.6841	0.9243	0.9352	3.5920	3.69
2661	0.6021	0.9451	0.9486	3.5966	3.50
B2963	0.9046	0.9511	0.9435	3.7358	3.53
B2975	0.3435	0.8156	0.9159	2.1529 7.4273	4.36
B3009	0.6914	0.9527	0.9460	3.7419	3.67
B3055	0.5394	0.9069	0.8961	4.2152	3.95
B3602	0.9975	0.9985	0.9696	4.1002	3.79
4473	0.6412	0.9843	1.000	3.7299	3.53
Average Variation	0.0315 ^a	0.0387 ^a	0.0171 ^a	—	—

^aStandard deviation.

TABLE 3
CHEMICAL COMPOSITIONS

Asphalt	Fraction Percentages ^a						HA PN	LA + PN HX + HA	LA + HA HX + PN
	HX	HA ₁	HA ₂	HA	LA	PN			
1370	15.00	14.32	4.80	19.12	34.78	31.11	0.615	1.931	1.169
2509	14.89	17.18	4.97	22.15	31.43	31.54	0.702	1.700	1.154
2661	16.76	12.36	3.90	16.26	35.49	31.39	0.518	2.025	1.073
B2963	13.65	12.89	2.86	15.75	31.11	39.94	0.399	2.401	0.8818
B2975	9.45	22.44	5.07	27.51	30.69	32.35	0.850	1.706	1.392
B3009	12.13	18.05	3.80	21.85	28.62	37.40	0.584	1.943	1.019
B3055	10.53	19.29	4.50	23.79	32.06	33.62	0.708	1.914	1.265
B3602	4.75	26.57	2.61	29.18	34.82	31.25	0.934	1.948	1.778
4473	11.74	13.15	4.87	18.02	37.20	33.05	0.545	2.361	1.233
Average Standard Deviation	0.26	0.94	0.36	1.27	1.35	2.40	0.054	0.072	0.086

^aHX = Asphaltenes, HA₁ = First Heavy Aromatics, HA₂ = Second Heavy Aromatics, HA = Total Heavy Aromatics, LA = Light Aromatics, and PN = Paraffins and Naphthenes.

No significant relationships were obtained between the rheological properties of the asphalts and the percentages of the composition fractions. When the three composition ratios in Table 3 were used to supplement the fraction-percentage data, regression equations were obtained for η_c , the apparent viscosity, and B, the non-Newtonian index, at 120 F. This indicated that the chemical composition method used in this study provided sufficient information for the characterization of the flow properties at 120 F. However, the composition data did not yield regression equations for the flow properties at the lower temperatures. Evidently, at the lower temperatures, factors other than the chemical composition, such as the colloidal state, have an influence on the flow behavior of the asphalts.

Table 3 contains coefficients of thermal expansion obtained from density data, using a pycnometer. When the coefficients of thermal expansion were included with the com-

TABLE 4
REGRESSION EQUATIONS

η_c at 45 F (90% confidence):

$$\log \eta_{c_{45}} = 9.48368 - 0.17511 (\text{HX}) + 0.22041 (\text{LA}) - 7.11288 \left(\frac{\text{HA}}{\text{PN}} \right) - 4.0187 \left(\frac{\text{LA} + \text{PN}}{\text{HX} + \text{HA}} \right) + 1.78584 (\alpha_T \times 10^4)$$

B at 45 F (85% confidence):

$$B_{45} = 4.4161 + 0.04841 (\text{HX}) - 0.1198 (\text{LA}) - 3.3140 \left(\frac{\text{HA}}{\text{PN}} \right) + 3.3279 \left(\frac{\text{LA} + \text{HA}}{\text{HX} + \text{PN}} \right) - 0.6097 (\alpha_T \times 10^4)$$

η_c at 77 F (99.5% confidence):

$$\log \eta_{c_{77}} = -8.45403 + 0.10255 (\text{HX}) + 0.11518 (\text{LA}) + 2.65554 (\alpha_T \times 10^4)$$

B at 77 F (99.9% confidence):

$$B_{77} = 1.8958 - 0.009740 (\text{HX}) - 0.2253 (\alpha_T \times 10^4)$$

η_c at 120 F (99.5% confidence):

$$\eta_{c_{120}} = \left[67.507 - 0.9763 (\text{LA}) - 1.355 (\text{PN}) - 7.808 \left(\frac{\text{HA}}{\text{PN}} \right) + 8.634 \left(\frac{\text{LA} + \text{PN}}{\text{HX} + \text{HA}} \right) \right] 10^4$$

B at 120 F (98.5% confidence):

$$B_{120} = 8.3343 - 0.1130 (\text{HA}_1) - 0.1981 (\text{LA}) - 0.05015 (\text{PN}) - 3.2272 \left(\frac{\text{HA}}{\text{PN}} \right) + 3.9992 \left(\frac{\text{LA} + \text{HA}}{\text{HX} + \text{PN}} \right)$$

m, Walther slope (99.5% confidence):

$$m = -1.8314 - 0.029628 (\text{LA}) - 2.9636 \left(\frac{\text{HA}}{\text{PN}} \right) + 1.7895 \left(\frac{\text{LA} + \text{HA}}{\text{HX} + \text{PN}} \right) + 1.7263 (\alpha_T \times 10^4)$$

position data, regression equations were obtained for the flow properties at 45 and 77 F, and for the Walther slope. No explanation can be given for the significant effect of the expansion coefficients on the regressions. The coefficients were included because of their apparent correspondence with rheological behavior. The significance of the expansion coefficient might be due to its relation to the free volume of the asphalts. Free volume is defined as the volume of material packing irregularities (3). Equations have been developed that show an inverse dependence of viscosity on the free volume of liquids (10). However, the coefficient of thermal expansion reflects the total change of both free and occupied volume with temperature. If the thermal expansion could be considered as reflecting primarily a change in free volume, the viscosity-temperature susceptibility would be expected to be a direct function of the expansion coefficient. This appears to be the case, as revealed by the equation obtained for m . The equation indicates that an increase in the expansion coefficient would increase the Walther slope.

Since the expansion coefficient is only a measure of the gross change in volume, its relationship to the viscosity or non-Newtonian index at particular temperatures is not apparent from the free-volume theory. No previous use of the expansion coefficient in relationships with rheological properties of asphalts has been discovered by the authors.

As indicated by the regression equations in Table 4, the effect of an increase in the expansion coefficient would be positive for the viscosities and negative for the non-Newtonian indices. That is, the viscosities would increase and the flow behavior would become more non-Newtonian. Due to the form of the equations, it is difficult to analyze the effect of specific chemical fractions. In the equation for B at 77 F, an increase in the asphaltene fraction would cause a decrease in B . However, substitution of data reveals that the expansion coefficient has a more significant effect than does HX . Likewise, in the equation for η_c at 77 F, the expansion coefficient is a more significant variable than are HX or LA . In the rest of the equations, the effect of the composition ratios further complicates the analysis of the effects of individual fractions. It is observed that each of the composition ratios appears in at least two of the equations.

The confidence levels shown for each equation in Table 4 are the confidence levels that the correlations are valid. Table 5 contains the values of the multiple R^2 obtained for each equation. These numbers are the fraction of the variability of the data that is explained by the regression equations.

Numerical comparisons between predicted and measured values are given in Table 5. The average differences between the predicted and measured viscosities at 45 F and 77 F are seen to be about three times as great as the variations given in Table 1 for replicate microviscometer determinations. The regression equation for η_c at 120 F provided predictions that differed from the measured values by an average of only 11.9 percent. This average difference is about the same as the experimental variation of 9.7 percent. When the viscosity range of the asphalts is considered, the predictions of the regression equations appear to be acceptable. For example, the range of η_c at 77 F was about a hundredfold, while the maximum difference for the predictions was about twofold.

The predictions for B showed close agreement with the measured results. In fact, for the temperatures of 77 F and 120 F, the variations in the predicted values of B

were smaller than the variations between replicate experimental determinations.

The results calculated from the regression equation for m showed excellent agreement with the experimental data. As mentioned earlier, the data for asphalt B2075 were not used in the derivation of the regression equation for m because of the nonlinearity of the viscosity-temperature plot. When the composition data and expansion coefficient for B2975 were substituted in the regression equation, a Walther slope of 4.7582 was predicted. This value of

TABLE 5
DEVIATIONS FROM REGRESSION EQUATIONS

Quantity	Multiple R^2	Average Difference	Maximum Difference
η_c at 45 F	0.93545	21.3%	83.5%
η_c at 77 F	0.90963	36.4%	79.9%
η_c at 120 F	0.94499	11.9%	28.8%
B at 45 F	0.87319	0.052	0.100
B at 77 F	0.98088	0.005	0.016
B at 120 F	0.97312	0.004	0.007
m	0.98682	0.42%	1.45%

m was greater than the values for the other asphalts, and indicated a slope between the two values of m obtained from the Walther plot for B2975.

CONCLUSIONS

The composition results as obtained in this study yielded information that provided significant relationships between flow properties at 120 F and composition of the nine asphalts examined. However, at lower temperatures, the data indicated that there is a poorer correspondence between the flow properties and chemical composition as revealed by the analytical technique used in this study. The coefficient of thermal expansion was found to be a significant quantity for the description of flow properties at lower temperatures. Since the coefficient of thermal expansion is a function of the composition and molecular structure of a material, and since at lower temperatures association of molecules is more likely to occur than at higher temperatures, then it is reasonable to conclude that the coefficient of thermal expansion would be more significant at lower temperatures. Indeed, the data obtained in this study supported this conclusion.

Results such as those presented here may prove useful in studies of asphalts from specific crudes. However, for more general correlations, a more sophisticated analytical method is needed to delineate or separate the chemical entities that are important in determining the flow properties at service temperatures.

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Discussion

H. E. SCHWEYER, Research Professor, University of Florida—The conclusions and comments of the authors as evaluated from their data seem to be both reasonable and technically correct for the type of studies carried out. In view of the results indicated, it was thought that the following points might be mentioned as corroborating the type of results obtained:

1. The paper points out the necessity for low-temperature rheological evaluations of viscoelastic responses. This is a definite indication of why there is interest being shown in such measurements by a large number of investigators. Among such determinations are the use of the glass transition temperature as well as other low-temperature rheological determinations.

2. It should be pointed out that simple shear rate-stress measurements are not sufficient to characterize asphaltic materials at a given temperature unless they are Newtonian liquids. Thus, at low temperatures the evaluation of viscoelastic responses is going to be more important as time goes on. Reference should be made to a paper in this RECORD by Majidzadeh and the writer that emphasizes this point.

3. The sliding plate viscometer is not the instrument for low-temperature sophisticated evaluation for three reasons: (a) this instrument merely measures simple shear-stress relations, which do not permit the low temperature evaluation of viscoelastic materials; (b) the instrument permits only limited deformations before calculations are invalid unless area-change corrections are made; and (c) the instrument is limited in its capacity to materials of relatively low consistency unless it is adapted for use in other machines.

4. The low-temperature rheological responses are not determined by gross group component quantities as has been shown by the authors. Rather, it is necessary, first, that the rheological responses be defined specifically and, second, that these responses be correlated with the material parameters of any component group. Such material parameters would be degree of aromaticity, molecular weight, branchiness index, etc.

5. The colloidal and structural effects of viscoelastic materials must be related in the long run to composition, but as yet we have not developed the necessary techniques to do so. This does not mean that this is an insurmountable task, but it will require considerably more research.

CHARLES W. LAMB and JAMES R. COUPER, Closure—The authors concur with Dr. Schweyer's comments on all points. However, we will comment upon each point raised.

1. There is a definite need for more low-temperature rheological evaluations of viscoelastic responses. If the thermal expansion could be considered as reflecting primarily a change in free volume, the viscosity-temperature susceptibility would be expected to be a direct function of the expansion coefficient. This appears to be the case, as revealed by the equation obtained for m . The equation indicates that an increase in the expansion coefficient would increase the Walther slope.

2. The authors are aware of the fact that simple shear rate-stress measurements are not sufficient to characterize materials at low temperatures, unless they are Newtonian liquids. Comments on this point were made in Lamb's dissertation (6). A paper by Majidzadeh and Schweyer in this RECORD elaborates on the fact that more low-temperature work is necessary.

3. In addition to using the sliding-plate microviscometer, viscoelastic measurements were made in this study in a conicylindrical viscometer. This latter instrument and the apparatus were adapted for low-temperature conditions and studies are currently continuing and, in addition, include obtaining of stress relaxation data. The results obtained from the microviscometer were corrected for area change. This point is discussed at length by Lamb (6). The reason for using the conicylindrical viscometer

was that a much broader range of consistencies could be handled in this instrument than in a sliding-plate microviscometer.

4. Studies are presently under way in which an attempt will be made to correlate rheological responses with molecular weight, branchiness index, etc.

5. Yes, considerably more research is required on rheological responses and chemical composition, but the ultimate determinant of the physical properties is obviously chemical composition.

Development of a Laboratory Durability Test for Asphalts

DAH-YINN LEE, Assistant Professor, Department of Civil Engineering, Iowa State University

A laboratory test procedure for evaluating the durability of paving asphalts is proposed which recognizes and is intended to simulate the two-stage hardening of asphalt during mixing processes and subsequent pavement service life. The test consists of first subjecting the asphalt to the thin film oven test (TFOT) and then treating the residue in oxygen at high pressures. The TFOT at 325 F is to simulate the changes that may occur in asphalt during hot-mixing and the pressure-oxidation process at 150 F is to simulate the changes that may occur in asphalt during pavement service life. A $\frac{1}{8}$ -in. film thickness is used in both treatments.

The effectiveness of the proposed test in accelerating the hardening and other changes of asphalt, the ability of the test in differentiating asphalts with respect to changes (both physical and chemical), and the effects of time and oxidation pressure are demonstrated by results of the proposed durability test on five 85-100 penetration grade asphalt cements and one of 120-150 penetration grade. The properties measured to indicate changes include penetration, softening point, absolute viscosity, asphaltene content, and percent oxygen.

The major conclusions from this study are that (a) the approach of the proposed durability test is sound and the procedure reproducible; (b) the procedure is capable of accelerating the hardening of asphalt in a relatively short period of time; (c) differences exist among asphalts in hardening during the pressure-oxidation procedure, and therefore the procedure can distinguish between asphalts that are susceptible to hardening and those that are not; (d) the hardening in the pressure-oxidation process is a hyperbolic function of time, which suggests that a definite correlation can be established between field hardening and the proposed laboratory durability test; and (e) continued study into the next phase of the durability test investigation is necessary and warranted so that information obtained can be put into useful and applied form in asphalt paving design and quality control.

•ALL bituminous paving materials undergo changes with time and under the action of heat, weather, and traffic. Such changes are, in general, detrimental to their function as binders and as waterproofing agents. Thus, the degree of resistance of a bituminous binder to these changes is usually referred to as its durability. Durability of asphalt has been studied for many years by a great number of investigators searching for knowledge of (a) mechanisms or causes of asphalt deterioration; (b) methods for controlling

or preventing undue hardening of asphalts; and (c) tests to predict the behavior of an asphalt during mixing, laying, and in pavement service.

It is generally agreed that the most important single factor that causes asphalt paving to crack and disintegrate is asphalt hardening. Therefore, the degree and rate of asphalt hardening has been considered as indicative of relative durability of asphalt, and many durability tests have been proposed centering around the evaluation of the resistance of asphalt to hardening.

Almost all durability tests that have been proposed involve a study of two phases: (a) subject asphalt to certain treatments to speed up the hardening process, and (b) compare the degree or the rate of hardening of the treated asphalt with actual hardening that occurred in asphalt during the mixing process or in the road. Hardening that occurred in the mixing process and in the road is usually determined by recovering the asphalt from the mix or pavement by the Abson method and comparing the penetration, softening point, ductility, viscosity, and chemical compositional properties of the recovered asphalt with those of the original asphalt. Major differences among various proposed durability tests are the treatments or the manner in which the hardening of the asphalts is accelerated.

A majority of the treatments used to speed up the hardening of asphalt in a durability test include heating at elevated temperatures, either alone in various thicknesses of films, temperature, and duration (1-9), or in a mixture (10-12). The more important ones in these groups are the Shattuck mixing test, the standard loss on heating test, and the thin film oven test (TFOT).

Many investigators believe that oxidation is a major factor causing asphalt hardening. Procedures for evaluating the susceptibility of asphalt to oxidation were developed by Thurston and Knowles (13), Anderson et al (14), and Ebberts (15). Van Oort (16) studied the durability of asphalts and showed by calculation that, under normal aging conditions, the oxygen diffuses into the asphalt films a depth of only a few microns. However, experiments by Blokker and Van Hoorn (17) showed that the penetration is much greater, on the order of 3 mm or more.

In recent years, particularly after the introduction of the microfilm viscometer, many investigators have used so-called microfilm durability techniques in which asphalt is aged in films of only 5 to 15 microns (16, 18, 19, 20). Hardening is measured by the viscosity ratio or aging index after the film is exposed to heat and air.

Some investigators considered the abrasion resistance of a paving mixture as a good indicator for the hardening and durability of the binder. The shot abrasion test (21, 22) was developed to measure the change in resistance of a compacted sand-asphalt mix to a falling stream of steel shot after extended exposure in the infrared oven.

Traxler (23) presented 15 effects that may cause changes in the chemical, rheological, and adhesion properties of asphalt during handling and under service conditions. The effects listed include oxidation, photo-oxidation under direct sunlight and under reflected light, volatilization, photochemical action of direct and reflected lights, polymerization, age hardening, exudation of oils, changes by nuclear energy, action of water, absorption of oils by solid, adsorption of asphaltic components at a solid surface, catalytic effects at the asphalt-stone interface, and microbiological deterioration. He also suggested possible ways of retarding the various effects and methods of study on 5 of the 15 effects by microfilm techniques.

In considering the various factors that may affect the durability of asphalt, it should be noted that (a) while the quantitative measurement of the individual factors in influencing the durability of asphalt is extremely complex, if not impossible, it is to be recognized that some of these effects are more important than others in various phases of use of asphalt; (b) one or more of the effects may function at the same time; and (c) all effects are influenced by time, temperature, and film thickness.

The durability of bitumen in theory and practice was reviewed by Blokker and Van Hoorn (17). An accelerated test procedure for assessing the aging characteristics of bitumens was investigated that involved treating bitumen in thin films (5 to 200 microns) in oxygen of 20 atm at 50 C (122 F) and measuring relative viscosity. The same approach was used by Martin (24). The British Road Research Laboratory (25) has developed a pressure-oxidation test for road tars by exposing tar films 7 mm thick to oxygen

at 300 psi and 65 C (149 F) for 64 hours and measuring the change in either Fraass brittle point or equiviscous temperature (evt).

In 1963, Hveem et al (26) presented results of an extensive study on the durability of asphalt by the shot-abrasion test and the microfilm viscometer technique. Weathering was achieved by subjecting asphalt-sand mixtures to infrared radiation in a weathering machine. A correlation study showed that exposure of 1000 hours in the weathering machine was about equal to 5 years of pavement service time for California conditions. For routine control testing purposes a new rolling thin film oven test (film thickness of 5 to 10 microns, exposed in oven at 325 F for 75 min) was developed to predict change in asphalt during mixing operation. To simulate weathering during service life, 20-micron films of residue from the rolling thin film oven test are weathered at 210 F for a period of 24 hours and viscosity is determined by microviscometer. It was found that these conditions produced hardening equivalent to 1000 hours in the weathering machine at 140 F or 5 years of service life.

Practical and reliable information can be obtained from a laboratory durability test only when the behavior of the asphalt in the durability test can be correlated with pavement durability in the field. Correlations on the TFOT are well established (27-34). Correlations between field hardening of asphalt and laboratory data were studied by Simpson et al (35), Traxler (36), Gallaway (37), and Heithaus and Johnson (19) on microfilm durability tests. Halstead and Zenewitz (38) studied the relation between the TFOT and the microfilm durability test. Their results showed greater hardening for the microfilm test for asphalts with aging indices greater than two.

In spite of the great amount of time and effort that have been put into the study of the durability and durability testing of asphalt, the paving industry is still in need of a logically conceived, well-designed, universally accepted, and yet relatively simple and rapid laboratory durability test for paving asphalt, which will enable the design engineer to select or specify an asphalt based on quality and to make a proper estimate of the service life of a selected asphalt.

It is believed that the true value of any laboratory durability test should be judged from the answers to the following questions: (a) How logical or realistic is the acceleration process in the laboratory as compared with what actually occurs in the field? (b) How well can the tests or properties measured indicate the actual changes that cause deterioration of asphalt? (c) How good is the correlation between laboratory and field data?

It is the purpose of this paper to describe a laboratory durability test for paving asphalts, the rationale from which the test is developed, and the tests and procedures involved.

The proposed durability test is intended to simulate as realistically and as completely as possible the two-stage hardening of asphalt during mixing and subsequent pavement service life. The test makes use of, and takes advantage of, the well-established BPR thin film oven test; it consists of first subjecting the asphalt to the TFOT and then treating the residue from the TFOT in oxygen at high pressures. The TFOT at 325 F is used to simulate the changes that may occur in asphalt during mixing and the pressure oxidation process at 150 F is to simulate the changes that may occur in asphalt during pavement service life.

The effectiveness of the proposed test in accelerating the hardening and other changes of asphalt, the ability of the test in differentiating asphalts with respect to resistance to changes (both physical and chemical), and the effects of time and oxygen pressure are demonstrated by results of the proposed durability test on five 85-100 pen. and one 120-150 pen. grades of asphalt cements.

This investigation is the initial phase of an overall long-range program undertaken at the Bituminous Research Laboratory, Iowa State University, in the development of a laboratory durability test sponsored by the Iowa Highway Research Board. The second and third phases of the program will be the establishment of field correlation and the derivation of quality criteria for paving asphalts based on durability studies.

DEVELOPMENT

In our study of the durability of asphalt and in the development of the test procedure, the following premises and concepts were formulated and followed:

1. The most important single factor that causes asphalt pavement to crack and disintegrate is the failure of the asphalt as a cementing and waterproofing agent in an asphalt mixture due to asphalt hardening. Therefore the extent and rate of asphalt hardening is considered to be indicative of the relative durability of asphalt.

2. The hardening and other pertinent changes that may occur in asphalt in an asphalt-concrete mix take place in two stages under two entirely different environments or conditions: hardening during short periods of time in the mixer at higher temperatures and higher rates, and hardening during longer periods of time of road service in pavement at relatively lower temperatures and lower rates. The hardening mechanisms and effects in these two stages are believed to be quite different.

3. It is believed that among the factors causing asphalt hardening, the evaporation of volatiles and high-temperature oxidation predominate during the mixing process. Oxidation at road service temperatures, especially in absence of light, seems to predominate under service conditions.

4. Any realistic durability test for asphalt should include consideration of the two stages of hardening processes of asphalt in their logical order and their differences in mechanisms and effects.

5. In evaluating the quality or durability of asphalts, one is concerned with not only the characteristics of the original asphalt but, even more important, the binder characteristics—the viscosity, the tendency to harden, the susceptibility to oxidation, the colloidal stability, etc.—of the asphalt in the finished pavement. This would include study of the asphalt after the first stage hardening and would provide assurance that the properties of the binder following construction are satisfactory for future pavement performance.

6. Hardening during the mixing process may be simulated and predicted in the laboratory by the BPR thin film oven test. Additional hardening and other changes in the asphalt in service may be simulated by laboratory pressure-oxidation tests at road service temperature on residue of the TFOT.

7. A definite correlation may be established, at least on a local basis, between field hardening and performance of asphalt and laboratory-accelerated hardening during a logically conceived and realistic durability test. The asphalt hardening in the field in terms of years could be reasonably predicted in terms of hours or days.

It was with these concepts and considerations that a durability procedure was devised. The overall program includes the following steps:

1. Determine the rheological and colloidal-chemical properties of the original asphalts.
2. Run the BPR thin film oven tests and determine the characteristics of asphalts on the residues.
3. Treat the TFOT residues in oxygen at 150 F under various pressures for various lengths of time.
4. Determine asphalt characteristics on pressure-oxidized TFOT residues.
5. Establish field service correlation.
6. Establish asphalt quality or usefulness criteria in terms of rheological or chemical properties or both.

It is expected that the results obtained from this program will provide a more realistic basis for quality control and durability prediction. Thus, by comparing results of tests on an asphalt from steps 1 to 4 and information or criteria established from 5 and 6, the quality of the asphalt can be specified or predicted.

This report is concerned with the feasibility and sensitivity of the laboratory test procedures (steps 1 to 4), the establishment of a working procedure, and the effects of

pressure and duration on rheological and chemical properties of the treated asphalts. A proposal to study the fifth and sixth steps of the overall program has been submitted for consideration.

PROCEDURES

Five 85-100 pen. grade asphalt cements and one 120-150 pen. grade were used in the study. All except the 120-150 pen. asphalt cements, which was obtained from the American Oil Co. at Sugar Creek, Mo., were taken from various actual construction projects in Iowa during the 1966 construction season. The physical and chemical properties of the asphalts are given in Table 1.

The simulation of hardening of asphalt in the first stage (during mixing) was achieved by the BPR thin film oven test (ASTM D 1754-63T). Properties of the residues from the TFOT are also given in Table 1.

The acceleration of the hardening of asphalt in the second stage (during road service) was achieved by (a) aging the residue from the TFOT in relatively thin films, (b) aging the residue in oxygen instead of air, and (c) increasing the oxygen pressure.

Three series of pressure-oxidation tests were investigated. Two series were run on residues of the TFOT and one series, for comparison purposes, was conducted on 2 percent sand-asphalt mixtures. Commercial pressure cookers of cast aluminum, 11 in. in diameter and 11 in. in height, were used for one series of pressure-oxidation treatments on residues of the TFOT. Samples of TFOT residues of 25 ml were weighed into 4-in.-diameter aluminum dishes, making films of $\frac{1}{8}$ in. Dishes with samples were then placed in the pressure cookers. After a leakage check, the cookers were evacuated and filled with oxygen twice and finally filled to a pressure (at room temperature) that would result in a pressure of 29 psig at 150 F. The cooker and contents were placed in the oven at 150 F. Samples were treated in oxygen at 29 psig for 24, 48, 96, and 240 hours. Viscosity at 77 F and rate of shear of $5 \times 10^{-2} \text{ sec}^{-1}$, softening point (R & B), compositional analysis, and percent oxygen were determined on the treated residues. Viscosity was determined by a Shell sliding-plate microviscometer. Percent asphaltenes and oils were determined by the selective solvent method proposed by Csanyi and Fung (39) using Skelly F as solvent. Percent oxygen was obtained by a Coleman Model 36 oxygen analyzer. Results on the first series of tests are given in Table 2.

The second series of pressure-oxidation treatments on TFOT residues was run at a higher oxygen pressure; the stainless-steel oxidation stability bombs (ASTM D 525) of 2-in. inside diameter and 4 $\frac{1}{2}$ -in. height were used. Samples of TFOT residues of 4 ml were treated in $\frac{1}{8}$ -in. diameter glass dishes (making films of $\frac{1}{8}$ in.) in pressure bombs at 132 psig of oxygen in 150 F water baths for periods of 24, 48, 96, and 240 hours. Changes in asphalt in terms of viscosity at 77 F, asphaltenes, and oxygen content were determined and are given in Table 3. Effects of pressure variation on viscosity and

TABLE 1
PROPERTIES OF ASPHALTS STUDIED

Asphalt Cement ^a	Penetration	Specific Gravity	Flash Point (F)	Fire Point (F)	Softening Point, R & B (F)	Viscosity, 77 F (megapoises)	Complex Flow "C" (Ref. 45)	Asphaltenes (%)	Oxygen (%)	Oxygen in Asphaltene (%)
1-O	88	1.012	575	665	116.5	2.10	0.901	18.8	0.79	0.99
1-R	50	1.015	—	—	130.5	7.50	0.510	22.8	1.00	2.13
2-O	88	1.001	650	710	116.5	1.90	0.781	14.4	0.48	1.37
2-R	55	1.015	—	—	126.5	4.90	0.553	17.9	0.72	1.73
7-O	90	1.016	650	715	112.5	1.25	0.966	16.6	0.81	1.14
7-R	56	1.020	—	—	126.5	3.10	0.933	18.7	1.01	1.59
9-O	90	1.035	595	680	116.5	2.10	1.000	19.1	0.73	1.10
9-R	55	1.038	—	—	122.5	5.10	0.900	21.0	1.10	1.32
10-O	90	0.998	650	725	118.0	1.70	1.040	12.9	0.63	1.85
10-R	55	1.010	—	—	129.0	6.15	1.000	15.9	1.13	2.18
11-O	134	1.024	595	660	106.5	0.53	1.040	15.3	0.64	1.58
11-R	79	1.030	—	—	116.0	2.15	1.040	18.9	0.97	1.92

^aO = original asphalt, R = residue from TFOT.

TABLE 2
 PROPERTIES OF ASPHALT RESIDUES FROM TFOT AGED IN PRESSURE COOKER
 AT 29 PSIG AND 150 F

Asphalt Cement ^a	Hours	Viscosity, 77 F (megapoises)	Complex Flow "C"	Relative Viscosity	Softening Point	Asphaltenes (%)	Oxygen (%)
1-O	0	2.10	0.901	1.00	116.5	18.8	0.79
1-R	0	7.50	0.510	3.58	130.5	22.8	1.00
	24	14.5	0.364	6.91	138.0	23.9	1.14
	48	19.0	0.213	9.05	141.5	25.3	1.20
	72	22.0	0.287	10.48	143.0	25.7	1.25
2-O	0	1.90	0.781	1.00	116.5	14.4	0.48
2-R	0	4.90	0.554	2.58	126.5	17.9	0.72
	24	7.50	0.384	3.95	135.5	20.7	1.18
	48	9.60	0.384	5.05	137.5	21.4	1.37
	72	11.50	0.306	6.06	139.5	21.2	1.46
7-O	0	1.25	0.966	1.00	112.5	16.6	0.81
7-R	0	3.10	0.933	2.48	128.5	18.7	1.01
	24	10.0	0.649	8.00	131.5	19.7	1.06
	48	14.5	0.510	11.60	134.0	20.6	1.17
	72	17.6	0.625	14.10	138.5	20.5	1.14
9-O	0	2.10	1.000	1.00	116.5	19.0	0.73
9-R	0	5.10	0.900	2.43	122.5	21.0	1.10
	24	8.90	0.577	4.24	128.5	22.3	1.12
	48	14.0	0.577	6.67	131.0	23.1	1.23
	96	18.5	0.601	8.82	137.0	24.7	1.15
	240	29.0	0.601	13.80	140.5	26.2	1.37
10-O	0	1.70	1.040	1.00	118.0	12.9	0.63
10-R	0	6.15	1.000	3.62	129.0	15.9	1.13
	24	12.2	0.510	7.18	137.5	19.5	1.26
	48	15.0	0.466	8.85	141.5	19.9	1.30
	96	21.5	0.384	12.63	146.5	21.0	1.42

^aO = original asphalt, R = residue from TFOT.

TABLE 3
 PROPERTIES OF ASPHALT RESIDUES FROM TFOT AGED IN PRESSURE
 BOMBS AT 132 PSIG AND 150 F

Asphalt Cement ^a	Hours	Viscosity, 77 F (megapoises)	Complex Flow "C"	Relative Viscosity	Asphaltene (%)	Oxygen (%)
1-O	0	2.10	0.901	1.00	18.8	0.79
1-R	0	7.50	0.510	3.58	22.8	1.00
	24	15.0	0.445	7.15	24.9	1.16
	48	18.2	0.325	8.68	26.4	1.25
	72	23.0	0.325	10.95	26.8	1.35
	240	28.0	0.176	13.35	27.2	1.64
2-O	0	1.90	0.781	1.00	14.4	0.48
2-R	0	4.90	0.554	2.58	17.9	0.72
	24	8.40	0.364	4.42	19.9	1.33
	48	13.1	0.306	6.90	20.7	1.48
	72	14.2	0.268	7.49	21.7	1.52
	240	24.0	0.176	12.62	24.3	1.75
7-O	0	1.25	0.966	1.00	16.6	0.81
7-R	0	3.10	0.933	2.48	18.7	1.01
	24	10.2	0.700	8.17	20.2	1.17
	48	16.2	0.638	12.96	21.0	1.30
	72	20.6	0.568	16.50	21.6	1.38
	240	32.5	0.424	26.00	23.6	1.45
9-O	0	2.10	1.000	1.00	19.1	0.73
9-R	0	5.10	0.900	2.43	21.0	1.10
	24	13.50	0.577	6.44	22.7	1.24
	48	19.50	0.577	9.29	23.5	1.34
	96	25.3	0.649	12.05	24.7	1.46
	240	34.0	0.601	16.20	26.3	1.56
10-O	0	1.70	1.040	1.00	12.9	0.63
10-R	0	6.15	1.000	3.62	15.9	1.13
	24	14.5	0.577	8.54	19.2	1.46
	48	18.0	0.445	10.60	20.6	1.62
	96	23.5	0.325	13.80	21.8	1.78
	240	31.0	0.231	18.20	23.3	1.82
11-O	0	0.53	1.040	1.00	15.3	0.64
11-R	0	2.15	1.040	4.06	18.9	0.97
	24	5.00	1.070	9.44	20.8	1.10
	48	6.45	0.900	12.15	21.8	1.13
	96	13.2	0.900	24.90	23.1	1.29
	240	18.7	0.466	35.30	24.7	1.43

^aO = original asphalt, R = residue from TFOT.

TABLE 4
EFFECTS OF PRESSURE VARIATION ON ASPHALT PROPERTIES

Condition	Asphalt 9		Asphalt 10		Asphalt 11	
	Viscosity, 77 F (megapoises)	Asphaltenes (%)	Viscosity, 77 F (megapoises)	Asphaltenes (%)	Viscosity, 77 F (megapoises)	Asphaltenes (%)
Original	2.10	19.1	1.70	12.9	0.53	15.3
Residue, TFOT	5.10	21.0	6.15	15.9	2.15	18.9
Vacuum, 24 hr	4.75	21.0	5.70	15.9	1.86	18.8
N ₂ , 1 atm, 24 hr	4.90	20.6	6.80	15.5	1.85	18.9
Air, 1 atm, 24 hr	8.50	21.0	7.20	16.3	1.95	18.6
O ₂ , 1 atm, 24 hr	10.5	21.4	10.0	16.9	2.50	18.9
O ₂ , 10 psig, 24 hr	10.8	21.6	10.5	16.4	2.65	19.7
O ₂ , 30 psig, 24 hr	11.4	22.0	11.0	17.6	2.80	19.5
O ₂ , 60 psig, 24 hr	12.5	21.5	12.5	17.7	3.50	20.7
O ₂ , 90 psig, 24 hr	13.0	23.0	14.0	18.0	—	—
O ₂ , 106 psig, 24 hr	13.5	22.7	—	—	—	—
O ₂ , 132 psig, 24 hr	13.5	22.7	14.5	19.2	4.30	20.8
O ₂ , 154 psig, 24 hr	14.1	23.3	15.4	18.5	—	—
O ₂ , 200 psig, 24 hr	15.5	23.7	17.8	19.4	6.90	22.0

chemical properties of treated TFOT residues in $\frac{1}{8}$ -in. films at 150 F were investigated up to 200 psig. Data on the effects of pressure variation on asphalts 9, 10, and 11 are given in Table 4.

The third series of pressure-oxidation studies were made on 2 percent sand-asphalt mixtures. Ottawa sand and asphalt were heated to 350 F and 300 F respectively and mixed, in proportions of 2 percent asphalt by weight of sand, for 3 minutes in a Kitchen-Aid mixer. After mixing under closely controlled conditions, mixtures of 800 g were loosely spread about $\frac{1}{2}$ in. deep in aluminum pans 9 in. in diameter and treated in oxygen in the cooker at 29 psig for 24, 48, and 96 hours at a temperature of 150 F. Asphalts were recovered from both treated and untreated sand-asphalt mixtures by the Abson method (ASTM D 1850-65) using benzene as a solvent and were tested for viscosity and chemical analysis. The results are given in Table 5.

TABLE 5
PROPERTIES OF ASPHALTS RECOVERED FROM PRESSURE-OXYGEN TREATED SAND-ASPHALT MIXTURES

Asphalt Cement ^a	Asphalt (%)	Hours Aging	Viscosity, 77 F (megapoises)	Complex Flow "C"	Relative Viscosity	Asphaltenes (%)	Oxygen (%)
1-O	0	0	2.10	0.901	1.00	18.8	0.79
1-Re	2	0	8.80	0.754	4.20	23.4	1.42
		24	9.40	0.510	4.48	24.5	1.53
		48	14.50	0.364	6.90	24.6	1.62
		96	17.00	0.287	8.10	25.1	1.63
2-O	0	0	1.90	0.781	1.00	14.4	0.48
2-Re	2	0	6.80	0.675	3.58	18.7	1.11
		24	10.6	0.325	5.59	21.5	1.35
		48	10.9	0.287	5.74	21.4	1.45
		96	11.5	0.268	6.05	21.7	1.50
7-O	0	0	1.25	0.966	1.00	16.6	0.81
7-Re	2	0	7.00	1.040	5.60	17.0	0.95
		24	8.80	0.839	7.03	18.9	1.14
		48	11.50	0.700	9.20	19.6	1.34
		96	15.10	0.554	12.10	19.7	1.30
9-O	0	0	2.10	1.000	1.00	19.1	0.73
9-Re	2	0	5.40	0.933	2.57	20.1	1.06
		24	9.10	0.900	4.33	22.0	1.26
		48	11.5	0.781	5.48	23.0	1.36
		96	16.0	0.700	7.63	23.5	1.64
10-O	0	0	1.70	1.040	1.00	12.9	0.63
10-Re	2	0	10.6	0.615	6.24	18.4	1.20
		24	14.5	0.601	8.55	20.2	1.55
		48	15.0	0.424	8.83	19.2	1.61
		96	16.5	0.404	9.70	20.9	1.70
11-O	0	0	0.53	1.040	1.00	15.3	0.64
11-Re	2	0	1.78	1.040	3.36	19.5	1.07
		24	3.60	0.933	6.80	20.3	1.09
		48	4.30	0.933	8.12	22.1	1.30
		96	5.60	0.754	10.56	23.3	1.51

^aO = original asphalt, Re = recovered asphalt.

Figure 1. Viscosity vs time of aging in pressure cooker.

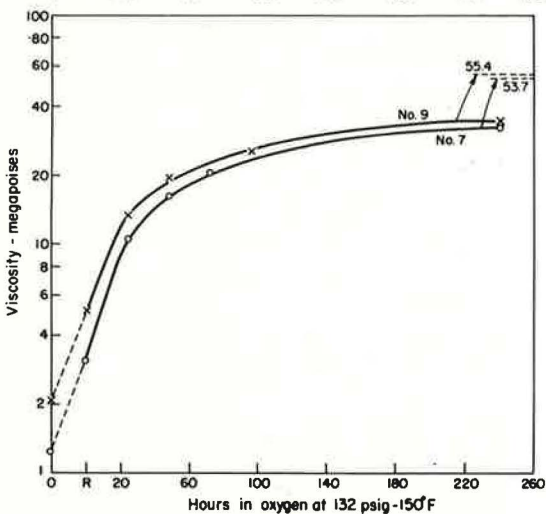
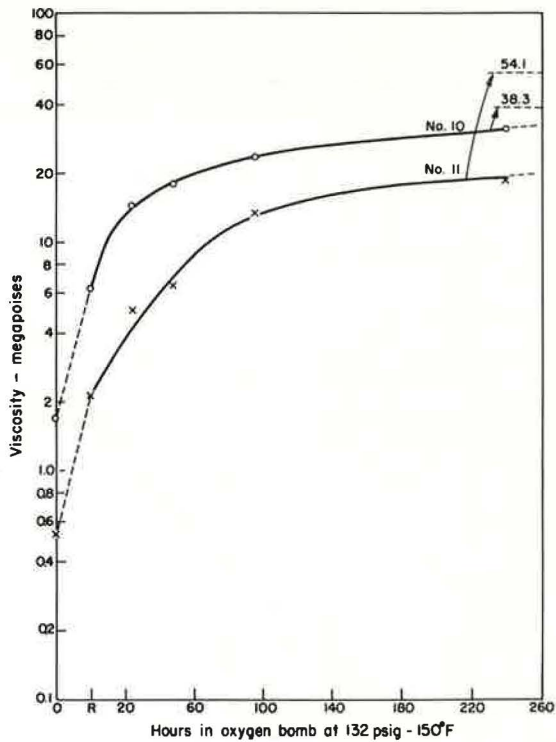
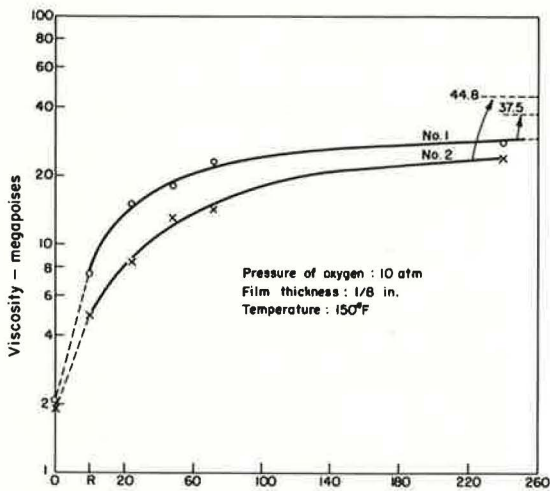
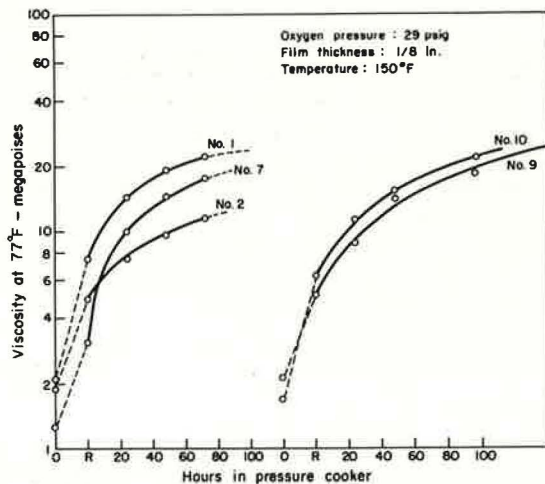


Figure 2. Viscosity vs time of aging in pressure bomb.

RESULTS

Behavior of Asphalt During the Pressure-Oxidation Treatments

The viscosity changes during the proposed durability test (the TFOT plus pressure-oxidation) are shown in Figure 1 for samples treated at 29 psig and in Figure 2 for samples treated at 132 psig, both in films of $\frac{1}{8}$ in. and at a temperature of 150 F. The general nature of the two sets of curves is similar, i.e., (a) effect of aging is reflected by increase in viscosity, and (b) the viscosity change appears to be a hyperbolic function of time of treatment, which is in good agreement with field findings (40-44).

Brown et al (40) have suggested the following to express mathematically the hardening of asphalts in the field:

$$\Delta Y = \frac{T}{a + bT} \quad (1)$$

or

$$\frac{T}{\Delta Y} = a + bT \quad (2)$$

where

ΔY = change in penetration (or softening point or ductility) with time T or the difference between the zero-life value and the value for any subsequent year,

T = time,

a = constant, the intercept of the Eq. 2 line on the ordinate,

b = slope of the line Eq. 2, and

$1/b$ = the ultimate change (limiting value of change) of penetration at infinite time.

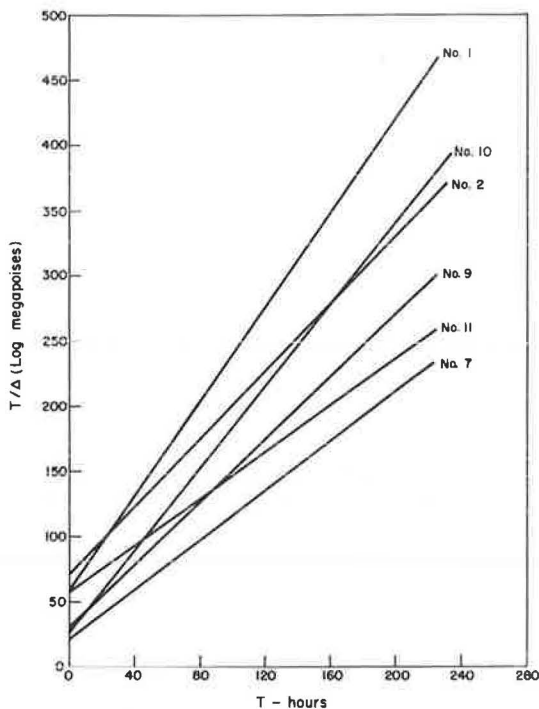


Figure 3. T/Δ log viscosity vs T.

Note that from the limiting values of change, $1/b$, the limiting values of properties can also be calculated. Both values could be used as numerical measures for comparison of the relative performances of asphalts. Thus an asphalt with a high value of limiting change of penetration or a low value of limiting penetration could be considered as inferior to one with a low value of limiting change of penetration or a high value of limiting penetration.

Limiting viscosities (viscosity at infinite time) for the six asphalts studied were calculated by applying Eq. 2 for viscosity change during the pressure-oxidation test at 132 psig. They are indicated by horizontal broken lines in Figure 2. The plots of T/Δ log viscosity vs T are shown in Figure 3. The concept of limiting value suggested by Brown et al is no doubt a useful tool in comparing performance or potential behavior of asphalts. However, when used as the only index in asphalt durability or quality evaluation it can be misleading. The reason is that, in reality, asphalt will not last forever, or to infinite time. More likely than not, the asphalt will reach a critical value of penetration or viscosity or ductility or other controlling

TABLE 6
COMPARISON BETWEEN TWO DURABILITY CRITERIA

Asphalt Cement	Limiting Viscosity at 77 F (megapoises)	Time to harden to 30 megapoises (hours)
1	37.5	250
2	44.8	310
7	53.7	160
9	55.4	140
10	38.3	220
11	54.1	360

property and fail before it reaches the limiting value or infinite time. Therefore, it is this critical value (or values) of the controlling property (or properties), and the time the asphalt in question takes to reach this value is of the utmost practical concern. It is entirely possible that an asphalt A that showed a higher limiting penetration than an asphalt B could reach a critical penetration quicker in service life and fail earlier than B, and would properly be considered a poorer asphalt.

For this reason, it is suggested that, instead of (or in addition to) limiting values of penetration or viscosity, the time an asphalt would take to reach a critical penetration—e.g., 20—or viscosity—say, 50 megapoises at 77 F—be calculated from the hyperbolic Eq. 2 and be used as an index to indicate the relative durability of asphalt. Limiting viscosities and times they would take to reach an arbitrarily selected critical viscosity of 30 megapoises at 77 F for the six asphalts during the pressure-oxidation test at 132 psig are given in Table 6.

Note that No. 10, having a lower limiting viscosity, would be considered a better asphalt than No. 11 by the limiting value concept. However, in reality, it may fail earlier than No. 11 because it will reach the critical viscosity of 30 megapoises earlier.

When comparing results from pressure-oxidation treatments between 29 psig and 132 psig, the apparent difference due to oxidation pressure is indicated by the lower viscosity increase during 29-psig treatment at all durations. However, there are other differences not shown in the graphs that are found in the comparison of viscosities between surface and bottom layers of asphalt treated under different pressures. Table 7 shows results of viscosity determinations on $\frac{1}{8}$ -in. films of asphalt No. 9 for 29-psig and 132-psig treatments, both at 150 F. Assuming that the viscosity increase under these conditions is due to oxidation, the data in Table 7 would seem to suggest:

1. Oxidation penetration progresses with time. The degree of difference in hardening between surface and bottom of the $\frac{1}{8}$ -in. asphalt films diminishes with time.
2. The difference in oxidation hardening between surface and bottom layers of the $\frac{1}{8}$ -in. film was higher for lower pressures than for higher pressures.
3. It is thus believed desirable to treat asphalt from the TFOT at higher pressures and longer durations, not only to achieve a higher acceleration rate but also to eliminate differences between surface and bottom layers of the treated asphalt films.

Other significant observations that can be made from the Tables and Figures are as follows:

1. The general shape of the hyperbolic curves during the pressure-oxidation treatment at 132 psig and 150 F can be defined with reasonable accuracy within 200 to 300 hours.

2. The treatment (132 psig and 150 F) is capable of accelerating the hardening process to an average of seven times that of the original asphalt in terms of absolute viscosity at 77 F in 24 hours, without deviating much from the field-hardening mechanism. This value is equivalent to about one year of hardening in the field under Iowa conditions (44). Higher acceleration factors can be obtained by increasing the oxygen pressure and time of oxidation.

TABLE 7
VISCOSITIES OF TREATED ASPHALT CEMENT NO. 9

Time (hours)	Viscosity at 77 F (megapoises) ($5 \times 10^{-2} \text{ sec}^{-1}$)			
	29 psig		132 psig	
	Surface	Bottom	Surface	Bottom
24	8.9	5.8	13.5	11.5
48	14.0	12.0	19.5	18.5
96	18.5	13.5	25.3	25.3
240	29.0	28.0	34.0	34.0

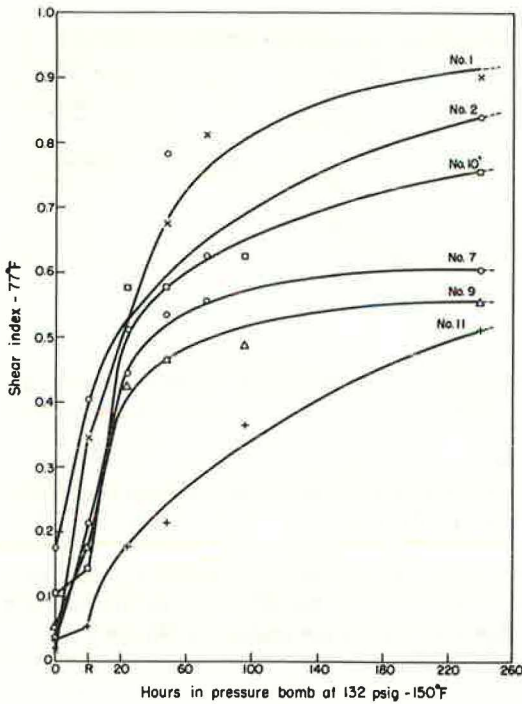


Figure 4. Shear index vs time of aging.

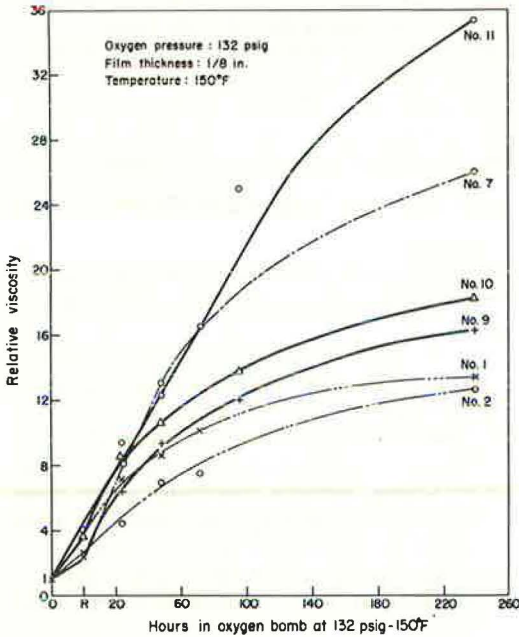


Figure 5. Relative viscosity vs time of aging.

3. The effect of the pressure-oxidation treatment during the proposed durability test is shown by decrease in the degree of complex flow "c" (46). This is also in agreement with field findings (41). The change in shear susceptibility or shear index of the asphalts during the proposed durability test at 132 psig is shown in Figure 4. The shear index is the tangent of the angle of log shear rate vs log viscosity plot. The behavior of asphalts in the proposed test procedure appeared to be in agreement with behavior of asphalts in Hveem's weathering machine and in the field (26).

4. The viscosity ratio or relative viscosity (ratio between treated or aged and original viscosities) was plotted against time in Figure 5. It will be noted that asphalt 11 hardened most by relative viscosity. However, if viewed from the absolute viscosity curves, it can be shown that, either by extrapolation or by calculation, asphalt 10 would reach a critical viscosity of, say, 30 megapoises at 77 F first and could be considered as the least durable. Thus the question arises as to the adequacy of using relative viscosity alone as the index of hardening for durability study purposes.

5. From the slopes of the curves in Figure 5, it is noted that the relative hardening during TFOT or during mixing may or may not reflect relative hardening during pressure-oxidation or in service aging. This illustrates the necessity of a durability test procedure that could simulate not only the changes in asphalt during handling but also changes during subsequent service life.

Asphaltene content changes in asphalt during pressure-oxidation tests are shown in Figures 6 and 7. The increase in asphaltenes also decreased with time. Effects of aging were also indicated by the decrease in oils and increase in percent oxygen in treated asphalts.

Effects of Pressure Variation on Pressure-Oxidation Treatment

The effects of oxygen pressure during the pressure-oxidation test on viscosity and asphaltene content changes for asphalts 9, 10, and 11 are given in Table 4. Data in Table 4 were obtained from TFOT residue, treated in the pressure bomb for

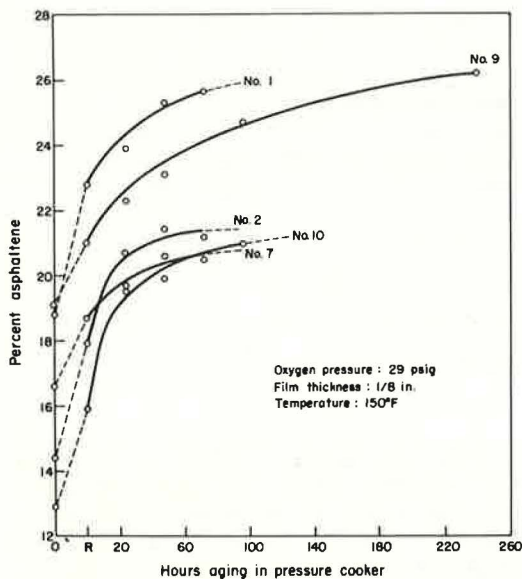


Figure 6. Asphaltene content vs time of aging.

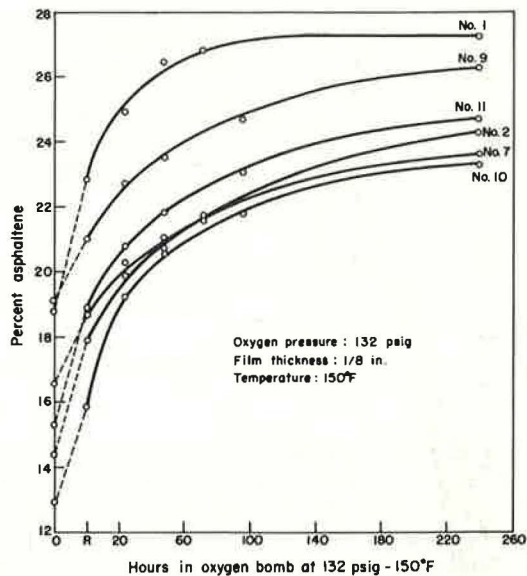


Figure 7. Asphaltene content vs time of aging.

24 hours at 150 F and in films of $\frac{1}{8}$ in. Viscosity is plotted against oxygen gage pressure in Figure 8. Percent asphaltene in asphalt vs oxygen gage pressure is shown in Figure 9. In both cases there appear to be linear relationships between property changes and oxygen pressure. The effect of oxygen on asphalt hardening is obvious when comparing viscosities between asphalt treated in a vacuum or nitrogen and treated in air or oxygen. However, the increase in viscosity is not very sensitive to an increase in oxygen pressure. An increase in oxygen pressure from 1 atm to 20 atm could increase the viscosity by only two to five times for the three asphalts studied. The effect of oxygen pressure on formation of asphaltenes during the test is more uniform for the asphalts studied, being about 1.5 to 2.0 percent over an increase of oxygen pressure from 1 atm to 10 atm. Nevertheless, an increase of oxygen pressure to 20 atm should accelerate the hardening process by a factor of about $1\frac{1}{2}$.

Behavior of Asphalts in Sand-Asphalt Mixtures During Pressure-Oxidation Treatments

The properties of asphalts recovered from the pressure-oxidation treated

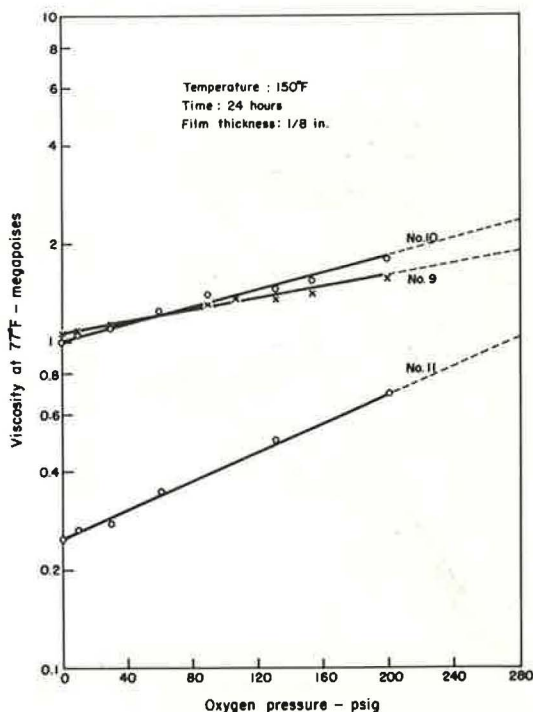


Figure 8. Effect of oxygen pressure on viscosity.

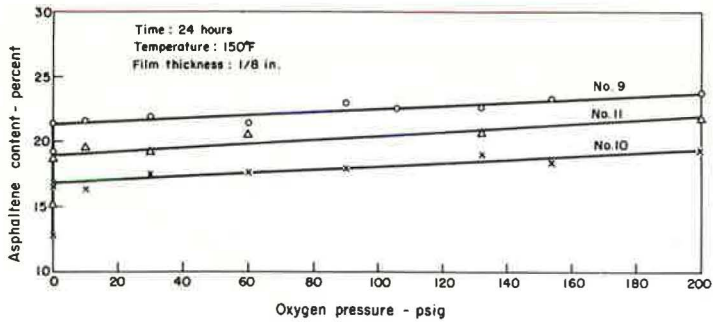


Figure 9. Effect of oxygen pressure on asphaltene content.

sand-asphalt mixtures are given in Table 5 and shown in Figures 10 and 11. Due to the relatively high mixing temperature (350 F) and low asphalt content (2 percent) used in the mixing process, the viscosity and asphaltene content increases during mixing were higher than those from the TFOT in a majority of the asphalts. However, the increases in viscosity and asphaltene content were relatively low compared with treated TFOT residues during the pressure-oxidation hardening process in spite of the thin films. The relative change and shape of the curves for the pressure-oxidation treatment were similar to those of the treated TFOT residues. Another difference found between treated sand-asphalt and TFOT residues was the marked percent oxygen increase in the asphalts recovered from the treated sand-asphalt mixtures.

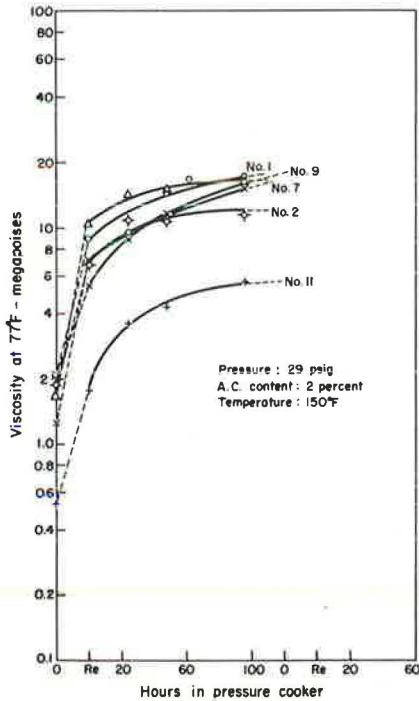


Figure 10. Viscosity of recovered asphalt vs time of aging.

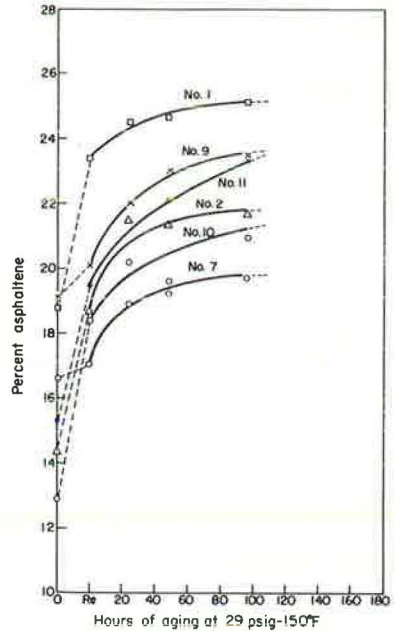


Figure 11. Percent asphaltene of recovered asphalts vs time of aging.

TABLE 8
 VISCOSITY AT 77 F ON TFOT RESIDUES TREATED IN
 OXYGEN BOMBS AT 132 PSIG, 150 F
 AND IN $\frac{1}{4}$ -IN. FILMS FOR 24 HR

Bomb	Asphalt 9	Asphalt 11
A	12.8	4.95
A	13.5	4.50
A	13.5	5.00
Average Bomb A	13.3	4.82
B	13.3	5.00
B	13.3	5.00
B	13.0	5.20
Average Bomb B	13.2	5.07
Grand average	13.2	4.15
Standard deviation	0.283	0.233
Maximum deviation from mean (%)	3.0	9.1
Average deviation from mean (%)	1.8	2.9

It was decided that the use of TFOT residue during the second phase treatment in the proposed durability test is superior to the use of a sand-asphalt mixture because (a) the TFOT procedure is simple and rapid, (b) less manipulation and fewer variables in the process contribute to better reproducibility, and (c) more asphalt can easily be obtained from the TFOT for more informative testings.

Repeatability

The repeatability and reproducibility of the TFOT were studied and reported

elsewhere (46, 47). The reproducibility of the pressure-oxidation test at 150 F and 132 psig oxygen pressure was determined by making repeat treatments under identical conditions of temperature, pressure, film thickness, and duration on one residue from TFOT on Asphalt 9 and one TFOT residue from Asphalt 11. Repeatability was measured by viscosity with a sliding plate microviscometer at 77 F and at a rate of shear of $5 \times 10^{-2} \text{ sec}^{-1}$. The results of six treatments on each asphalt are given in Table 8.

It is concluded that the pressure-oxidation test is reproducible. The variability or accuracy of the proposed durability test procedure is controlled by the variability and reproducibility of the TFOT and viscosity determinations.

CONCLUSIONS

The work reported in this paper may be considered as both a progress report and a testing of ideas and philosophy or a testing of the feasibility and logicity of the proposed durability test. The more significant conclusions are:

1. The pressure-oxidation procedure is considered sound and reproducible. The procedure is simple and the conditions can be easily controlled.
2. The BPR Thin Film Oven Test is superior to the sand-asphalt mixture recovery method in simulating the first-stage hardening in asphalt. The reasons are that (a) it is simple, rapid, and well established; (b) the facilities are inexpensive; (c) with fewer variables the results have better reproducibility; and (d) more asphalt can easily be obtained for testing, not only for viscosity, but for chemical changes, ductility, brittleness, etc. The availability of material for testing, in addition to viscosity measurement, is considered important until a test or property of asphalt is found that can truly represent or define the deterioration of asphalt completely and reliably.
3. The procedure is capable of accelerating the hardening process to an average of seven times that of the original asphalt in terms of absolute viscosity at 77 F in 24 hours, without deviating much from the hardening mechanism. This value is equivalent to about one year of hardening in the field under Iowa conditions. Higher acceleration factors can be obtained by increasing the oxygen pressure and time of oxidation. The exact laboratory acceleration equivalency factors or curves have to be established through field correlation.
4. Differences exist among asphalts in the rate and degree of hardening during the pressure-oxidation procedure. Therefore, the procedure can distinguish between asphalts that are susceptible to hardening and those that are not.
5. The viscosity increase or hardening in the pressure-oxidation test is a hyperbolic function of time. This is in good agreement with actual asphalt hardening in service (40-44). It is believed that a definite correlation can be established, at least on a local basis, between field hardening and performance of asphalt and the proposed laboratory durability test.
6. Continued study into the next phase of the durability test investigation—i.e., field correlations—is necessary and warranted in order that information obtained can be put into useful and applied form in asphalt paving design and quality control. It will be noted

that, in the planned future study, a new pressure vessel will be designed to hold eight 5½-in. diameter TFOT pans so that the TFOT residues can be treated in oxygen directly without transferring and more sample will be available for additional tests such as ductility and Fraass brittle point. Treatment will be made both in 10 and in 20 atmospheres oxygen pressure up to 240 hours.

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Viscoelastic Response of Aged Asphalt Cements

KAMRAN MAJIDZADEH, Department of Civil Engineering, Ohio State University, and
HERBERT E. SCHWEYER, Department of Chemical Engineering, University of Florida

The viscoelastic response of aged and unaged asphalt cements at 32 F was investigated. It has been known that aging of asphalt cements results in an increase in viscosity and degree of non-Newtonian behavior. However, the relative change in viscosity alone is not sufficient to characterize the durability of asphalt cements and the response of these materials under severe temperatures and loading conditions. To analyze aging phenomena from a viscoelastic point of view, cylindrical asphalt specimens were subjected to a creep test and strain-time data were obtained. Using curve-fitting techniques, the viscoelastic parameters characterizing aged and unaged asphalts at the selected temperature were calculated. The dynamic response of the asphalts was obtained by transforming the strain-time data into frequency domains.

The viscoelastic analysis indicates that aging results in the development of an initial elastic deformation mechanism and an increase in the coefficient of viscous traction. Similarly, it is shown that the storage modulus $E'(\omega)$ and phase angle are greatly affected by aging conditions. Due to the limitations of a standard aging index, to include the effect of aging on other deformation mechanisms, a dynamic aging index is proposed and its merits are discussed. The results of chemical analysis and rheological and durability tests on these asphalts are also presented.

•THE material characteristics responsible for the complex physicochemical changes occurring in bituminous mixtures have been subject to extensive studies ever since asphalt paving became useful. Because of the importance of aging phenomena on the life of a bituminous pavement, researchers have directed their studies toward the effects of aging on the properties of binder as well as the mixture itself. These durability studies, however, have been mostly confined to analyzing the changes in the properties of asphaltic binder, since it is this main constituent that contributes to the cohesiveness and adhesiveness of the mixture. The aging of the binder generally results in loss of adhesiveness, reduction of ductility, and increase in brittleness, and then eventually leads to a reduction in serviceability under induced traffic and climatic conditions.

In searching for a simple engineering tool for the analysis of aging phenomena, as well as to reveal the basic mechanisms involved in asphalt durability, three distinct approaches have been utilized by asphalt technologists encompassing physical, chemical, and rheological subject areas.

The simple physical tests such as penetration, softening point, and ductility, which are used by highway engineers as a measure of consistency, have yielded valuable information with respect to aging. The results of laboratory and field studies have indicated that the penetration of asphalt cement in the bituminous mixture drops significantly during mixing operations and the service life (1, 2, 3, 4). The occurrence of cracking of

the bituminous surfaces has also been found to be related to the drop in the penetration of the bituminous binder. The decrease in the ductility and the increase in the softening point temperature due to aging also result in the brittle behavior of bituminous mixtures and a loss of load-carrying capacity (5, 6). Based on these field and laboratory observations, the thin film oven test and other tests have been developed to evaluate the durability of asphaltic materials (7, 8). However, it should be noted that these tests are largely empirical in nature, and it is rather difficult to establish a characteristic index relating the results of these tests, nor has it been possible to incorporate aging indices such as percent loss in penetration in any rational pavement design method.

In the physicochemical approach to the analysis of durability, extensive studies have been conducted to reveal the chemical reactions and mechanisms responsible for aging as well as to determine the quantitative changes in the chemical composition of the binder (9, 10, 11, 12). The controlled laboratory experiments conducted to elucidate the factors affecting durability have indicated that four basic mechanisms are involved in the aging phenomena: (a) evaporation of volatile components, (b) oxidation, (c) age hardening due to the development of internal structures, and (d) polymerization. It is obvious that other secondary mechanisms might also be involved. However, it is not the intent of this report to investigate the relative significance of these aging mechanisms and their methods of evaluation.

The physicochemical studies have conclusively indicated that aging results in changes in the colloidal structure of the binder and the proportions of chemical components and, possibly, in the formation of a complex internal structure. It has been frequently reported that aging in the bituminous binder has resulted in a substantial increase in the percent of asphaltene content (13, 14, 15, 16).

Investigations by Moavenzadeh and Stander have also shown that the increase in percent asphaltene content due to aging is related to the change in the flow characteristics as well as to the molecular weight distribution. At an earlier date Majidzadeh and Schwyer (17), investigating the non-Newtonian behavior of asphalts, had shown that structural changes occurring in the binder due to shear deformation might be related to the asphaltene content. These investigators, observing the variations in the magnitude of reaction rate equilibrium constant and the size of flow units among different asphalts, have also stated that the asphaltene content is one of the major parameters controlling the flow characteristics. However, other chemical components as well may contribute to the rheological properties of bituminous binder. Recently, Moavenzadeh (18), studying the fracture mechanics of asphalt cements at low temperatures, again has confirmed the significance of asphaltene content and the effect of chemical changing due to aging on the magnitude of critical strain energy release rate. It has been indicated that the asphalt, which showed a relatively large gain in the asphaltene content due to aging, also exhibited greater change in the magnitude to critical strain-energy release rate. In short, the physicochemical approach to the aging phenomenon emphasizes the effects of aging on the chemical components of the binder which might significantly alter the rheological properties of bituminous material. However, realizing the complex chemical structure of asphalt, greater effort is needed to understand all the micromechanics involved in aging phenomena.

In the rheological approach to the aging of asphalts, the basic objective is to relate the fundamental flow characteristics of the binder to the aging mechanism. In earlier attempts the change in viscosity and in the non-Newtonian constant due to aging have been investigated and indices for durability of asphalt have been established (19). In these analyses aging indices, AI, have been proposed as the ratio of aged and unaged viscosity at a selected reference temperature. Moavenzadeh and Stander (15), using the Arrhenius viscosity model, have related this index to the free energy of activation; that is,

$$\text{Aging Index, AI} = \frac{\eta_{\text{aged}}}{\eta_{\text{unaged}}} = \exp \left[\left(\Delta F_a - \Delta F_u \right) / RT \right] \quad (1)$$

where indices a and u refer respectively to the aged and unaged conditions, and the term ΔF is the free energy of activation. The other terms are defined in the list of

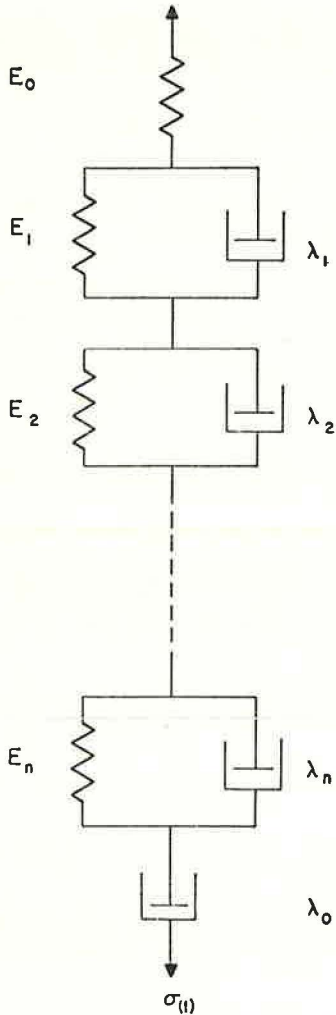


Figure 1. A rheological model.

formation mechanisms can be represented by one mechanical model, shown in Figure 1. Mathematically, this model corresponds to the operator equation

$$\epsilon(t) = \left[\frac{1}{E_0} + \frac{1}{\lambda_0} \frac{d}{dt} + \sum_{i=1}^n \frac{\frac{1}{E_i}}{\tau_i \left(\frac{d}{dt} + \frac{1}{\tau_i} \right)} \right] \sigma(t) \quad (3)$$

where n refers to the number of Kelvin elements corresponding to the delayed elastic deformation mechanism and τ_i is the retardation time, λ_i/E_i . For the materials used in this study, it has been shown that two Kelvin elements will suffice, expressing the viscoelastic response of asphalts. As shown in an earlier paper (20), some asphalt cements, depending on the composition and test temperature, may not exhibit any initial elastic deformation, represented by modulus E_0 .

To investigate the effect of aging on the response of asphalts, the material constants given in Eqs. 2 and 3 can be evaluated using a creep test $\sigma = \sigma_0 = \text{constant}$. The method

nomenclature at the end of this section. It is unfortunate that the data presented by Moavenzadeh, due to the scatter of experimental points, did not result in a mathematical expression relating the aging index, temperature, aging condition, and thermodynamic variables. Nevertheless, it should be pointed out that the results show only a trend that could be approximated by a linear relation at certain aging conditions. A major limitation to the use of the aging index as a criterion for the durability of asphalts is the accuracy of the determination of viscosities at low temperatures. Since, as the environmental condition approaches the glass transition temperature and asphalts become more non-Newtonian and complex in nature, the significance of the aging index as a criterion for material selection becomes more apparent (16, 18). However, the determination of AI, which is based on viscosity measurement at these low temperatures, even with the most sophisticated viscometer is not considered possible with any degree of confidence.

To overcome the difficulty of obtaining an accurate measure of aging indices at low temperatures, the method of viscoelastic analysis has been utilized in this paper. Previously, Majidzadeh and Schweyer (20) had shown that asphalt cements at low temperatures, similar to polymeric systems, are characterized by linear viscoelastic equations of state represented in differential operators form given by

$$\left[a_n \frac{d^n}{dt^n} + \dots + a_0 \right] \sigma = \left[b_n \frac{d^n}{dt^n} + \dots + b_0 \right] \epsilon \quad (2)$$

where $a_n \dots a_0$ and $b_n \dots b_0$ are material parameters related to the distinct deformation mechanism observed in viscoelastic materials. By proper determination of these constants, the viscoelastic response as well as the factors affecting these behaviors, such as aging, can be investigated. For the asphalt cements, it had been previously reported that the de-

of successive approximations and curve fitting techniques (20, 21), as used in the previous study, has been used to determine these constants. To study the dynamic response of the materials, the observed strains are transformed into a frequency (ω) domain, written as

$$\epsilon^*(i\omega) = \frac{\sigma_0}{i\omega} \left[\frac{1}{\frac{E_1}{\lambda_1} + i\omega} + \frac{1}{\frac{E_2}{\lambda_2} + i\omega} + \frac{1}{i\omega\lambda_0} + \frac{1}{E_0} \right] \quad (4)$$

For a constant stress, σ_0 , applied at $t = 0$, where $\sigma^*(\omega) = \frac{\sigma_0 i}{\omega}$, the complex dynamic modulus is obtained by

$$E^*(i\omega) = \frac{1}{\frac{1}{E_1 + i\omega\lambda_1} + \frac{1}{E_2 + i\omega\lambda_2} + \frac{1}{i\omega\lambda_0} + \frac{1}{E_0}} \quad (5)$$

This modulus in turn can be resolved into a real part or storage modulus $E'(\omega)$ corresponding to the stored energy and an imaginary part or loss modulus E'' representing the energy loss in the system. Similarly, the phase angle, ϕ , between stress and strain, which is a measure of the dissipation of the energy per cycle or internal damping, is given by

$$\phi = \tan^{-1} \frac{E''(\omega)}{E'(\omega)} \quad (6)$$

With respect to the derivation of an aging index criterion, the loss modulus $E''(\omega)$ is possibly of greater value than other viscoelastic parameters. In the field of polymer rheology a term designated as dynamic viscosity $\lambda'(\omega)$ has been defined as given by

$$\lambda'(\omega) = \frac{E''(\omega)}{\omega} \quad (7)$$

This parameter has been previously used by Sisko (23) to study the dynamic response of aged asphalt cements. It has also been shown that the relation existing between dynamic viscosity and frequency is very similar to that of steady state viscosity-rate of shear. This similarity is expected, since during the deformation process coiled molecules experience oscillatory forces with a frequency proportional to the rate of shear even though the material is only subject to a shear force. That is, the randomly coiled molecules in a viscous material rotate as they undergo a translatory motion. The dynamic viscosity at very low frequency approaches the ordinary steady state flow viscosity, λ . With increasing frequency λ falls monotonically, reaching values much smaller than steady state flow.

Then, in analogy with the aging index for the steady state flow, a dynamic aging index, $AI(\omega)$, can be defined as

$$AI(\omega) = \frac{\lambda'_a(\omega)}{\lambda'_u(\omega)} = \frac{\left(\frac{E''(\omega)}{\omega} \right)_a}{\left(\frac{E''(\omega)}{\omega} \right)_u} = \frac{E''_a(\omega)}{E''_u(\omega)} \quad (8)$$

where a and u refer to the aged and unaged conditions. At low frequencies, where the dynamic viscosity approaches that of steady state flow, $AI(\omega)$ equals the aging index (AI) of Eq. 1. However, with increasing frequency, the aged asphalt exhibits a more elastic response compared with that for the unaged specimens, and $AI(\omega)$

decreases substantially. Therefore, at a desired frequency, the $AI(\omega)$ might yield valuable information with respect to the effect of aging on the asphaltic materials.

Nomenclature

- AI = aging index, η_a/η_u
 $AI(\omega)$ = dynamic viscosity aging index $E_a''(\omega)/E_u''(\omega)$
 a, b = constants
 ϵ = strain response
 E = moduli; E' is real or the storage modulus and E'' is imaginary or the loss modulus
 ΔF = energy of activation, subscript a for aged sample, subscript u for original sample
 i = any i th item
 λ = viscosity
 $\lambda'(\omega)$ = dynamic viscosity
 n = number of Kelvin elements
 η = viscosity, subscript a for aged sample, subscript u for original sample
 o = initial condition
 ϕ = phase angle
 R = universal gas constant
 σ = stress
 T = absolute temperature
 t = time
 τ = retardation time λ/E
 ω = frequency
 * indicates transformed equation

MATERIALS AND TEST PROCEDURE

In this investigation four types of asphalts selected from different sources have been utilized. These asphalts were aged according to the standard procedure for thin film oven test at 325 F for a period of 5 hours. After aging, the penetration, ductility, and viscosity of these asphalts were determined and compared with the original test properties. The results of the thin film oven test and the relative changes in consistency are given in Tables 1 and 2.

The effect of aging on the chemical composition of asphalts was also studied. The aged and unaged asphalts were separated into four components using the Schwyer-Chipley method of analysis (22). The results of this chemical analysis (Table 3) indicate that aging causes an increase in the percent asphaltene content, as well as changes in the proportions of other components. The asphalt cement designated S63-13 is an air-blown asphalt with a high percentage of paraffinic-naphthenic (PN) component. The aging, as shown in Table 3, results in a small increase in percent PN and the light aromatic fraction (LA) of this asphalt. On the other hand, asphalts S63-6 and S63-9 exhibit a substantial gain in their percent of LA fraction and asphaltene content. Asphalt S63-4, in contrast to the other asphalts, showed some reduction in the LA fraction due to aging. It is also observed that the PN component of asphalts S63-4, S63-6, and S63-9, in contrast to S63-13, was slightly reduced. It should be pointed out that work is in progress at present to relate these chemical changes with the flow characteristics of asphalts. Since the results of these correlations have not yet been completed, no attempt will be made in this paper to relate composition to the aging phenomenon.

For rheological studies, cylindrical specimens with diameter of 1.3125 in. and a height of 2.816 in. were prepared, using the Harvard miniature molds. Asphalt cements first were heated to a liquid state and poured into the molds, which were then cooled down gradually over a period of three hours to 32 F temperature. The specimens were cured at this temperature for an additional two hours. The solidified specimens were then removed from the 32 F water bath and the excess asphalt was removed to obtain a cylinder with the specified height. These samples were then transferred to a

TABLE 1
PROPERTIES OF ASPHALT CEMENTS

Property	Smackover S63-4	Florida AC-8 S63-6	Steam Refined Intermediate S63-9	Air Blown, Low Sulfur Naphthenic S63-13
Penetration, 77 F 100 g/5 sec	77	91	84	91
Softening point, deg F	116	118	115	119
Ductility, 77 F, cm	125	140+	200+	170
Specific gravity, 60 F/60 F	1.021	1.037	1.033	0.988
Sulfur, %	3.56	5.83	4.24	0.69
Hexasphaltene, %	12.9	19.4	16.8	12.8
Glass transition Temperature, deg F	-11.8	-12.2	-13.9	-10.8

TABLE 3
COMPOSITION ANALYSIS OF AGED AND UNAGED ASPHALTS, PERCENT

Component	S63-4		S63-6		S63-9		S63-13	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Paraffinic- Naphthenic	9.8	8.6	8.0	7.5	13.1	11.1	23.9	24.9
Light aromatic	34.6	31.5	26.4	32.7	28.3	35.7	23.6	23.9
Heavy aromatic	43.9	42.8	46.0	37.4	43.7	33.4	37.1	32.2
Hexasphaltene	10.9	14.1	17.8	22.0	15.8	19.2	12.1	15.1

TABLE 2
PROPERTIES OF ASPHALT CEMENTS BEFORE AND AFTER THIN FILM OVEN TEST

Identification	Penetration at 77 F			Ductility at 77 F		Viscosity at 140 F		
	Original	Residual	% Ret.	Original	Residual	Original	Residual	Ratio
S63-4	77	56	72.7	125+	125+	1912	3778	1.98
S63-6	91	54	59.3	140+	145	2579	6632	2.57
S63-9	84	54	64.3	150+	150+	1704	4318	2.53
S63-13	91	64	70.3	170	105	1726	4002	2.32

TABLE 4
VISCOELASTIC PARAMETERS OF AGED AND UNAGED ASPHALTS AT 32 F
(All numbers should be multiplied by 10⁸)

Model Parameters	Condition	S63-4	S63-6	S63-9	S63-13
E ₀ , dynes/cm ²	Aged	1.204	0.895	2.023	1.340
	Original	(-)	(-)	(-)	(-)
λ ₀ , poises	Aged	144.6	83.63	92.99	56.66
	Original	113.3	73.68	50.84	110.6
E ₁ , dynes/cm ²	Aged	0.4959	0.3043	0.3699	0.2727
	Original	0.4688	0.2658	0.3725	0.2510
λ ₁ , poises	Aged	94.07	47.38	48.88	24.68
	Original	66.14	53.16	32.34	41.60
E ₂ , dynes/cm ²	Aged	0.9146	1.098	0.9410	0.6466
	Original	1.735	0.7081	0.9292	0.5944
λ ₂ , poises	Aged	11.56	19.14	6.413	7.609
	Original	24.47	14.75	9.308	7.753

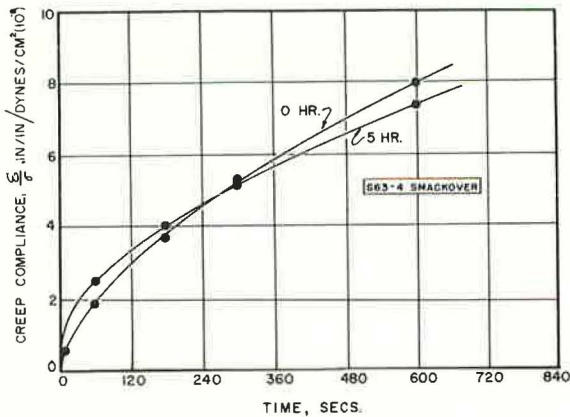


Figure 2. Effect of aging on creep response at 32 F of certain asphalt cements.

elastic response as well as other changes in the flow mechanism (Fig. 2). The presence of an elastic deformation mechanism in aged specimens might be attributed to the formation of certain molecular bonds similar to crosslinking phenomena observed in rubber-like materials. It has been recognized that aging results in structural changes in asphalts, classically known as sol-gel transformation. These structural effects are often associated with changes in the composition, such as the increase in percent asphaltene and changes in other components shown in Table 3.

The other effect of aging is on the viscous flow characteristics of asphalts, which is evident from the increase in the coefficient of viscous traction as measured by the slope of the steady-state flow portion of the creep curves. An increase in viscosity is often taken as an indication of aging susceptibility of asphalts and is expressed by the aging index as previously discussed. Among all the asphalts studied, only one has exhibited a decrease in viscosity. This asphalt (S63-13) had previously exhibited certain peculiar rheological behavior (20).

Dynamic Response

As discussed earlier, the dynamic response of asphalts can be calculated using the viscoelastic parameters obtained from a creep test. In Figures 3, 4, 5, and 6 the variations of the dynamic moduli and phase angle with frequency and aging condition are shown. Similar relations have also been obtained for other asphalt cements.

The comparison of these dynamic moduli indicates that aging results in significant changes in the dynamic response of asphalt cements. The storage modulus $E'(\omega)$, representing the energy stored in the system per cycle of deformation, increases with aging as well as frequency as evaluated by the proposed constitutive equation. The increase of $E'(\omega)$ with aging is due to the presence of the instantaneous elastic deformation and stiffer dashpot flow mechanisms which contribute to the behavior of asphalts. At higher frequencies the storage modulus approaches an ultimate value of the order of 10^8 dynes/cm². Values of a similar order of magnitude had been previously reported for asphalt cements (23). Similarly, the loss modulus $E''(\omega)$, representing the energy loss per cycle of deformation, is greatly affected by aging and frequency. Aged asphalt cements which exhibit initial elastic response and stiffer dashpot responses (λ_0 in Table 4) dissipate less energy per cycle than unaged materials. This difference becomes more pronounced at the higher frequencies, where aged asphalts approach a perfectly elastic body. At low frequencies, where an ample time is available for the molecular motions, and the energy loss $E''(\omega)$ becomes proportional to frequency, the behavior of viscoelastic materials approaches that of steady-state flow conditions. In these frequency ranges the aged asphalts exhibit greater amounts of energy loss compared with unaged specimens.

controlled-temperature water bath kept at 32 F and were cured there for three hours before testing. For viscoelastic characterization, prepared specimens were subjected to a creep test, constant stress σ_0 at $t = 0$, and appropriate strain-time data were analyzed as previously (20).

DISCUSSION AND ANALYSIS OF RESULTS

Creep Response

The viscoelastic analysis of creep data for both aged and unaged asphalts indicates that parameters describing the material characteristics are significantly affected by aging (Table 4). The analyses reveal that aging results in development of an instantaneous

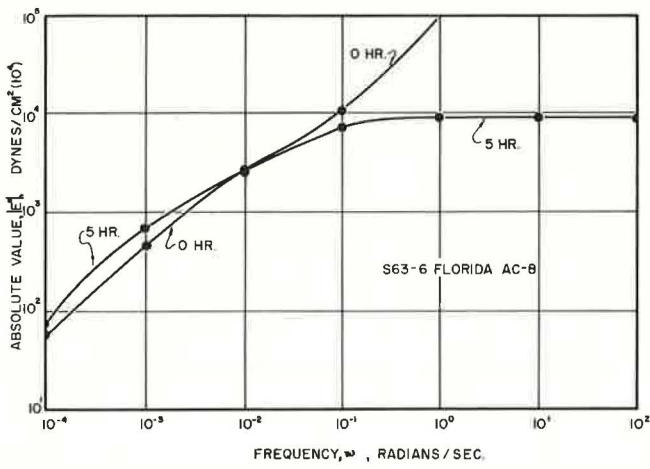


Figure 3. The complex modulus of original and aged (TFOT) Florida asphalt cement.

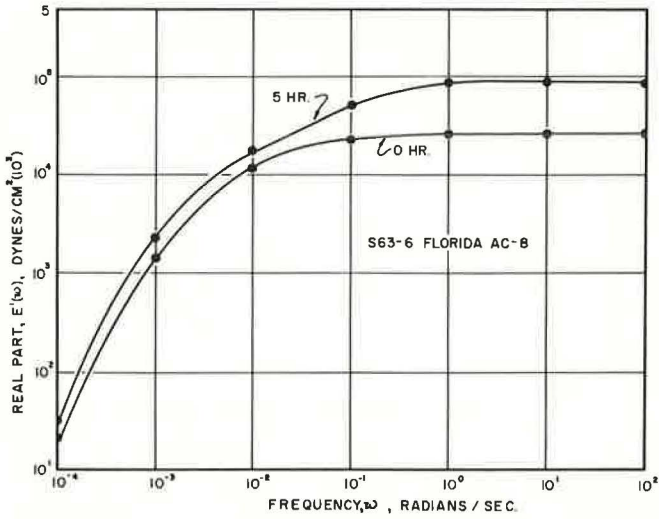


Figure 4. The storage modulus of original and aged (TFOT) Florida asphalt cement.

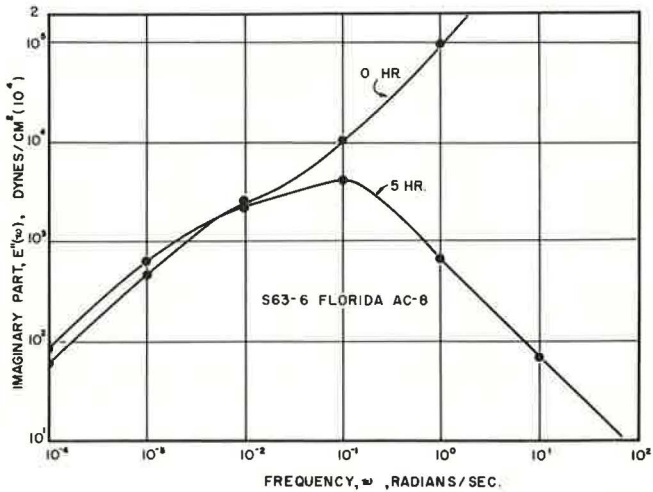


Figure 5. The loss modulus of original and aged (TFOT) Florida asphalt cement.

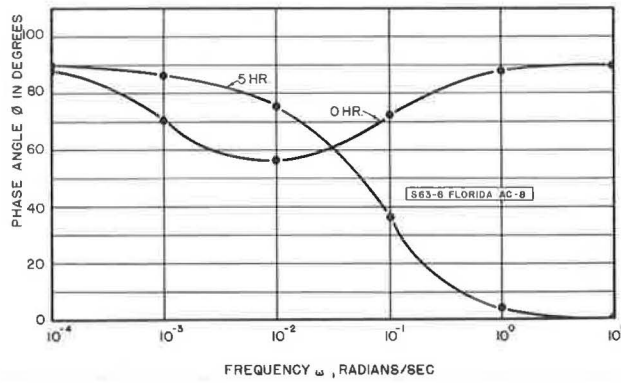


Figure 6. The phase angle of original and aged (TFOT) Florida asphalt cement.

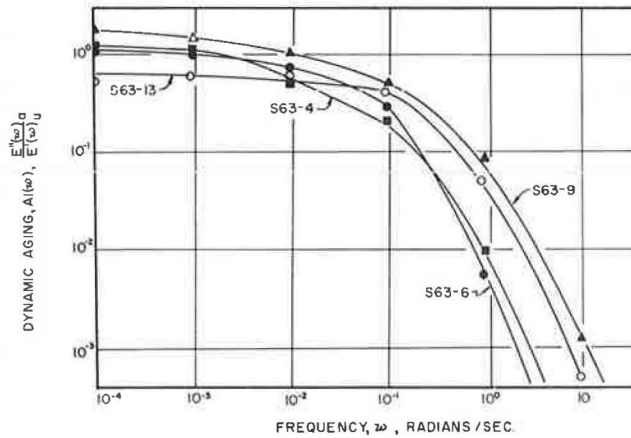


Figure 7. Variations of dynamic aging index with frequency.

TABLE 5
DYNAMIC AGING INDEX OF FOUR ASPHALT CEMENTS
AT VARIOUS FREQUENCIES

Frequency, Radians/Sec	AI(ω)			
	S63-4	S63-6	S63-9	S63-13
1×10^{-4}	1.219	1.134	1.826	0.514
1×10^{-0}	1.05	1.096	1.621	0.646
1×10^{-2}	0.56	0.768	1.062	0.629
1×10^{-1}	0.20	0.293	0.502	0.519
1×10^0	0.900×10^{-2}	0.675×10^{-2}	9.6×10^{-3}	5.0×10^{-2}
10	0.98×10^{-4}	0.685×10^{-4}	12.14×10^{-4}	5.5×10^{-4}
10^2	0.98×10^{-6}	0.685×10^{-6}	121.7×10^{-6}	5.5×10^{-6}

The variation of phase angle with frequency also explains in a similar manner the differences in the storage and dissipation of energy per cycle of deformation. At low frequencies the stress and strains in both aged and unaged asphalts are 90 deg out of phase, corresponding to the presence of a dashpot flow mechanism. However, at higher frequencies, the phase angle of aged asphalt approaches zero, indicating a perfectly elastic response. The unaged asphalt, on the other hand, due to the immobilization of a retarded deformation mechanism, still exhibits a viscous flow behavior which is represented by a 90 deg out-of-phase angle. At intermediate frequencies, the variations of dynamic moduli and phase angle depend on the differences in the viscoelastic responses and the relative contribution of different flow mechanisms.

Dynamic Aging Index

In the discussion of the aging phenomena, it was pointed out that aging susceptibility of asphalts is commonly measured by an aging index, which is the ratio of aged and unaged viscosities at a standard temperature. It has also been shown that asphaltic binders during their service life become harder and may eventually result in severe road failures. The aging index, then, should reveal these detrimental hardening tendencies and predict the possible fatigue of bituminous mixtures under adverse service conditions. However, this aging index has certain limitations. First, it has been shown in this paper that the aging not only changes the viscosity of the binders, but also alters the initial elastic (related to E_0) and delayed elastic (related to E_n) responses of asphalts; therefore, the relative viscosity change is not a sufficient criterion for the aging phenomena. Second, the fatigue type failures of road surfaces which might be due to asphalt hardening never occur under steady-state deformation. Rather, they are always associated with the repeated nature of wheel loads. Thus, the aging index should be related to the frequency of load applications as well as to the increase in the resistance to steady-state deformation. Third, the loss of flexibility and the subsequent road cracking are more pronounced at low temperatures where the present aging index cannot be evaluated accurately using conventional rheometers.

Considering the foregoing discussions, a dynamic aging index as given by Eq. 8 has been utilized in this paper. In Figure 7, the dynamic aging index calculated for the asphalts studied has been plotted as a function of frequency (Table 5). As observed at low frequencies, when the asphalt response approaches that of steady-state flow, the dynamic aging index reaches a limiting value that is a function of the steady-state viscosity. At this range of frequency, there is little difference in the aging susceptibility of the four asphalts. However, at higher frequency ranges, the dynamic aging index is reduced considerably and the effect of aging and the type of asphalt on this index becomes more apparent. The smaller values of the dynamic aging index in this range indicate changes to a more elastic behavior of asphalt cements. Therefore, the magnitude of the aging index at high frequencies can be taken as a measure of the increase in the stiffness of asphalts due to aging and might have many applications in the pavement performance analysis.

SUMMARY AND CONCLUSIONS

In this investigation the effect of aging on the viscoelastic response of four different asphalt cements tested at 32 F was studied. Cylindrical specimens were subjected to a constant stress level and the strain-time data were obtained. These data were analyzed and the viscoelastic responses describing the deformation mechanism of asphalts were determined. The time responses of the asphalts were then transformed into a frequency domain and appropriate dynamic moduli were calculated. The following conclusions can be drawn from this study:

1. Aging phenomena result in the development of instantaneous elastic response as well as other changes in the deformation mechanisms of asphalts such as steady-state flow.
2. The dynamic responses of asphalts are significantly affected by aging. At high ranges of frequency, due to the presence of instantaneous elastic response, the dynamic behavior of aged asphalts approached that of perfectly elastic bodies.

3. The limitations of the steady-state aging index are discussed and a dynamic index is utilized to include the effect of repeated loading.

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Tensile Strength of Asphalt Films and Road Life

A. W. SISKO, American Oil Company, Whiting, Indiana

The tensile strength of thin films of 12 asphalts in different conditions of aging—unaged, aged in the thin film oven test, and aged in roads for up to eleven years—increased by as much as 140 percent as the temperature decreased from 80 to 0 F. Experimental conditions insured failure by brittle fracture. At low temperatures, TFOT aging produced no significant differences in the tensile strength of the asphalts but road aging produced large differences. The tensile strength of road-aged asphalts appears unrelated to asphalt source or composition.

• ASPHALT roads can crack under the tensile stresses produced by traffic, by changes in the subgrade, and by thermally induced expansions and contractions. Road life can therefore be expected to depend on how long the thin asphalt films in the road can resist tensile rupture. Nonetheless, little or no work has been done to determine how aging affects the tensile strength of asphalt in a road. Part of the difficulty has been the lack of samples that would permit significant correlation studies.

Tensile tests on asphalt concrete have shown that the locus of failure moves from within the film of asphalt between the stones to the asphalt-stone interface, and finally the stones fracture as the rate of loading is increased or the temperature is decreased (1). Since such tests do not clearly indicate the fracture properties of the thin, 5- to 15-micron, asphalt films themselves, alternative procedures have been developed to test the strength of thin films held between metal surfaces. A study of the variables in the latter test showed that the mode of failure of the films changes from ductile flow, through a mixed region, to brittle fracture with a decrease in temperature, a decrease in film thickness, and an increase in rate of extension, and that the strength of a film increases in the transition from the ductile to the brittle state (2). However, that study was made with a single, unaged asphalt and did not extend to temperatures low enough to reveal the maximum that must exist in the tensile strength of asphalt.

Twelve aged asphalts became available in the course of an investigation of the dynamic mechanical properties of asphalts in relation to road durability (3). Eleven came from the 1954-1955 survey of the Bureau of Public Roads (4, 5) and had been used to make roads which are 11 years old. The twelfth came from a 3-year-old road in Illinois. The roads are well distributed around the country and the condition of each was evaluated, using a standard rating form, by state highway personnel. The asphalts represented a variety of crude sources and manufacturing processes.

The tensile strength of the asphalt was determined at three stages of aging—unaged, aged in the thin film oven test (TFOT) (6), and aged in the road. The TFOT was run to reproduce approximately the condition of the asphalt in the new road after the hot plant mixing and laying operations.

It would not be unexpected if the extent of cracking in the roads did not correlate with the asphalt tensile strength. The roads were not uniformly made and therefore the thicknesses and moduli of the stone layers and the asphalt concrete layers varied from one road to another. Furthermore, the strain in the asphalt film depends on other factors such as the film thickness, the interlock between the stones, and the ambient temperature. Nevertheless, if the contribution of asphalt tensile strength to road life is to be determined, the earlier work (2) must be extended to include more asphalts and several

TABLE 1
PROPERTIES AND CHARACTERISTICS OF ASPHALT SAMPLES

Asphalt	BPR No. ^a	Location	Process ^b	Crude Source	Penetration at 77 F			Viscosity at 140 F, Kilopoises		
					Unaged	TFOT	Road	Unaged	TFOT	Road
1	92	California	V, S	California	89	47	29	1.41	3.70	25.0
2	39	Kentucky	—	—	88	51	18	1.66	4.74	114.0
3	—	Illinois	—	Midcontinent	78	46	38	1.46	4.80	9.4
4	19	Maryland	V	Venezuela	91	53	17	1.92	5.54	96.0
5	9	Massachusetts	V	Venezuela and Texas	91	51	22	1.82	5.08	16.0
6	62	Nebraska	V, P, B	Kansas, Oklahoma, Texas	85	55	57	1.61	4.58	5.0
7	71	Oklahoma	V, P, B	Midcontinent	82	54	46	1.62	2.72	3.9
8	97	Oregon	V, S	California	94	36	29	1.25	6.27	11.0
9	25	Tennessee	S	Venezuela and Mexico	85	51	24	3.00	11.10	390.0
10	74	Texas	V, P, O	Texas	93	64	28	1.16	2.12	29.0
11	185	Wisconsin	V, B, S	Midcontinent	78	48	28	1.47	3.29	43.0
12	114	Wyoming	V	Wyoming	94	54	48	1.27	3.37	2.4

^aSee references 4 and 5.

^bProcess codes: V = vacuum distillation; P = propane fractionation; B = blending different asphalt grades; O = blowing (oxidation); S = steam distillation.

conditions of aging, among them road aging. The data may provide a valuable background for future work.

EXPERIMENTAL

Samples

Table 1 gives the properties and characteristics of the asphalt samples. Eight crude sources and five processes are represented. Compared with the unaged samples, the viscosity of the TFOT samples increased by no more than a factor of five, indicating that the asphalts are representative of those currently being manufactured. The viscosity of the road asphalts is the average obtained with two samples extracted from different sections of the same pavement.

Table 2 gives the asphalt compositions determined by a combined solubility and chromatographic procedure. The asphaltenes were separated by insolubility in n-hexane. To obtain hard resins, soft resins, and oils, the asphalt was adsorbed on alumina and washed successively with n-hexane and ether. Asphaltenes varied from a low of 1 percent for the unaged Sample 10 (Texas) to a high of 37 percent for Sample 9 (Tennessee) extracted from the road. In general, asphaltenes increased with aging, hard

TABLE 2
ASPHALT COMPOSITION

Component ^a	Location	Unaged	TFOT	Road	Location	Unaged	TFOT	Road
A	California	15	19	24	Oklahoma	8	10	12
HR		28	25	30		26	27	32
SR		35	34	22		44	42	36
O		22	22	24		22	21	20
A	Kentucky	12	15	24	Oregon	15	20	21
HR		20	19	28		28	26	29
SR		40	39	24		30	28	26
O		28	27	24		27	26	24
A	Illinois	16	20	22	Tennessee	23	26	37
HR		20	20	24		18	19	18
SR		37	34	29		39	37	26
O		27	26	25		20	18	19
A	Maryland	19	22	24	Texas	1	1	3
HR		19	18	27		38	39	52
SR		36	35	29		41	40	26
O		26	25	20		20	20	19
A	Massachusetts	15	19	28	Wisconsin	14	16	26
HR		22	19	26		23	25	25
SR		36	39	27		39	38	26
O		25	23	19		24	21	23
A	Nebraska	11	14	15	Wyoming	15	18	18
HR		24	22	24		20	21	23
SR		39	38	35		43	40	35
O		26	26	26		22	21	24

^aComponent codes: A = asphaltenes, HR = hard resins, SR = soft resins, O = oils.

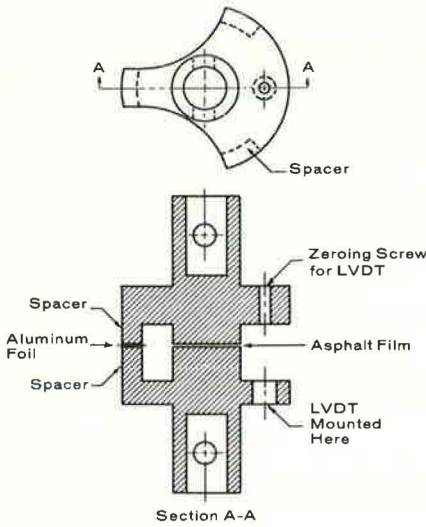


Figure 1. Sectional view of holder.

Equipment and Procedure

All tensile tests were performed on 0.0005-in. (13-micron) asphalt films in an Instron tester operated at an extension rate of 0.1 in./min. These conditions were selected to cause failure by brittle fracture.

The films were prepared between aluminum holders designed to produce a uniform film thickness by means of spacer legs ground and lapped to be coplanar with the surface of the holder in contact with the asphalt film. Figure 1 shows how spacers of aluminum foil are used to produce uniform films. The holders also provide a mounting for a Daytronic Model 103A-80 linear variable differential transformer (LVDT) extensometer. The Instron was equipped with an environment control chamber and with ball-and-socket joints similar to those used by Majidzadeh and Herrin (2).

Attempts to use holders with stone faces in contact with the film were unsuccessful. These holders were difficult to manufacture, and, at low temperatures, fracture occurred sometimes in the asphalt and sometimes in the stone.

To prepare a film, a small quantity of asphalt was spread on one of two holders that had been preheated to 250 F in an oven. Small squares of foil were quickly positioned on the spacer arms and the holders were clamped together in the position shown in Figure 1 with a C-clamp across each of the spacer arms. Four sets of holders were made up and each test was run in quadruplicate. The loaded holders were cooled for 30 minutes at room temperature and finally were held for an additional 30 minutes in the Instron chamber at the selected test temperature before testing.

Just before testing, the LVDT was attached and zeroed with the zeroing screw. Finally, the C-clamps were removed and the Instron tester started. The Instron recorder gave the breaking force and the carrier amplifier indicator of the LVDT gave the extension at break.

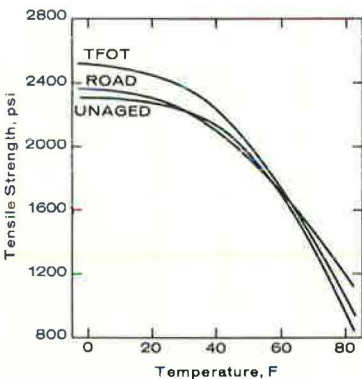


Figure 2. Dependence of tensile strength on temperature.

TABLE 3
EVALUATION OF ROAD CONDITION

Location	Cracking	Plastic Deformation	Ride ^a
California	Moderate	None	3.5
Kentucky	Large	Slight	3.5 ^b
Illinois	None	None	4.0
Maryland	Large	Slight	3.5 ^a
Massachusetts	Large	None	3.5
Nebraska	Slight	Moderate	3.5
Oklahoma	None	Moderate	3.7
Oregon	Slight	None	4.0
Tennessee	Slight	Severe	2.5
Texas	None	None	3.5
Wisconsin	Moderate	None	2.2 ^a
Wyoming	Slight	Slight	3.0

^aRide Evaluation: 4-5 very good, 3-4 good, 2-3 fair, 1-2 poor, 0-1 very poor.

^bRoad in need of service.

resins increased or remained about the same, soft resins decreased, and oil decreased or remained about the same.

Highway personnel in each state walked and rode over the sampled roads to evaluate the extent of cracking, the amount of plastic deformation, and the riding quality. Table 3 gives a qualitative summary of these findings.

TABLE 4
TENSILE STRENGTH OF ASPHALT FILMS
(in psi)

Asphalt	Unaged			TFOT					Road		
	0 F	40 F	80 F	0 F	20 F	40 F	60 F	80 F	0 F	40 F	80 F
1	1850	2110	970	2520	2570	2330	1640	1150	2430	2180	1760
2	2340	2040	840	2550	2340	2290	1530	930	2180	1860	1440
3	2300	1810	970	2410	2180	1960	1570	1070	2240	2100	1200
4	2440	2150	780	2430	2250	2270	1670	920	2510	2140	1480
5	2200	2020	970	2470	2200	2190	1680	1070	2090	1870	1440
6	2340	2040	790	2650	2390	2160	1540	970	2200	2010	1020
7	2010	2190	1030	2700	2570	2340	1730	1170	2230	2340	940
8	2550	2340	1060	2550	2670	2360	1920	1180	2840	2550	1170
9	2710	2080	1080	2610	2550	2360	1660	1210	2190	1710	900
10	2570	2040	810	2530	2950	2320	1530	880	2360	2240	1000
11	1820	1970	1020	2340	2140	2240	1590	1120	2470	2190	1060
12	2320	2160	810	2340	2480	2290	1670	970	2420	1990	1070
Average	2290	2080	930	2510	2440	2260	1640	1050	2350	2100	1210

Failure was always by brittle fracture. The stress-time recording was linear right up to the time of fracture and there was a sharp report at failure. The broken film was divided equally between the two surfaces. The fracture started at a small defect and propagated along the parabolic lines characteristic of the fracture surfaces of amorphous brittle materials. Because the area of the new surface could not be readily determined, the tensile strength was assigned on the basis of the initial area of the film.

RESULTS

The tensile strengths of the aged and unaged asphalts at temperatures from 0 to 80 F are given in Table 4. More temperatures were used in testing the TFOT asphalts in order to better establish how tensile strength changes with temperature. The data for the unaged and TFOT samples are averages of four determinations; those for the road samples are averages of eight determinations because two samples of asphalt concrete were supplied from each road. Statistical analysis was applied to determine objective criteria for the acceptability of individual determinations. Less than 1 percent

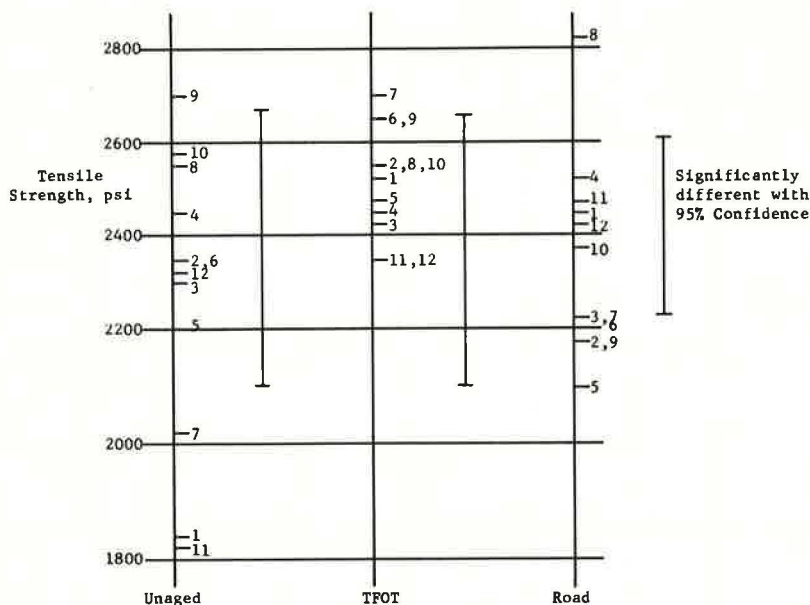


Figure 3A. Ranking of tensile strengths at 0 F.

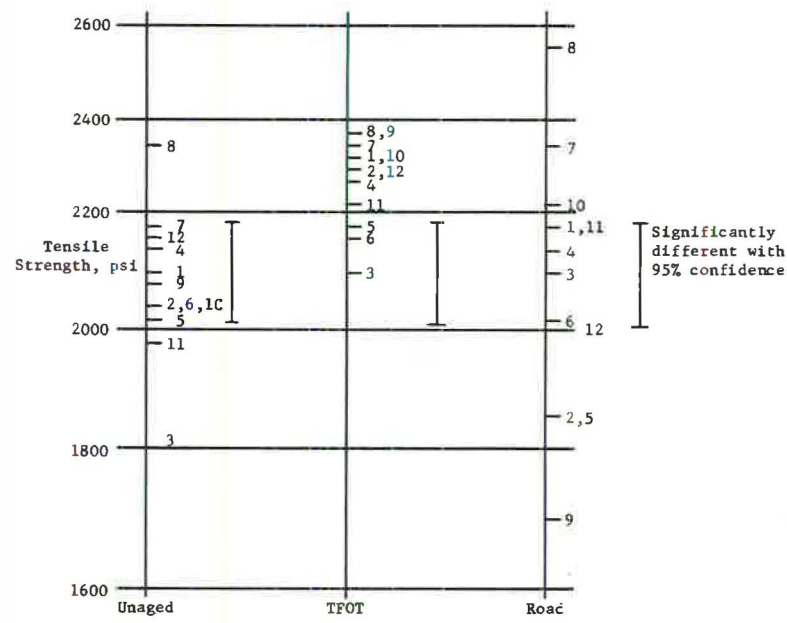


Figure 3B. Ranking of tensile strengths at 40 F.

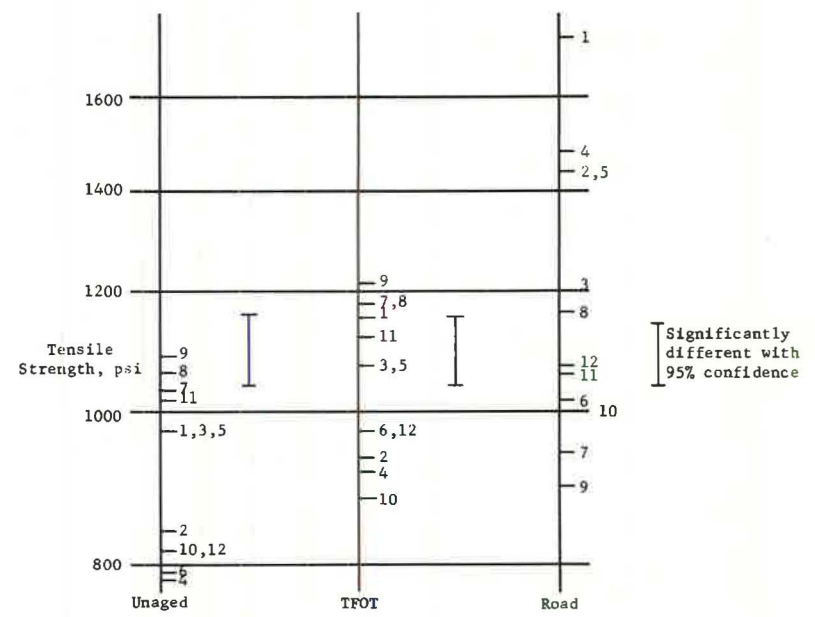


Figure 3C. Ranking of tensile strengths at 80 F.

of the data were rejected. Finally, the 95 percent confidence level for significant difference between samples was determined for 0, 40, and 80 F and for each condition of aging.

The general dependence of tensile strength on temperature is given by the averages in Table 4, which are also plotted in Figure 2. At 80 F the order of average tensile strengths is road >TFOT > unaged; at 60 F unaged and aged asphalts are about the same; and at 0 F the TFOT films are strongest with the unaged and road being about the same. A maximum tensile strength, averaging from 2300 to 2500 psi, was reached for all conditions of aging.

Figure 3 shows rankings of the asphalt samples according to tensile strength at 0, 40, and 80 F. The tensile strength scale is logarithmic so the 95 percent confidence level applies any place on the scale. At 0 F there are differences between the unaged and road asphalts, but there is no significant difference between the asphalts after the TFOT. The same is approximately true at 40 F; however, at 80 F there is a greater spread in the data.

Failure occurred at extensions of about 3×10^{-4} in. when the applied load was 2000 pounds. For the gage length involved, an extension of this order would be expected if the two holders were made as one piece with no asphalt film present (the tensile elastic modulus of aluminum is about 1×10^7 psi). Whatever the tensile modulus of asphalt in thin films is, at a minimum it is within an order of magnitude of that of aluminum. Extension measurements were discontinued after establishing the relative closeness of the strain in the aluminum to the total strain.

Neither asphaltene nor resin content correlated with tensile strength. The interesting experiment that could be made by separating asphalt components with a preparative-type gel permeation chromatography column and determining the tensile strength of the components was not performed.

DISCUSSION AND CONCLUSIONS

Thin asphalt films, of about the thickness found in roads, increase in tensile strength with decrease in temperature to a maximum value which is about the same at low temperatures for all asphalts in newly constructed roads. Subsequent weathering develops appreciable differences in tensile strength between asphalts. The TFOT shows that there is no correlation between tensile strength and the source of the asphalt or its composition. Furthermore, the amount of cracking of the road does not appear to correlate with asphalt tensile strength. Changes in asphalt composition are not large enough to show the contribution that the individual components make to the tensile strength of asphalts. In addition, the failure of thin films is a complicated mixture of the strengths of cohesive and adhesive bonding.

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Rheological Aspects of Aging

KAMRAN MAJIDZADEH, Associate Professor of Civil Engineering, Ohio State University

•ALL bituminous paving materials change with time in one way or another. This change is altered in form and/or extent by different traffic and climatic environments. The material characteristics that resist these complex physicochemical changes have been investigated since asphalt was first used as a binding agent. Asphalt is by no means an ideal binding agent because of these changes with time; however, it offers the requisite cohesion and adhesion needed for the design of a stable mixture. The ability of the asphalt to retain its initial design durability characteristics during the service life of the pavement is of prime importance.

Because the aging of the bituminous mixture is primarily due to the alteration of the properties of the binder, the greatest effort in the study of durability has been directed toward the evaluation and characterization of those properties that may be responsible for the aging phenomena. Asphalt technology has been marked by many achievements in the areas of rheology and of the fundamental approach to the behavior of the binder and the asphaltic mixture. With respect to durability phenomena, however, the greatest effort has been concentrated on understanding the mechanisms involved in the rheological and physicochemical changes occurring in the binder alone. This paper attempts to find a relationship between the fundamental aging mechanisms in the bituminous binder and the corresponding rheological response of the bituminous-aggregate system.

FUNDAMENTALS OF AGING

Bituminous mixtures are designed to support traffic-induced stresses and strains as well as adverse effects of climatic conditions. The ability of the pavement structure to resist these forces during its service life depends on the rheological properties of the pavement system, which in turn are related to the properties of the constituents of the bituminous mixture. Aging phenomena, when altering properties such as adhesion and ductility of the binder, may result in instability of the pavement structure under traffic and climatic conditions. In a rational approach to pavement design, it is of utmost importance to relate quantitatively these changes in the properties of the binder to the overall rheological response of the paving mixture.

Aging of Binders

The effect of aging on the properties of bituminous binder has been studied at great length in the last 50 years. These studies have searched not only for the cause of aging but also for the relative changes in the flow properties and their method of evaluation. Relating pavement cracking and distress to asphalt hardening due to aging, many empirical and semi-empirical physical tests have been developed to measure the rate of change of flow properties. Hubbard and Gollomb (1) and Powers (2) have utilized the penetration test as a criterion for pavement cracking. The relative change in the ductility characteristics of asphalts, measured by ductility tests as well as others such as softening point tests, has also been used as a measure of asphalt hardening (3, 4, 5).

When the limitations of these empirical methods in rational pavement analysis are realized, the need for a more fundamental approach is apparent. The result of extensive field and laboratory evaluations has left no doubt at this time that aging results in the

hardening of the bituminous binder (6, 7, 8). This hardening and other alterations in the rheological properties are associated with physicochemical changes in asphalt cements (9, 10, 11). Sisko and Brunstrum (12) reported that the changes in asphalt composition generally show a consistent trend with aging; that is, asphaltene content changes at the expense of resins and resins change at the expense of oils. However, their data revealed that only the asphaltene content increases consistently with increased aging. The variations in the other components were rather erratic. The data by Majidzadeh and Schweyer (13) and Schweyer and Chipley (14) similarly indicate that aging considerably increases the asphaltene content. The other components, such as light aromatic, heavy aromatic, and paraffinic-naphthenic content, increased or decreased depending on the type of asphalts studied. Similar conclusions have been reached by other investigators with respect to the effect of aging on composition (15, 16, 17, 18). From an engineering standpoint, we are not only interested in the physicochemical interpretation of these compositional changes, but also in their macro- and micro-rheological significance and their application to pavement design. With respect to the macro-rheological properties, research data indicate that both steady-state and dynamic response of asphalts are significantly affected by aging. Depending on the type and composition of asphalts, aging generally results in an increase in viscosity and degree of non-Newtonian behavior (17, 18). The aging index, which is a measure of relative increase in viscosity, has been introduced in specifications to safeguard against selection of materials susceptible to aging. The results of creep tests at low temperature also indicate that aging results in the development of an instantaneous elastic response and a decrease in the steady-state flow characteristics (13). Similarly, dynamic responses of the asphalts, such as storage modulus, loss modulus, and dynamic viscosity, indicate an increasing trend with aging (13, 12).

These phenomenological observations cannot reveal the micro-mechanisms involved in the deformation process. To investigate the effect of internal structure and composition on the aging phenomena, the micro-rheological approach is of greater promise. One of the classical flow theories used in asphalt rheology is the Eyring rate processes, which relates the movement of molecules to the potential energy barrier required for the formation of suitable "holes" or environment. The Eyring equation relating the shear strain rate, $\dot{\gamma}$, and shear stress, τ , is written as

$$\dot{\gamma} = 2 \frac{\delta}{\delta_1} \frac{KT}{h} \exp\left(\frac{-\Delta F}{RT}\right) \sinh \frac{\delta \delta_2 \delta_3}{2KT} \tau \quad (1)$$

or

$$\dot{\gamma} = A \sinh B \tau$$

where K , h , and R are respectively the Boltzmann, plank, and universal gas constants; ΔF is the free energy change, δ is the distance between equilibrium position which molecules would occupy, and δ_1 , δ_2 , and δ_3 are center-to-center distances along 3 axes. A molecular parameter of great interest in this equation is the term $V_f = \delta_1 \delta_2 \delta_3$, known as volume of flow units. The Herrin and Jones (19) study indicates that this parameter decreases with increasing temperature. Majidzadeh and Schweyer (20) have reported that the volume of the flow units varies among asphalt cements. However, recently Moavenzadeh and Stander have presented data quite contrary to the previous independent observations of Herrin and Majidzadeh. Their results not only showed an increase of flow volume with temperature, but also that there was no significant difference among various aged and unaged asphalts. They state, "There is a possibility that the values of A and

$B \left(B = \frac{V_f}{2KT} \right)$ are dependent on this particular evaluation procedure. . . "However, it

appears that their conflicting viewpoint should be interpreted cautiously at this time. Particularly, Eyring and Ree (21) have recently generalized their approach by assuming that the flow system might be composed of more than one flow unit type, each char-

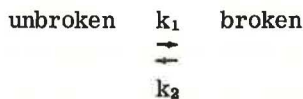
acterized by a different set of A and B constants. The viscosity is then given by the summation of these flow mechanisms as

$$\eta = \sum_{i=1}^n \frac{\lambda_n A_n}{B_n} \frac{\sinh^{-1} A_n \dot{\gamma}}{A_n \dot{\gamma}} \quad (2)$$

where λ is the fraction of flow surface occupied by the flow unit. It is quite probable that a liquid such as asphalt would possess two Newtonian and one non-Newtonian flow mechanisms and/or other combination needed to explain the micromechanics of deformation.

It appears that extensive work is needed to clarify the confusion arising from the Moavenzadeh and Stander paper and to explore the application of the modified Eyring equations to asphalt cements.

Another micro-rheological approach for the study of asphalt flow characteristics and aging phenomena is the application of the kinetic reaction rate principle as postulated by Denny and Brodkey (22). According to this concept, a non-Newtonian fluid undergoes a structural breakdown and reformation represented by



which has the kinetic reaction equation

$$-\frac{d(1-F)}{dt} = k_1 (1-F)^n - k_2 F^m \quad (3)$$

where k_1 and k_2 are forward and backward reaction rates and F is the broken portion of the structure; m and n in this equation are constants. Denny and Brodkey have shown that the ratio of $k_1/k_2 = K$, known as the equilibrium constant, is related to shear stress, τ , and shear susceptibility, P , given by

$$K = \frac{k_1}{k_2} = \frac{F^m}{(1-F)^n \tau^P} \quad (4)$$

Majidzadeh and Schweyer (20) have shown that equilibrium constant, K , varies considerably among different asphalts. It appears that there is a certain correlation between K and asphaltene content, volume of flow unit, and other rheological properties of asphalts. However, sufficient research data are not available to permit development of a sound hypothesis with respect to the flow of asphalt and the aging phenomena.

Aging of Mixtures

The purpose of previous rheological and physicochemical analyses of asphaltic binders was to reveal the mechanical response of a mixture under induced external conditions. However, to incorporate the results of these analyses into bituminous mix design, one should recognize that the behavior of the binder in a compacted mix differs from that of bulk asphalt. This difference, which is due to the thickness and the induced boundary effects, has been reported by many investigators. Mack (23) and Majidzadeh and Herrin (24) have shown that the rheological properties of asphalts, depending on thickness, vary from the behavior of a solid to that of a liquid. Krokosky et al (25), in the analysis of viscoelastic response of an asphalt-aggregate combination, points out the effect of aggregate interference and the interlock phenomena on the temperature dependency of the mixture. Majidzadeh and Herrin (26) have also shown that the induced boundary condition in a solid-asphalt-solid system alters the temperature dependency of the binder. In

TABLE 1
PROPERTIES OF ASPHALT CEMENTS

Property	60/70	B3056
Specific gravity, 77/77 F	1.010	1.020
Softening point, ring and ball, deg F	123	—
Ductility, 77 F, cm	150+	250+
Penetration, 100 gm, 5 sec, 77 F	63	—
Percent asphaltene, unaged	18.75	15.88
Percent asphaltene, 375-3 hr aged	24.38	18.85
Percent asphaltene, 375-9 hr aged	27.00	28.25
Percent asphaltene, 425-7 hr aged	31.51	30.44

importance of such an interrelation is quite obvious, since it could aid in the prediction of the pavement response and thus aid the adoption of proper guidelines for material selection.

MATERIALS AND PROCEDURES

Materials

In this report the results of an investigation on two asphalt cements are documented. These asphalts are a 60-70 penetration grade from Venezuelan crude and the AC-20 grade designated as B3056, used in the Asphalt Institute-Bureau of Public Roads cooperative study of viscosity graded asphalts. In Table 1 the test characteristics of these asphalts are given, along with the asphaltene content at unaged and 3 different aging conditions. The shear stress-rate of shear relations of these materials as previously reported are also shown in Figures 1 and 2. The results of rheological tests on these asphalts indicate that, at temperatures below 45 C, B3056 is much more non-Newtonian than the 60-70 asphalt.

The aggregate used in this study was an Ottawa sand with a powdered silica

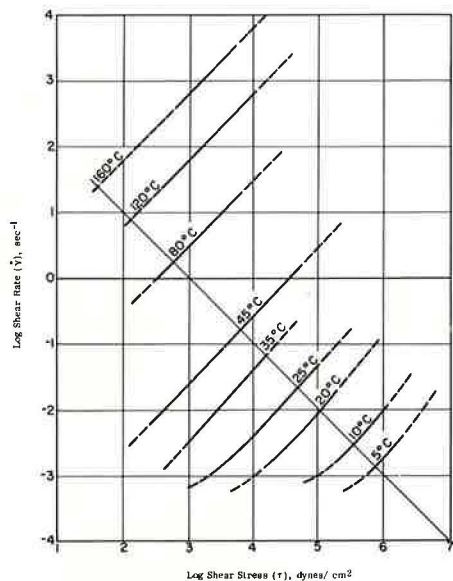


Figure 1. Shear rate vs shear stress on log-log scale for the 60-70 penetration grade asphalt at all test temperatures.

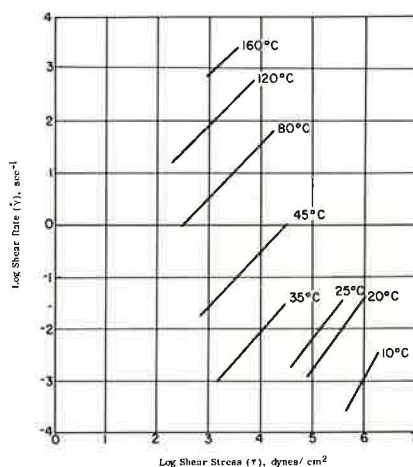


Figure 2. Shear rate vs shear stress on log-log scales for the B3056 asphalt at all test temperatures.

TABLE 2
GRADATION OF AGGREGATE

Sieve No.	ASTM Specification D 1663-59T	Selected Gradation, Percent Passing
16	85-100	100
30	70-95	75
50	45-75	45
100	20-40	26
200	9-20	15

filler. The sand was sieved and recombined in proportions putting it within the specification limits of ASTM D 1663-59T for sheet asphalts; it had the gradation shown in Table 2. The specific gravity of the aggregate was determined to be 2.65.

Procedures

Mixing of the aggregate and asphalt was done manually under infra-red lamps to maintain a mixing temperature of 275 F. The mix batch was 750 gm aggregate and

6 percent asphalt cement, sufficient to make six samples. Mixing was continued until a uniform coating of all particles was achieved. The batches were then stored in sealed, carbon-dioxide filled cans until needed for further testing.

Aging of the materials was carried out by two different methods, aging of the asphalt cement only and aging of the sand-asphalt mixture. The asphalt cement was aged in a tilted-rotating shelf oven according to the procedure used by Moavenzadeh and Stander (17) for five different degrees of aging as follows: 325 F for 3 and 9 hours, 375 F for 3 and 9 hours, and 425 F for 7 hours.

In order to age the sand-asphalt mixture under conditions more closely associated with natural conditions, each batch of the mixture was placed in an oven in two pans so that the mixture had a loose depth of approximately $1\frac{1}{2}$ in. The mixture was stirred each hour, and aged at three degrees as follows: 325 F for 3 and 9 hours, and 375 F for 3 hours. It was found that the other two aging degrees, 375 F for 9 hours and 425 F for 7 hours, produced a mix too highly aged to compact properly when made into test specimens.

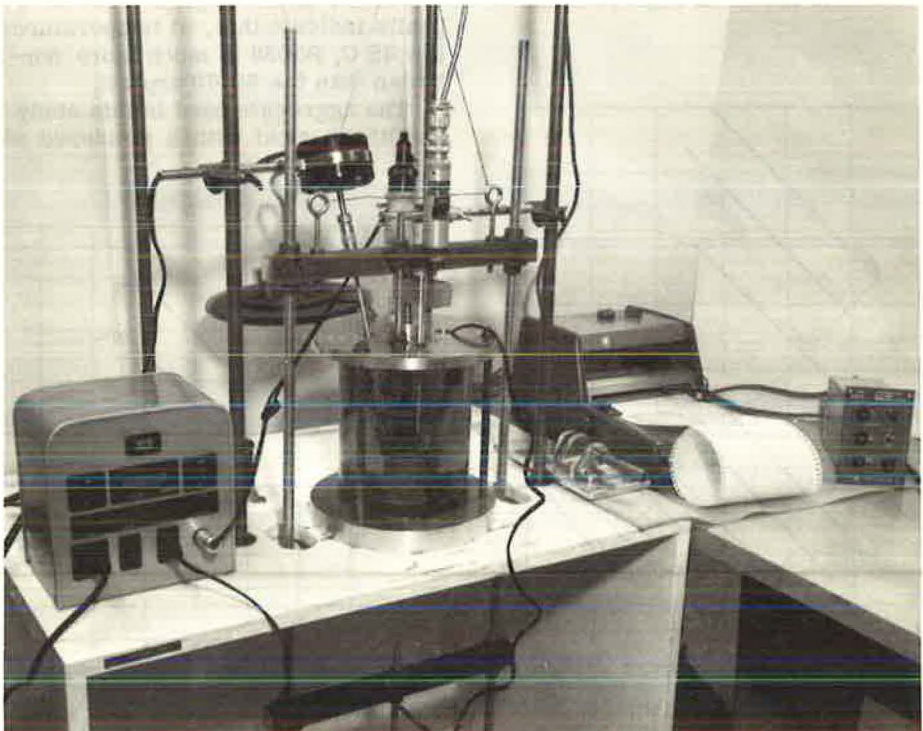


Figure 3. Creep setup.

To compact the specimens, Harvard miniature molds, 1.312 by 2.624 in., were heated in a water bath, removed, dried, and oiled. The sand-asphalt mixture was put in the mold in three layers; each layer was spaded 25 times. Compaction was done using a double plunger arrangement and a static load of 3000 psi maintained for two minutes. Compaction temperature was 275 F and enough material was used to make a sample 2.624 in. in height. After compaction the sample was ejected and allowed to air-cool to room temperature. The average height and bulk specific gravity of each sample was determined and they were stored in dark carbon-dioxide filled cans until needed for testing.

The sand-asphalt samples were tested in creep at 15, 25, 45, and 60 C, and at appropriate stresses to give an approximate strain of 0.5 percent after 10 minutes. The temperature was maintained in an environmental cell (Fig. 3) to ± 0.1 C. An LVDT and a Varian Model G-14 recorder were used to establish the time-deformation curve of each specimen. Because it was necessary to determine the elastic deformation of the sample, a preconditioning of the sample was carried out. The load to be used was applied for a period of 1 minute, then removed for 5 minutes. This seated and somewhat mechanically conditioned the samples so that consistent results could be obtained during the creep test.

A number of viscosity tests were run on both the aged and unaged asphalt cements to determine their basic flow characteristics. These tests were run with a sliding-plate microviscometer and a Haake Rotovisco. Their operation and procedures are explained in detail elsewhere (17) and are not given here.

ANALYSIS AND DISCUSSION OF RESULTS

Creep Data

The creep response of rheological systems is governed by three deformation mechanisms—instantaneous elastic, retarded, and steady state—each affected by the aging phenomena to some extent. To investigate the effect of aging on the creep response of asphaltic mixtures, aged and unaged specimens, as described in the previous section, were tested in creep under controlled laboratory conditions. Figures 4 and 5 show the resulting strain-time data for one of the asphalt cements at various aging conditions and at two test temperatures. These figures clearly indicate that the creep compliance of bituminous mixtures decreases as the degree of aging increases. The greatest aging effects are shown by the asphalt mixture in which the binder was aged at 425 F for 7 hours and the asphalt mixture that was aged as a mixture. It should be pointed out, however, that the aging of asphaltic binders at 375 F for 3 hours and 9 hours has a lesser effect on the creep response of mixtures at high temperatures.

From the changes in the rheological parameters corresponding to the three deformation mechanisms, it appears that the instantaneous elastic response is not significantly affected by aging. This observation is supported by previous rheological analyses of asphalt binders and mixtures. At the test temperatures selected in this study, the asphalt cements are not expected to exhibit any significant elastic response. Thus, the observed instantaneous elastic deformation is primarily attributable to the aggregate effect.

The second mechanism, retarded deformation, appears to be somewhat affected by aging. However, a detailed discussion relating to this effect awaits a computer analysis and the determination of the distribution function of relaxation and retardation times.

The third mechanism, which is also affected by aging, is the steady-state deformation represented by the slope of the creep data. Figures 4 and 5 indicate that this slope decreases as the degree of aging increases.

In Figures 6 and 7, the relative effects of aging on two different asphalts are shown. Previous analysis on these asphalts had indicated that B3056 asphalt was more non-Newtonian than 60-70 penetration. The comparison of the creep response of these two asphalts (unaged) at 45 C similarly exhibits significant differences. However, as a result of aging, the differences in the deformation of the mixtures become less significant. This indicates that 60/70 asphalt is much more susceptible to aging than B3056. A similar conclusion has been reached from the comparison of the creep curves at all temperatures and aging conditions.

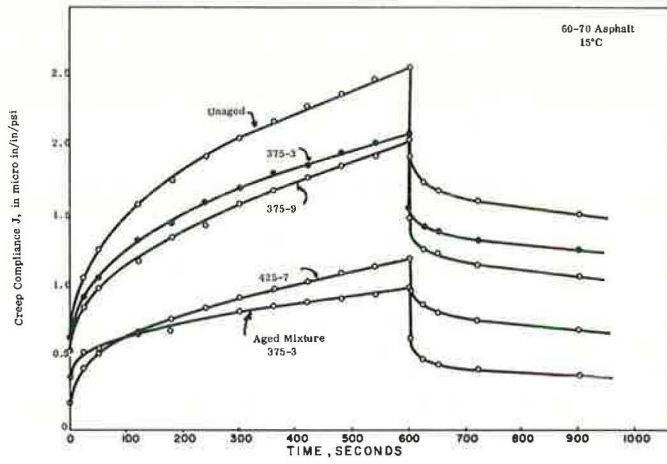


Figure 4. Creep response of 60-70 asphalt mixture at 15 C.

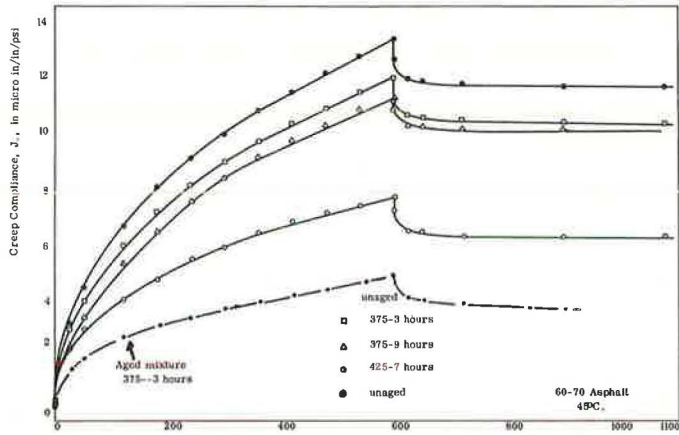


Figure 5. Creep response of 60-70 sand-asphalt mixture.

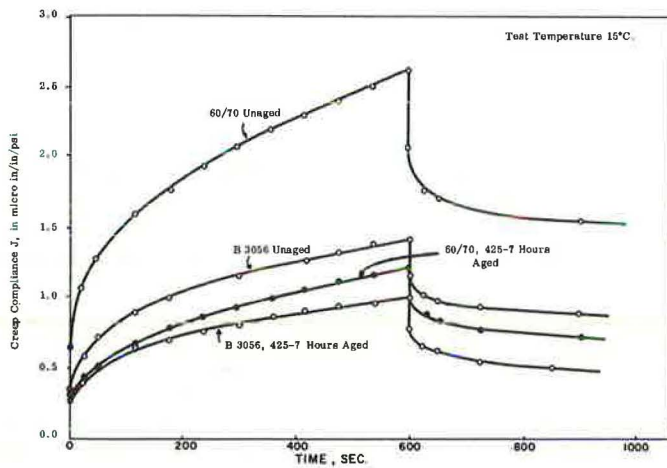


Figure 6. Comparison of creep response of two asphalts at 15 C.

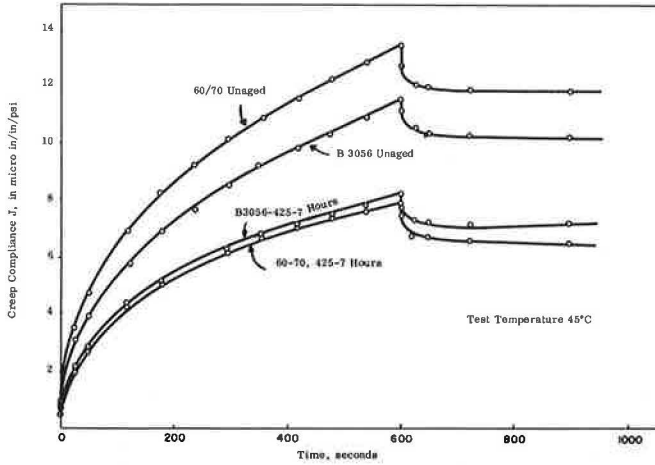


Figure 7. Comparison of creep response at 45 C.

The comparison of the creep data in Figures 4 and 5 also brings out the effect of the aging environment on the deformation of bituminous mixture. It is clearly shown that the sand-asphalt mixture aged at 375 F for 3 hours is much stiffer than the mixture prepared with an asphalt aged at 375 F for 3 hours. That is, for the same temperature and exposure period, the presence of aggregate during the aging process has a great influence on the rheological response of the bituminous material. From a practical standpoint, aging of the binder always occurs in the presence of aggregate; therefore, the

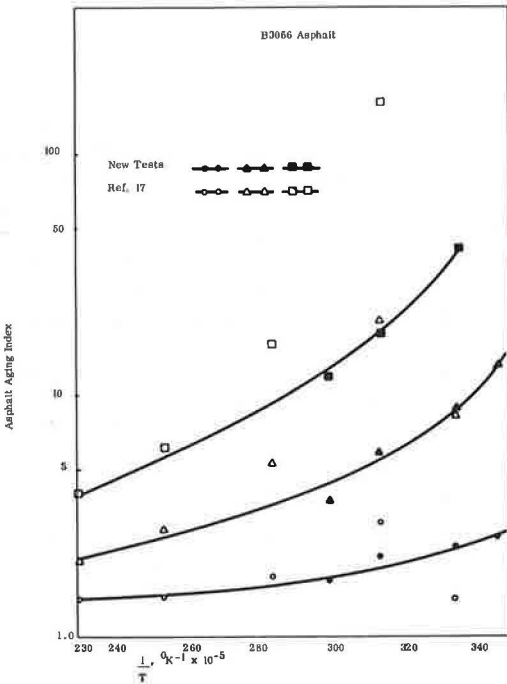


Figure 8. Effect of test temperature on asphalt aging index.

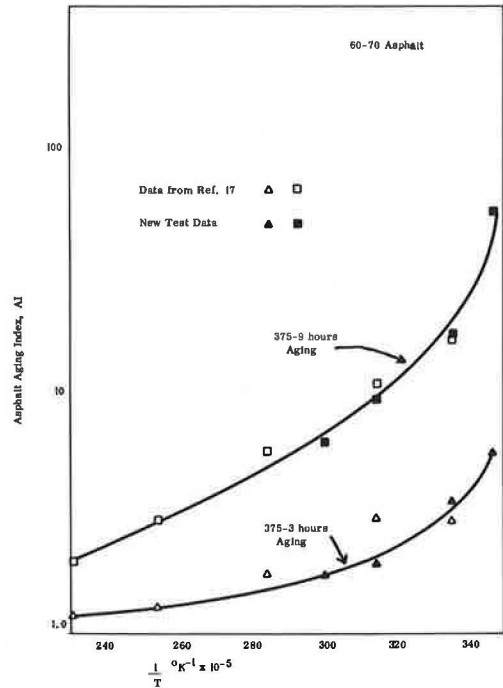


Figure 9. Effect of test temperature on asphalt aging index.

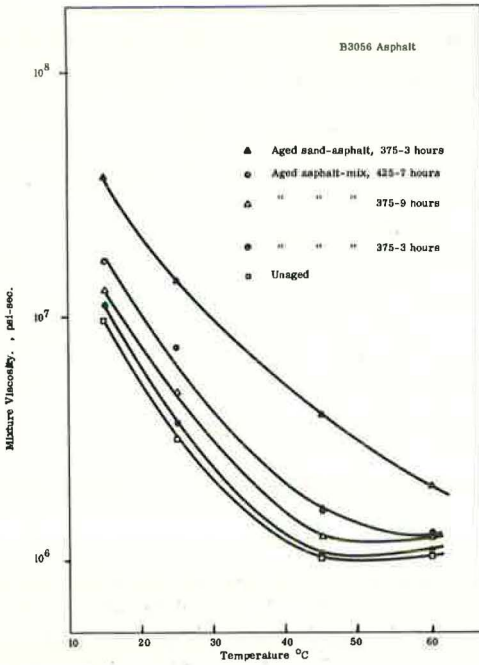


Figure 10. Effect of temperature on mixture viscosity.

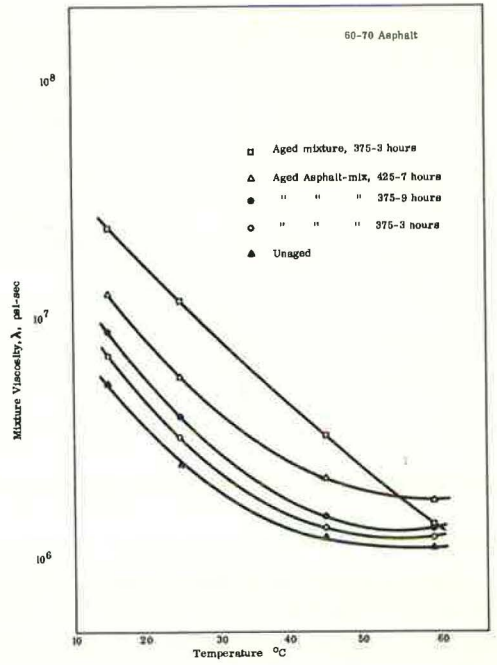


Figure 11. Effect of temperature on mixture viscosity.

foregoing observation bears much engineering significance. At the present time, similar analyses are being carried out for other aging conditions. The results of this work will be presented in subsequent papers.

Aging Index

In the previous section, it was shown that the creep response of asphaltic mixtures depends on the type of material and the aging conditions used. In order to relate aging susceptibility of mixtures to durability characteristics of binders, rheological tests were conducted on both aged and unaged asphalt cements. In Figures 8 and 9, the calculated aging indices for two asphalt cements at different test temperatures and aging conditions are shown. The test results are represented by solid data points and the open points correspond to the values of aging indices reported by Moavenzadeh and Stander (17). As shown, the newly calculated aging indices, except for aging at 425 F for 7 hours, confirm the previously reported relations. The analysis of the data for the 60-70 penetration asphalt at 425 F and 7 hours aging has not been completed at this time. In these figures, the aging index-temperature relationships are represented by smooth curves, which appear to be more justified than the straight-line relations used previously (17). The point of interest is that comparison of these figures shows a slightly higher aging susceptibility for the 60-70 asphalt over the B3056 asphalt. The same phenomenon was also observed from the analysis of creep data.

Since the aging mechanism affects the steady-state deformation of asphaltic mixtures, the mixture viscosity was calculated to show the relative significance of this parameter. The mixture viscosity is defined by

$$\frac{\sigma_0}{\lambda} = \frac{d\epsilon}{dt}$$

or

$$\lambda = \frac{\sigma_0}{d\epsilon/dt} \tag{5}$$

where $d\epsilon/dt$ is the slope of strain-time data for $\sigma = \sigma_0 = \text{constant}$. In Figures 10 and 11 the calculated mixture viscosities at different agings and test temperatures are shown. These figures indicate that the mixture viscosity increases as the degree of aging increases. The greatest effects of aging on mixture viscosities correspond to the sand-asphalt mixtures aged at 375 F for 3 hours and aging of the asphaltic binders at 425 F for 7 hours. To compare the aging susceptibility of these mixtures, the mixture aging indices of these two asphalts at various temperatures are calculated. This index

$$\text{Mixture aging index} = \frac{\lambda_{\text{aged}}}{\lambda_{\text{unaged}}} \quad (6)$$

In Figure 12, the mixture aging indices of these asphalts at different aging conditions are compared. It is again evident that the 60-70 asphalt cement, despite of its lesser non-Newtonian response, is more susceptible to aging than B3056. At the present time, two other asphalts with different rheological properties are also being tested to further substantiate the differences in aging susceptibility in relation to the rheological response of binders.

Temperature Effect

Recent extensive investigations of the rheological properties of bituminous mixtures have indicated that these materials are temperature-dependent. This temperature dependency, similar to that of polymeric systems, can be expressed by a unique function representing the effect of temperature on all viscoelastic parameters. In the introduction to this paper it was pointed out, however, that the temperature dependency of the asphaltic binder is expected to differ from that of the bituminous mixture. This is due to the presence of aggregate and induced boundary conditions.

The temperature dependence function a_T of asphalt cements, deduced from the Rouse theory, is written as

$$a_T = \frac{(\tau_p)_T}{(\tau_p)_{T_0}} \quad (7)$$

where τ_p is the relaxation or retardation of the molecular system given by

$$\tau_p = \frac{6\eta M}{n^2 p^2 \rho RT} \quad (8)$$

in which M is the molecular weight and p^2 is the summation index. Then the a_T function can be written as

$$a_T = \frac{\eta \rho_0 T_0}{\eta_0 \rho T} \quad (9)$$

This equation, which is based on the movement of submolecules in their surroundings, obviously cannot be used for a rheological system such as the asphalt-aggregate composition. The Al-Ami (28) results have similarly indicated that the a_T function derived from asphalt viscosity does not satisfactorily superimpose creep data. The use of mixture viscosity for the derivation of an a_T function is also technically unsound. This method, which is based on the analogy between the mixture viscosity λ and the asphalt viscosity η , is expressed by

$$a_T (\text{mixture}) = \frac{\lambda \rho_0 T_0}{\lambda_0 \rho T} \quad (10)$$

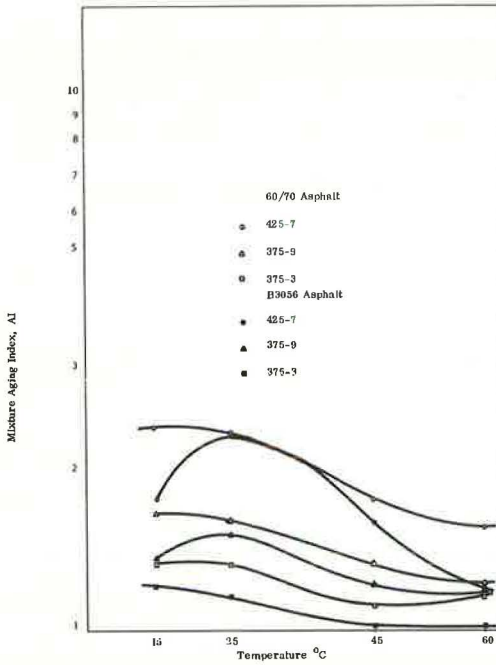


Figure 12. Variation of mixture aging index with temperature.

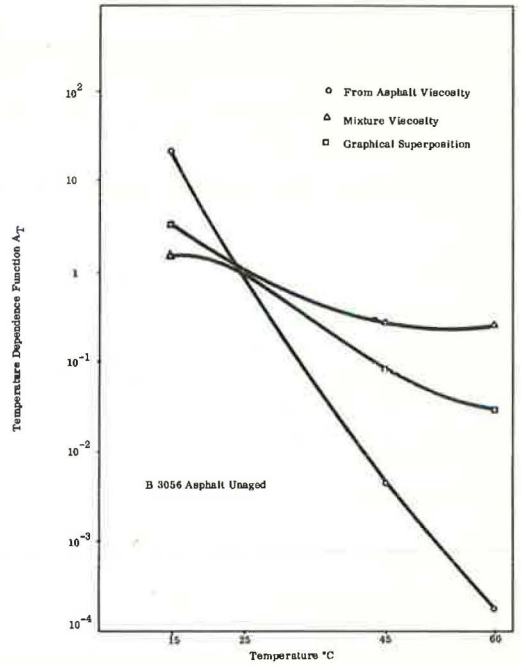


Figure 13. Relation of a_T and temperature for B3056.

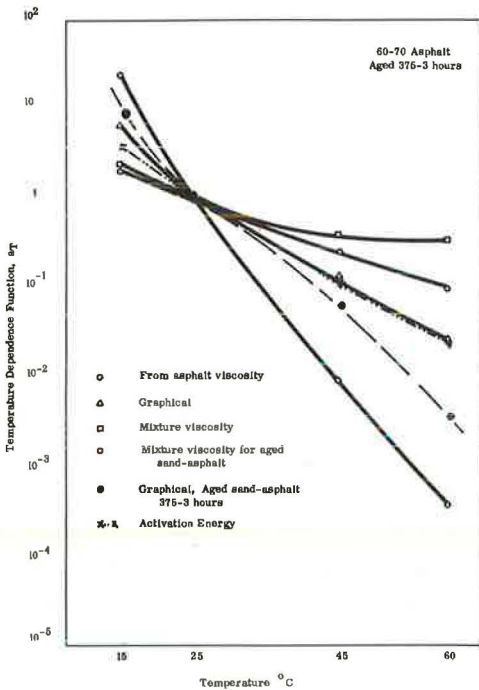


Figure 14. Relations of a_T and temperature.

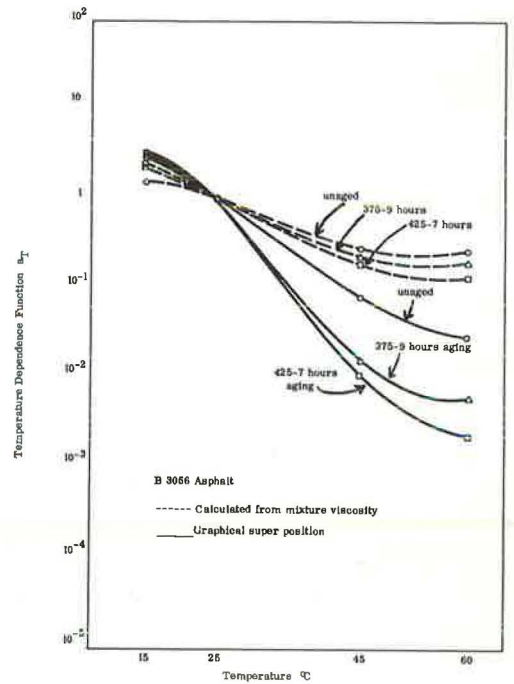


Figure 15. Effect of aging on a_T function.

It is obvious that the molecular mobility concept of the Rouse theory, which is the basis of the above equation, cannot be applied to the deformation of asphalt mixtures.

In Figures 13 and 14 the a_T function calculated by these two methods and the function obtained by graphical techniques are compared. These figures and the similar results obtained for other aging conditions confirm the previous observation that the temperature dependency of bituminous mixtures cannot be explained by asphalt viscosity or mixture viscosity. Furthermore, a_T functions for different aging conditions, when calculated by these methods, do not appear to be significantly affected by aging. On the contrary, however, the a_T functions obtained by graphical superposition exhibit considerable variation due to aging (Fig. 15).

Al-Ami (28) has shown that there is a very good agreement between the values of a_T obtained by graphical superposition and by use of activation energy. The results shown in Figure 14 similarly confirm this observation. Work is in progress to calculate the temperature dependence function by use of an Arrhenius form equation and to show the effect of aging on the activation energy function.

In Figures 16 and 17, the master curves obtained from the superposition of creep curves are shown. These figures clearly show the effect of aging on the deformation response of the bituminous mixtures. As has been noted previously, the 60-70 penetration asphalt, although less non-Newtonian than the B3056 asphalt, is more age-susceptible. Another point of practical significance may also be taken from these figures. The B3056 asphalt may be aged at 375 F for at least 3 hours with no discernible change in creep characteristics; however, somewhere between 3 hours and 9 hours at this temperature a major amount of aging takes place. For the 60-70 asphalt, the major amount of aging at 375 F takes place in less than 3 hours, and little further aging is noticed for times up to 9 hours. Of importance here is not the individual interpretation of each asphalt, but that the effects of aging times and temperatures may be interpreted using the master creep curves.

SUMMARY AND CONCLUSIONS

This is a progress report of a study concerned with the durability characteristic of asphalts and asphaltic mixtures. In this paper the rheological response of sand-asphalt mixtures prepared with two different asphalt cements and tested at various temperatures and aging conditions were studied. The aging conditions consisted of two methods: aging the asphalt binder alone, and aging the sand-asphalt mixture.

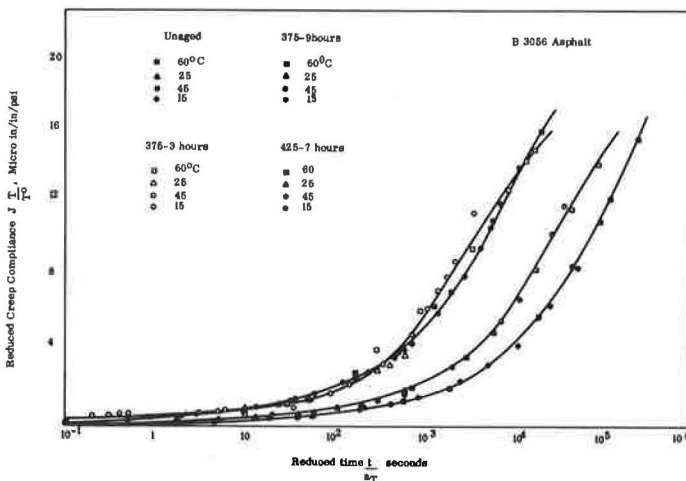


Figure 16. Master creep curve of B3056 at different aging conditions.

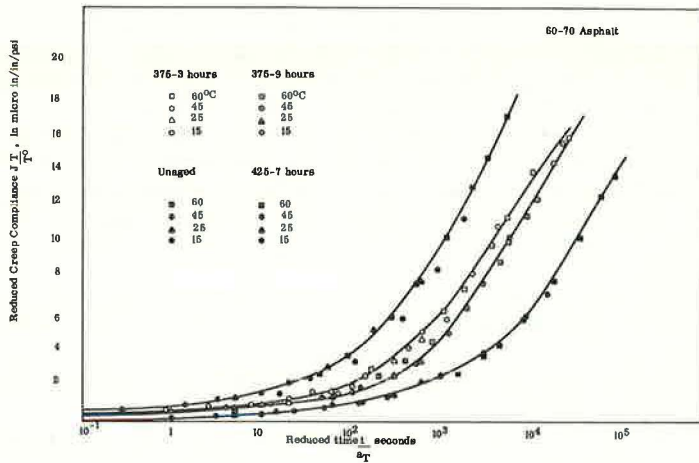


Figure 17. Master creep curve of 60-70 asphalt mix at different aging conditions.

The following conclusions are reached from this study:

1. Aging affects the creep response of bituminous mixtures. The greater the degree of aging the greater the effect on the creep responses; that is, there is a correlation between the degree of aging and the deformation of the sand-asphalt mixtures.
2. There is an apparent correlation between the aging susceptibility of asphalt cements and the aging susceptibility of bituminous mixtures.
3. The rheological response of aged bituminous mixtures appears to differ significantly from the response of mixtures prepared with aged asphaltic binders at identical aging conditions. Further study is in progress to reveal the mechanisms involved.
4. The temperature dependence function, a_T , of sand-asphalt mixtures is affected by the aging conditions.
5. For these asphaltic mixtures and these aging conditions, the master creep curves could be a valuable tool in interpreting the effects of aging on the creep response of the mixtures.

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