

Development of a Laboratory Durability Test for Asphalts

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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	126.5	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-ASPALT 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	1.08
		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.

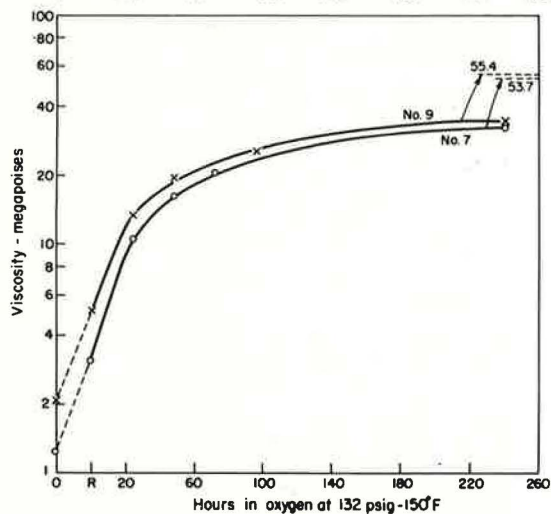
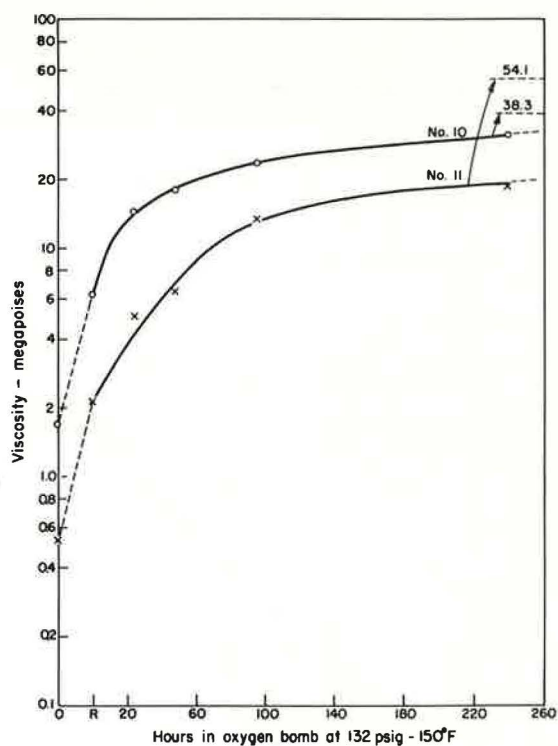
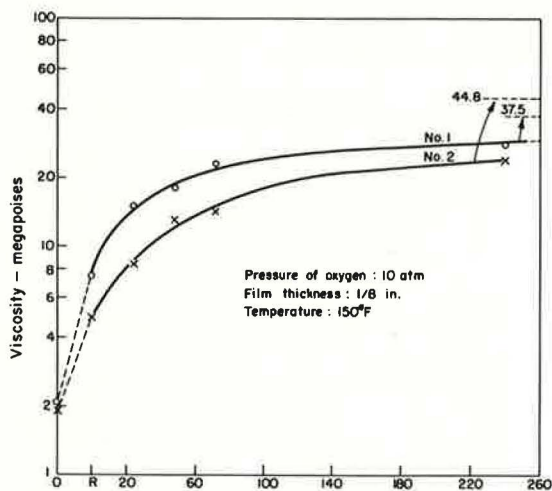
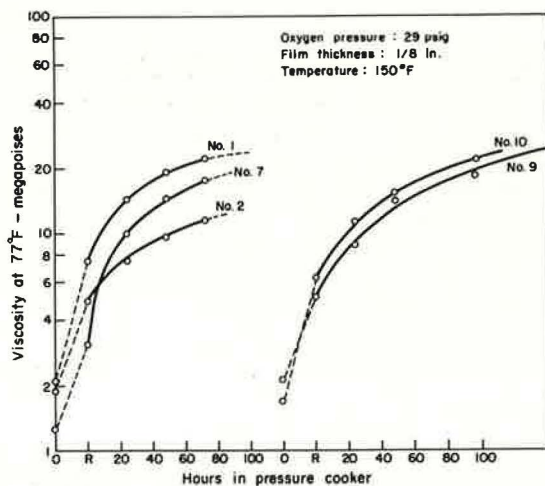


Figure 2. Viscosity vs time of aging in pressure bomb.

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.

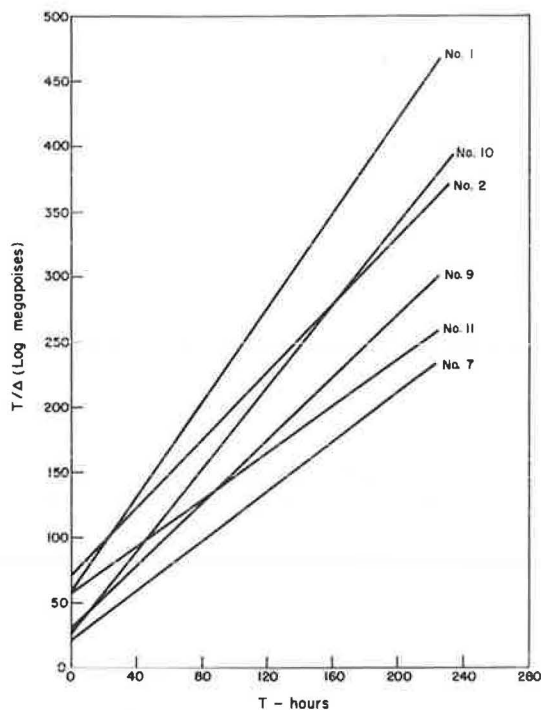


Figure 3. T/Δ log viscosity vs T .

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

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 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

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

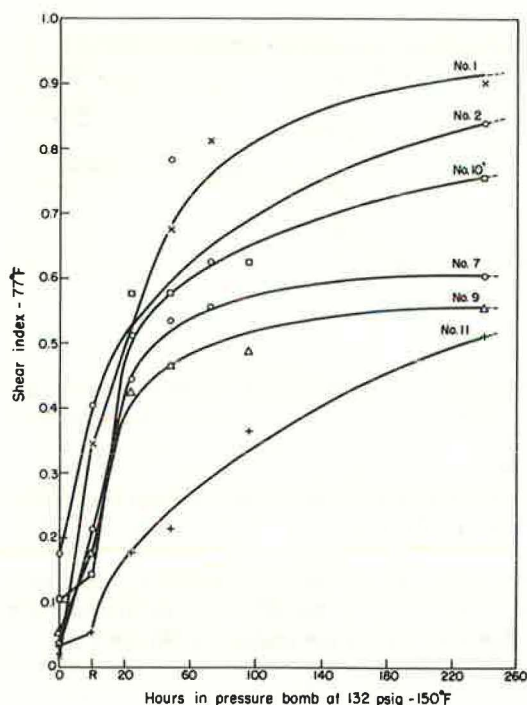


Figure 4. Shear index vs time of aging.

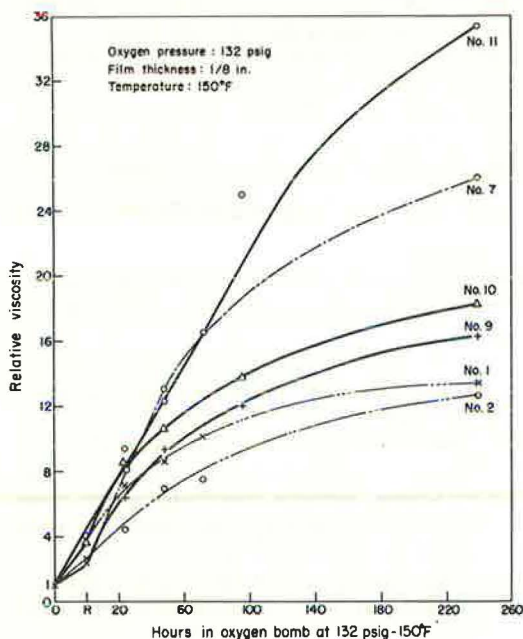


Figure 5. Relative viscosity vs time of aging.

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

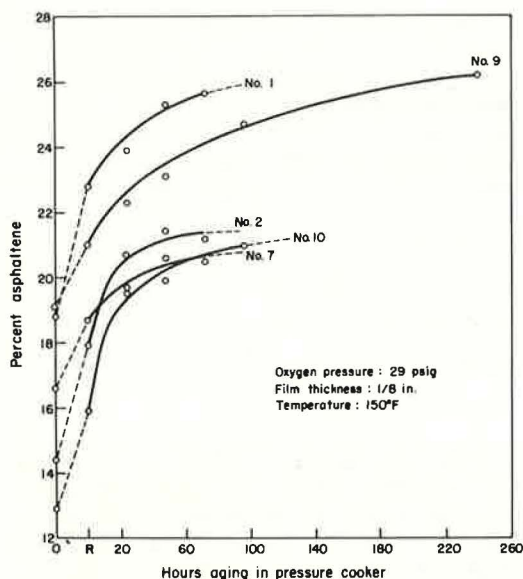


Figure 6. Asphaltene content vs time of aging.

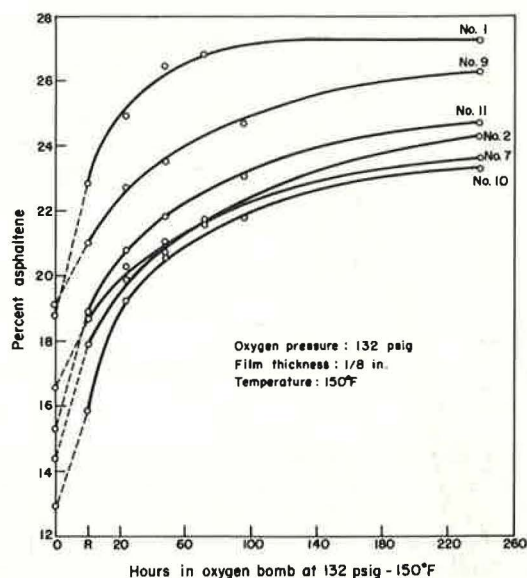


Figure 7. Asphaltene content vs time of aging.

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

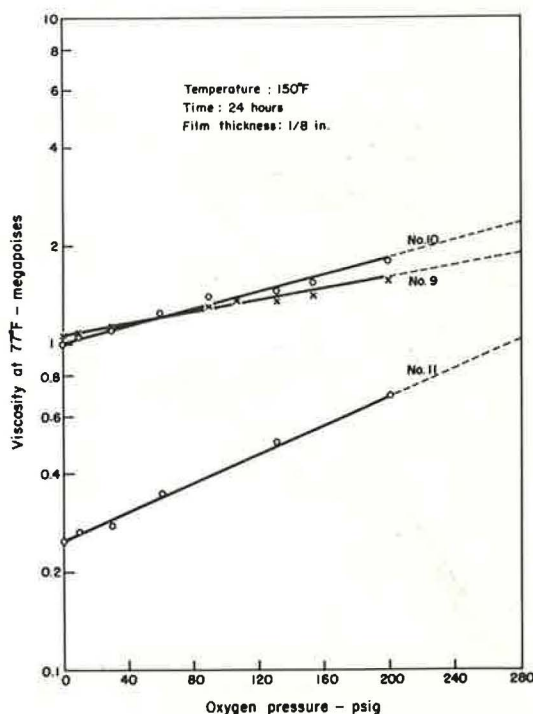


Figure 8. Effect of oxygen pressure on viscosity.

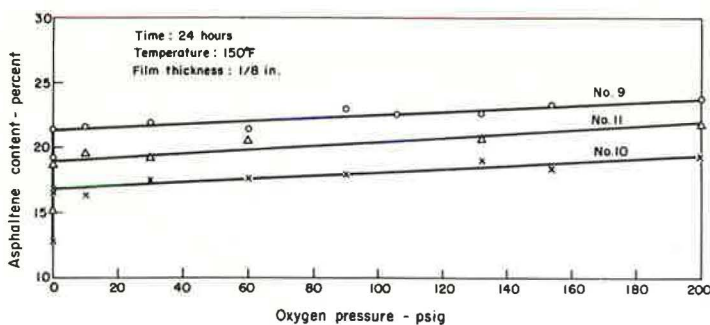


Figure 9. Effect of oxygen pressure on asphaltene content.

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.

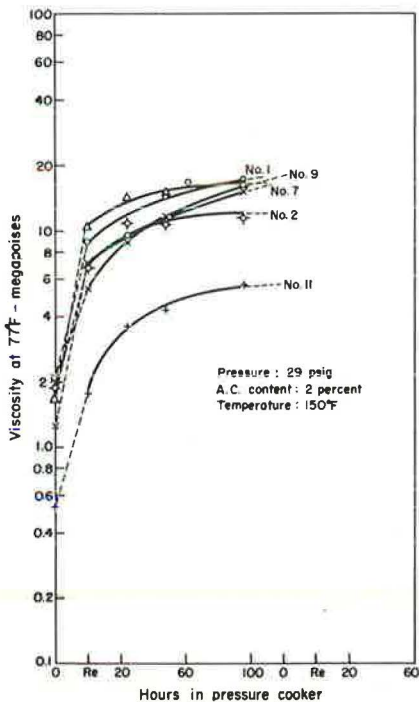


Figure 10. Viscosity of recovered asphalt vs time of aging.

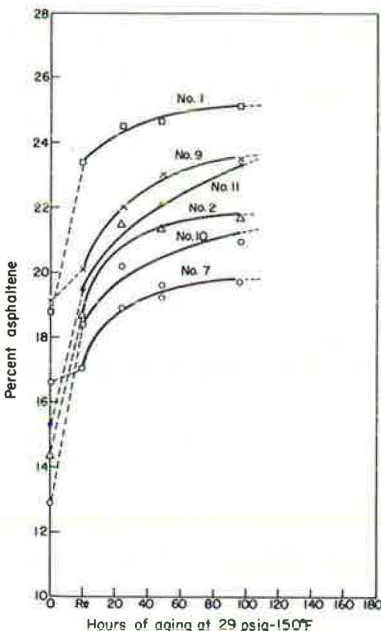


Figure 11. Percent asphaltene of recovered asphalts vs time of aging.

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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