progress report

Engineering Research Institute

Development of a Laboratory Durability Test for Asphalts

Project HR--124
Iowa Highway Research Board

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Ames, Iowa

August 1967

EPO68-036
Project No. 624-S

Iowa State University
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Part One

The Nature of the Thin Film Oven Test

Authorization

The Iowa Highway Research Board at its May 1966 meeting approved Project HR-124 entitled, "Development of a Laboratory Durability Test for Asphalts." Upon approval of the Iowa Highway Commission and allocation of funds, a contract for the execution of the work on the project was awarded to the Engineering Research Institute of Iowa State University with the date for completion of the work set for May 31, 1967. This study under the same title was designated Project 624-S of the Engineering Research Institute.

This report recovers the work completed up to May 31, 1967. This work encompassed studies in the initial two phases of an overall study in the development of a durability test for paving asphalts.

Summary

Fruitful research on durability of paving asphalts may come from two approaches:

- The improvement of the asphalt for durability.
- The development of relatively rapid laboratory tests which will enable the design engineer to select or to specify an asphalt based on quality and to make a correct estimate of the service life of a selected asphalt when used in a specific paving mixture.

Research Project HR-124, "Development of a Laboratory Durability Test for Asphalts," sponsored by the Iowa Highway Research Board is in the second category and was intended to be the initial stage of an overall study in the development of a durability test for paving asphalts.

The original proposed study involves work in the following phases:

A. The identification and ascertainment of predominant factors causing hardening during mixing, laying and in road service, their mechanisms and their effects,

B. Development of an accelerated laboratory test that will simulate changes in asphalt (including hardening and other colloidal-chemical changes) both during mixing and in road service,

C. Correlation of hardening and other changes in asphalt during the developed laboratory durability test and changes in asphalt in pavement, and

D. Establishment of durability criteria for paving asphalts by means of established laboratory durability tests on original asphalt.

Research Project HR-124 encompassed work in the first two phases and has been completed. A new proposal has been submitted to the Iowa

Highway Research Board to undertake the third and fourth phases of the durability test study so that information obtained from HR-124 and from the extension of HR-124 can be applied to asphalt paving design and quality control.

This is a progress report on the work accomplished in HR-124. For clarity, the Report is presented in two parts. Part One is a critical examination of the BPR Thin Film Oven Test (TFOT). This includes the review of the background from which the test was developed; the study of the factors that affect the test, including film thickness, heating temperature, heating atmosphere, and duration; the investigation of the evaluation that may be derived from the test and the significance and potential of the test as related to quality control and laboratory durability test for asphalts. Part Two is a report on the development of a laboratory durability test. This includes a review of the state-of-the-art in the durability of paving asphalts and the actual development of the test.

The major conclusions drawn from the study in HR-124 are:

- The approach of the proposed durability test is considered sound and the procedure reproducible.
- The procedure is capable of accelerating the hardening of asphalt in a relatively short period of time.
- Differences exist among asphalts in hardening during the pressure-oxidation procedure. Therefore the procedure can distinguish between asphalts that are susceptible to hardening and those that are not.
- The hardening in the pressure-oxidation process is a hyperbolic function of time. This is in agreement with actual asphalt hardening

found in service. It suggests that a definite correlation can be established between field hardening and the proposed laboratory durability test.

● 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.

Introduction

Investigations have shown that asphalts produced from different crude sources and methods of production can have various degrees of durability under equivalent conditions of construction, traffic, and climate. Investigations have also demonstrated that the present specifications for paving asphalts do not exclude the possibility of the use of poor durability asphalts. A need exists in the paving industry to develop test methods and specifications to enable the effective exclusion of the use of nondurable asphalts and a reasonable prediction of the useful life of asphalts used.

All bituminous paving materials are affected by heat, weather, traffic, and time. The combined effects result in a hardening of the asphalt and less desirable adhesion and rheological characteristics. The ability of an asphalt to resist these changes due to the heat and oxidation is defined as its durability.

It is agreed that the most important single factor causing asphalt to crack and disintegrate is asphalt hardening. Therefore the degree and rate of hardening of asphalt under specific weathering and traffic conditions is indicative of the relative durability of the asphalt.

The hardening that occurs in asphalt takes place in two steps: hardening during short periods of time in a mixer at high temperatures and higher rates, and hardening over long periods of time in pavement at relatively lower temperatures and lower, decreasing rates. There is evidence that the hardening mechanisms in these two stages are quite different. Heat and oxidation are believed to be the predominant factors in the mixing process and essentially the hardening during pavement service is caused by oxidation.

Hardening during hot mixing can reduce the useful life of asphalt by as much as ten years. Obviously the degree and nature of hardening in asphalt during this relatively short time should be one of the most important factors to be considered in selection of the asphalt, in construction control, and in developing durability tests for paving asphalts.

Considerable study has been given to the development of tests and techniques for evaluating the hardening properties of asphalt as related to asphalt durability and quality control. One approach to the problem is various forms of oven heating tests. Among all oven heating tests, the Bureau of Public Roads Thin Film Oven Test (TFOT) is now recognized as one of the most valuable in predicting the hardening of asphalt during mixing, in measuring the potential durability of asphalt in pavement, and in quality control. The test was first proposed by Lewis and Welborn in 1940 and has been adopted as an ASTM tentative standard in 1963[1,2]. The proposed requirement of minimum retained penetration has been included by majority of specifications for paving asphalts. However, the test itself has lacked systematic study since the first few papers by the Bureau of Public Roads[1-4]. Owing to the increasing acceptance of the TFOT and its potential in asphalt durability evaluation, a close examination of the test is highly desirable.

This study examines the nature of the test; the factors affecting the test including film thickness, temperature, heating duration, and heating medium; the evaluation that can be derived from the test such as hardening, chemical changes, and volatility; and the significance, value, and potential of the TFOT as related to quality control and laboratory durability test.

The properties of the asphalts used in this study are given in Table 1. The results of the study are presented separately under the following headings:

Background

Effect of Temperature in the TFOT

Effect of Film Thickness in the TFOT

Effect of Heating Time in the TFOT

Effect of Heating Medium

TFOT and the Volatility of Asphalt

TFOT and the Hardening of Asphalt

TFOT and the Ductility of Asphalt

Applications of the TFOT

Conclusions

Table 1. Characteristics of original asphalts.

Code	Penetration 77/100/5	Specific gravity	Flash point (°F)	Fire point (°F)	Viscosity 77 °F (Megapoises)	Softening point (°F)	Percent Asphaltenes	Percent Oxygen	Co. & Plant[a]
A	59	1.035	620	710	3.60	125.0	--	--	a
B	75	1.033	615	695	2.50	119.0	--	--	a
1	88	1.012	575	665	2.10	116.5	18.8	0.79	b
2	88	1.001	650	710	1.90	116.5	14.4	0.48	c
7	90	1.016	650	715	1.25	112.5	16.6	0.81	d
9	90	1.035	595	680	2.10	116.5	19.1	0.73	e
10	90	0.998	650	725	1.70	116.0	12.9	0.63	a
C	112	1.028	610	680	0.80	112.0	--	--	a
11	134	1.024	595	660	0.53	106.5	15.3	0.64	a
D	238	1.020	590	650	0.16	101.0	--	--	a

(a) American Oil Co., Sugar Creek, Mo.

(b) American Petrofina Co., Mt. Pleasant, Texas.

(c) Mobiloil Co., Augusta, Kansas.

(d) Sinclair Refining Co., Harford, Ill.

(e) Texaco Oil Co., Casper, Wyo.

Background

The importance of heat stability or resistance of paving asphalt was recognized early in the history of asphalt paving technology.

It was reported that in 1897 Allen Dow suggested two methods for determining asphalt hardening when heated to high temperatures[5]. One of the methods involved heating 20 g of asphalt in a 2-oz glass retort at 400 °F for 30 hours and determining weight and penetration loss. Specifications based on this test required a maximum loss on heating of 8 percent and minimum retained penetration of 75 percent. This was probably the original loss on heating test. Prior to 1911, there were a number of other heat tests proposed; all were used to determine weight loss and penetration drop. Clifford Richardson[6], in his book, The Modern Asphalt Pavement, gave the name of the test as "Loss on Heating." The heating time was arbitrarily set at 7 hours and the temperature at 325 °F and 400 °F. A sample weight of 20 g was used in a crystallizing dish 2-¼ in. in diam, making a film of 0.788 cm or 0.31 in. The major concern of the test was the volatile loss.

In 1911, Hubbard and Reeve prepared a bulletin on methods used by the Office of Public Roads, for the examination of bituminous road materials[7]. The bulletin included a "volatilization test", the object being the determination of the weight loss the material underwent when 200 g in a standardized 6-cm-diam tin box (making a film of 0.71 cm or 0.28 in.) were subjected to a temperature of 163 °C for 5 hours. Changes in the character of the material due to such heating were also to be ascertained. The changes were meant to be in general appearance and in hardening using a float or penetration test. The volatilization test was made on practically all bitumens except tars and was also occasionally made at 400 °F for 5 hours. The same year, ASTM issued a method for the determination of the loss on heating of oil and asphaltic compounds. A 20-g sample was placed in a flat bottom tin, 6 cm in diam, and heated for five hours at 325 °F. In 1916 the loss on heating test was made on ASTM Standard Test Method D6-11. The size of the sample was increased to 50 g and the 3-oz tin in use today was specified, making a film of 13/16 in. The present ASTM designation for this test is D6-64. The basic conditions of the test ASTM D6-16 are still the same.

Many attempts were made to explain the field behavior of asphalts in terms of results obtained from the standard loss on heating tests. Anderson et al. developed a "resistance to hardening" value based on the penetrations of residues of the standard loss on heating test after 5 and 10 hours[8]. The "resistance to hardening" value is equal to

$$5\left(\frac{Y_1 - 1}{Y_1 - Y_2}\right) + 5$$

in which Y_1 = log penetration after 5 hours at 325 °F.

Y_2 = log penetration after 10 hours at 325 °F.

They set a resistance to hardening value of 55 as the dividing line between satisfactory and unsatisfactory materials. Resistance value could also be interpreted as the hours it would take to harden the asphalt in the standard loss on heating test at 325 °F to a penetration of 10.

Clark studied the volatility of asphalts by the standard loss on heating test[9,10]. He concluded that the hardening of asphalt during mixing, as measured by loss in penetration, was proportional to the volatility of the asphalts as measured by the standard loss on heating.

Nevertheless, the value of the standard loss on heating test in predicting the hardening of asphalt was questioned by many technologists[11-15]. It is now generally agreed that, because of the depth of the sample in a standard loss on heating test, the conditions are not sufficient severe to evaluate and differentiate the hardening properties of asphalts. With the advent of vacuum distilled asphalts, the value of the test in characterizing the early steam-refined petroleum asphalts was also lost.

The first thin film exposure test on asphalt was probably developed by Hubbard and Reeve in 1913[16]. In a paper entitled, "The Effect of Exposure on Bitumens" they described the exposure of eight bituminous materials in films of 1/8 in. to the action of natural light, air, and solar heat. Their conclusion was that the hardening of bitumen upon exposure was not due to loss by volatilization of the light constituents alone. The data indicated that the increase in asphaltenes due to oxidation were also responsible for the hardening. Natural exposure tests in films of 1/8 in. were also made on liquid asphalts[17-20].

Realizing the inadequacy of the standard loss on heating test in providing more information on the quality of asphalts, the Bureau of Public Roads investigated oven heating tests of asphalt in films thinner than the 7/8-in. layer of the old loss test. This work was first reported by Lewis and Wolborn[22]. This report represented the results of tests on eighty 50-60 and 85-100 pen. (penetration) asphalts made on the residues from the standard loss on heating tests as well as residues from the thin film oven tests. Sixteen 50-60 pen. grade asphalts were used to study the effects of heating time from 2 to 10 hours and film thicknesses of 1/8, 1/16, and 1/32 in. The properties of eight residues from the TFOT were compared with those of the same asphalts recovered from Ottawa sand and sheet asphalt mixtures used in the Shattuck mixing tests[23]. In addition test sections of sheet asphalt were constructed using one of the 50-60 pen. asphalts. Samples were taken immediately after the hot mix was laid and compacted. Penetration, ductility, and softening point of the reocvered asphalt were compared with those of the residue from the TFOT on the original asphalt. The most significant conclusions from this study were:

- The standard loss on heating test does not furnish adequate information concerning the probable behavior of asphalts for use in hot-mix paving.
- The changes that occur during the TFOT for 5 hours with 1/8-in. films in asphalts of the 50-60 grade are comparable to the changes that may be expected in bitumen recovered from mixtures prepared in paving plants.
- The ability of asphalts to retain their original characteristics after the 5-hour, 1/8-in.-film oven tests offers a means of evaluating their relative durability.

A second paper in 1946 by Lewis and Halstead reported the results of TFOT on asphalts of 60-70, 100-120, and 120-150 penetration grades[24]. The data in this report generally supported the earlier findings for the 50-60 and 85-100 grades. Requirements of percent weight loss, retained ductility and penetration on their film oven test (1/8-in. film heated 5 hours at 325 °F) for all grades of asphalts were suggested.

Winniford[25] studied the reproducibility of the standard loss on heating test (ASTM D 6) and TFOT as affected by oven design such as the levelness of the rotating shelves and the rate of air circulation in the ovens and as affected by testing procedures such as the position of the thermometer, the sample size, type of container, and the manner the penetration on residue is determined. The TFOT proved to be a more sensitive measure of the changes in weight and penetration occurring in the ovens than was the standard loss on heating test for paving asphalts.

The TFOT was modified by Vallerga et al. to study the effect of heat, infrared and ultraviolet lights on the aging of asphalts[26]. The major modification was that the rotating-shelf was tilted at a 15 degree angle to horizontal resulting in thinner films.

The most recent studies including the TFOT were the reports on a general study of properties of asphalts produced in the U. S. for highway construction which were reported in 1959[27] and 1960[28].

Table 2 shows the evolution of the various oven tests proposed and the present standards.

Table 2. Parameters in various oven heating tests.

Name	Wt. of Sample	Film Thickness (in.)	Temp (^oF)	Time (hours)
Dow (1897)	20	(a)	400	30
Richardson (1905)	20	0.31	325	7
Richardson (1905)	20	0.31	400	7
Hubbard & Reeve (1911)	20	0.28	325	5
Hubbard & Reeve (1911)	20	0.28	400	5
ASTM (1911)	20	0.28	325	5
ASTM D6-16 (1916)	50	0.83	325	5
Lewis & Welborn (1940)	50	0.13	325	5
Germany (DIN 1995)	100	0.31	325	5
British (IP 45/58)	50	0.83	325	5
ASTM D6-64	50	0.83	325	5
ASTM D 1754-63T	(b)	0.13	325	5

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[a] 2 oz glass retort was used

[b] 50.0 ml

Effects of Temperature

Both the physical and chemical properties of asphalt undergo changes due to time and exposure to heat and oxygen. In general, these changes are detrimental to its function as binder and waterproofing agent. Since in most applications of asphalt heating is almost an essential step, the effects of heat in air has been related to asphalt quality. The resistance of asphalt to change due to heating is considered one of the most important qualities of asphalt and has been the basis for all oven heating tests for asphalt.

Since the TFOT is basically a heating test and since almost all effects that cause changes in asphalt are influenced by temperature, this factor was studied. Five 85-100 pen. asphalts and one 120-150 pen. asphalt were used in the study. A standard TFOT was run on all asphalts at temperatures from 150 °F to 400 °F. To study the influence of oxygen, samples of 1/8-in. films were also heated in oxygen and 27 in. mercury of vacuum for five hours at all temperatures. Physical changes in asphalts were determined by penetration, softening point, and absolute viscosity at 77 °F. Chemical changes as indicated by asphaltenes content changes and oxygen content changes were also determined. The results obtained at various temperatures are given in Tables 3 and 4. Figure 1 shows the effect of temperature in a TFOT on the viscosity change. Figure 2 shows the influence of heating in a TFOT (1/8-in. film, 5 hours) in 1-atm oxygen, 1-atm air, and 27-in. mercury vacuum on log penetration. Typical curves showing the effects of temperature on softening point are presented in Fig. 3. The following can be observed:

Table 3. Effects of temperature.

A.C.	Temperature (^oF)	Medium	Penetration 100/5/77	S.P. (^oF)	Viscosity 77 ^oF (megapoises)	Asphaltenes (%)
1	225	O_2	66	128.0	4.60	22.5
		Air	81	122.5	2.40	20.5
		Vac	87	119.0	2.10	19.0
	325	O_2	32	150.5	18.6	28.7
		Air	48	131.5	7.50	22.7
		Vac	72	120.5	2.80	19.4
	400	O_2	16	168.0	25.5	33.8
		Air	20	163.0	22.5	26.5
		Vac	60	128.5	5.50	20.0
2	225	O_2	68	123.0	3.75	18.8
		Air	77	120.0	3.25	16.0
		Vac	87	116.5	2.10	14.7
	325	O_2	34	146.5	11.7	24.4
		Air	54	133.0	5.64	18.1
		Vac	79	119.5	2.80	15.6
	400	O_2	19	191.5	24.7	30.5
		Air	25	158.5	22.5	27.4
		Vac	72	131.0	6.20	18.5
7	150	O_2	78	115.0	1.58	17.0
		Air	83	115.5	1.36	16.7
		Vac	89	114.0	1.28	16.5
	225	O_2	74	117.5	2.45	19.3
		Air	81	116.5	1.85	17.3
		Vac	88	114.5	1.35	16.7

(Table 3. Cont.)

A.C.	Temperature (^{o}F)	Medium	Penetration 100/5/77	S.P. (^{o}F)	Viscosity 77 ^{o}F (megapoises)	Asphaltenes (%)
	325	O_2	34	144.5	23.0	24.8
		Air	55	127.0	4.65	18.8
		Vac	78	117.5	1.72	17.1
	400	O_2	--	--	--	28.0
		Air	24	150.5	32.5	23.3
		Vac	68	122.5	2.25	19.1
9	150	O_2	78	117.5	2.10	19.8
		Air	79	117.5	2.00	19.2
		Vac	87	116.5	1.95	19.1
	225	O_2	59	120.5	4.15	20.8
		Air	73	119.0	2.40	19.6
		Vac	81	117.5	2.05	19.5
	325	O_2	33	147.5	17.0	25.9
		Air	55	124.0	5.50	21.4
		Vac	75	119.5	2.45	20.2
	400	O_2	14	188.0	--	35.2
		Air	21	158.5	66.0	27.6
		Vac	62	121.5	3.21	19.8
10	150	O_2	79	119.5	2.45	13.3
		Air	83	117.5	1.95	12.8
		Vac	86	116.5	1.73	12.9
	225	O_2	65	125.5	3.05	14.8
		Air	74	122.0	2.45	13.7
		Vac	80	120.0	2.36	13.0

(Table 3. Cont.)

A.C.	Temperature (^{o}F)	Medium	Penetration 100/5/77	S.P. (^{o}F)	Viscosity 77 ^{o}F (megapoises)	Asphaltenes (%)
	325	O_2	29	144.5	26.5	25.1
		Air	55	130.0	6.45	16.0
		Vac	74	121.5	3.90	13.3
	400	O_2	20	159.5	52.0	26.2
		Air	29	151.0	31.5	22.6
		Vac	65	122.5	4.75	13.8
11	150	O_2	120	108.5	0.64	16.0
		Air	123	108.0	0.56	15.7
		Vac	128	108.0	0.54	15.2
	225	O_2	95	111.5	1.10	17.6
		Air	110	110.5	0.71	16.4
		Vac	123	109.0	0.55	16.2
	325	O_2	44	128.5	10.0	23.2
		Air	76	117.0	2.35	19.0
		Vac	114	110.5	0.71	16.5
	400	O_2	27	--	--	--
		Air	32	143.5	23.5	27.1
		Vac	98	112.5	0.98	17.6

Table 4. Chemical changes vs TFOT.

A.C.	Original Penetration	Temp (^{o}F)	Medium	Original Asphaltenes	Original % O_2	Treated Asphaltenes	Treated % O_2
1	88	--	--	18.8	0.79	--	--
		225	O_2			22.0	1.11
			Air			20.9	1.06
			Vac			19.0	0.90
		325	O_2			28.7	1.85
			Air			25.2	1.45
			Vac			19.4	1.12
		400	O_2			33.8	1.90
			Air			30.6	1.48
			Vac			20.0	1.08
		325	CO_2			22.1	1.02
2	88	--	--	14.4	0.48	--	--
		225	O_2			18.8	0.86
			Air			18.0	0.73
			Vac			14.7	0.68
		325	O_2			24.1	1.16
			Air			22.5	1.04
			Vac			15.6	0.94
		400	O_2			30.5	1.66
			Air			27.4	1.22
			Vac			18.5	1.01
		325	N_2			17.5	0.71
			CO_2			17.5	0.64

(Table 4. Cont.)

A.C.	Original Penetration	Temp (^{o}F)	Medium	Original Asphaltenes	Original % O_2	Treated Asphaltenes	Treated % O_2
9	90	--	--	19.1	0.73	--	--
		225	O_2			20.8	0.77
			Air			19.3	0.69
			Vac			19.5	0.70
		325	O_2			25.9	1.00
			Air			23.4	0.81
			Vac			20.2	0.75
		400	O_2			35.2	1.40
			Air			27.6	0.95
			Vac			19.8	0.85
		325	N_2			21.3	0.86
			CO_2			21.3	0.80
10	90	--	--	12.9	0.63	--	--
		150	O_2			13.3	0.62
			Air			12.8	0.63
			Vac			12.9	0.68
		225	O_2			14.8	1.01
			Air			13.7	0.74
			Vac			13.0	0.75
		325	O_2			25.0	1.19
			Air			16.8	1.05
			Vac			13.3	0.91

(Table 4. Cont.)

A.C.	Original Penetration	Temp (^oF)	Medium	Original Asphaltenes	Original % O_2	Treated Asphaltenes	Treated % O_2
		400	O_2			26.2	1.10
			Air			24.6	1.10
			Vac			13.8	0.91
		325	N_2			14.5	1.00
			CO_2			14.2	1.09
11	134	--	--	15.3	0.64	--	--
		150	O_2			16.0	0.93
			Air			15.7	0.87
			Vac			15.2	0.77
		225	O_2			17.6	1.13
			Air			16.4	0.82
			Vac			16.2	0.75
		325	O_2			23.2	1.48
			Air			20.6	0.86
			Vac			16.5	0.85
		400	O_2			24.0	0.82
			Air			27.1	1.22
			Vac			17.6	0.83

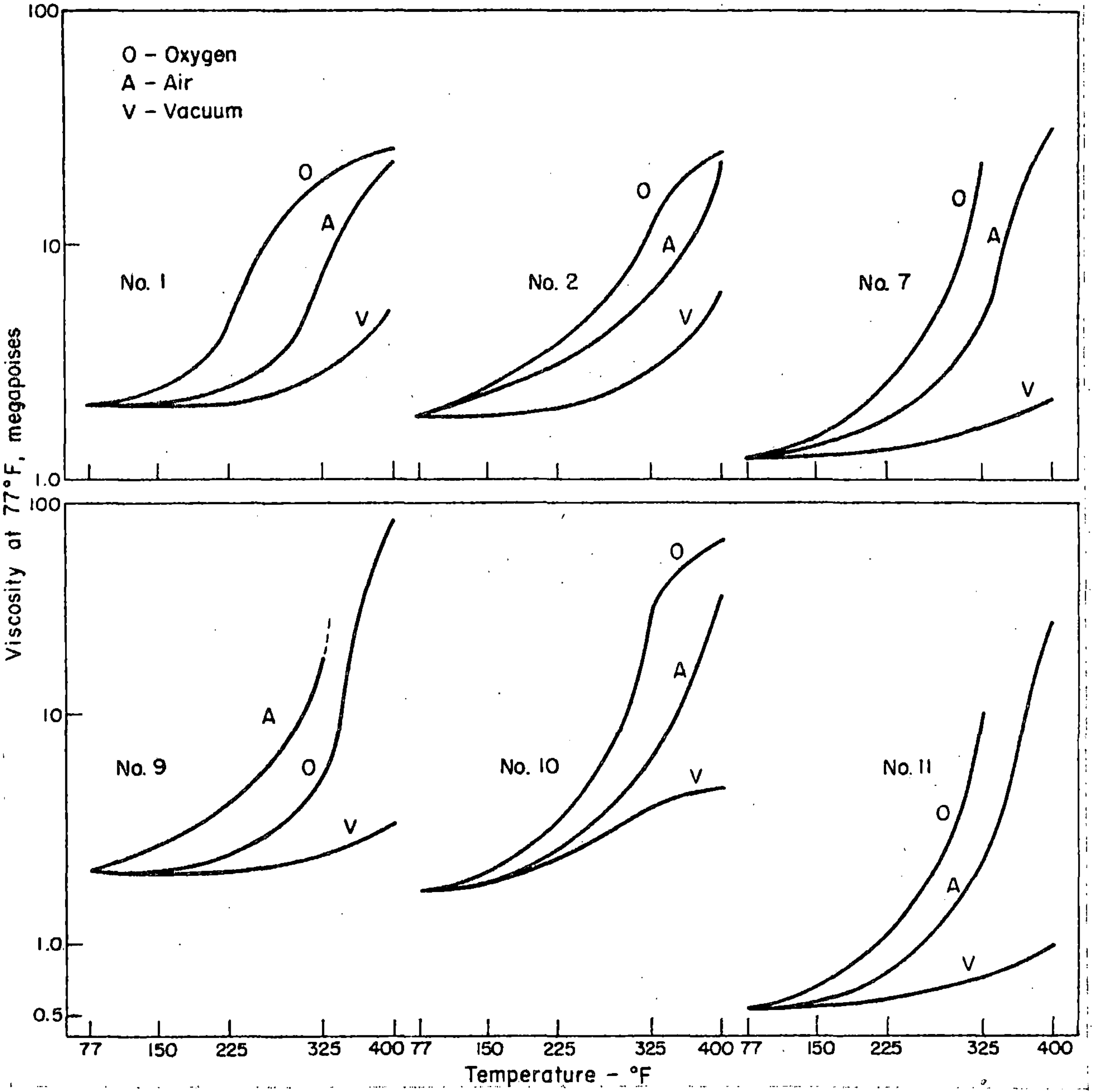


Fig. 1. Log viscosity vs temperature.

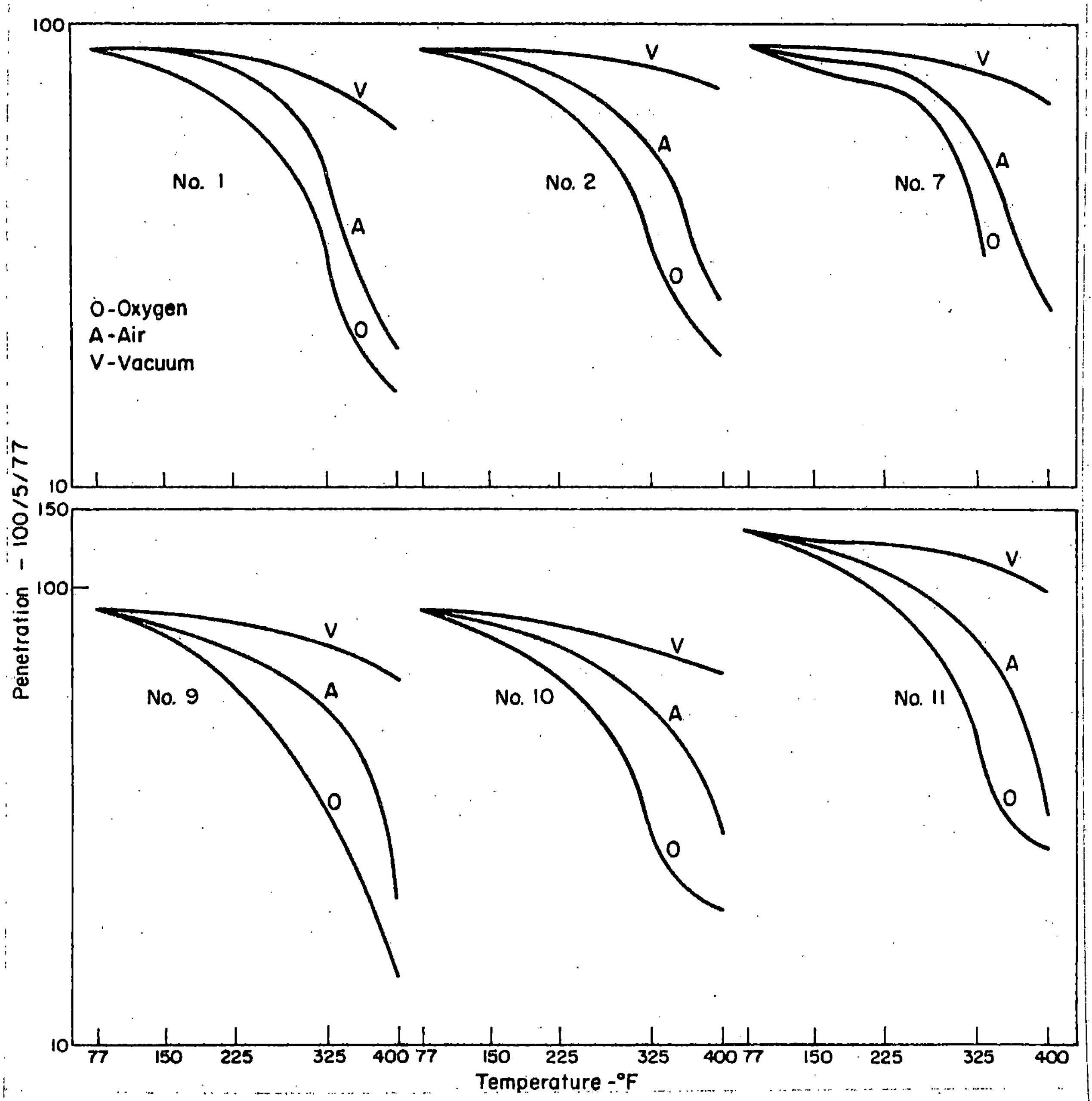


Fig. 2. Log penetration vs temperature.

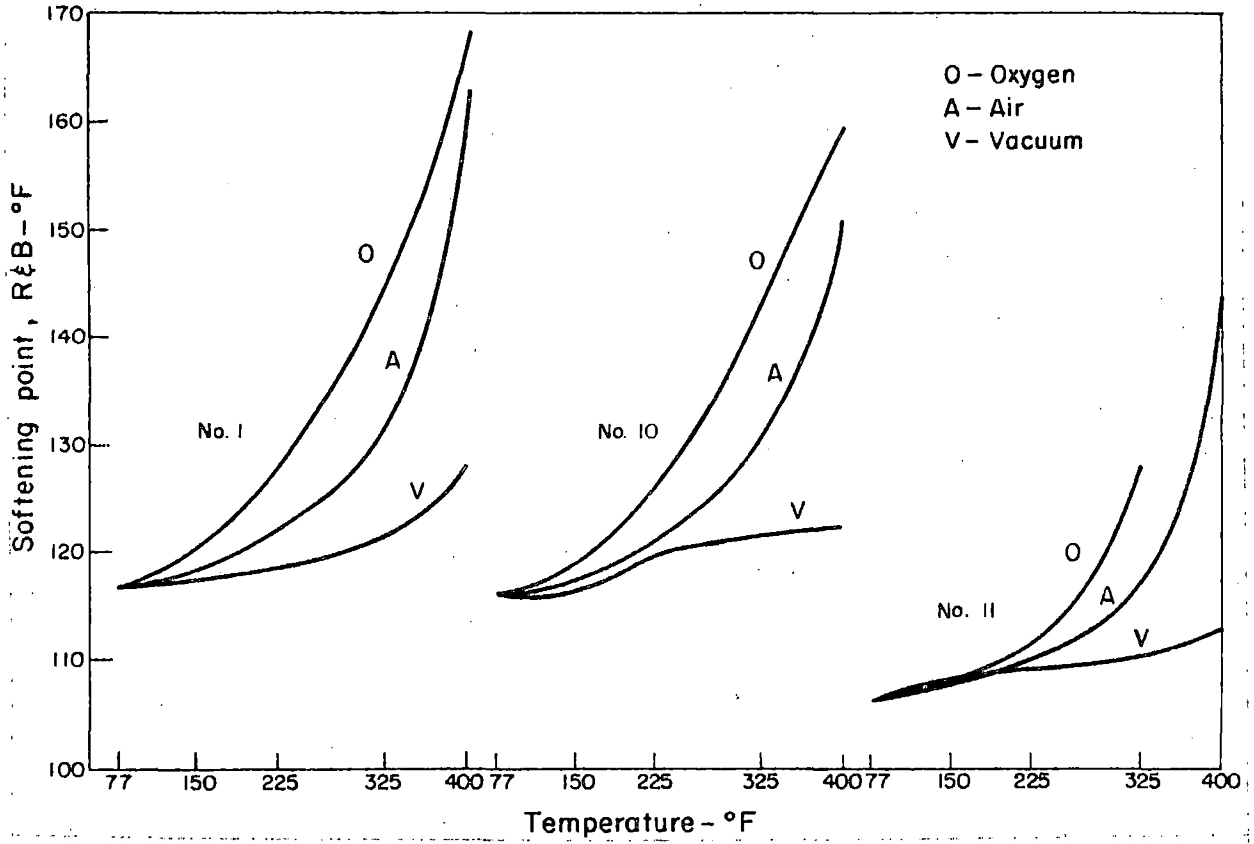


Fig. 3. Softening point vs temperature.

- Hardening and rate of hardening increase with increasing temperature. However, the hardening due to temperature alone as shown for samples heated in vacuum is not pronounced even under relatively severe TFOT conditions, especially at lower temperatures. In most cases heating in a vacuum at 400 °F causes hardening only roughly equivalent to heating in oxygen at 225 °F. Relations between volatility and hardening will be discussed later in the report.
- When heating asphalts in the presence of air or oxygen, the effects of temperature on hardening are drastically compounded due to oxidation (A and O curves). This demonstrates the profound oxidation factor in the hardening of asphalt.

- A marked increase in hardening during TFOT (A curves) as indicated by viscosity and penetration changes occurs from 250 °F upwards. Some asphalts, e.g. Asphalts 1 and 11, the rate of hardening decreased somewhat after 350°F when heated in presence of oxygen. This suggests: (a) Reaction of different asphalts to heat in presence of oxygen may vary considerably, and (b) The behavior of asphalt in the presence of oxygen and the mechanisms of hardening below and above 350°F may differ.

The influence of oxygen on the effect of temperature on hardening during TFOT is further demonstrated by Figs. 4 and 5. Figure 4 is a plot of penetration change against log partial pressure of oxygen in the oven at various temperatures for Asphalts 9 and 10. Figure 5 shows the effect of oxygen on viscosity change at various temperatures for Asphalts 1, 2, 7, and 10. At least two facts are clearly indicated by these curves: (a) The effect of oxygen is more pronounced at high temperatures than at low temperatures, and (b) The effect of oxygen in asphalt hardening is more obvious at low oxygen partial pressures than at high oxygen partial pressures. The influence of oxygen on the asphaltene formation is shown in Fig. 6. This again demonstrates that the asphaltene increase in asphalt during TFOT is a function of oxygen partial pressure as well as temperature.

The effect of temperature on the chemical properties of asphalts during TFOT is indicated by an increase in asphaltene and percent oxygen in the residue. The relations between the asphaltene change and temperature of heating is shown in Fig. 7. The relation between the oxygen content of treated asphalt and heating temperature is shown in Fig. 8. The

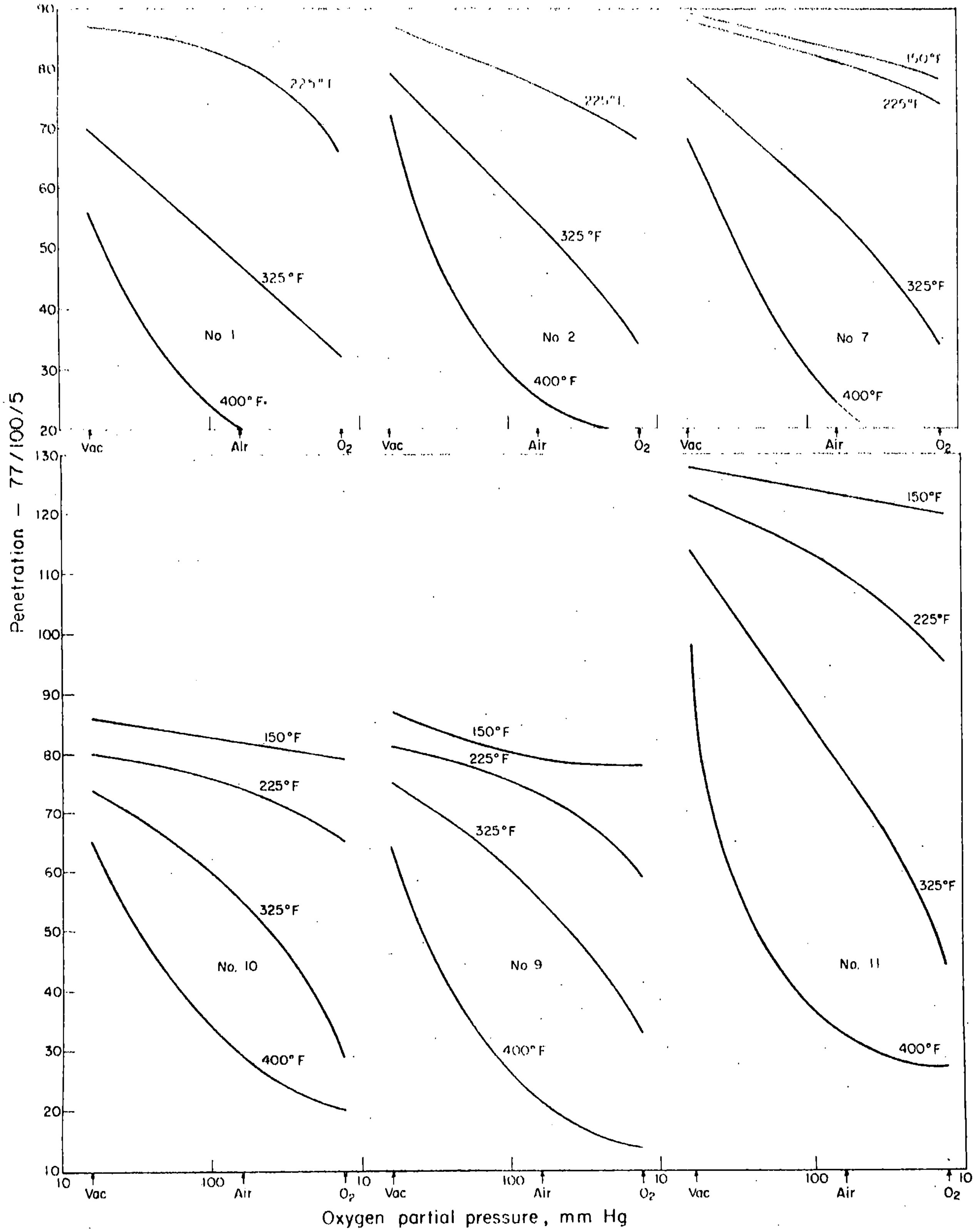


Fig. 4. Penetration vs log oxygen partial pressure.

contributions of both oxygen and temperature in bringing about changes in asphalt during TFOT was again very evident.

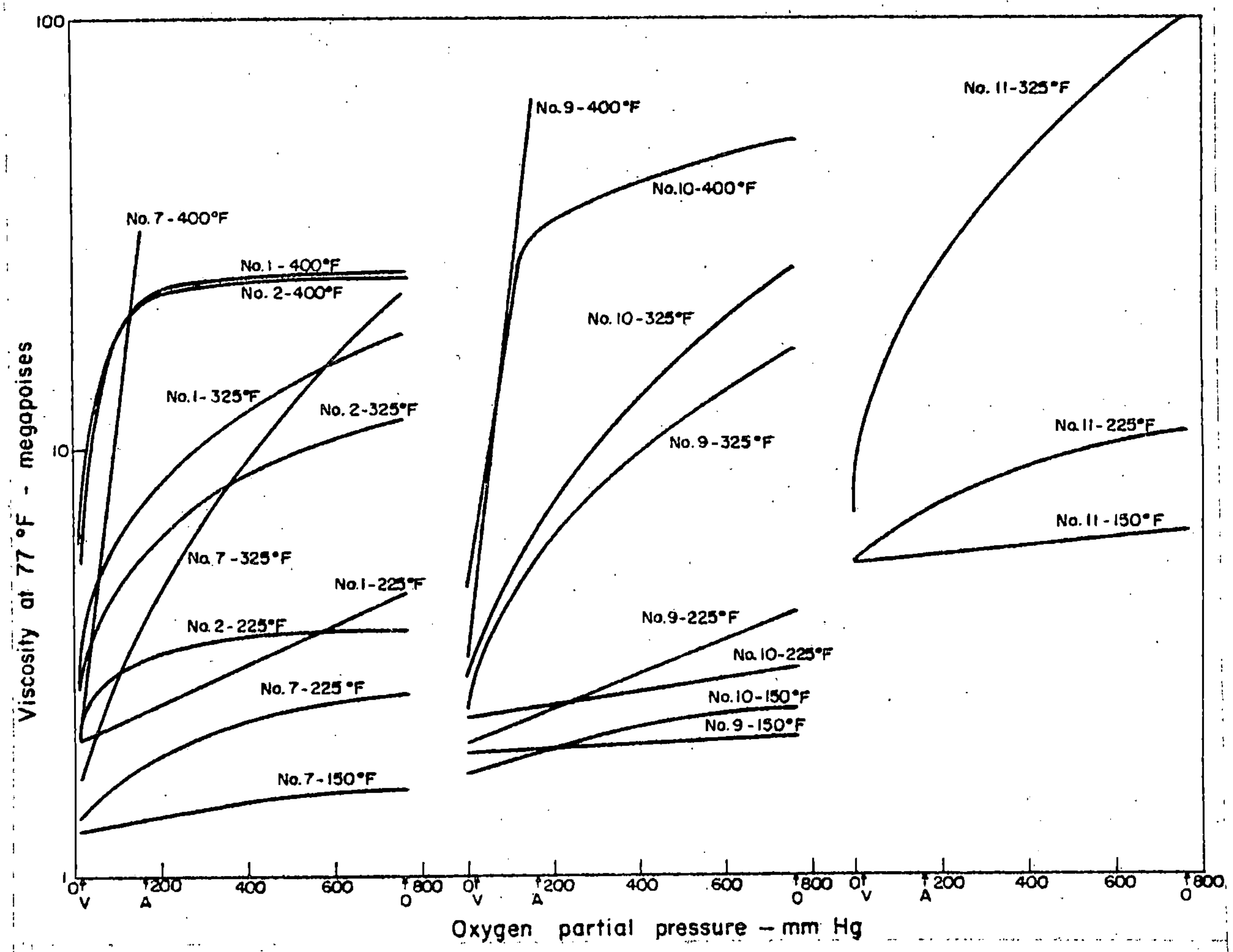


Fig. 5. Log viscosity vs oxygen partial pressure.

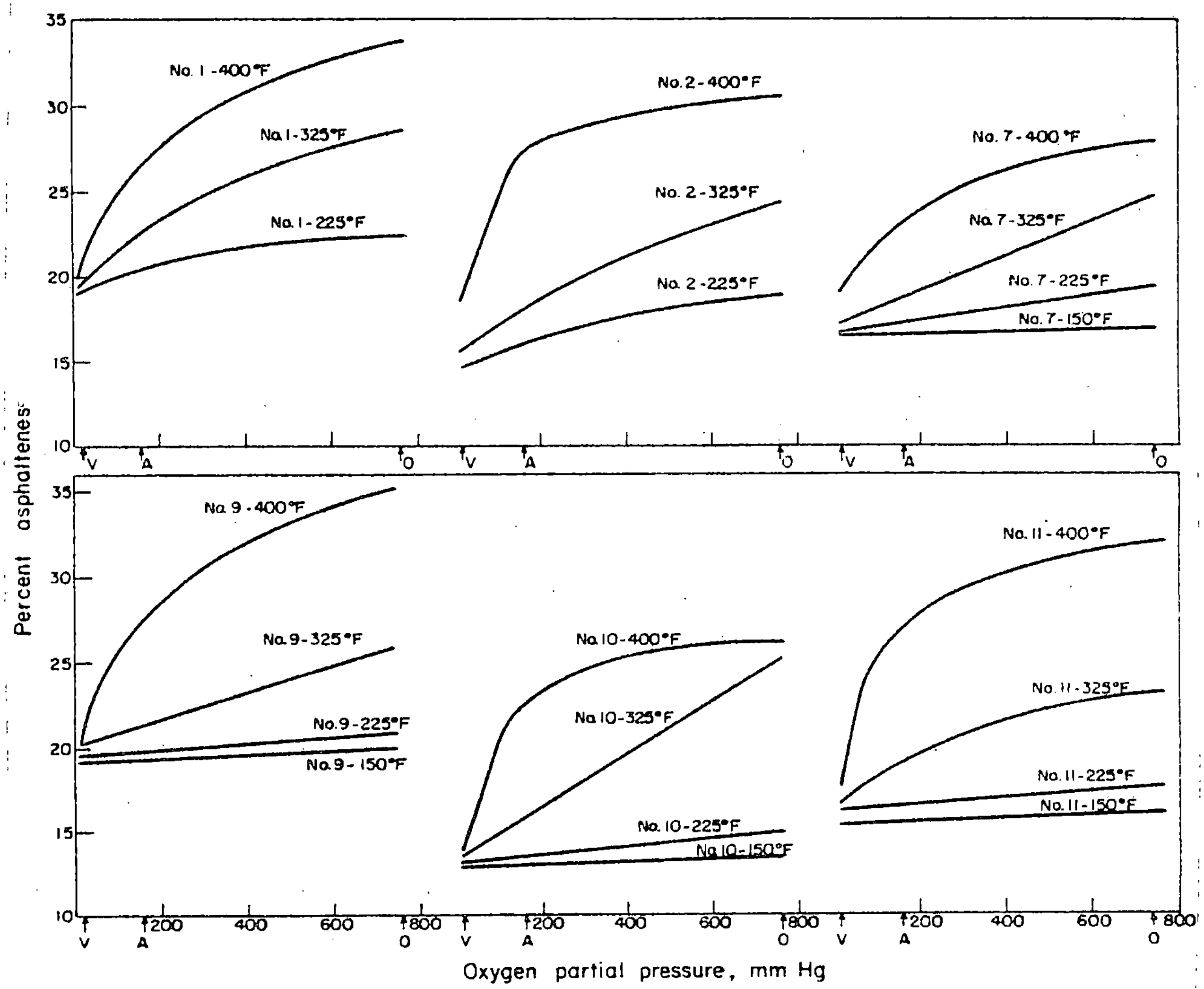


Fig. 6. Percent asphaltenes vs oxygen partial pressure.

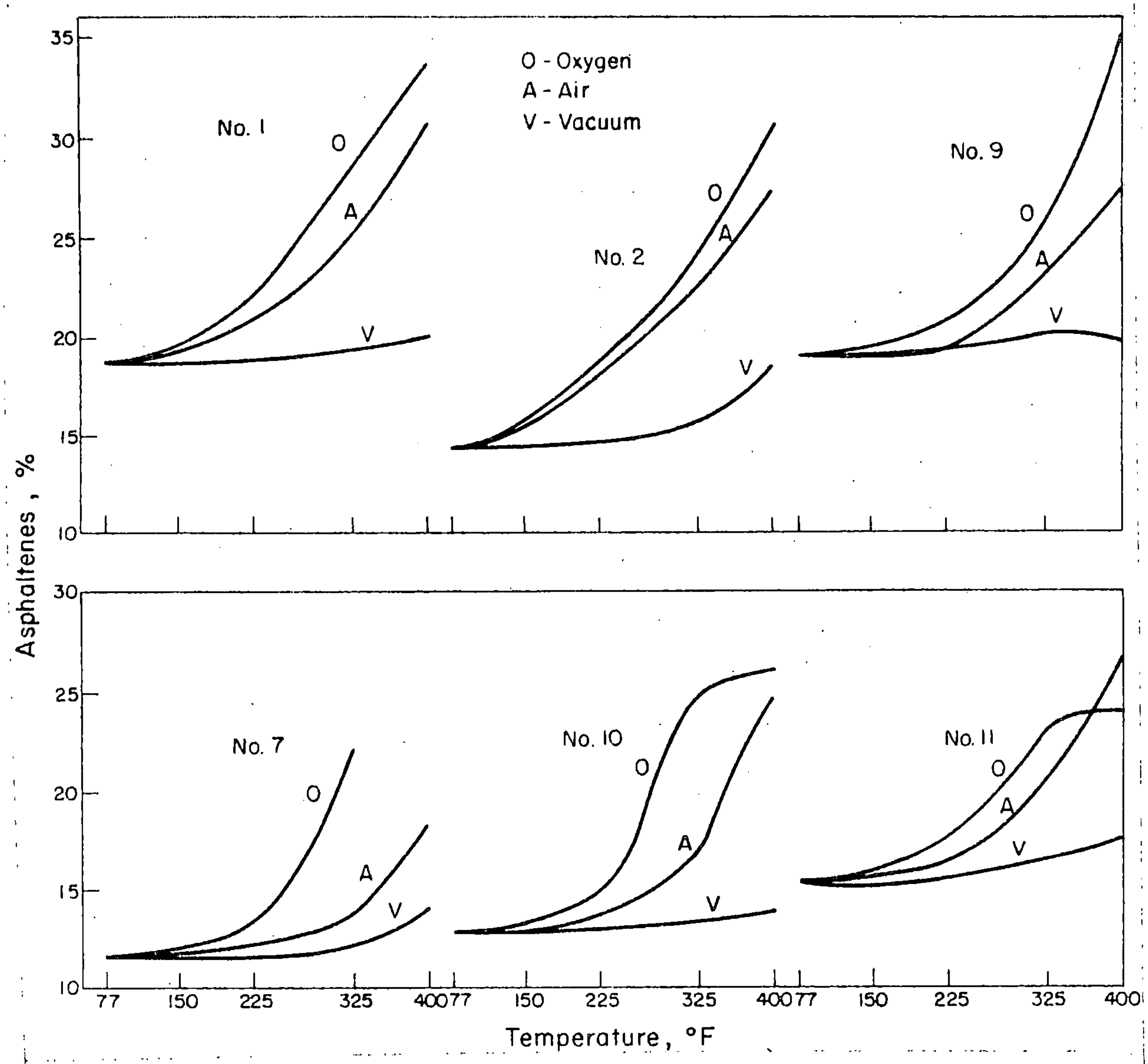


Fig. 7. Percent asphaltene vs temperature.

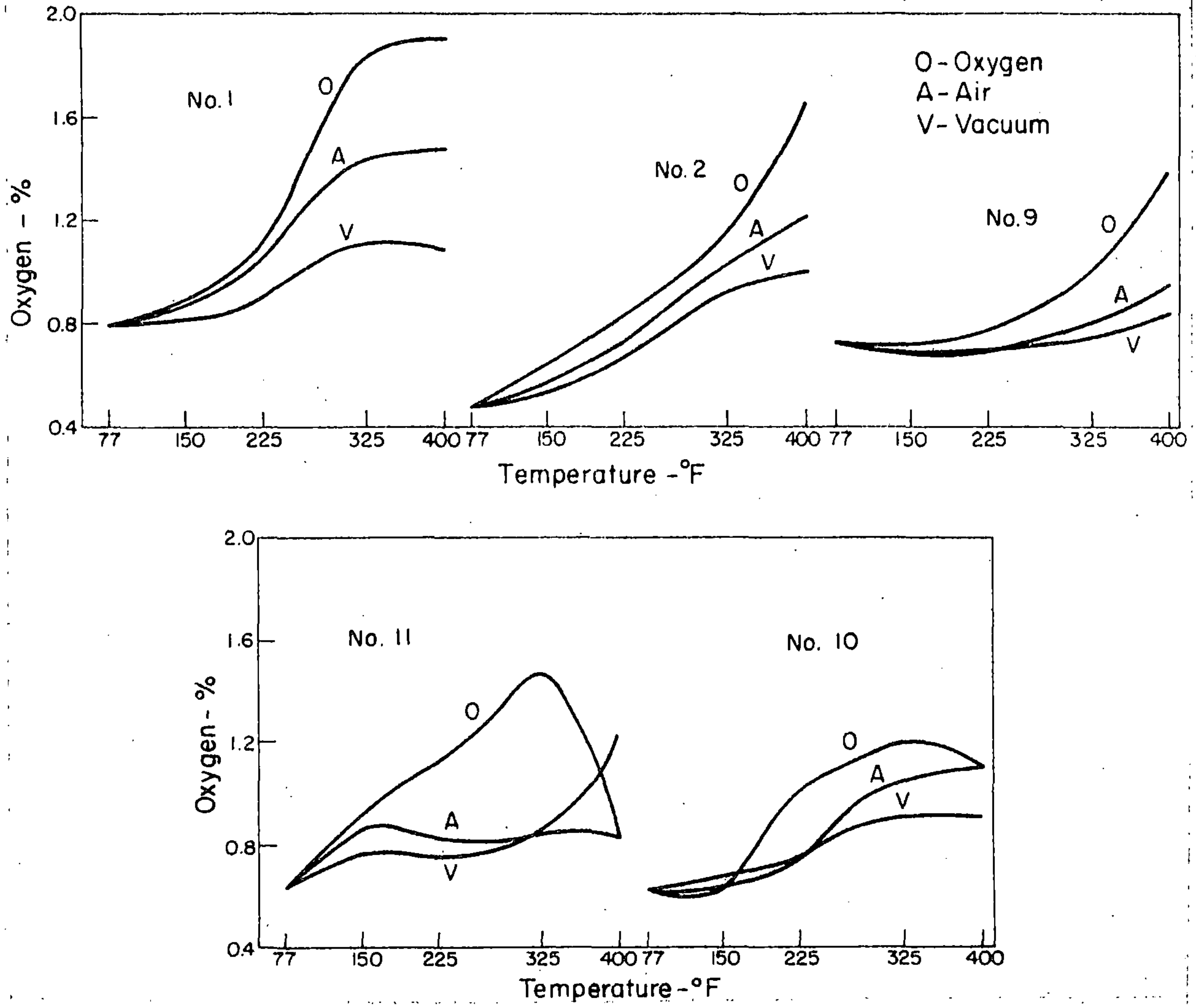


Fig. 8. Percent oxygen vs temperature.

Effects of Film Thickness

The major difference between the standard Loss on Heating Test (LOH) and the Thin Film Oven Test (TFOT) is the film thickness. Film thickness has been recognized as one of the most important factors in influencing asphalt hardening not only in oven heating tests, various microfilm durability tests of asphalt, but also in the field application of asphalt.

Film thickness as a factor was studied on Asphalts 9, 10, and 11. Asphalts in films from 1/64 in. (0.4 mm) to 1-½ in. (38.5 mm) were heated in standard oven at 325 °F for 5 hours. Metal containers with surface area of 23.8 sq cm (3 oz cans) to 153.9 sq cm (TFOT pans) were used. Changes in asphalt after heating in various film thicknesses were determined by sliding plate microviscometer, R&B softening point test, and percent asphaltene[29]. The film thickness, exposed surface area of sample, volume of asphalt used, specific surface and resulted viscosity at 77 °F (rate of shear of $5 \times 10^{-2} sec^{-1}$), softening point, and percent asphaltenes for the asphalts studied are given in Tables 5, 6, and 7. Relations between film thickness and viscosity of the residue is shown in Fig. 9. Effects of film thickness on softening point of residue is shown in Fig. 10. Asphaltene content change due to change in film thickness in TFOT is shown in Fig. 11. For comparison the plot of softening point versus log specific surface is given in Fig. 12. The following conclusions have been made:

- Hardening and chemical change in asphalt during TFOT is a function of film thickness.

Table 5. Effects of film thickness, A.C. No. 9

Film Thickness (in.)	(mm)	Surface area (cm^2)	Volume (cm^3)	Specific surface (cm^2/g)	Viscosity 77 °F (poises)	Softening point (°F)	Asphaltenes (%)
1½	38.1	38.5	146.6	0.26	2.35×10^6	--	19.0
1	25.4	38.5	97.8	0.39	2.50×10^6	115.5	19.1
13/16	21.1	23.8	50.0	0.48	2.70×10^6	--	19.1
3/4	19.1	38.5	73.3	0.53	2.55×10^6	--	--
1/2	12.7	38.5	48.9	0.79	2.85×10^6	--	--
1/4	6.4	38.5	24.4	1.58	3.00×10^6	121.0	--
1/4	6.4	153.9	97.8	1.58	3.20×10^6	118.5	19.3
3/16	4.8	38.5	18.4	2.10	3.65×10^6	119.5	--
3/16	4.8	153.9	73.4	2.10	3.90×10^6	119.5	19.4
1/8	3.2	38.5	12.2	3.15	5.40×10^6	123.0	--
1/8	3.2	153.9	50.0	3.15	5.10×10^6	122.5	20.0
1/16	1.6	153.9	24.4	6.31	1.73×10^7	132.5	23.2
1/32	0.8	153.9	12.2	12.62	4.00×10^7	--	28.0
1/64	0.4	153.9	6.1	25.24	2.50×10^8	--	30.6

- No appreciable change took place in the asphalt during 5 hours at 325 °F in films of more than about 1/4 in. thicknesses indicated by all properties determined. However, asphalts in films less than 1/4 in. to 1/8 in., significant changes occurred both in consistency as measured by absolute viscosity and softening point, and in chemical changes as indicated by the increase in percent asphaltenes.
- In both log viscosity vs log film thickness (Fig. 13) and asphaltene vs log film thickness, Fig. 14, plots, there appear to be a critical or transitional film thickness. Below and above these points there is a linear relation between log viscosity and log film thickness, and percent asphaltene and log film thickness over the range studied.

Table 6. Effects of film thickness, A.C. No. 10.

Film Thickness (in.)	(mm)	Surface area (cm^2)	Volume (cm^3)	Specific surface (cm^2/g)	Viscosity 77 °F (poises)	Softening point (°F)	Asphaltenes (%)
1½	38.1	38.5	146.6	0.26	1.85×10^6	--	13.0
1	25.4	38.5	97.8	0.39	2.40×10^6	116.0	13.1
13/16	21.1	23.8	50.0	0.48	2.55×10^6	--	13.4
3/4	19.1	38.5	73.3	0.53	2.50×10^6	--	13.3
1/2	12.7	38.5	48.9	0.79	2.50×10^6	--	13.4
1/4	6.4	38.5	24.4	1.58	3.50×10^6	124.0	14.0
1/4	6.4	153.9	97.8	1.58	2.80×10^6	122.5	13.6
3/16	4.8	38.5	18.4	2.10	4.50×10^6	125.5	16.6
3/16	4.8	153.9	73.4	2.10	4.40×10^6	125.0	15.2
1/8	3.2	38.5	12.2	3.15	5.70×10^6	127.5	18.6
1/8	3.2	153.9	50.0	3.15	5.30×10^6	128.0	16.7
1/16	1.6	153.9	24.4	6.31	1.55×10^7	136.0	19.1
1/32	0.8	153.9	12.2	12.62	3.15×10^7	153.0	22.6
1/64	0.4	153.9	6.1	25.24	5.70×10^7	--	26.0

The change in slope of the straight lines could indicate change in the mechanisms causing hardening and increase in asphaltene content. It is suggested that in asphalt films thicker than the "transitional thickness" volatilization and heat are major effects, while in films thinner than the "transitional thickness" oxidation and heat assume more significant importance.

Note that the straight line portions of Asphalt 9 intersect at a film thickness of 4 mm on both viscosity-film thickness and asphaltene content-film thickness plots; for Asphalt 10 these points occurred at 7 mm and at 5 mm, while for Asphalt 11 they were 7 mm and 4 mm. It is interesting to note that, according to Blokker and Van Hoorn[30], hardening of asphalt due to oxidation in the dark may occur down to depths of 3 mm or more by measurement of the rate of oxygen absorption and to depths

Table 7. Effects of film thickness A.C. No. 11

Film Thickness (in.)	(mm)	Surface area (cm^2)	Volume (cm^3)	Specific surface (cm^2/g)	Viscosity 77 °F (poises)	Softening point (°F)	Asphaltenes (%)
1	25.4	38.5	97.8	0.39	5.30×10^5	108.5	16.2
13/16	21.1	23.8	50.0	0.48	6.20×10^5	--	16.5
3/4	19.1	38.5	73.3	0.53	7.80×10^5	--	16.9
1/2	12.7	38.5	48.9	0.79	8.20×10^5	--	17.2
1/4	6.4	38.5	24.4	1.58	1.00×10^6	112.5	18.0
1/4	6.4	153.9	97.8	1.58	8.70×10^5	112.0	17.5
3/16	4.8	38.5	18.4	2.10	1.26×10^6	114.0	17.9
3/16	4.8	153.9	73.4	2.10	1.06×10^6	113.5	18.1
1/8	3.2	38.5	12.2	3.15	2.23×10^6	116.0	19.4
1/8	3.2	153.9	50.0	3.15	2.15×10^6	116.0	18.9
1/16	1.6	153.9	24.4	6.31	3.45×10^6	--	21.4
1/32	0.8	153.9	12.2	12.62	9.80×10^6	138.5	23.4
1/64	0.4	153.9	6.1	25.24	2.20×10^7	--	26.1

depths of about 5 mm by theoretical calculation on the depth of oxygen penetration.

- Since slopes of the straight line portions of the viscosity-film thickness plots for various asphalts are not necessarily the same (possibly due to the differences in the reactivity of asphalts towards oxygen and in the volatiles available in the asphalt) and since the consistency change is not a linear function of film thickness throughout the entire range of film thickness, it is not difficult to understand the poor correlation between hardening during LOH and TFOT.
- The effects of the sample volume on TFOT results were studied by heating asphalts in 1/8-in. film at 325 °F for 5 hours in volumes of 7.6 ml to 51.8 ml. The viscosity of residues was determined

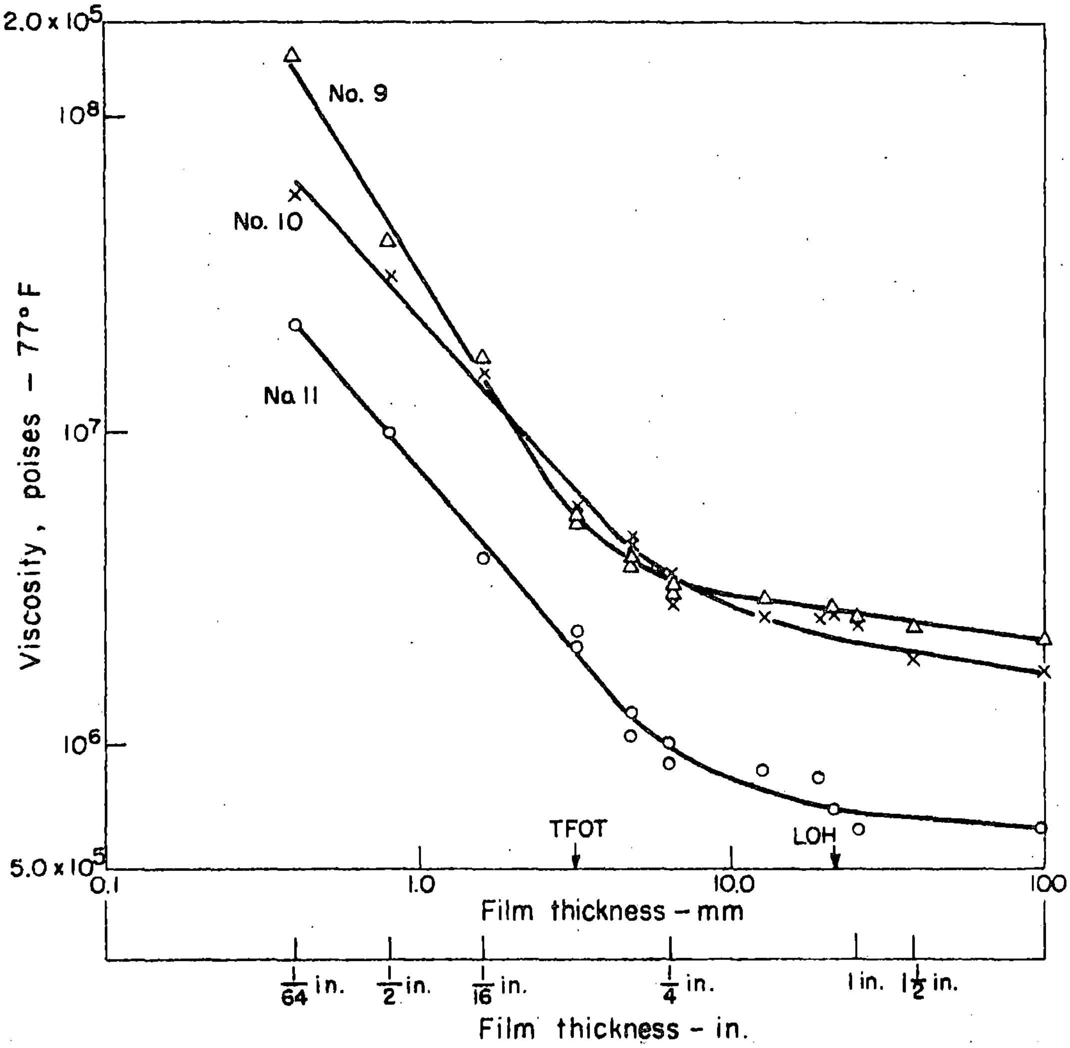


Fig. 9. Viscosity vs film thickness, TFOT.

at 77 °F. Results on two asphalts are given in Table 8. It was concluded that, within the range studied, the volume of sample has no effect on TFOT results as long as other conditions remain constant. Data on 1/4 in. and 3/16 in. films on all three asphalts also support this conclusion.

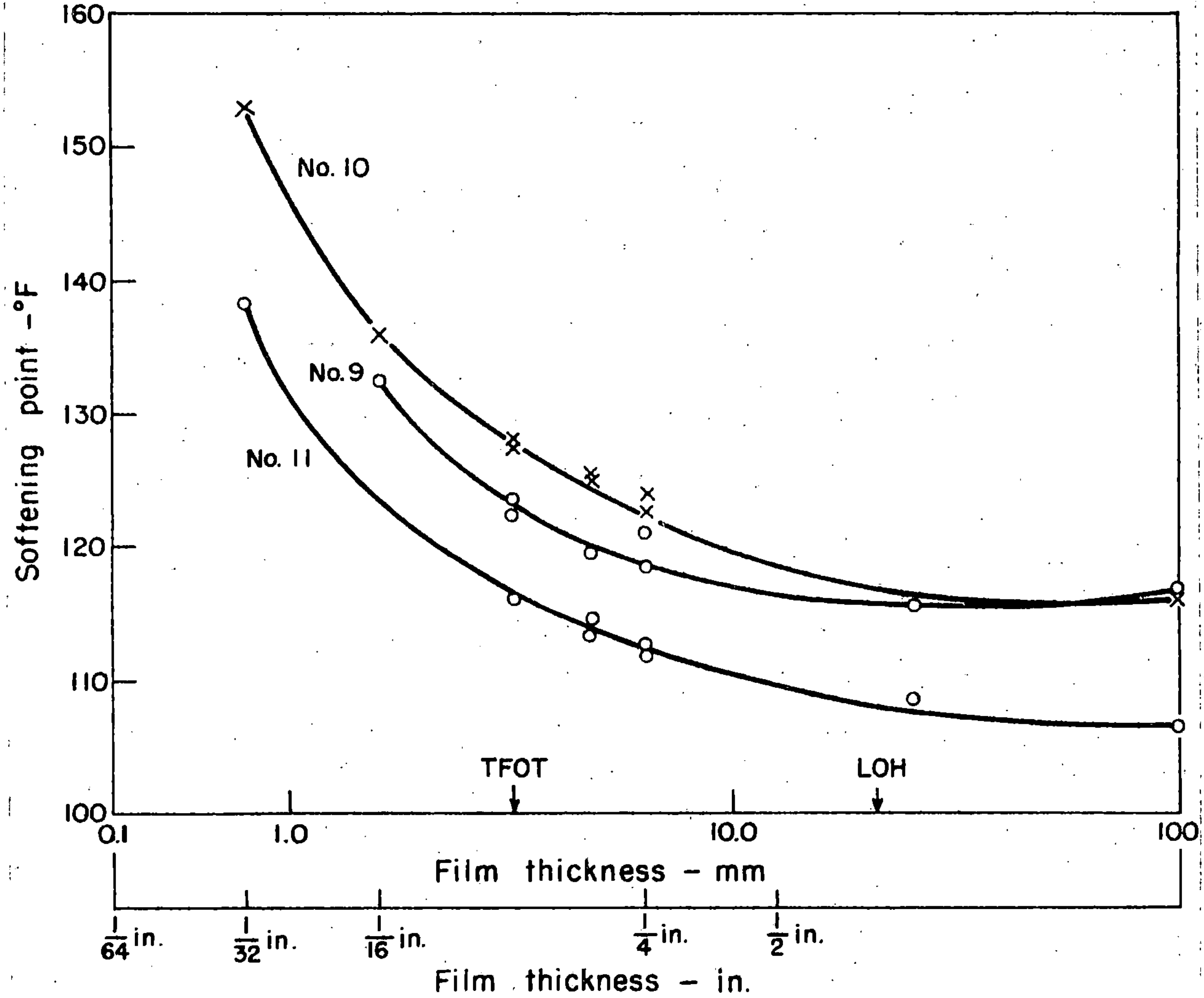


Fig. 10. Softening point vs film thickness.

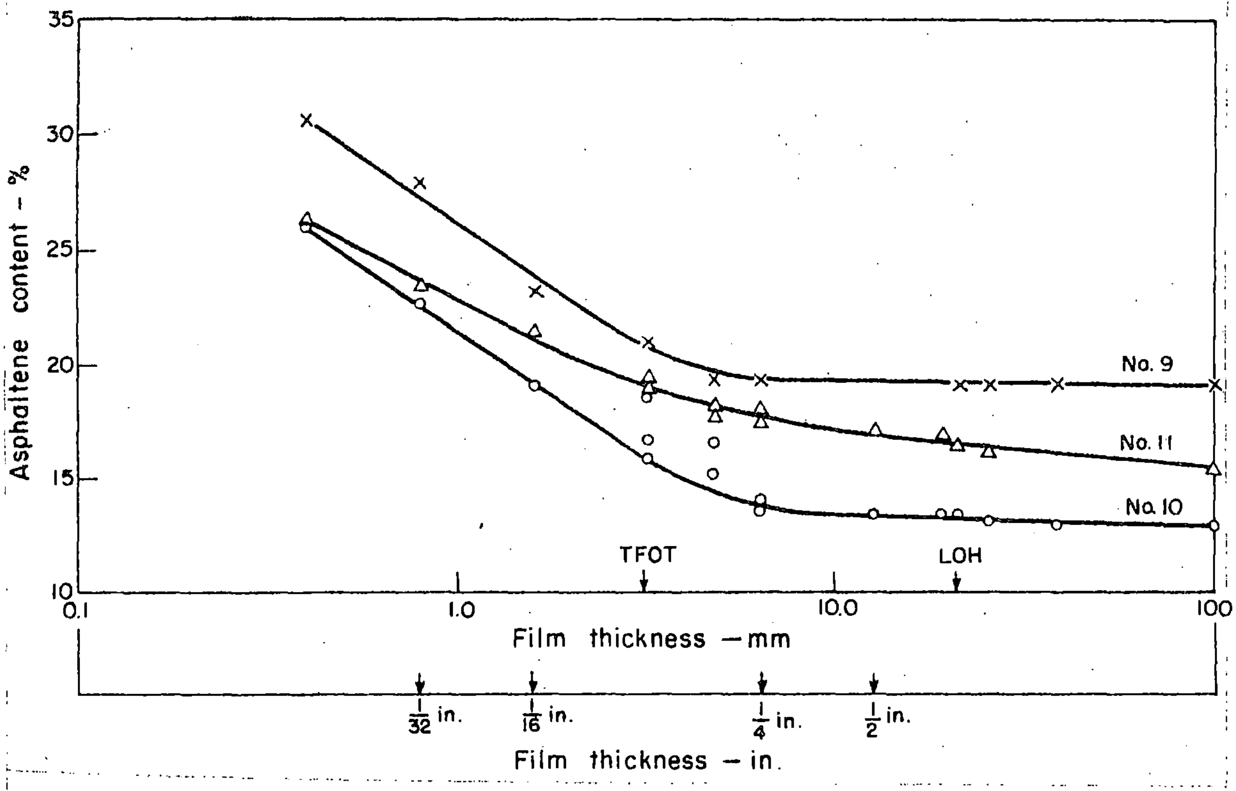


Fig. 11. Asphaltene content vs film thickness, TFOT.

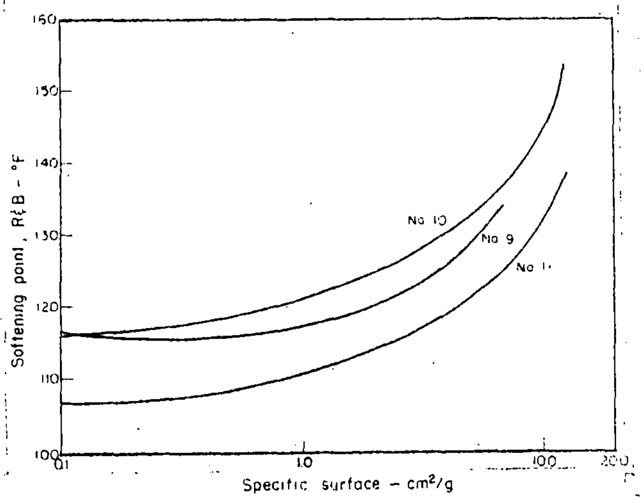


Fig. 12. Specific surface softening point.

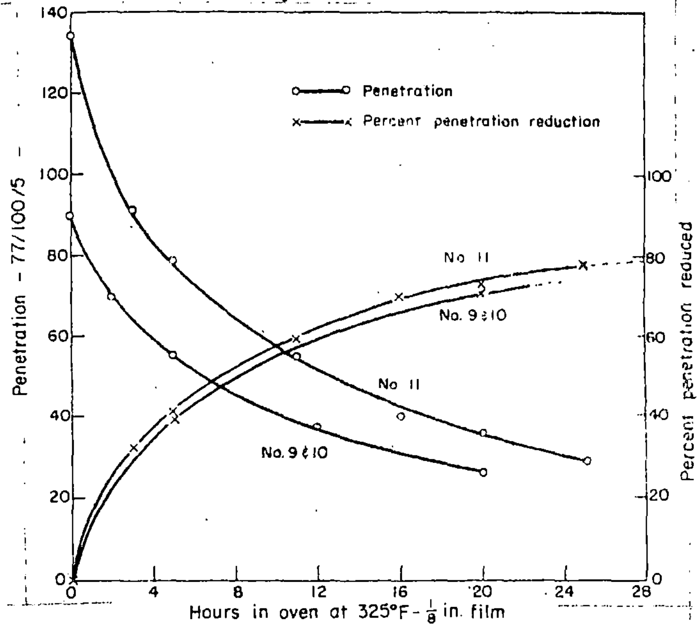


Fig. 13. Effect of heating vs time on penetration.

Table 8. Effects of volume on TFOT.

A.C.	Film thickness (in.)	Volume of sample (ml)	Viscosity at 77 ^{o}F (megapoises)
10	1/8	7.6	5.85
	1/8	8.1	6.60
	1/8	12.2	5.70
	1/8	12.3	6.30
	1/8	25.0	6.60
	1/8	26.0	6.05
	1/8	50.0	6.15
	1/8	51.8	6.30
11	1/8	8.1	2.25
	1/8	12.2	2.23
	1/8	25.0	2.20
	1/8	50.0	2.15

Effects of Heating Time

The effect of heating time on the TFOT (1/8-in. film, 325 °F) was studied by Lewis and Welborn[31], on sixteen 50-60 pen. asphalts up to 10 hours. To obtain more definite information concerning the behavior of 85-100 pen. and 120-150 pen. asphalts in the TFOT with respect to time and in terms of absolute viscosity and chemical changes, Asphalts 9, 10, and 11 were heated at 325 °F in 1/8-in. films for periods up to 25 hours. Penetration, softening point, absolute viscosity at 77 °F, and percent asphaltene were determined on residues after various periods of heating. Results of the tests are given in Table 9. The effect of heating time on penetration is shown in Fig. 13. Also shown in Fig. 13 is the plot of percent penetration loss with time. Figure 15 shows the increase in viscosity with time for all three asphalts. Hardening takes place at decreasing rate with time of heating. When hardening is evaluated in terms of penetration ratio, a linear relationship was found between penetration ratio and time of heating, Fig. 14. A straight line relationship was also found between softening point of the residue and the time of heating, as shown in Fig. 16. The TFOT is relatively insensitive to variation in time of heating at 5 hours. A variation of 15 minutes would vary the penetration on TFOT residue by less than 2 percent. The increase in asphaltene content in asphalt with time of heating was expected and is shown in Fig. 17.

Table 9. Effect of heating time, 1/8-in. film, 325°F.

A.C. No.	9				10				11			
Hours	Penetration 77/100/5	Viscosity, 77 °F (megapoises)	Asphaltenes (%)	Softening point (°F)	Penetration 77/100/5	Viscosity, 77 °F (megapoises)	Asphaltenes (%)	Softening point (°F)	Penetration 77/100/5	Viscosity, 77 °F (megapoises)	Asphaltenes (%)	Softening point (°F)
1	90	2.10	19.1	116.5	90	1.70	12.9	116.0	134	0.53	15.3	106.5
2	--	3.50	19.7	118.5	--	2.80	14.9	121.5	--	--	--	--
3	--	--	--	--	--	3.20	15.0	--	91	1.11	17.6	111.5
4	--	4.25	20.2	--	--	4.60	16.4	--	--	--	--	--
5	55	5.10	21.0	122.5	55	6.15	16.7	129.0	79	1.62	18.9	116.0
6	--	7.40	21.8	--	--	--	--	--	--	--	--	--
7	--	--	--	--	--	7.77	16.6	--	--	--	--	--
8	--	10.5	22.4	--	--	--	--	--	--	--	--	--
10	--	--	--	--	--	12.7	17.2	134.5	--	--	--	--
11	--	--	--	--	--	--	--	--	55	5.10	21.6	124.5
12	37	16.5	24.4	131.5	--	--	--	--	--	--	--	--
14	--	18.0	25.0	--	--	--	--	--	--	--	--	--
16	--	21.0	25.3	--	--	19.5	17.4	--	40	11.5	23.2	130.5
18	--	23.0	25.7	--	--	--	--	--	--	--	--	--
20	26	27.5	26.2	143.5	26	22.1	17.8	150.5	36	14.5	23.7	136.5
22	--	28.5	25.9	--	--	--	--	--	--	--	--	--
24	--	--	--	--	--	26.0	19.1	--	--	--	--	--
28	22	33.0	26.6	--	--	--	--	--	29	17.5	25.0	142.5

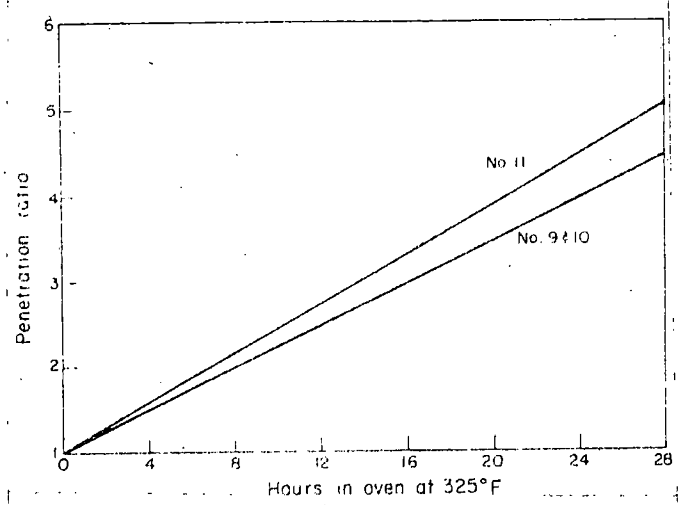


Fig. 14. Time of heating at $325^{o}F$ vs penetration ratio.

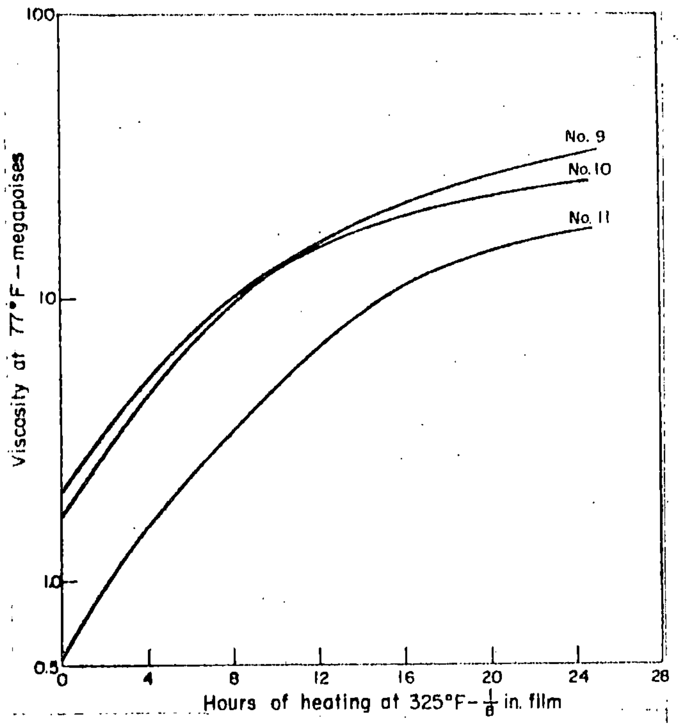


Fig. 15. Viscosity vs heating time.

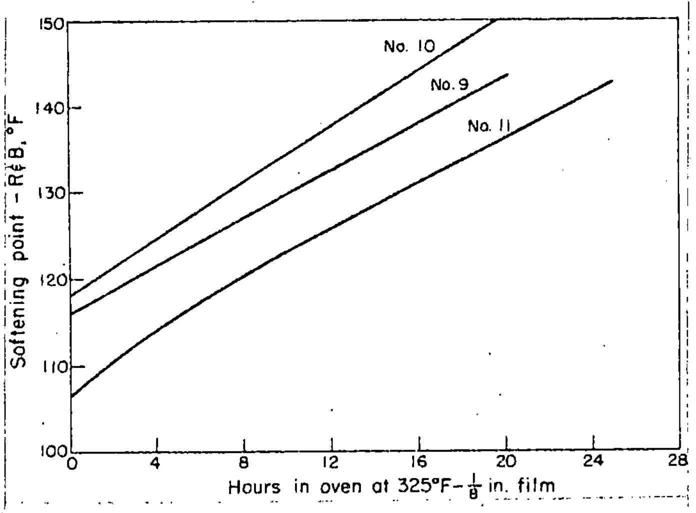


Fig. 16. Softening point vs heating time.

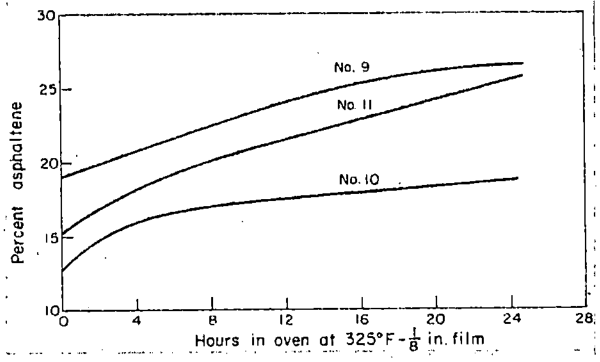


Fig. 17. Asphaltene content heating time.

Effects of Heating Medium

When the oven heating test for asphalt was first developed, the major concern was the weight loss during the test. The purpose of the test was obviously the evaluation of the volatility of asphalt and thus was named by many as the Volatilization Test and by the ASTM as the Loss on Heating Test.

While it seems to be the concensus of opinion that the TFOT is an evaluation of the combined effects of volatilization, oxidation, and heat on asphalt, the nature or the relative importance of each factor in the test has not been agreed and clearly defined.

To evaluate the relative effects of volatility, oxidation, and heat on the TFOT, asphalts were exposed to 27-in. vacuum, air, oxygen, nitrogen, and carbon dioxide for 5 hours in 1/8-in. films at 325 °F. Penetration, softening point, viscosity at 77 °F, and percent asphaltenes were determined on the residues. Results on these tests are presented in Table 10. Percent loss in penetration during heating at 325 °F in 1/8-in. films in various atmospheres are shown graphically in Fig. 18. The following can be noted:

- Oxygen is the most important element causing hardening during the TFOT. When the availability of oxygen decreased from heating in oxygen to heating in vacuum, hardening also decreased.
- Nonoxidative hardening exists during the TFOT since hardening occurs when asphalt is heated in absence or limited amount of oxygen.
- Comparing the average penetration loss of 40 percent when asphalt was heated in air and the 15 percent loss in vacuum, it can be

Table 10. Effects of heating medium in TFOT, 325°F, 5 hours, 1/8-in. film.

A.C. No.	Medium	Penetration 100/5/77	Softening point (°F)	Viscosity 77 °F (megapoises)	Percent Asphaltenes
1	Original	88	116.5	2.10	18.8
	N_2, 1 atm	71	121.0	2.56	19.1
	CO_2, 1 atm	70	121.5	2.80	19.5
	27 in vac	72	120.5	2.80	19.5
	Air, 1 atm	48	131.5	7.50	22.7
	O_2, 1 atm	32	160.5	18.6	28.7
2	Original	88	116.5	1.90	14.4
	N_2, 1 atm	71	122.5	2.64	16.1
	CO_2, 1 atm	72	121.0	2.63	16.0
	27 in vac	79	119.5	2.80	15.6
	Air, 1 atm	54	133.0	5.64	18.1
	O_2, 1 atm	34	146.5	11.70	24.4
7	Original	90	112.5	1.25	16.6
	N_2, 1 atm	67	118.5	2.80	16.7
	CO_2, 1 atm	67	121.5	2.30	19.5
	27 in vac	78	117.5	1.72	17.1
	Air, 1 atm	55	127.0	4.65	18.8
	O_2, 1 atm	34	144.5	23.0	24.8
9	Original	90	116.5	2.10	19.1
	N_2, 1 atm	67	121.5	2.95	18.9
	CO_2, 1 atm	68	120.0	2.80	19.0
	27 in vac	75	119.5	2.45	20.2
	O_2, 1 atm	33	147.5	17.0	25.9
	Air, 1 atm	55	124.0	5.50	21.4
10	Original	90	117.0	1.70	12.9
	N_2, 1 atm	62	128.5	5.30	13.5
	CO_2, 1 atm	60	128.5	5.80	14.2
	27 in vac	74	121.5	3.90	13.3
	Air, 1 atm	55	130.0	6.45	16.0
	O_2, 1 atm	29	144.5	26.5	25.1

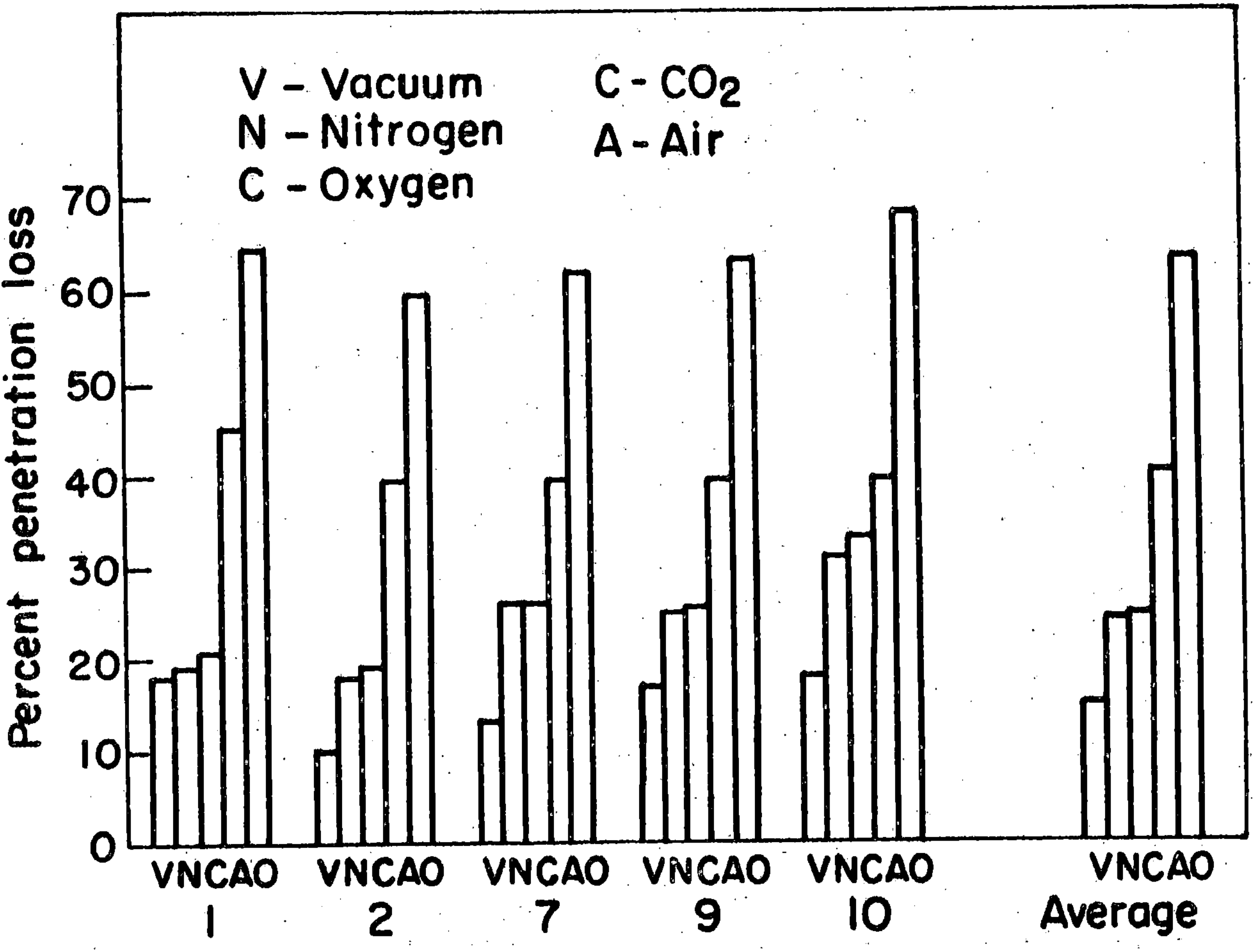


Fig. 18. Effect of healing medium in penetration loss.

concluded that, at 325 ^{o}F, only about 40 percent of hardening in terms of penetration loss can be attributed to heat (polymerization) and volatilization, the rest being due to essentially oxidation.

● The minor role volatility plays in the TFOT hardening can be observed from the facts that: (a) The weight loss in asphalt heated in vacuum was greater than weight loss in asphalt heated in either air or oxygen, however, asphalt hardened much less when heated in vacuum; and (b) when asphalt was heated in absence of oxygen, hardening occurred where little or no weight loss due to volatilization was observed.

Thin Film Oven Test vs Volatility of Asphalt

Many factors contribute to changes in asphalt during handling and under service conditions. Traxler[31] suggested 15 of them. The more important ones include oxidation, volatilization, polymerization, and age hardening. When considering or evaluating these factors in relation to asphalt quality or durability it should be remembered that: (a) Some factors are more important in influencing asphalt durability in one phase of asphalt use than in others, (b) One or more of the factors may function simultaneously, and (c) Almost all the effects are affected by time and heat.

Volatilization can be defined here as the evaporation of volatiles or lighter constituents from asphalt. Exposed surface area, temperature, pressure, and heating time can all have effects on the process. The degree and rate of volatilization of any asphalt depends upon the composition of asphalt, the nature and quantity of its volatiles, and to a certain extent on its source and refining procedure.

Volatile evaporation from asphalt cements produced by a modern refining process at road service temperatures is unlikely or not in the order of any significance. However, when hot asphalt is mixed with hot aggregate and spread in thin films, as in the mixing process of an asphaltic concrete, the conditions are very favorable to loss of volatiles. Many investigators[32-34] believe that during mixing process volatilization is one of the major causes for hardening of asphalt. Hardening of asphalt due to evaporation of volatiles has been included in the study of durability of paving asphalts.

Qualitative detection of existence of volatiles in asphalt can be determined by the Flash and Fire Point Test. To assess quantitatively how much hardening during hot mixing of asphalt is due exclusively to volatilization, or the relative importance of volatilization in asphalt hardening is difficult, if not impossible. This is due to the closely associated mechanisms of volatilization, oxidation, and polymerization. One way to evaluate the hardening of asphalt due to volatilization is by heating asphalt in inert atmosphere. In this approach while oxidation is eliminated still only a portion of the asphalt hardening may be attributed to the loss of volatiles since heat is involved. Another approach to the problem has been various forms of oven heating or volatilization tests, especially Loss on Heating (LOH) and Thin Film Oven Test (TFOT).

There are many questions in relation to the value and interpretation of LOH and TFOT results and volatility of asphalt. Among these more basic ones are:

- Does weight loss correspond to hardening or viscosity change?
- Does LOH or TFOT weight loss reflect total amount of volatiles?
- What are the relationships between standard LOH test and TFOT?
- What are the mechanisms of weight change during oven tests?
- What are the effects of temperature and oxidation on weight loss during oven tests?

In attempting to answer some of these questions, 10 asphalt cements were studied, ranging from 50-60 to 200-300 pen grades. Weight losses, penetration, viscosity at 77 ^{o}F, softening point, and asphaltene content were determined both on standard LOH tests and on TFOT. In addition, weight change histories of all asphalts both under LOH

(13/16-in. film, 325 °F) and TFOT (1/8-in. film, 325 °F) conditions were recorded until up to 480 hours or until a definite weight gain was obtained. Also weight and consistency changes during TFOT in air, in oxygen, in 27-in. mercury vacuum and in nitrogen (or carbon dioxide) at temperatures of 150, 225, 325, and 400 °F were determined. Weight change and percent hardening of the 10 asphalts during standard LOH tests are tabulated in Table 11. The same information on TFO tests is shown in Table 12. Weight change histories of asphalts during TFOT and LOH were plotted graphically against time in Fig. 19 and Fig. 20, respectively.

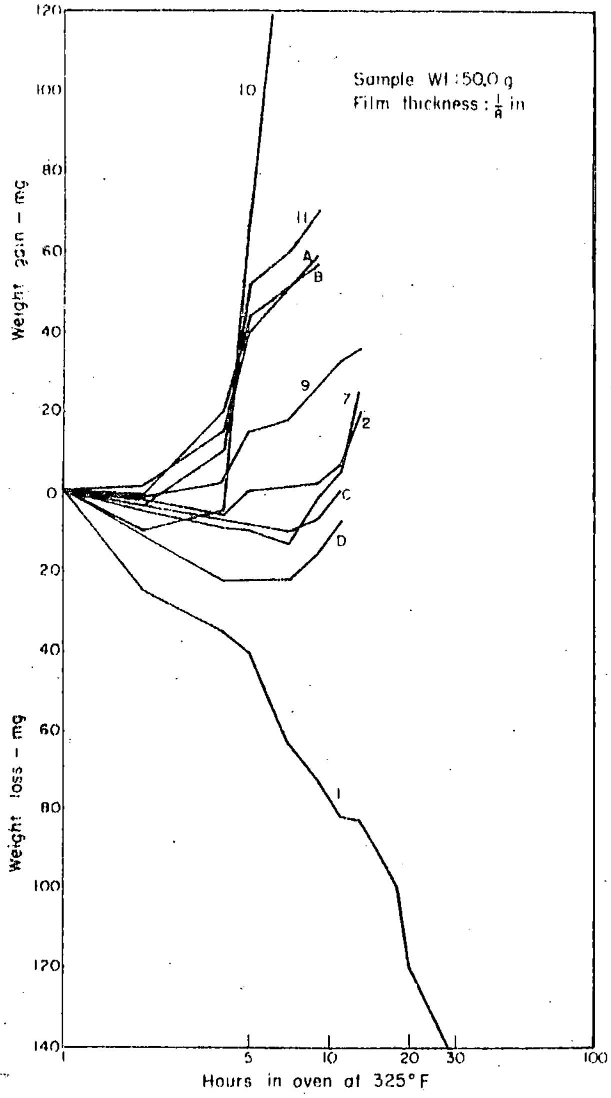


Fig. 19. Weight change during TFOT.

Asphalt	Original penetration (Po)	Original viscosity at 77 °F (megapoises)	Maximum weight loss (mg)	Hours at maximum loss	Loss during LOH (%)	Penetration LOH Pl	Percent retained	Percent hardening Po/Pl	Viscosity LOH, megapoises (Nℓ)	Percent hardening Nℓ/No
A	59	3.60	7	10	0.01	50	85	118	4.50	124
B	75	2.50	7	4	0.01	66	88	114	3.35	134
1	88	2.10	127[a]	55[a]	0.10	77	88	114	2.90	138
2	88	1.90	35	25	0.04	83	94	106	2.35	124
7	90	1.25	15	8	0.03	80	89	112	2.10	168
9	90	2.10	7	5	0.01	71	79	127	2.70	129
10	90	1.70	74[b]	480[b]	0.03	80	89	112	2.55	150
C	112	0.80	176[b]	480[b]	0.04	88	79	128	1.67	209
11	134	0.53	1	4	0.00	110	82	122	0.69	130
D	238	0.16	210[b]	480[b]	0.03	203	86	117	0.25	150

[a] Stopped at 55 hours.

[b] Stopped at 480 hours.

Table 11. Weight change vs consistency change during LOH tests.

Asphalt	Original penetration (Po)	Original viscosity at 77 °F (megapoises)	Maximum weight loss (mg)	Hours at maximum weight loss	Weight change during TFOT (%)	Penetration TFOT Pt	Percent retained Pt/Po	Percent hardening Po/Pl	Viscosity TFOT, megapoises (Nt)	Percent hardening Nt/No
A	59	3.60	0	--	+0.08	36	61	164	11.0	306
B	75	2.50	1	2	+0.09	48	64	160	5.45	218
1	88	2.10	140[a]	28[a]	-0.08	50	57	176	7.50	357
2	88	1.90	13	7	-0.02	55	63	160	4.90	258
7	90	1.25	8	4	-0.00	56	62	161	3.10	248
9	90	2.10	2	2	+0.03	55	61	164	5.10	243
10	90	1.70	10	2	+0.14	55	61	164	6.15	361
C	112	0.80	10	7	-0.01	65	58	172	2.75	344
11	134	0.53	3	2	+0.10	79	59	170	2.15	416
D	238	0.16	22	5	0.04	131	55	182	0.55	338

[a] Stopped at 28 hours.

Table 12. Weight change vs consistency change during TFOT.

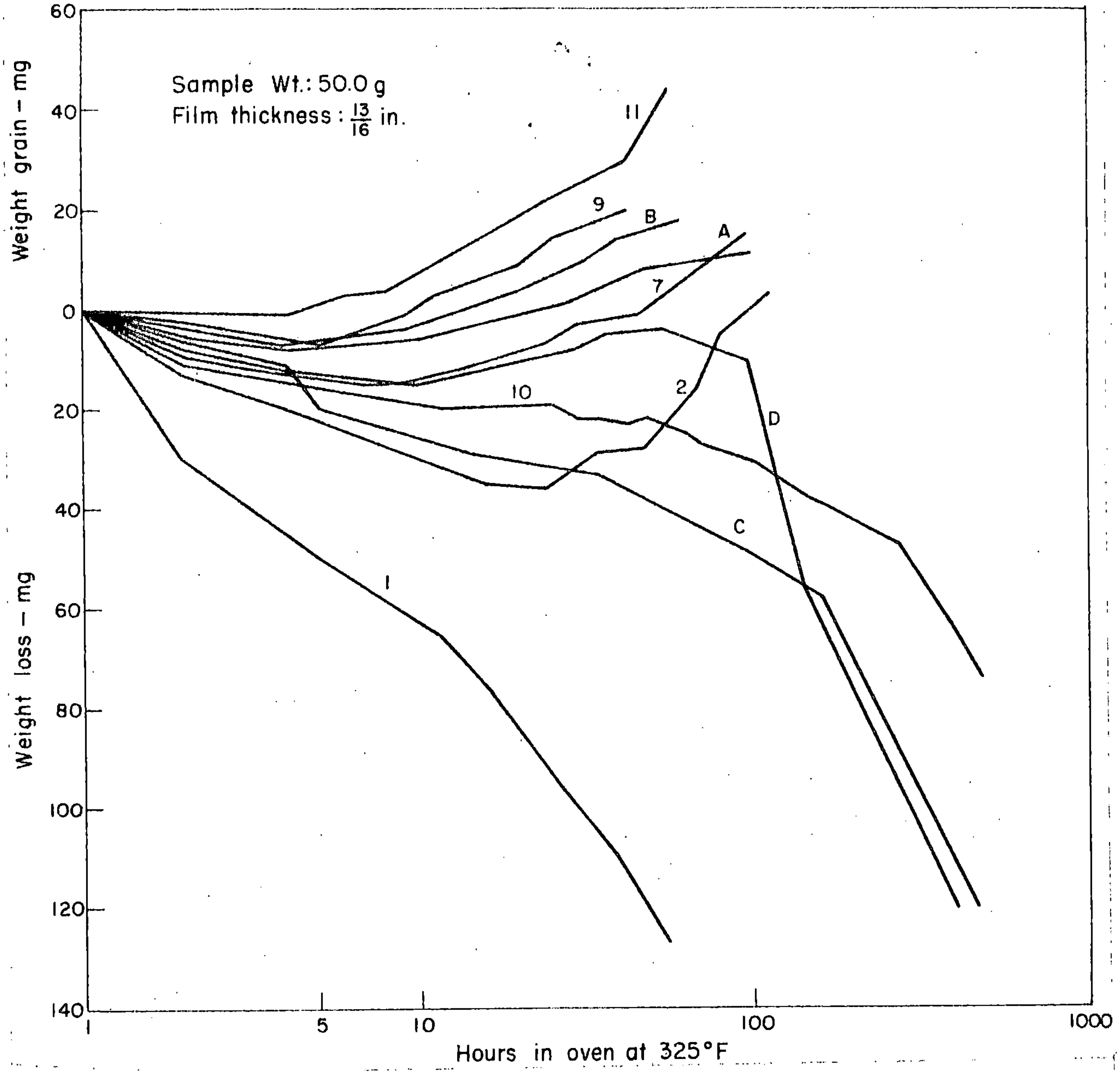


Fig. 20. Weight change during loss on heating tests (LOH).

Weight Loss During Oven Tests

From Figs. 19 and 20, it is seen that, under both Loss on Heating (LOH) and Thin Film Oven (TFO) tests conditions, the majority of asphalts studied showed initial weight loss and, after continued heating in the oven at 325 °F, showed weight gain. Most of the asphalts eventually showed net weight gain. The time when weight gain occurs varied for different asphalts, depending mainly on the difference in amount and nature of volatiles in asphalt. It is noted that this generally occurred earlier in TFO tests than in LOH tests, because of the thinner film, more available surface area and thus more favorable conditions for weight gain through oxidation. For TFO tests, the points of inflection occurred between 4 to 8 hours and for the LOH tests, 5 to 20 hours. Asphalt 1 showed continuous weight loss during the TFOT beyond 28 hours. Asphalts 10, C and D showed net weight loss up to 480 hours during the LOH test.

Based upon the preceding observation a hypothesis on weight change during the LOH and TFO tests is proposed and is represented graphically in Fig. 21. It is suggested that, during the oven test at 325 °F, two major factors (opposing each other) contribute to weight changes of asphalt. Oxidation constitutes weight gain and is shown by line OG. The rate of weight gain is influenced essentially by oxidation susceptibility or reactivity (or chemical makeup) of asphalt, coefficient of diffusion of asphalt, and available surface area. Loss of volatiles results in weight loss and is shown by line OLO'. Weight loss continues until time O', when all available volatiles (at prevailing temperature and pressure) are evaporated. The rate of weight loss depends upon the nature and amount of volatiles. The net weight change at any time during

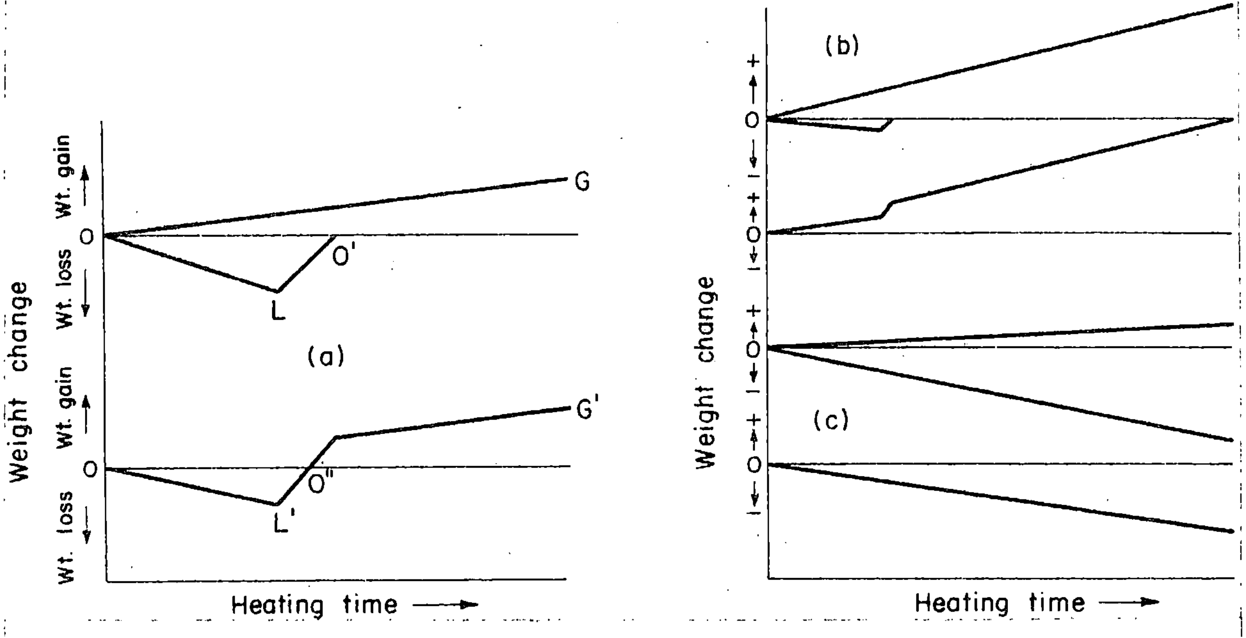


Fig. 21. Hypothetical weight change with time during oven heating tests.

an oven test is therefore the difference between the two factors and is represented by OL'O''G' in lower diagram of Fig. 21-a. Eight of the ten asphalts studied during TFO tests and seven of the asphalts during TFO tests and seven of the asphalts during LOH tests followed this pattern.

Some asphalts, especially lower penetration asphalt cements such as Asphalt A, have a weight gain larger than weight loss due presumably to more oxygen up-take or small amount of volatiles. Then there will be net weight at all heating times, shown in Fig. 21-b. On the other hand, for some asphalts with mere 325 ^{O}F volatiles as compared with weight gain due to oxidation, a weight gain will be observed for some time during the oven heating tests. This is indicated by Fig. 21-c.

Weight Change During LOH and TFOT

From Figs. 19 and 20 and from the suggested mechanism of weight change during oven heating tests, the following conclusions have been drawn with respect to weight change during LOH and TFO tests:

- Referring to Fig. 21-a, it is obvious that during either LOH or TFO test, if point O" (change from net weight loss to net weight gain) occurs within 5 hours, a weight gain will be noted, and if O" occurs after 5 hours, a weight loss will be noted. Since asphalts can behave either way, a definite weight loss during either LOH or TFO test is not to be expected.

- Maximum weight loss does not necessarily occur at 5 hours heating as in the case of LOH and TFOT, and weight change versus time is not linear. However, if there is a weight loss indicated in LOH or TFOT, this loss does reflect the potential volatility or maximum weight loss can be expected for this asphalt at this temperature. This is illustrated in Table 13.

- There is no simple relationship between weight loss in LOH and weight loss in TFOT. If any relationship exists it is only in broad and qualitative terms.

Weight Loss and Hardening During Oven Tests

Opinion differs among asphalt paving technologists on the significance of weight loss and its relationship to hardening during either LOH or

Table 13. Rank of asphalts according to weight loss and hardening during the LOH and TFOT.

Loss on Heating (LOH)				Thin Film Oven Test (TFOT)			
Maximum weight loss	Percent weight loss 5 hours	Hardening		Maximum weight loss	Percent weight loss (gain) 5 hours	Hardening	
		penetration	viscosity			penetration	viscosity
11	11	2	2	2	7 (9)	B	B
A	A	10	A	A	C (A)	2	9
B	B	7	9	9	2 (B)	7	7
9	9	B	11	11	D (11)	10	2
7	7	1	B	B	1 (10)	A	A
10	2	D	1	1		9	D
D	10	A	D	D		11	C
2	C	11	10	10		C	1
C	D	9	7	7		1	10
1	1	C	C	C		D	11

TFOT. One line of thought is that increase in hardening is roughly in direct proportion to the volatility, as measured by the increase in loss for LOH or TFOT. Other technologists find no relation between weight loss and hardening during heating.

For comparison, the 10 asphalts studied are listed in Table 13 in order of increasing maximum loss, weight loss (or gain) at 5 hours, hardening by retained penetration, and hardening by viscosity ratio, for both LOH and TFOT. The following observation can be made:

- No exact correlation between weight loss and the hardening during LOH or during TFOT. However, when the weight change is excessive, either loss or gain, it could indicate a high degree of hardening.

- Relationships between hardening during LOH and during TFOT are plotted in Figs. 22 and 23. The degree of hardening during LOH does not necessarily reflect hardening during TFOT. The correlation coefficient is 0.3742 for hardening measured by penetration, and 0.2233 for hardening measured by viscosity ratio.

- The relationship between hardening as measured by retained penetration and by viscosity ratio is shown in Fig. 24. Hardening during the TFOT showed better correlation than that during the LOH.

Since hardening during oven heating tests is resulted from a combination of mechanisms including oxidation, loss of volatiles and polymerization, and only loss of volatiles contributes to weight loss, it is reasonable not to expect a simple relationship between weight loss and hardening under normal LOH or TFOT tests.

To eliminate to some degree the weight gain factor due to oxidation, asphalts were heated in a vacuum of 27-in. mercury under TFOT conditions (1/8-in. film, 5 hours) at temperatures from 150 °F to 400 °F. Weight loss and viscosity of residue at 77 °F were determined and are shown in Table 14. The percent weight loss appears to be related to a viscosity change when oxidation is eliminated. The same relationship was noted between penetration and weight loss during the TFOT in vacuum. Even under this condition, it is doubtful that the hardening observed is due entirely to volatilization, because temperature is involved.

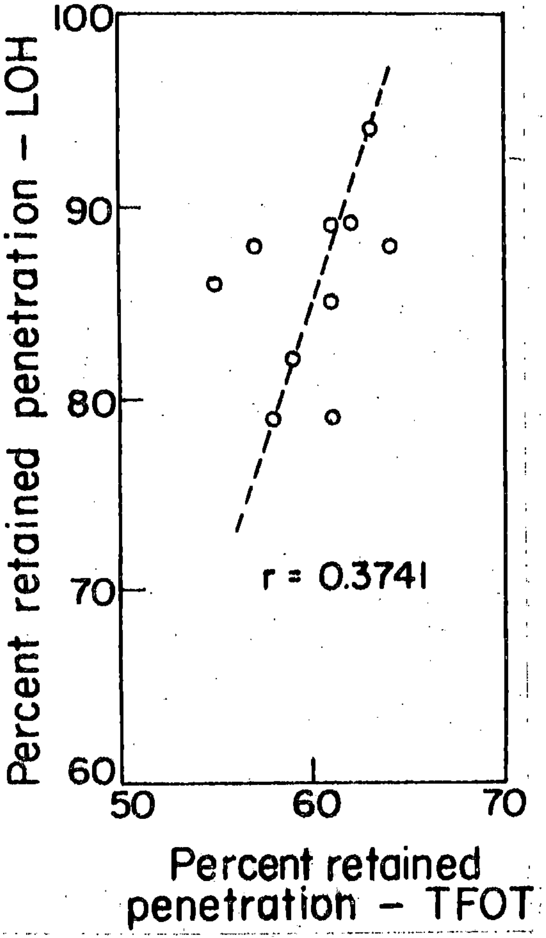


Fig. 22. Hardening LOH vs hardening TFOT, by retained penetration.

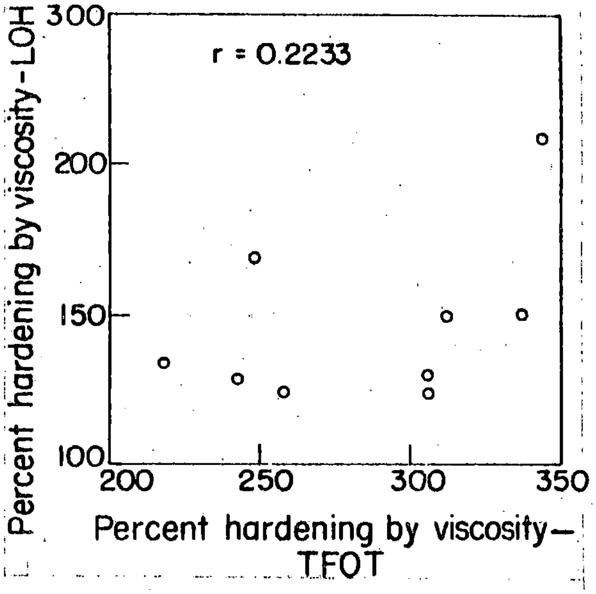


Fig. 23. Hardening LOH vs hardening TFOT, by viscosity.

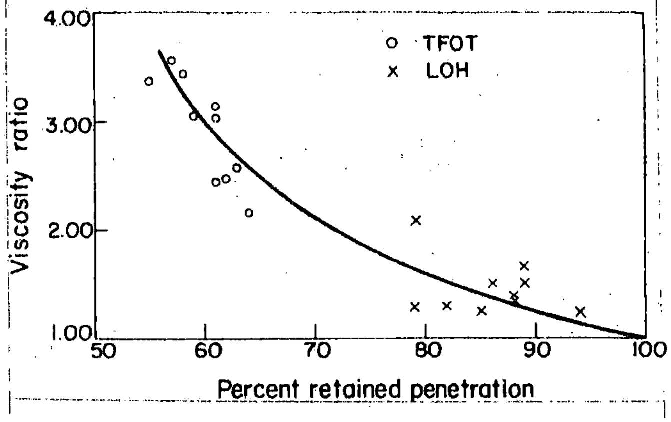


Fig. 24. Hardening by viscosity ratio vs hardening by retained penetration.

The Effect of Temperature on Weight Loss

The effects of temperature on weight loss during TFOT were investigated by heating asphalts in 1/8-in. films for 5 hours at temperatures from 150^{oo}F to 400 ^{o}F and in oxygen, air, and a vacuum. Percent weight loss of six asphalts at various temperatures is tabulated in Table 14 and is plotted in Fig. 25. The following observations are made:

Table 14. Percent weight change vs temperature and medium during TFOT.

A.C.	Medium	150 °F	225 °F	325 °F	400 °F
1	O_2	+0.01	+0.10	-0.12	-1.40
	Air	--	-0.005	-0.08	-1.60
	Vac	--	-0.08	-0.80	-1.60
	N_2	--	--	-1.06	--
2	O_2	--	+0.14	+0.32	-0.37
	Air	--	+0.07	-0.03	-0.13
	Vac	± 0	-0.04	-0.19	-0.48
	N_2	--	--	-0.06	--
	CO_2	--	--	-0.13	--
7	O_2	± 0	+0.10	+0.20	-0.56
	Air	+0.03	+0.05	± 0	-0.48
	Vac	+0.004	-0.05	-0.12	-0.76
	N_2	--	--	+0.04	--
9	O_2	+0.04	+0.14	+0.30	-0.76
	Air	+0.01	+0.02	+0.03	-2.03
	Vac	-0.004	-0.05	-0.32	-1.30
	N_2	--	--	-0.10	--
	CO_2	--	--	-0.06	--
10	O_2	± 0	+0.10	+0.30	-0.20
	Air	+0.003	+0.06	+0.14	-0.25
	Vac	± 0	-0.18	-0.30	-0.46
	N_2	--	--	-0.03	--
	CO_2	--	--	-0.14	--
11	O_2	+0.08	+0.18	+0.30	-0.80
	Air	+0.02	+0.08	+0.10	+0.26
	Vac	± 0	-0.04	-0.14	-0.28

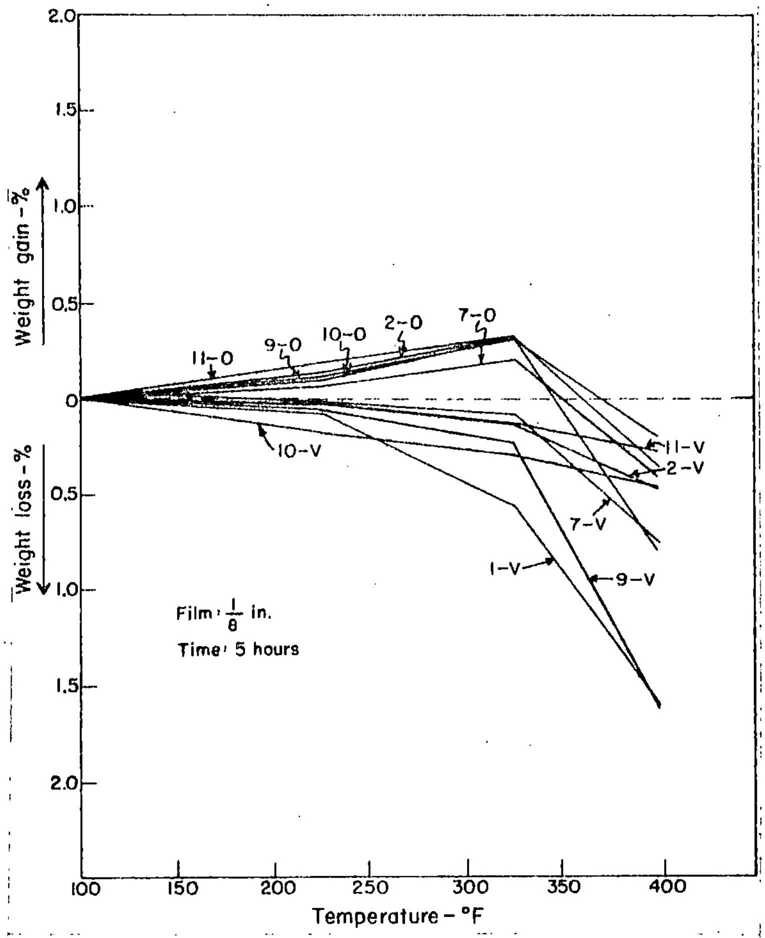


Fig. 25. Weight change vs temperature.

● The effects of temperature alone on the weight loss is that the increased temperature will increase the rate and degree of evaporation and thus weight loss during TFOT.

● However, if oxygen is available and oxidation occurs at the same time, as in the case of heating in air and in oxygen, the weight change is no longer a simple function of temperature and will depend on the relative weight change due to oxidation and to evaporation at various temperatures. All the asphalts studied showed a weight gain up to 325 °F. The weight gain caused by oxidation is about a linear function of temperature up 325 °F. At 400 °F (204 °C) all asphalts heated in oxygen showed a loss in weight, indicating a change in mechanism. The net loss in weight at 400 °F seems to be in line with Pfeiffer's postulation that at high temperatures the oxidation reaction results in formation of water instead of combining of oxygen in the bitumen[35]. The loss in weight at this temperature could then be partially interpreted as the formation of water through dehydrogenation and loss of water due to evaporation.

General Conclusions on Weight Loss During Oven Heating Tests

The following conclusions have been made concerning the weight change during LOH and TFOT:

- Observed weight loss during LOH and TFOT is the result of a combination of several mechanisms and cannot be expected for all asphalts.
- Weight loss during LOH and TFOT can be related to volatility of asphalt only in very general terms and is significant only when it is substantial.
- Weight loss during LOH and TFOT does not relate to hardening due to volatility in simple form.
- No relationship was found between weight losses during LOH and during TFOT.

Hardening During TFOT

All asphalts harden in the presence of heat and oxygen, as in the case of the TFOT. The degree of hardening in asphalt during the TFOT approaches that occurring during hot mixing. The hardening and chemical changes during the TFOT for the 85-100 pen. asphalts studied are shown in Table 15 and summarized as follows:

- Asphalts harden during TFOT at different rates and degrees as indicated by reduction in penetration, increase in softening point and viscosity at all temperatures.
- Chemical changes during TFOT are indicated by increases in asphaltene and percent oxygen as well as an increase of percent oxygen in asphaltene.
- Hardening during the TFOT is accompanied by a decrease in complex flow "C" or deviation from Newtonian characteristics of the asphalt.
- Hardening during the TFOT is accompanied by an increase in shear index or shear susceptibility.
- Hardening during TFOT is accompanied by reduction in Kinnaird's "characterizing factor," indicating existence of non-oxidative hardening during the test. However, oxidation is considered the predominant factor (see the discussion on volatility and effect of heating medium during TFOT).
- The temperature susceptibility of asphalt during TFOT remains unchanged.
- Since it is the properties of asphalt in the finished pavement that dictate the performance of the pavement and since the TFOT has been able to duplicate changes in asphalt after mixing and laying, the properties of the TFOT residue should be of prime concern not only in specifying asphalts but also in durability study of asphalt.

Table 15. Changes in 85-100 pen asphalts during the TFOT.

A.C.	Penetration 77/100/5	Softening point (°F)	C.F.[a]	Viscosity 77 °F (megapoises)	Viscosity 140 °F (poises)	Log temp. coef. of viscosity[b]	Complex flow "c"[c] at 77 °F[d]	Shear index at 77 °F[d]	Percent asphaltenes[e]	Percent oxygen	Percent oxygen in asphaltenes
1-O	88	116.5	22	2.10	1510	11.29	0.901	0.017	18.8	0.79	0.99
1-R	50	130.5	19	7.50	5320	11.29	0.510	0.344	22.8	1.00	2.13
2-O	88	116.5	22	1.90	1740	11.43	0.781	0.176	14.4	0.48	1.37
2-R	55	126.5	18	4.90	2940	11.43	0.554	0.404	17.9	0.72	1.73
7-O	90	112.5	19	1.25	1330	12.86	0.966	0.035	16.6	0.81	1.14
7-R	56	126.5	16	3.10	2970	12.86	0.933	0.213	18.7	1.01	1.59
9-O	90	116.5	23	2.10	1550	12.86	1.000	0.052	19.1	0.73	1.10
9-R	55	122.5	14	5.10	3060	12.86	0.900	0.176	21.0	1.10	1.32
10-O	90	118.0	25	1.70	1860	11.43	1.040	0.105	12.9	0.63	1.85
10-R	55	129.0	20	6.15	4720	11.43	1.000	0.141	15.9	1.13	2.18

O – Original

R – Residue from the TFOT.

[a] Characterizing factor. Kinnaird, R. N., Jr. Proc. AAPT 27:155 (1958).

[b] Temperature susceptibility. Slope of the log viscosity vs log temperature plot.

[c] The slope of the log rate of shear vs log shearing stress plot. Traxler, R. N. Asphalt. Its Composition, Properties and Uses. p. 53 (1961).

[d] The slope of the log viscosity vs log rate of shear plot. Hveem, F. N., Zube, E. and Skog, J. Proc. AAPT 32: 271 (1963).

[e] Csanyi, L. H. and Fung, H. P., Proc. AAPT 23:64 (1954).

Thin Film Oven Test and Ductility

Since its introduction by Dow[36] in 1903, the ductility test has been the subject of frequent discussion and remains the most controversial test in the specifications for paving asphalts. Some asphalt technologists[37-40] consider that the ductility test is a measure of cementitiousness or adhesiveness, elasticity, mobility, cohesiveness or tensile strength of asphalt and that these properties are essential qualities of asphalts. Others[41-43] feel that the test, at least at standard testing conditions, has little or doubtful meaning or is misleading.

Many research efforts have been directed toward the study of low temperature ductility[44-47], the effects of rate of elongation and ductility-temperature or ductility-penetration relationship[48]. Findings from these studies can be summarized as:

- There is an optimum temperature or penetration at which each asphalt has a maximum ductility and
- Low temperature ductility has more significance than ductility measured at 77 °F.

Data on correlation between standard ductility (77 °F, 5 cm per minute pull) of asphalt and its field performance have been lacking. From the limited studies conducted over the years the following are noted:

- Ductility, especially tested at low temperatures, can be related to pavement cracking[49,50] and
- Ductility of an asphalt after it is incorporated into the pavement is of prime importance in determining the quality of a bituminous structure[51].

Therefore, it appears that the ductility of residue from TFOT is more important than that of the original asphalt.

Halstead[52] did an extensive study on the relationship between pavement performance and ductility-penetration relations. There proved to be a critical ductility-penetration curve for asphalts below which low ductility would be a potential cause of poor service. Above this cause ductility would not be a significant factor affecting pavement durability. The loss in ductility during the TFOT could also be considered to represent the minimum change expected in service. It is noted that the limiting values of ductility for the TFOT residues contained in most asphalt specifications were derived from these concepts.

The effects of temperature, atmosphere and heating time in TFOT on ductility were studied on Asphalts 2, 10, and 11. Microductility specimens were used so that the differentiation among asphalts is possible within the limits of the ductility machine at 77 °F. Tests were run at both 60 °F and 77 °F. The effects of temperature and oxygen during TFOT on micro-ductility of Asphalts 2 and 10 are given in Table 16 and plotted in Fig. 26. Data on the effects of heating time are presented in Table 17 and Fig. 27.

The general effects of increasing temperature and oxidation in reducing ductility is obvious. The ability of a low temperature micro specimen in differentiating Asphalts 2 and 10 was clearly demonstrated; both asphalts have standard ductility at 77 °F of 150 cm+ but Asphalt 10 gave a microductility at 60 °F of 28 cm while Asphalt 2 had a microductility at 60 °F of only 8 cm. Since the effects of heating time during TFOT is essentially a continuous hardening of asphalt, shown in Fig. 28,

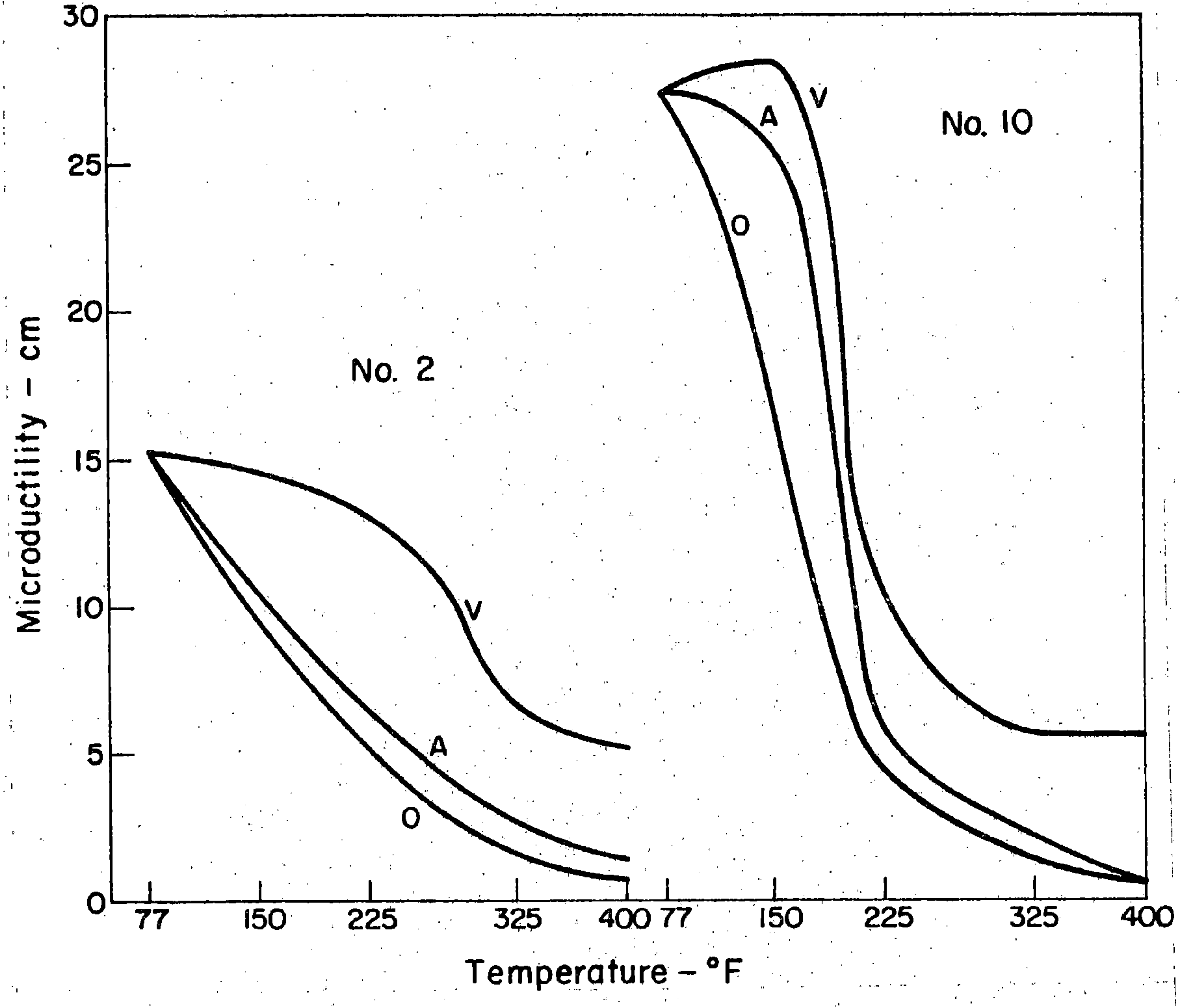


Fig. 26. Microductility at $60^{\circ}F$ vs temperature and medium.

it can also be plotted in terms of change of ductility with respect to change in penetration due to increase in heating time. Both figures reveal the fact of maximum ductility. In the case of Asphalts 2 and 10 they occurred at approximately the same consistency. A reduction in penetration during TFOT is not always accompanied by a reduction in ductility. The data also suggest the desirability of:

- evaluating the ductility property of asphalt in terms of ductility-penetration relationship,

Table 16. Effects of temperature and medium on microductility at 60 °F and 77 °F TFOT

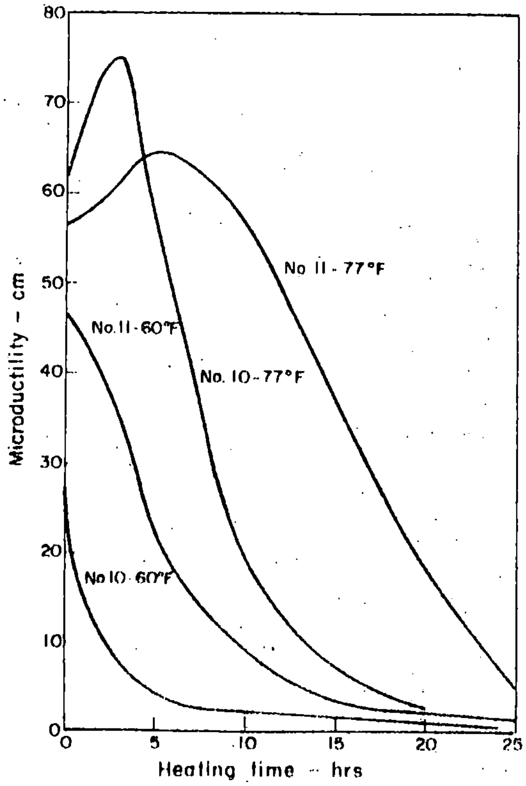
A.C. No.	Temperature	Medium	Microductility, cm 60 °F	77 °F
2	--	--	15.1 (original)	53.1
	225	O_2	5.1	--
		Air	6.0	--
		Vac	13.1	--
	325	O_2	1.3	--
		Air	3.0	25.3
		Vac	5.5	--
		N_2	3.9	--
		CO_2	4.8	--
	400	O_2	0.7	--
		Air	1.3	--
		Vac	5.1	--
10	--	--	27.3 (original)	61.8
	150	O_2	16.5	--
		Air	25.6	--
		Vac	28.5	--
	225	O_2	4.0	--
		Air	5.5	--
		Vac	10.3	--
	325	O_2	1.3	--
		Air	2.5	57.3
		Vac	5.6	--
	400	O_2	0.5	--
		Air	0.5	--
		Vac	5.5	--

Table 17. Microductility vs heating time, TFOT

A.C. Time (hours)	A.C. No. 10			A.C. No. 11		
	Penetration 77/100/5	Microductility (cm)		Penetration	Microductility (cm)	
		60 °F	77 °F		60 °F	77 °F
0	90	27.3	61.8	134	46.3	56.1
2	70	10.3	--	--	--	--
3	64	8.3	75.0	91	35.5	61.0
4	59	--	63.0	--	--	--
5	55	2.5	57.3	79	21.2	64.8
7	--	--	44.1	--	--	--
10	44	2.0	19.3	--	--	--
11	--	--	--	55	7.0	52.7
16	--	--	--	40	2.7	33.0
20	26	1.4	2.6	36	2.0	18.1
24	--	0.5	--	--	--	--
25	--	--	--	29	1.5	4.9

- specifying ductility of residue from TFOT in terms of absolute minimum instead of percent original, and
- testing ductility at low enough temperatures so that interpretation of the results can be made on ductility alone.

However, it is felt that further research is needed to study: (a) the most informative conditions of a ductility test, (b) the significance of ductility with respect to pavement behavior, (c) the relationship between ductility and basic chemical and rheological



properties of asphalt, and (d) the justified specification limits for ductility for both original asphalts and for residues from the TFOT.

Fig. 27. Microductility vs heating time.

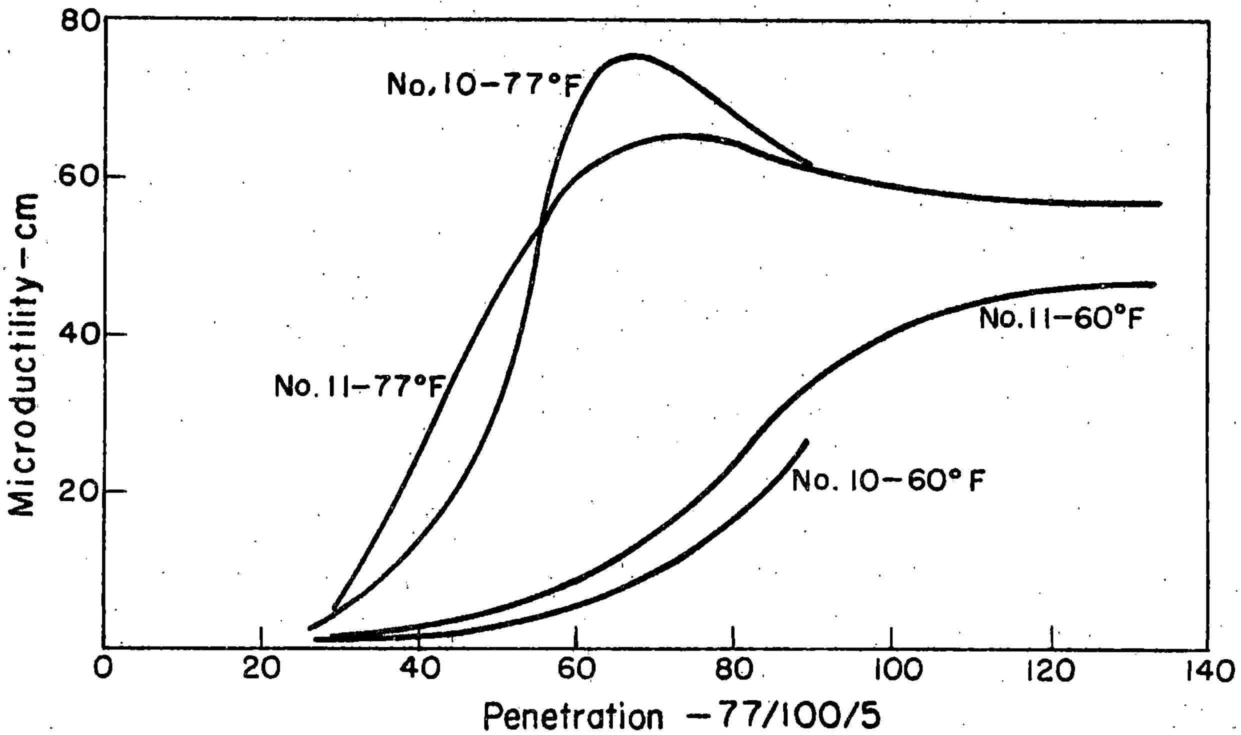


Fig. 28. Microductility vs penetration.

Applications of the Thin Film Oven Test

In view of the recognized ability of the TFOT in duplicating the changes, especially hardening, in asphalt during hot mixing and the recognized importance of the ability of an asphalt to retain its original consistency and ductility, the TFOT and the requirements on the retained penetration and ductility of an asphalt after TFOT have been adopted by majority of specifications for paving asphalts.

In addition to the use of the paving industry in specifying asphalts the TFOT has been used or proposed for use in various phases of asphalt research, operation and quality control.

Nevitt[53], in his proposed specifications for paving asphalts, stressed the importance of residual properties of asphalt and suggested a Ten Hour Thin Film Oven Test (1/8 in. film, 325 °F and 10 hours) for durability control.

Way _et al._[54] correlated the TFOT with the limiting penetration. The limiting penetrations were calculated from field data, considering the hardening of bitumen in the field is a hyperbolic function of time and the penetration at infinite time as the limiting penetration. Figure 29 is a plot of limiting penetration against penetration of the TFOT residue, where the percentage of the original penetration is used for both ordinates.

Speer _et al._[55], in their study of pavement performance using simulated traffic on a miniature test track, found that pavement performance in terms of rut depth could be correlated with the TFOT residue viscosity at pavement temperatures. Cowan[56] suggested the use of the TFOT residue viscosity to determine optimum compacting viscosity.

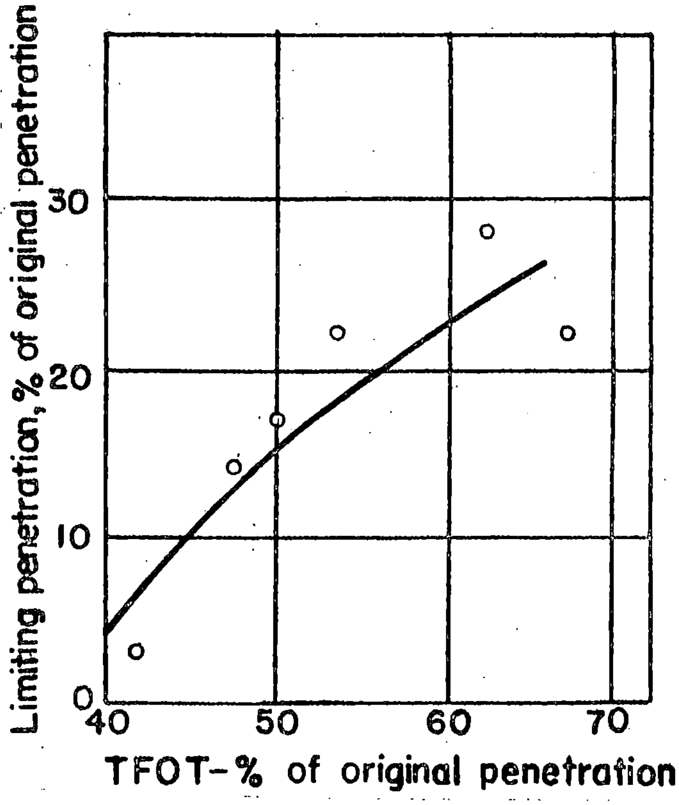


Fig. 29. Limiting penetration vs thin film oven test, after Way et al.

In evaluating the potential of the TFOT as a durability test for asphalt, Halstead and Zenewitz[57] made a comparison study of hardening using the sliding plate microviscometer between the microfilm test durability test (5 microfilm, 225 °F and two hours) and the TFOT. Their results showed greater hardening for the former test for asphalts with aging indices greater than two.

Wurstner et al.[58] used the TFOT in evaluation of the effectivenss of antioxidants for asphalts.

The Bituminous Research Laboratory, Iowa State University, uses the TFOT as an initial treatment in a durability test. The test involves first treating asphalt under standard TFOT conditions and then in oxygen at 150 °F and at high pressures. A detailed description of the developed durability test follows in Part Two of the report.

Conclusions

Major findings from the study of the nature of the Thin Film Oven Test, in addition to the established relationships between hardening, weight and chemical changes and temperature, time, film thickness variables, are:

●The Thin Film Oven Test is a measure of resistance of asphalt to heat and oxidation.

●Weight loss during the TFOT is not related to hardening in simple form. The volatility factor during the TFOT is significant only qualitatively.

●No relation was found between weight loss during the LOH and TFOT.

●The ability of the TFOT in duplicating the changes that occur during hot mixing makes it a valuable tool in laboratory durability study of paving asphalts.

A detailed description of the developed durability test follows in Part Two of this report.

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Part Two

Development of a Laboratory Durability Test for Asphalts

Introduction

All bituminous paving materials undergo changes with time and under the action of heat, weather, and traffic. In general such changes are detrimental to their function as binders and water-proofing agents. Consequently, the degree of resistance of a bituminous binder to these changes is usually referred to as its durability.

Durability of asphalt has been studied by many investigators for many years to find:

- Mechanisms or causes of asphalt deterioration.
- Methods for controlling or preventing undue hardening of asphalts.
- 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 causing asphalt paving to crack and disintegrate is asphalt hardening. Therefore, the degree and rate of asphalt hardening is considered indicative of the relative durability of asphalt. Many proposed durability tests center around the evaluation of asphalt's resistance to hardening.

Almost all proposed durability tests involve a study of the following two phases: (a) subject asphalt to certain treatments which speed up the hardening process, and (b) compare the degree or rate of hardening of the treated asphalt with actual hardening that occurred in asphalt during mixing process or in the road. Hardening occurring 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 way the hardening of the asphalts is accelerated.

A majority of the treatments used to speed up the hardening of asphalt in a durability test are heating of asphalt at elevated temperatures, either alone (in various thicknesses of films, temperature and duration) 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 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, Stross and Ellings[14], and Ebberts[15]. Van Oort[16] studied the durability of asphalts and showed by calculation that, under normal aging conditions, oxygen diffuses into the asphalt films to 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, especially 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[16,18-20]. 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 a good indicator of the hardening and durability of the binder. The shot abrasion test was developed to measure the change in resistance of a compacted sand-asphalt mix to a falling stream of steel shot after prolonged exposure in the infrared oven[21,22].

Traxler presented 15 effects that may cause changes in the chemical, rheological, and adhesion properties of asphalt during handling and under service conditions[23]. 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, adsorption of oils by a 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 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. The procedure 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 (e.v.t.).

In 1963, Hveem et al.[26] reported the 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 their 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 minutes) was developed to predict change in asphalt during the mixing operation. To simulate weathering during service life, 20-micron films of residue from the Rolling Thin Film Oven Test were weathered at 210 °F for a period of 24 hours and viscosity was determined by microviscometer. These conditions produced hardening equivalent to that of 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, Griffin, and Miles[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 has been put into the study of the durability and durability test of asphalt, the paving industry still needs a logically-conceived, well-designed, universally accepted, and yet relatively simple and rapid laboratory durability test for paving asphalt. This test would 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 that should be judged from: (a) How logical or realistic is the acceleration process in the laboratory compared with what actually occurs in the field? (b) How well do 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?

Part Two of this progress report describes the proposed durability test for asphalts, the approach from which the test is developed, the tests and procedures involved.

The proposed durability test will simulate as realistically and completely as possible the two-stage hardening of asphalt during mixing and the subsequent pavement service life. The test makes use of, and takes advantage of, the established BPR Thin Film Oven Test. It includes first subjecting the asphalt to TFOT and then treating the residue from the TFOT in oxygen at high pressures. The TFOT at 325 ^{o}F simulates the changes that may occur in asphalt during mixing. The pressure oxidation process at 150 ^{o}F simulates 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 120-15 pen. grades of asphalt cements.

This investigation is the initial phase of a long range program at 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.

Approach

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:

- The most important single factor causing 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 indicative of the relative durability of asphalt.
- Hardening and other pertinent changes that may occur in asphalt in an asphaltic 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 quite different.
- 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.
- Any realistic durability test for asphalt should consider the two stages of hardening processes of asphalt in their logical order and their differences in mechanisms and effects.
- 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 includes study of the asphalt after the first stage hardening and assures that the properties of the binder following construction are satisfactory for future pavement performance.

● 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.

● 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 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 of the TFOT.

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. By comparing results of tests on an asphalt from the first four steps and information or criteria established from the last two steps, the quality of the asphalt can be specified or predicted.

The report and the first year study in this project are concerned with the feasibility and sensitivity of the laboratory test procedures (in the first four steps), 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 last two steps of the overall program on the development of the laboratory durability test, i.e., (a) correlation of the behavior of asphalts during the proposed durability test and performance in pavement and (b) establishment of durability criteria for paving asphalts has been submitted to the Board for consideration.

Procedures

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

Table 1. Properties of asphalts studied.

A.C.	Penetration	Specific gravity	Flash point (^{o}F)	Fire point (^{o}F)	Softening point, R&B (^{o}F)	Viscosity 77 ^{o}F (megapoises)	Complex$^{(a)}$ flow "C"	Asphaltenes (%)	Oxygen (%)	Oxygen in asphaltene (%)
1-0	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
2-0	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
7-0	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
9-0	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
10-0	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
11-0	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

0 – original asphalt

R – residue, TFOT

(a) Traxler, R. N. "Asphalt. Its Composition, Properties, and Uses". Reinhold Publishing Co. N. Y. p. 53 (1961).

The simulation of asphalt hardening 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 aging the residue from the TFOT in relatively thin films, aging the residue in oxygen instead of air, and 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 two percent sand-asphalt mixtures. Commercial pressure cookers of cast aluminum, 11 in. diam and 11 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.-diam aluminum dishes (making films of 1/8 in.). Dishes with samples were then placed in the pressure cookers. After a leakage check, the cookers were evacuated, filled with oxygen twice, and finally filled to a pressure (at room temperature) that would result in a pressure of 29 psig at 150 ^{o}F. The cooker and contents were put into the oven at 150 ^{o}F. Samples were treated in oxygen at 29 psig for 24, 48, 96, and 240 hours. Viscosity at 77 ^{o}F and rate of shear of $5 \times 10^{-2} \sec^{-1}$, 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 Colemen Model 36 Oxygen Analyzer. Results from the first series of tests are given in Table 2.

The second series of pressure-oxidation treatments on TFOT residues were run at a higher oxygen pressure and the stainless steel oxidation Stability Bombs (ASTM D 525) of 2-in. i.d. and 4-½ in. height were used.

Table 2. Properties of asphalts residues from TFOT aged in pressure cooker at 29 psig (3 atm) and 150 °F.

A.C.	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

O — original asphalt
R — residue from TFOT

Samples of TFOT residues of 4 ml were treated in 1-5/8-in.-diam glass dishes (making films of 1/8 in.) in pressure bombs at 132 psig of oxygen in 150 °F water bath for periods of 24, 48, 96, and 240 hours. Changes in asphalt in terms of viscosity at 77 °F, asphaltenes, oxygen content were determined and are given in Table 3. Effects of pressure variation on viscosity and chemical properties of treated TFOT residues in 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 presented in Table 4.

Table 3. Properties of asphalts residues from TFOT aged in pressure bombs at 132 psig (10 atm) and 150 °F.

A.C.	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

Table 3. (Cont.)

A.C.	Hours	Viscosity 77 ^{o}F (megapoises)	Complex flow "C"	Relative viscosity	Asphaltene (%)	Oxygen (%)
	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	36.3	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

O – original asphalt

R – residue from TFOT

Table 4. Effects of pressure on pressure-oxygen tests.

	9		10		11	
A.C.	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
Vac. 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, 10psig, 24 hr	10.8	21.6	10.5	16.4	2.65	19.7
O_2, 30psig, 24 hr	11.4	22.0	11.0	17.6	2.80	19.5
O_2, 60psig, 24 hr	12.5	21.5	12.5	17.7	3.50	20.7
O_2, 90psig, 24 hr	13.0	23.0	14.0	18.0	--	--
O_2, 106psig, 24 hr	13.5	22.7	--	--	--	--
O_2, 132psig, 24 hr	13.5	22.7	14.5	19.2	4.30	20.8
O_2, 154psig, 24 hr	14.1	23.3	15.4	18.5	--	--
O_2, 200psig, 24 hr	15.5	23.7	17.8	19.4	6.90	22.0

The third series of pressure-oxidation studies were made on two percent sand-asphalt mixtures. Ottawa sand and asphalt were heated to 350 °F and 300 °F respectively and mixed, in proportions of two percent asphalt by weight of sand, for three minutes in a Kitchen-aid mixer. After mixing under closely controlled conditions, mixtures of 800 g were loosely spread in aluminum pans 9 in. in diam in thicknesses of about ½ in. 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 by the Abson method (ASTM D 1850-65) using benzene as a solvent from both treated and untreated sand-asphalt mixtures and 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

A.C.	Asphalt (%)	Hours aging	Viscosity 77 F (megapoises)	Complex flow "C"	Relative viscosity	Asphaltenes (%)	Oxygen (%)
1-0	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
2-0	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
7-0	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
9-0	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

Table 5. (Cont.)

A.C.	Asphalt (%)	Hours aging	Viscosity 77 F (megapoises)	Complex flow "C"	Relative viscosity	Asphaltenes (%)	Oxygen (%)
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

O — original asphalt

Re — recovered asphalt

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 Fig. 1 for samples treated at 29 psig and in Fig. 2 for samples treated at 132 psig, both in films of 1/8 in. and at a temperature of 150 °F. The general nature of the two sets of curves are 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 agreement with field findings[40-44].

Brown *et al.*[40] have suggested expressing the hardening of asphalts in the field mathematically as follows:

$$\Delta Y = T/(a + bT) \tag{1}$$

or

$$T/\Delta Y = a + bT \tag{2}$$

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.

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.

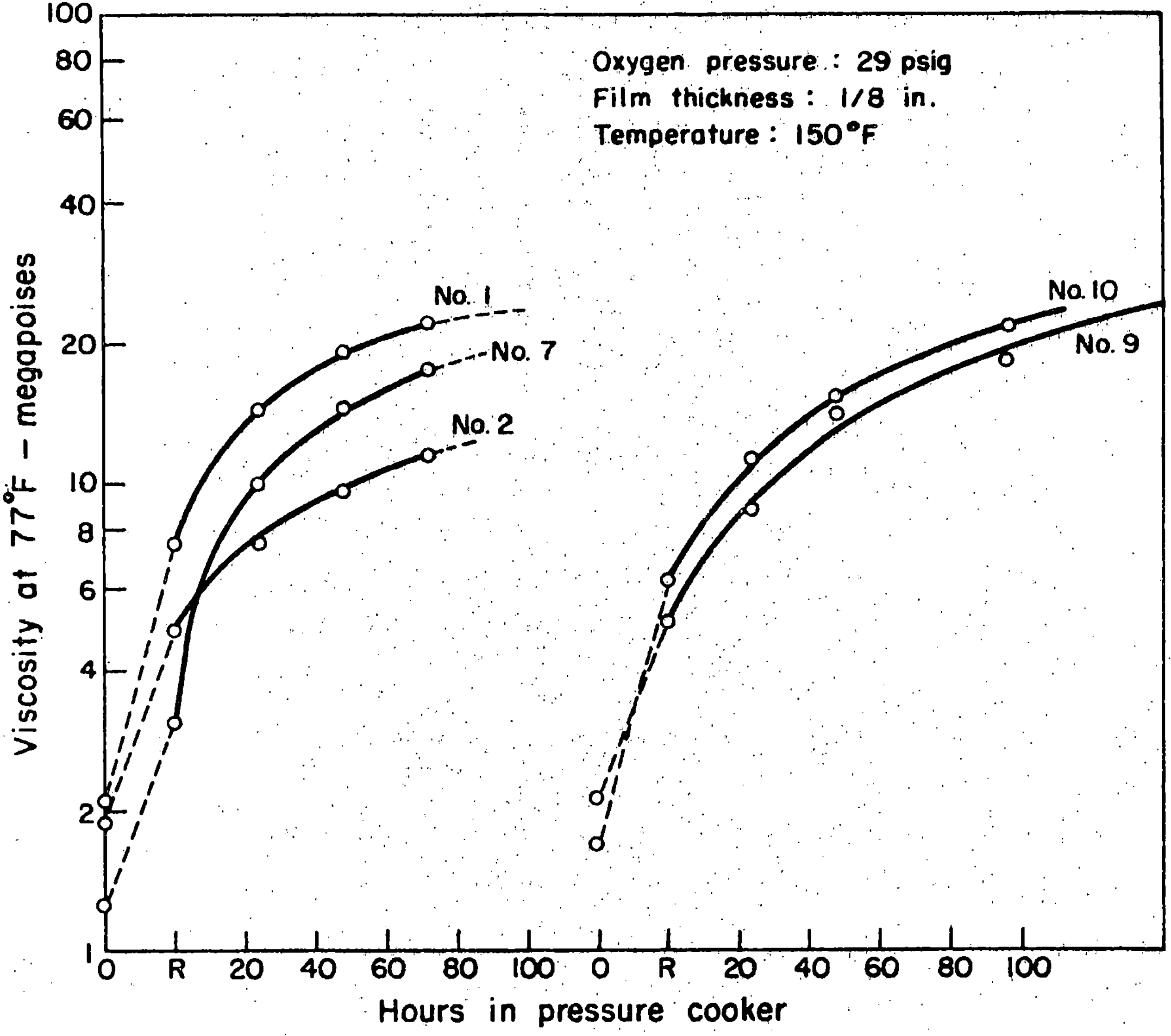


Fig. 1. Viscosity vs time of aging in pressure cooker.

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

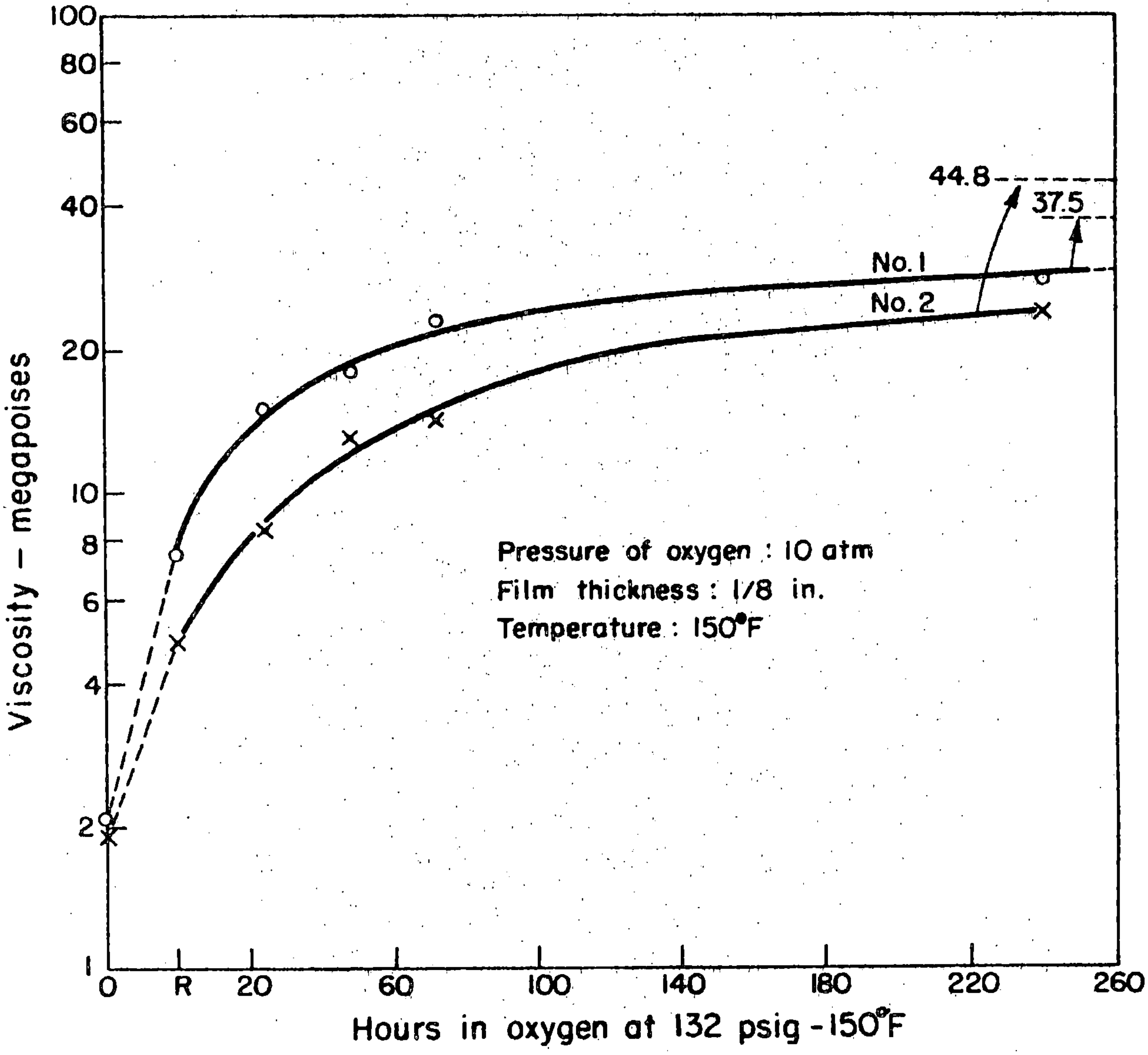
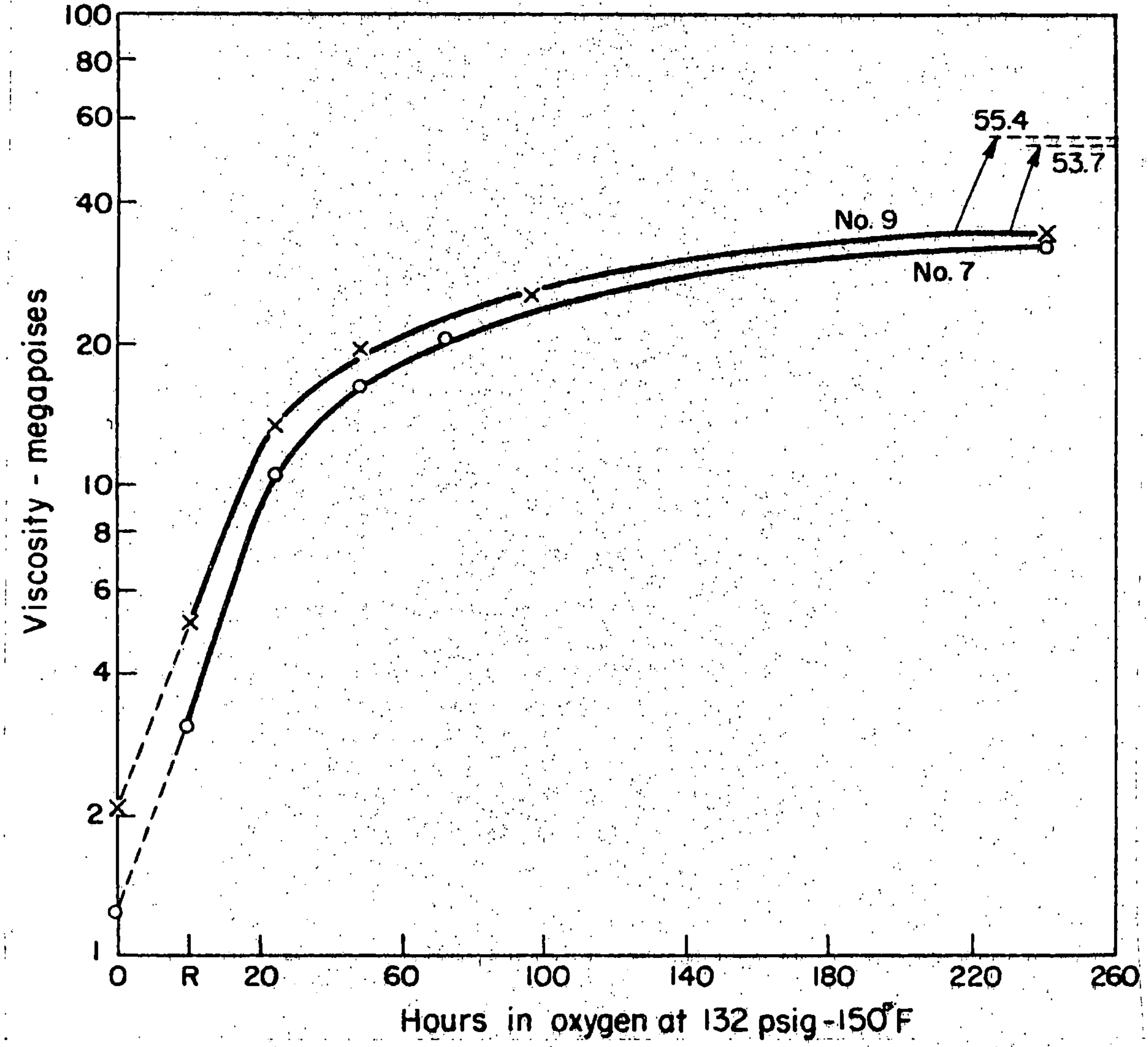


Fig. 2. Viscosity vs time of aging in pressure bomb.



100
80
60
40
20
10
8
6
4
2
1
Viscosity - megapoises
0
R
20
60
100
140
180
220
260
Hours in oxygen at 132 psig - 150°F
55.4
53.7
No. 9
No. 7

Fig. 2. (Cont'd.)

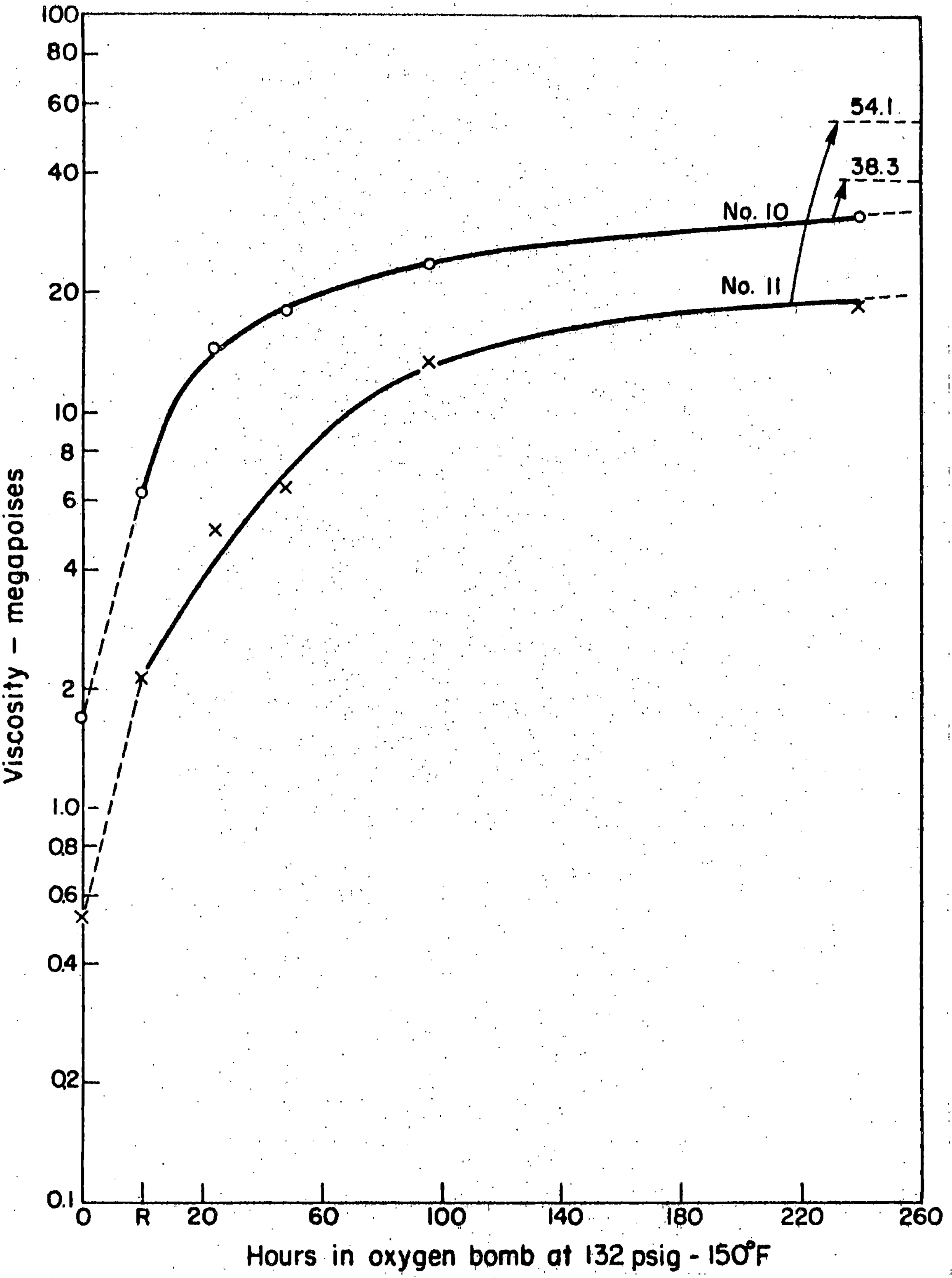

100
80
60
40
20
10
8
6
4
2
1.0
0.8
0.6
0.4
0.2
0.1
Viscosity – megapoises
0
R
20
60
100
140
180
220
260
Hours in oxygen bomb at 132 psig - 150°F
No. 10
No. 11
54.1
38.3

Fig. 2 (Cont.)

during the pressure-oxidation test at 132 psig. They are indicated by horizontal broken lines in Fig. 2. The plots of T/Δ Log viscosity vs T are shown in Fig. 3. The concept of limiting value suggested by Brown et al. is a useful tool in comparing performance or potential behavior of asphalts. However, it can be misleading when used as the only index in asphalt durability or quality evaluation. 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, viscosity, ductility, or other controlling property and fail before it reaches the limiting value or reaches the 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 possible that an Asphalt A showing a higher limiting penetration than an Asphalt B could reach a critical penetration, e.g. 20, quicker in service life and fail earlier than B, and would properly be considered a poorer asphalt.

So 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 meagpoises at 77 °F, be calculated from the hyperbolic Eq. (2) and 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.

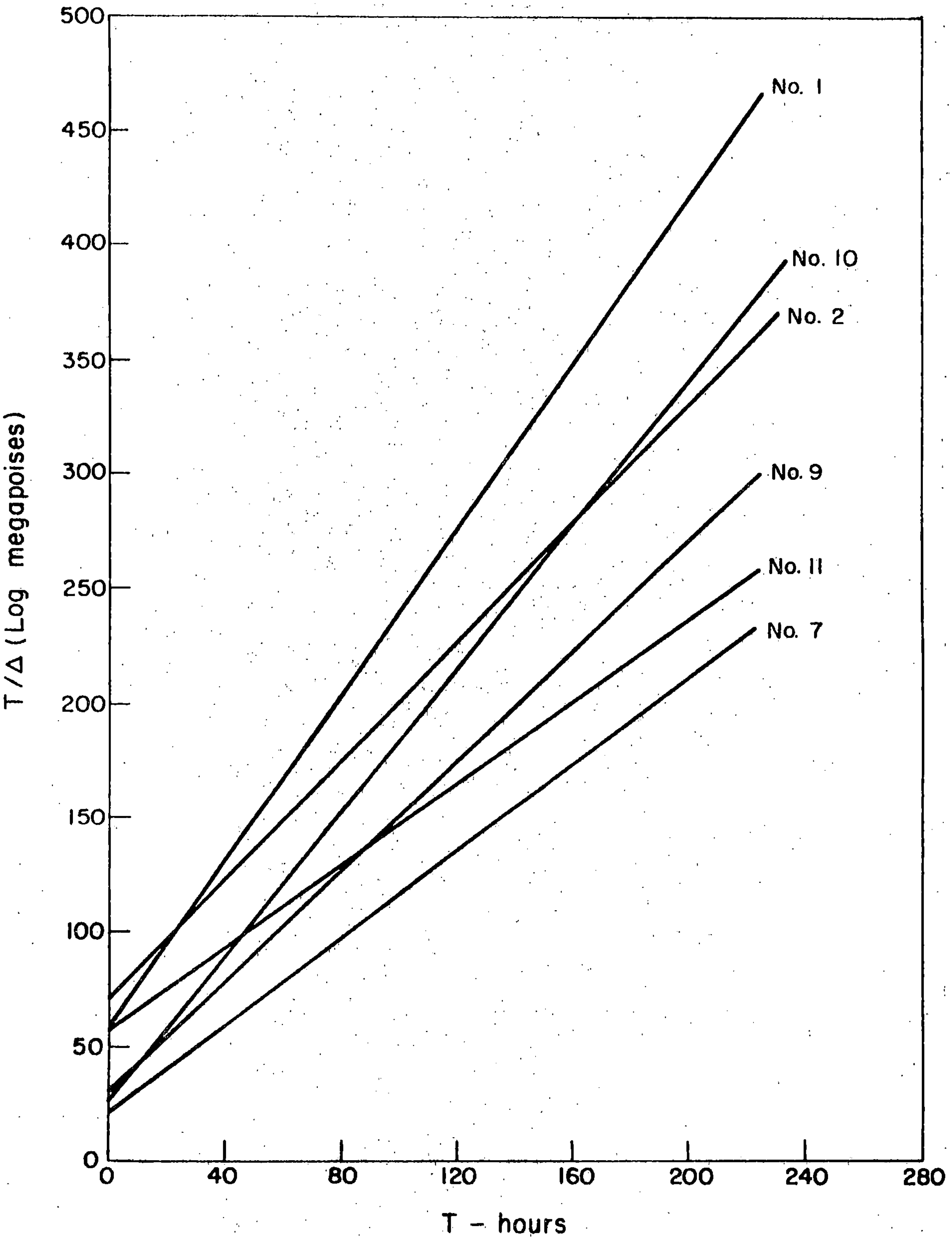


Fig. 3, T/Δ log viscosity vs T.

Table 6. Comparison between two durability criteria

A.C.	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

Note that A.C. 10, having a lower limiting viscosity, would be considered a better asphalt than A.C. 11 by the limiting value concept. In reality, it may fail earlier than A.C. 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, other differences not shown in the graphs 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 A.C. 9 for 29 psig and 132 psig treatments, both at 150 °F. Assuming the viscosity increase under these conditions is due to oxidation, then data in Table 7 would seem to suggest:

- Oxidation penetration progresses with time. The degree of difference in hardening between surface and bottom of the 1/8-in. asphalt films diminishes with time.
- The difference in oxidation hardening between surface and bottom layers of the 1/8-in. film was higher for lower pressures than for higher pressures.
- Thus it is desirable to treat asphalt from the TFOT at higher pressures and longer durations, not only to achieve a higher acceleration rate but to eliminate differences between surface and bottom layers of the treated asphalt films.

Table 7. Viscosities of the treated 1/8 in. film, A.C. 9

Time (hours)	Viscosity at 77 F (megapoises) (5×10^{-2} sec^{-1}) 29 psig Surface	29 psig Bottom	132 psig Surface	132 psig 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

Other significant observations that can be made from Table 2 and Fig. 2 are:

- 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.

- The treatment (132 psig and 150 °F) can accelerate 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 hardening in the field under Iowa conditions[44]. Higher acceleration factors can be obtained by increasing the oxygen pressure and time of oxidation.

- 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 the field finding[41].

The change in shear susceptibility or shear index of the asphalts during the proposed durability test at 132 psig is shown in Fig. 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 appears to be in agreement with behavior of asphalts in Hveem's weathering machine and in the field[26].

- The viscosity ratio or relative viscosity (ratio between treated or aged and original viscosities) was plotted against time in Fig. 5. It will be noted that A.C. 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, A.C. 10 would reach a critical viscosity of, say, 30 megapoises at 77 °F first and could be considered as the least durable. Thus a question arises regarding the adequacy of using relative viscosity alone as the index of hardening for durability study purposes.

- From the slopes of the curves in Fig. 5, the relative hardening during TFOT or during mixing may or may not reflect relative hardening

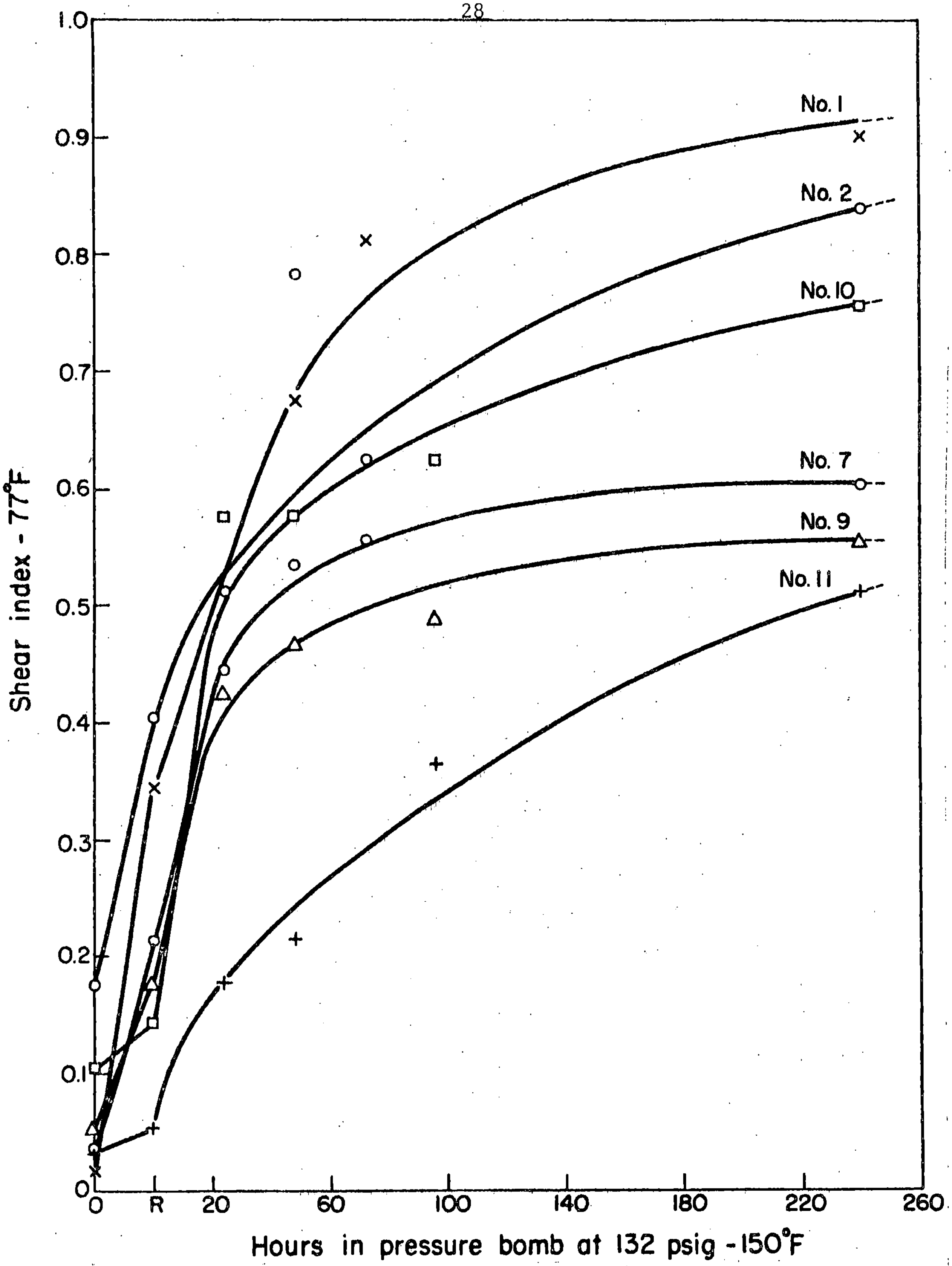


Fig. 4. Shear index vs time aging.

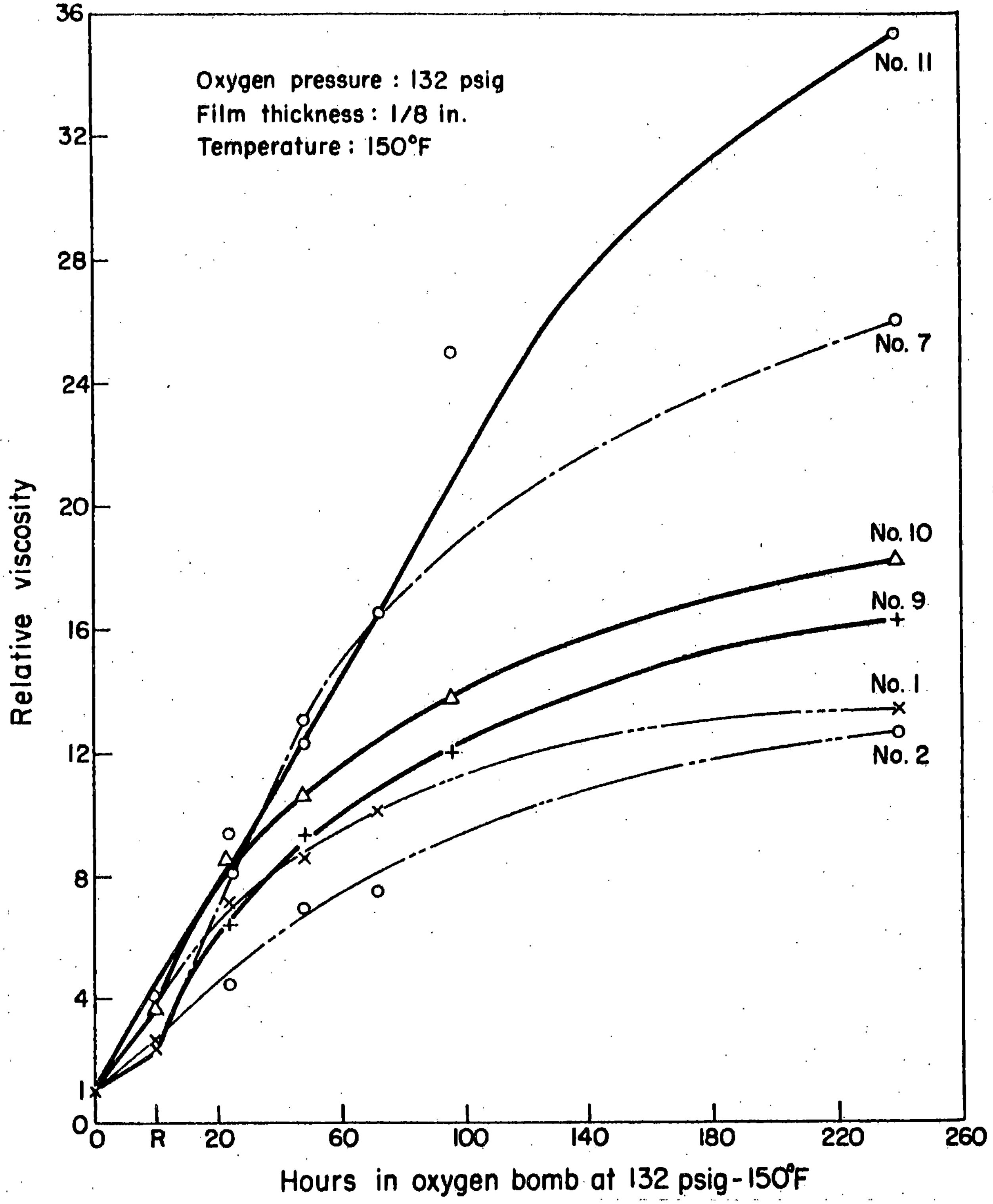


Fig. 5. Relative viscosity vs time of aging.

during pressure-oxidation or in service aging. This illustrates the necessity of a durability test procedure to 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 Figs. 6 and 7. The increase in asphaltenes 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 24 hours at 150 °F and in films of 1/8 in. Viscosity is plotted against oxygen gage pressure in Fig. 8. Percent asphaltene in asphalt vs oxygen gage pressure is shown in Fig. 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 nearly uniform for the asphalts studied, about 1.5 to 2.0 percent over an increase of oxygen pressure from 1 atm to 10 atm.

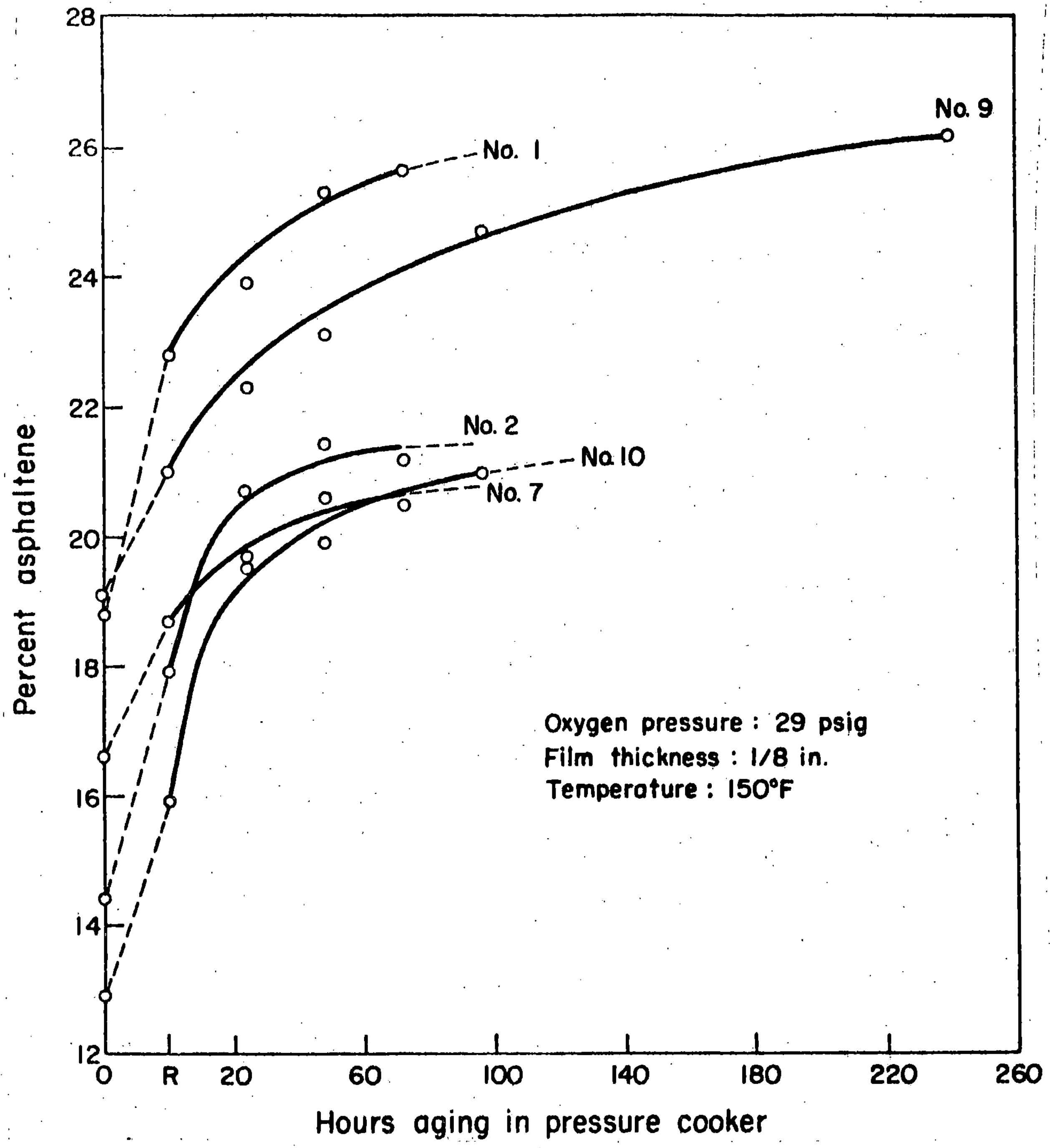


Fig. 6. Asphaltene vs time of aging.

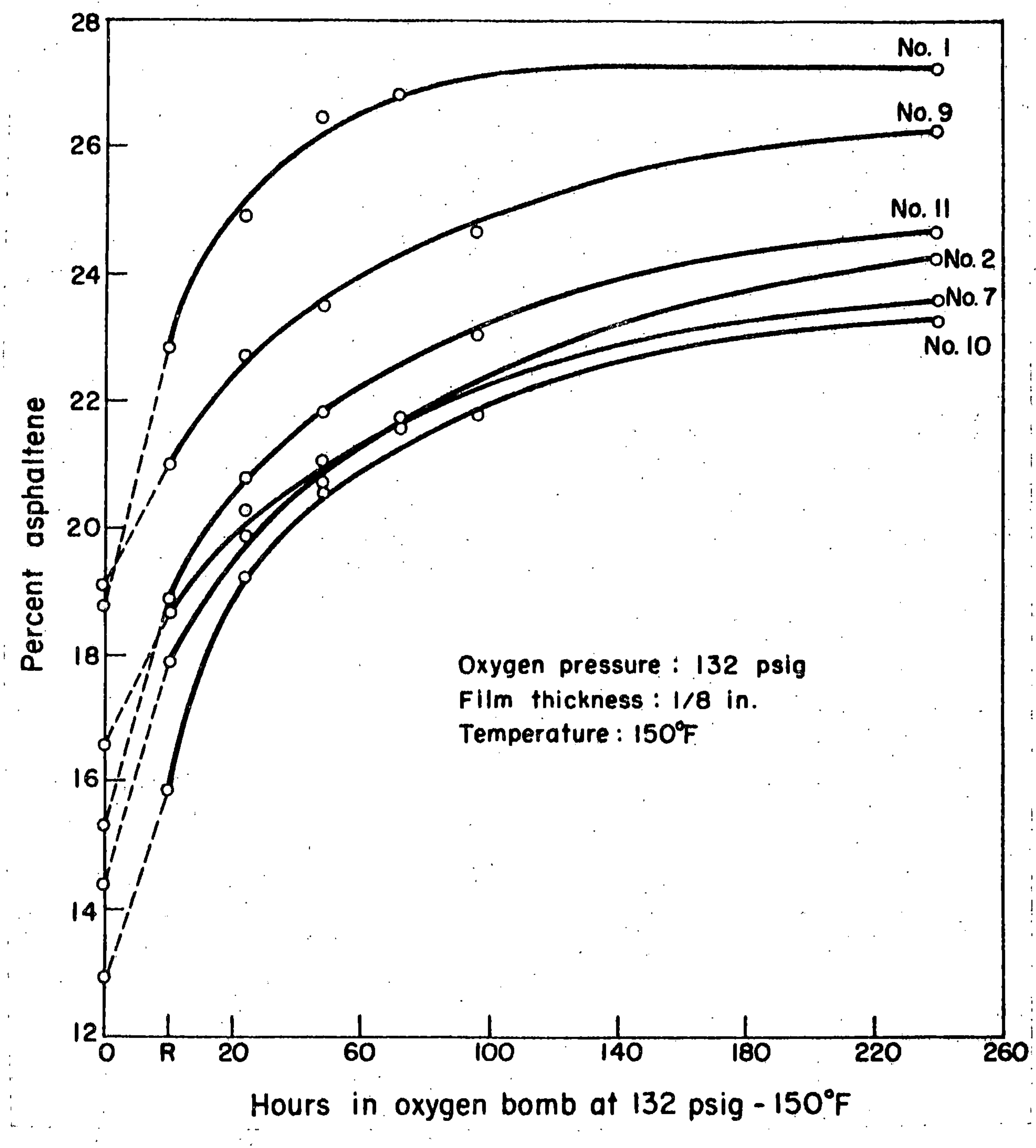


Fig. 7. Asphaltene content vs time of aging.

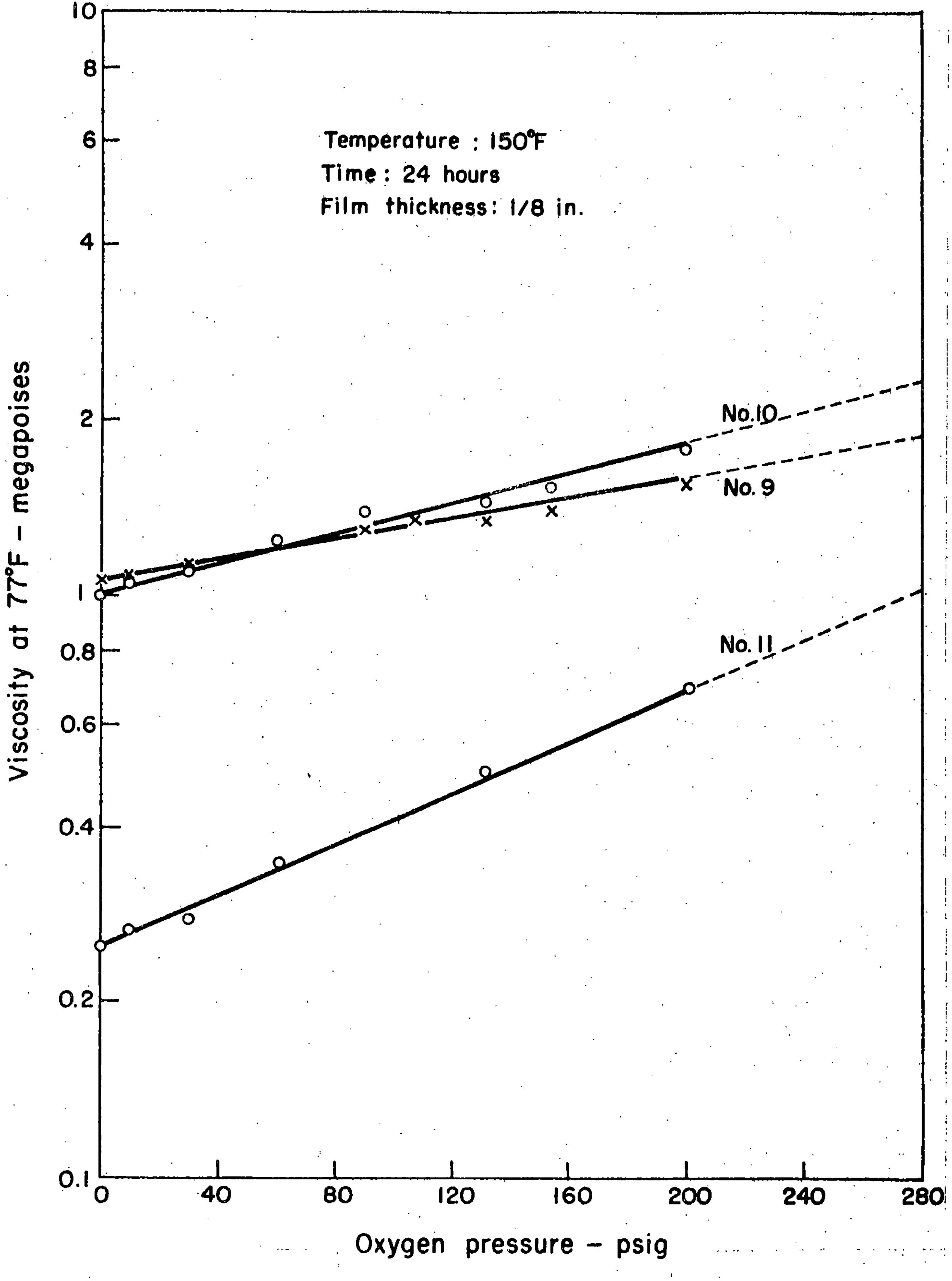


Fig. 8. Effect of oxygen pressure on viscosity.

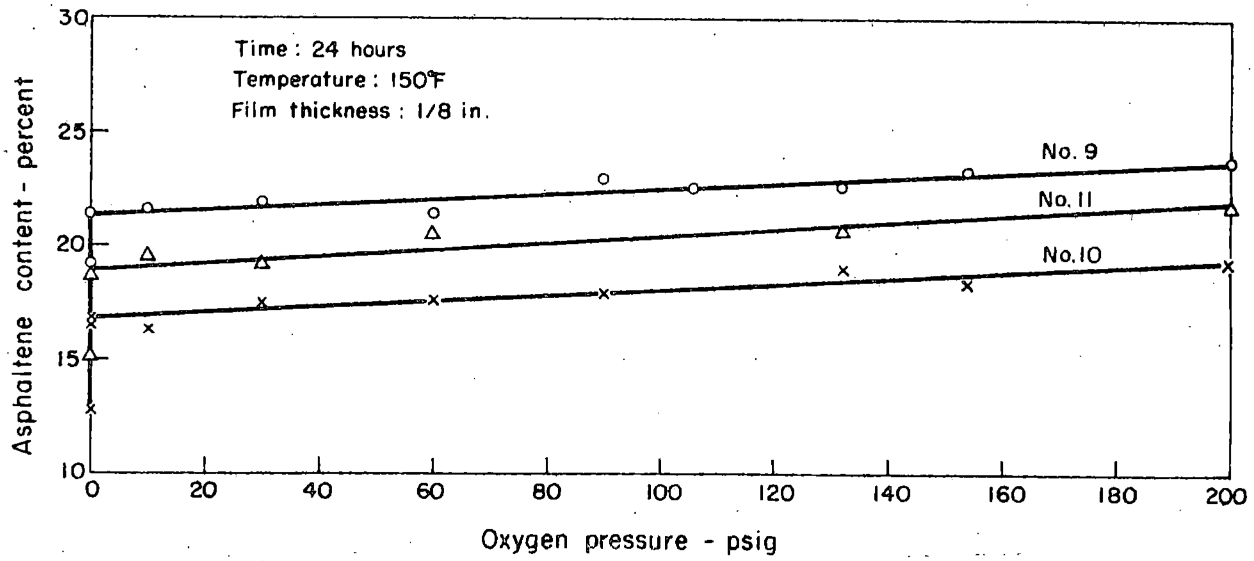


Fig. 9. Effect of oxygen pressure on asphaltene content.

Nevertheless, an increase of oxygen pressure to 20 atm should accelerate the hardening process by a factor of about 1-1/2.

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

The properties of asphalts recovered from the pressure-oxidation treated sand asphalt mixtures are given in Table 5 and shown in Figs. 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 increase in viscosity and asphaltene content were relatively low compared to treated TFOT residues during the pressure-oxidation hardening process, in spite of the thin films. The relative change and shape of the curves

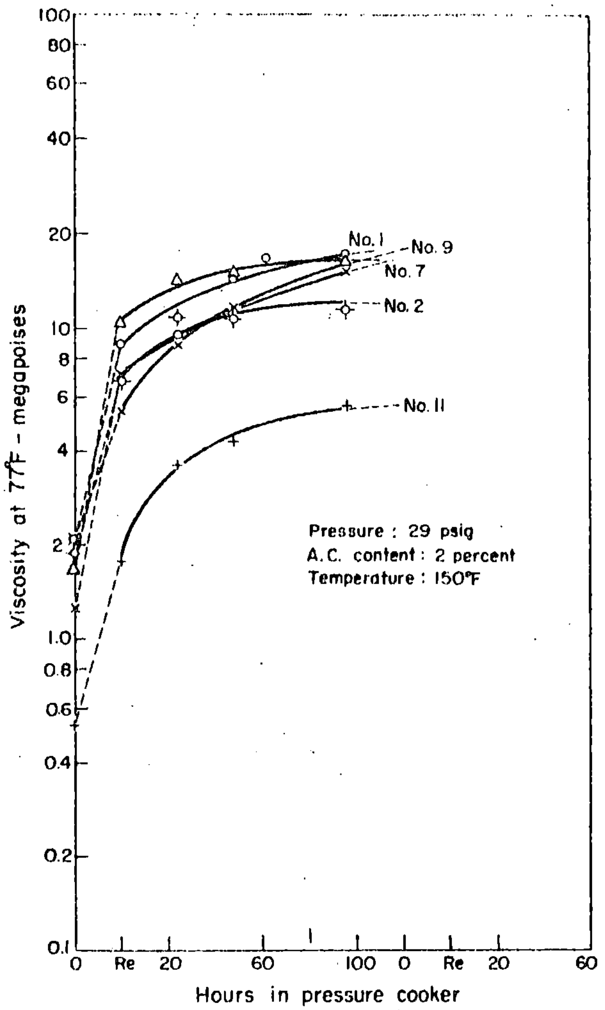


Fig. 10. Viscosity of recovered asphalt vs time of aging.

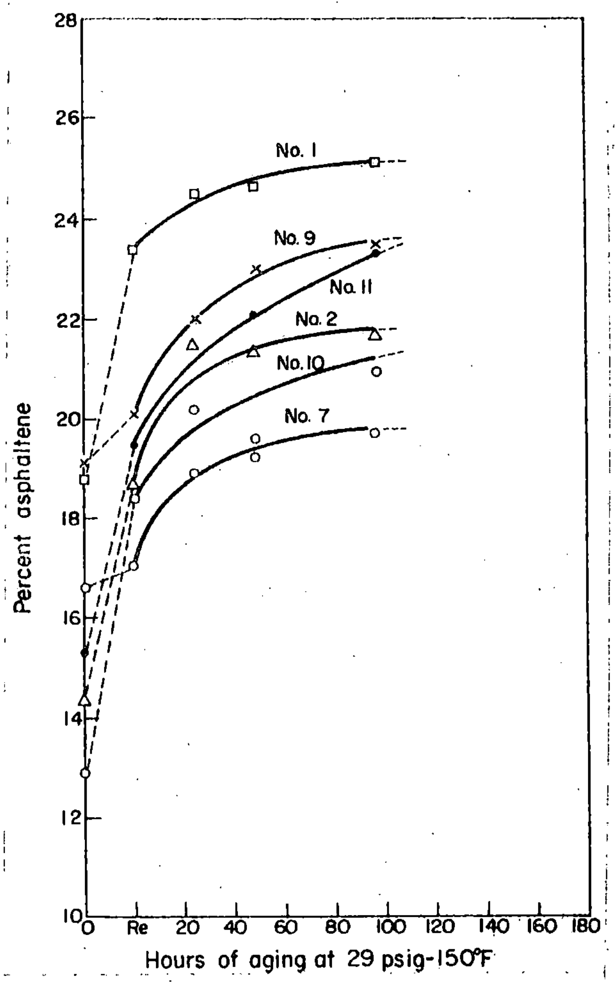


Fig. 11. Percent asphaltene of recovered asphalts vs time of aging.

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.

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 sand-asphalt mixture because:

- The TFOT procedure is simple and rapid,
- Less manipulation and fewer variables in the process contribute to better reproducibility, and
- 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 A.C. 9 and one TFOT residue from A.C. 11. Repeatability was measured by viscosity with a sliding plate microviscometer at 77 °F and at a rate shear of 5×10^{-2} $\sec^{-1}$. 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.

Table 8. Viscosity at 77°F on TFOT residues treated in oxygen bombs at 132 psig, 150°F and in films of 1/8 in. for 24 hr.

Bomb	A.C. 9	A.C. 11
A	12.8	4.95
A	13.5	4.50
A	13.5	5.00
Av bomb A	13.3	4.82
B	13.3	5.00
B	13.3	5.00
B	13.0	5.20
Av 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

Conclusions

The work described in this report may be considered both a progress report and a testing of ideas and philosophy, or a testing of the feasibility and logicality of the proposed durability test. The most significant conclusions are:

- The pressure-oxidation procedure is sound and reproducible. The procedure is simple and the conditions can be easily controlled.

- 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 important until a test or property of asphalt is found that can completely and reliably represent or define the deterioration of asphalt.

- The procedure can accelerate the hardening process to an average of seven times of the original asphalt in terms of absolute viscosity at 77 °F in 24 hours, without deviating much from the hardening mechanism. This value equals about one year 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 must be established through field correlation.

- 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.

- The viscosity increase or hardening in the pressure-oxidation test is a hyperbolic function of time. This is in 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.

- Continued study into the next phase of the durability test investigation, i.e. field correlations, is necessary so that information obtained can be put into useful and applied form in asphalt paving design and quality control.

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

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Acknowledgment

This report is the result of the study under Project 664-S of the Engineering Research Institute, Iowa State University, under the sponsorship of the Iowa Highway Research Board and theIIowa State Highway Commission. The author is indebted to the Board for its support of this study and the engineers of the Iowa Highway Commission for their interests and cooperation.

The author wishes to thank Professor L. H. Csanyi for his interests and guidance and Miss Pam Long for carrying out much of the testing.