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HARDENING OF PAVING ASPHALTS AND RELATION TO COMPOSITION

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Hardening of Paving Asphalts and Relation to Composition

by

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Abstract

Report Progress Report No. 1 - Research Project No. 15

Title Hardening of Paving Asphalts and Relation to Composition

Period February 1, 1959 to February 1, 1961.

Objectives
(1) Investigate paving asphalts used by THD to determine how they can be evaluated for quality
(2) Establish specifications to assure use of superior asphalts by the Department, and
(3) Determine how the durability of asphalts can be improved.

Experimental Increase in absolute viscosity, determined by the microfilm apparatus, was used to evaluate the effect of heating asphalts at various temperatures and different times. Fifteen micron films were used because 15 microns seems to be within the range of average thickness of the asphalt in paving mixtures. Most of the work was done in an atmosphere of air, but measurements were also made in nitrogen at 225°F to determine the effect of volatility without oxidation. Component analyses and asphaltene content were obtained on 25 asphalts.

Conclusions A modified Shell Film Test was found to be more satisfactory than the Bureau of Public Roads Film Test. Data obtained by heating 15 micron films of asphalts in air at 275 to 350°F for times ranging from 15 to 60 minutes are useful for calculating the hardening of a particular asphalt for many of the temperature-time combinations that may be encountered in the preparation and laying of hot paving asphalts. Most asphalts show less hardening by volatilization than by oxidation. Causes for hardening of asphalts in decreasing order of importance are oxidation, volatilization, polymerization induced by actinic light (sunlight) and condensation polymerization (caused by relatively high temperatures). Less stable asphalts may show a decrease in viscosity when subjected to elevated temperatures for several hours. This is caused by depolymerization or thermal cracking.

Component analyses together with the asphaltene content of an asphalt can be used to calculate a Dispersion Coefficient which, in most cases, predicts the resistance of the asphalt to hardening.

Recommendations None at present.

Future Work
(1) The effect of actinic light at various temperatures will be determined on representative asphalts.
(2) Hardening in nitrogen at temperatures above 225°F will be measured to determine the relative effects of oxidation and volatilization at higher temperature.
(3) Temperature-viscosity relationships for the various asphalts will be established. These data will be used in developing specifications to assure use of asphalts possessing superior properties.
(4) Additives and refining methods will be studied as means of improving the durabilities of asphalts.

CONTENTS

CONTENTS (cont'd)

Hardening of Paving Asphalts and Relation to Composition

I. OBJECTIVES OF RP-15

The goals of this project are to:

(1) Investigate the paving asphalts used by the Texas Highway Department and determine how these binders can best be classified as to quality.

(2) Establish specifications to assure use of superior asphalts by the Department, and

(3) Determine how the durability of paving asphalts can be improved.

II. HISTORY

Research Project 15, "Modification of Properties of Asphalt," was initiated on February 1, 1959. This progress report gives information obtained, on item (1) under Objectives, up to February 1, 1961.

III. CONCLUSIONS

The following conclusions are drawn from the data presented below:

1. The thin film type of viscometer is a useful apparatus for evaluating any increase in hardness (reduced durability) of asphalts caused by heat, oxygen and sunlight.
2. A modified Shell Thin Film Test is more satisfactory than the Bureau of Public Roads Film Test for evaluating the susceptibility of paving asphalts to the hardening by heat and air (oxygen).
3. Prolonged heating of paving asphalt films in air even at relatively low temperatures (e.g. 225°F) results in excessive hardening. The time-relative viscosity curve for each asphalt tends to become asymptotic to the time axis.
4. Heating films of asphalts in air at 275 to 350°F for times ranging from 15 to 60 minutes gives data by which the degree of hardening for any temperature-time combination can be calculated. These temperature and time ranges may be encountered during the preparation and laying of a hot mix pavement.
5. Heating 15 micron films of asphalt in an atmosphere of nitrogen yields data on hardening caused by volatilization alone. Most asphalts show less hardening by volatilization than by oxidation.
6. Heating enclosed films of 85-100 penetration asphalts out of contact with light or air results in appreciable hardening at temperatures above 225°F. This hardening, caused by condensation polymerization, is of minor importance at the temperatures normally used in the preparation and laying of paving mixtures. Some asphalts undergo depolymerization (cracking) at 350°F and above when heated between glass plates in the absence of light.

7. In general, the causes for hardening of asphalts, in decreasing order of importance are:

   Oxidation

   Volatilization

   Polymerization induced by actinic light

   Condensation polymerization

8. Of the 12 sources of asphalt studied, No. 1, 1A and 1B showed the greatest and No. 6, 6A and 6B the least susceptibility to hardening (loss in durability).

9. Component analysis together with the asphaltene content of an asphalt is useful in predicting its resistance to the hardening caused by heat and oxygen. Of the 12 sources studied, only one (No. 8) failed to show a good correlation between composition (Dispersion Coefficient) and hardening by heating in air or nitrogen (Relative Viscosity).

IV. RECOMMENDATIONS

No recommendations are made at this time.

V. FUTURE WORK

The following items will be investigated:

1. The effect of actinic light on all 25 asphalts or at least on representative sources.
2. Additional measurements of hardening in an atmosphere of nitrogen at temperatures between 225 and 325°F.
3. A study of the temperature-viscosity relationships of representative asphalts over a wide temperature range. These data in conjunction with some of the facts discussed in this report should make possible the establishment of specifications which will assure use of superior asphalts by the Texas Highway Department.
4. Work on the improvement of durability of paving asphalts. Adjustment of chemical composition by selection of crude oil and alteration of refining procedures can reduce hardening by volatilization and oxidation. Use of additives, which are anti-oxidants, might aid in reducing hardening of asphalts. Additives which act as inhibitors of free radical initiated polymerization will be used with representative asphalts. This phase of the future work will be subordinated to the three previous items.

TABLE 1

Paving Asphalts Studied

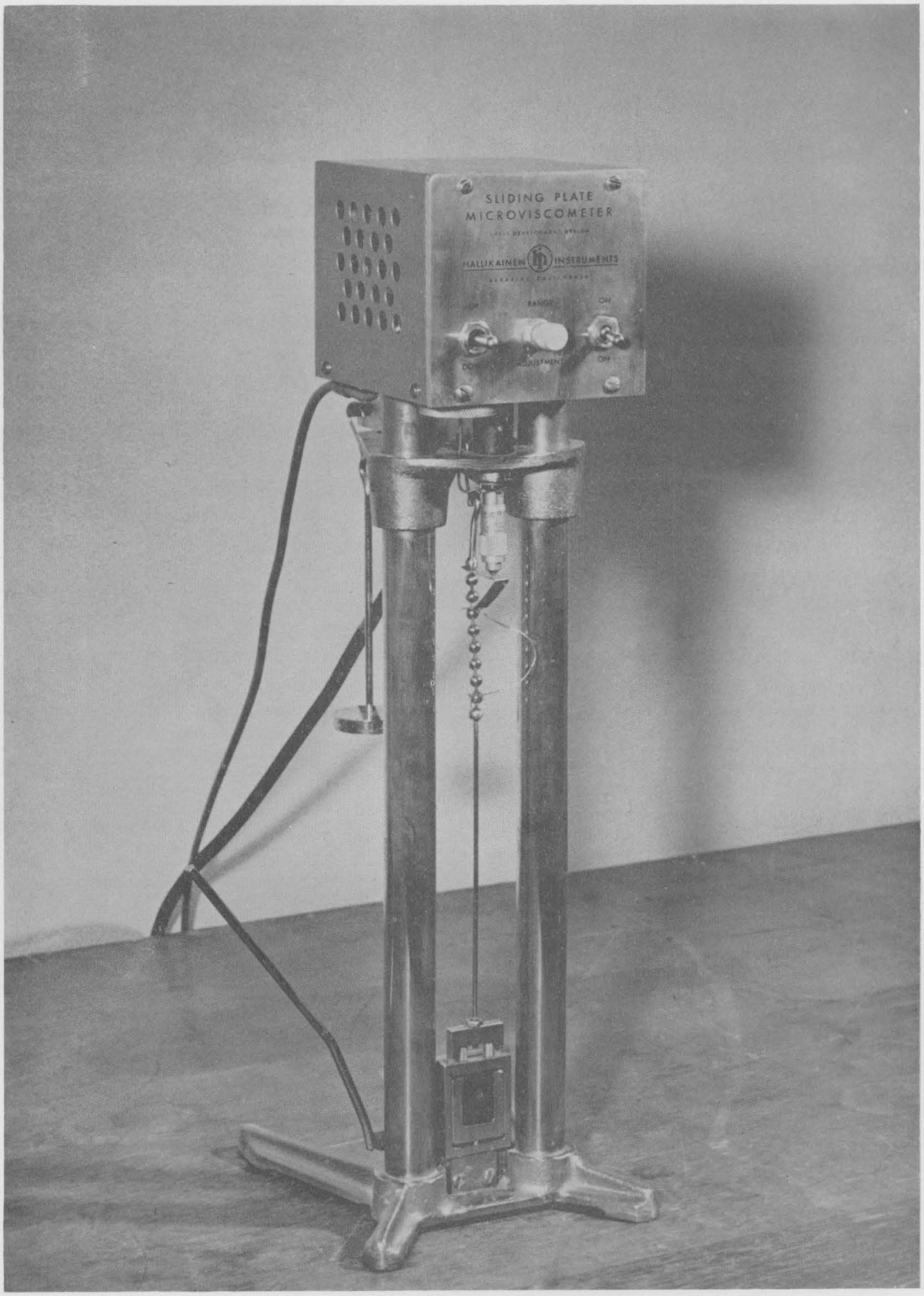
Asphalt No.	Viscosity, Megapoises* at 77°F	Penetration 77°F/100 gms/ 5 sec.	Softening Point, R & B °F
	OA-90 Asphalts		
6	0.70	89	118
4	0.80	93	115
7	0.80	94	117
5	0.85	90	115
8	0.90	98	116
9	0.90	90	117
2	0.90	92	111
10	1.00	92	119
1	1.10	92	117
3	1.20	90	117
11	1.30	93	117
	OA-135 Asphalts		
6A	0.36	133	111
7A	0.40	144	111
11A	0.49	133	111
3A	0.54	142	111
1A	0.59	132	111
	OA-175 Asphalts		
6B	0.21	170	104
8B	0.21	188	106
2B	0.22	185	103
11B	0.23	177	107
12B	0.24	168	104
10B	0.27	160	109
5B	0.29	150	109
7B	0.30	172	108
1B	0.30	163	108

*One megapoise is one million poises. One megapoises is about 100 million times the viscosity of water.

VI. EXPERIMENTAL

1. Materials Investigated

Twenty-five different asphalts prepared by 12 producers were obtained from the field by THD during the spring and summer of 1959. Table 1, facing, lists the asphalts by grade of asphalt and number. Viscosity in poises at 77°F, penetration at 77°F/100 gms/5 sec., and softening point, R & B are given. Within each grade the asphalts are listed in increasing order of absolute viscosity at 77°F. Standard tests, obtained in the THD laboratories, are shown in Table A-1 of the Appendix.



THIN FILM VISCOMETER

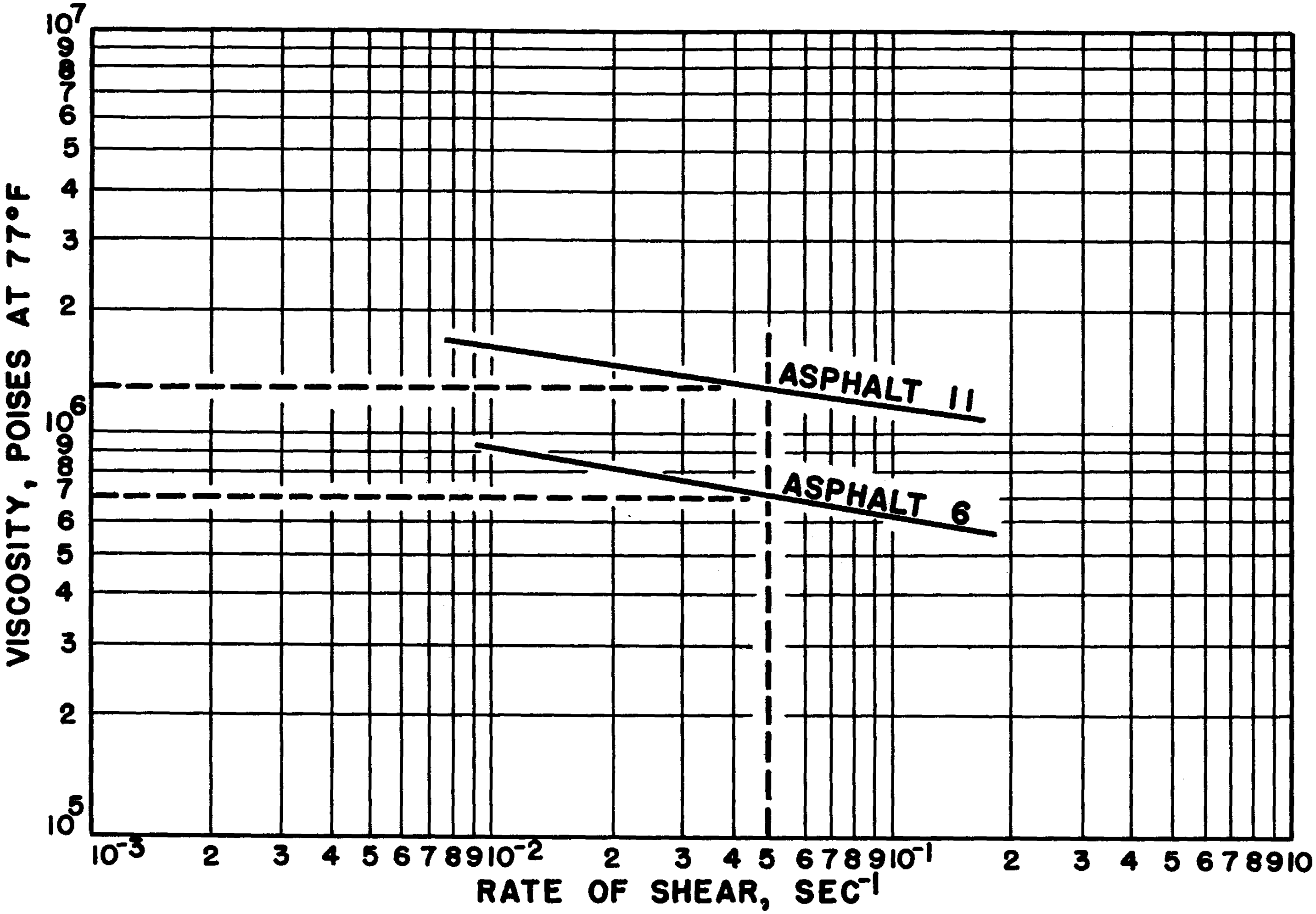
FIGURE I

2. Method for Measuring Viscosity

Viscosities in poises were obtained by the microfilm type viscometer, one form of which is illustrated in Figure I, facing. A film of each asphalt 25-30 microns thick was prepared between 3 x 2 cm. glass plates. Thickness of the asphalt film was determined by weighing the assembly. After a sample had been brought to the test temperature (usually 77°F) measurements were made at four different shearing stresses (applied loads), which resulted in four different rates of shear. The viscosity, in poises, was calculated for each rate of shear. Then, the rate of shear in reciprocal seconds versus viscosity in poises was plotted on log-log coordinates. The best straight line was drawn through the points on the resulting graph and the viscosity determined at 5×10^{-2} reciprocal seconds. This makes possible the comparison of all the asphalts (including any non-Newtonian materials) at a common rate of shear. Figure II, following, shows the type of plot by which the viscosities at $5 \times 10^{-2} \mathrm{sec}^{-1}$ were obtained.

FIGURE II

TYPE OF PLOT USED TO CALCULATE VISCOSITY AT 5 X 10^{-2} SEC^{-1}



3. Hardening of Asphalts - Discussion

Increase in viscosity (hardening) of asphalts under various conditions was selected as a measure of the durability of the binder under service conditions. It may be argued that the deterioration of an asphalt in service is not entirely a matter of hardening. However, the changes that take place in asphalt because of volatilization, oxidation and the action of actinic light are readily and accurately evaluated by measuring increases in absolute viscosity. It will be shown below that asphalts prepared from different crude oil sources and by different refining procedures possess marked differences in response to heat and oxygen. The effect of actinic light on representative asphalts will be determined in the near future.

The changes in viscosity which are reported below are related to the cohesive forces within the asphalt and in considerable degree to its adhesion to solid surfaces.

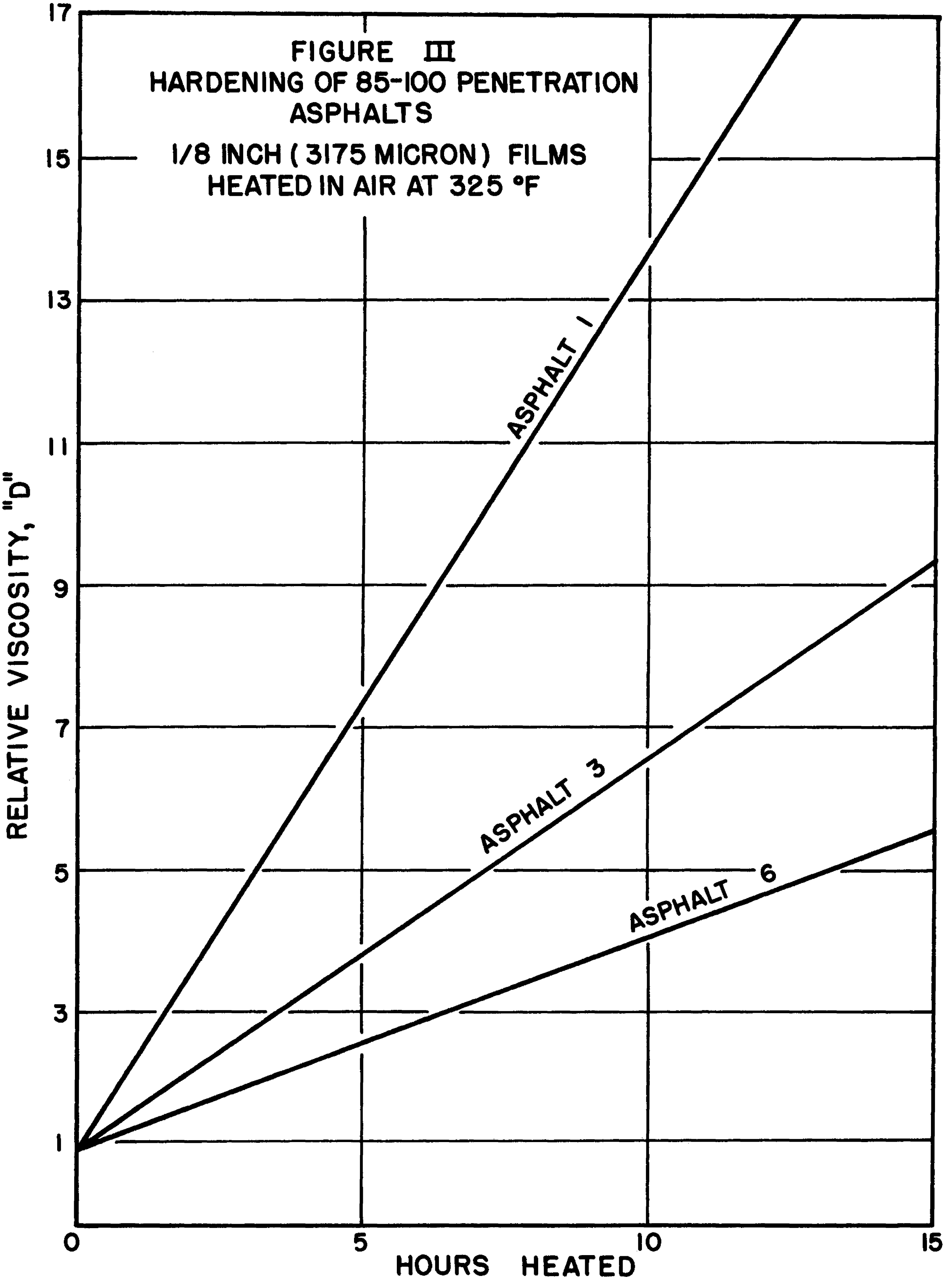


FIGURE III
HARDENING OF 85-100 PENETRATION ASPHALTS
1/8 INCH (3175 MICRON) FILMS HEATED IN AIR AT 325 °F
ASPHALT 1
ASPHALT 3
ASPHALT 6
RELATIVE VISCOSITY, "D"
HOURS HEATED
17
15
13
11
9
7
5
3
1
0
5
10
15

4. Hardening in Bureau of Public Roads Film Test

Hardening of the asphalts by heat and oxygen was first investigated by means of the Bureau of Public Roads Film test. This is not a thin film test in the true sense because the layer of asphalt used is about 1/8 inch thick. A large mass of asphalt is used in this procedure in order to have sufficient sample for determination of penetration, softening point and ductility. The OA-90 and OA-135 asphalts listed in Table 1 were subjected to this test which specifies that the asphalt be heated in air for 5 hours at 325°F. Some of the asphalts were also subjected to the same conditions for 10 to 15 hours and viscosities then determined. Data are shown in Table A-2 of the Appendix.

Figure III, facing, gives comparative data on Asphalts 1, 3 and 6. Hours heated in air at 325°F are plotted versus relative viscosity, which is a fundamental measure of the hardening. Relative viscosity is obtained by dividing the viscosity of the heated (and hardened) sample by the viscosity of the original asphalt. For example, if the original material has a viscosity of one megapoise and the viscosity of the hardened sample 12 megapoises, the relative viscosity of the treated asphalt is 12.

The three materials shown in Figure III were selected because they represent the range of hardening rates encountered. Asphalt 1 shows the most rapid hardening and Asphalt 6 the lowest rate. Asphalt 3 is representative of a large group of materials used by THD which are intermediate in their susceptibility to hardening by heat and oxygen.

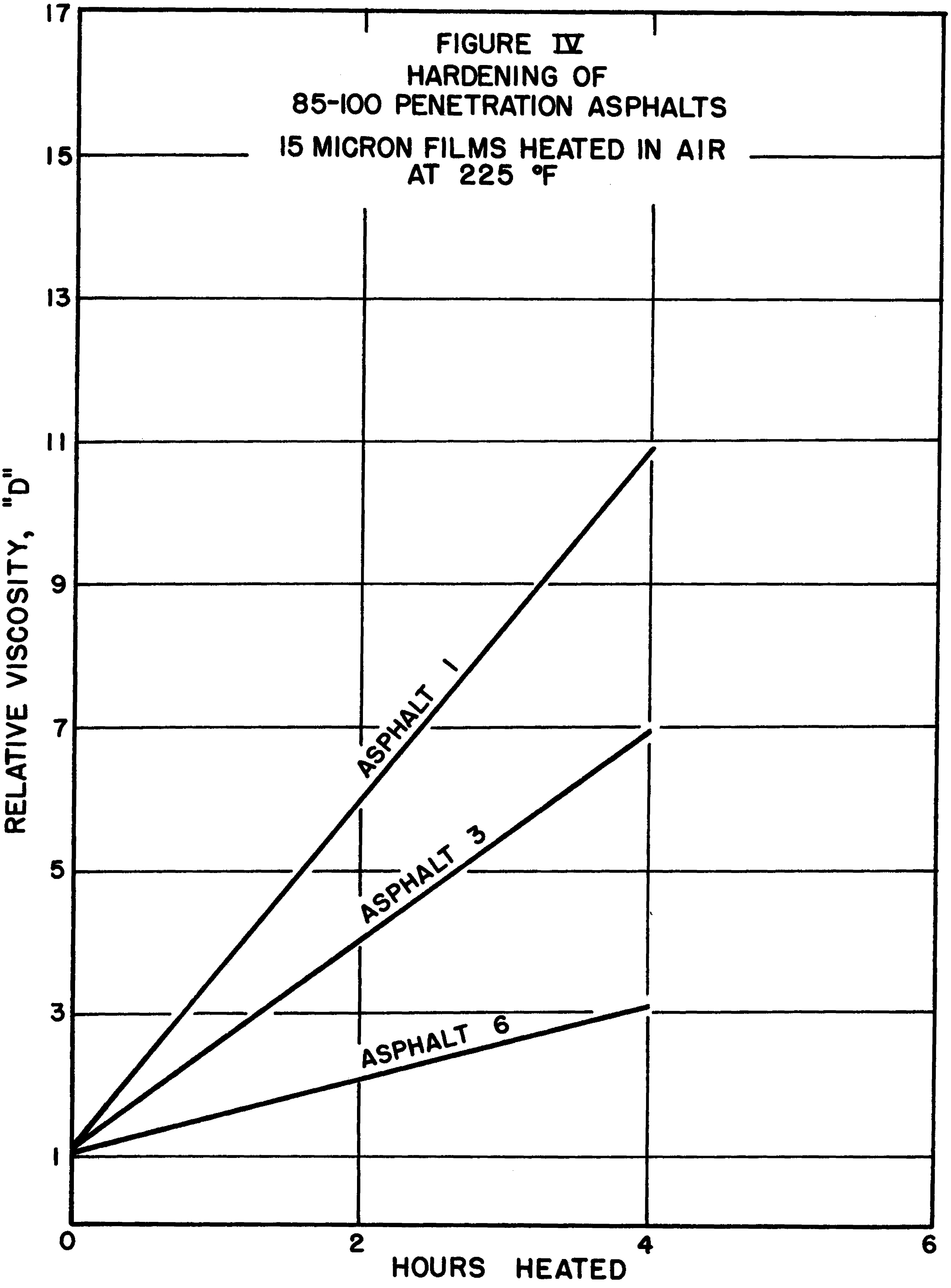


FIGURE IV
HARDENING OF
85-100 PENETRATION ASPHALTS
15 MICRON FILMS HEATED IN AIR
AT 225 °F

5. Hardening in Modified Shell Thin Film Test

The Shell Development Company has advocated a test in which a 5 micron film of asphalt is heated for 2 hours at 225°F and the resulting increase in viscosity is determined by the microfilm viscometer. In our preliminary work this test was modified to the extent that 15 micron films were heated for 2 and 4 hours in order to establish more definitely the hardening rate of the different asphalts. Fifteen micron films were used in this study because 15 microns seems to be in the range of optimum average thickness for the asphalt films in most types of pavement.

Table A-3 of the Appendix gives data on the 25 asphalts studied by this procedure. Figure IV, facing, illustrates the data obtained on the OA-90 asphalts previously shown in Figure III. As mentioned in the preceding section, these samples (Asphalts 1, 3 and 6) encompass the range of hardening rates encountered.

The two procedures used for evaluating the asphalts give the same general classification for all of the samples. However, data obtained with the 15 micron films were more reproducible than those obtained on the 1/8 inch (3175 micron) layer. More uniform data would be expected from the thin films for the following reason. When a 3175 micron layer is heated a hardened film develops on the surface, which frequently can be noted visually after heating for 10 to 15 hours. Prior to testing in the viscometer it is necessary to blend thoroughly this hard surface film with the softer asphalt under it. Even with most careful attention to this operation, mixing may not be perfect. The final sample is in reality a mass of original asphalt contaminated with some hardened material. The same problem is presented by the hardened 15 micron film but to a much lesser degree.

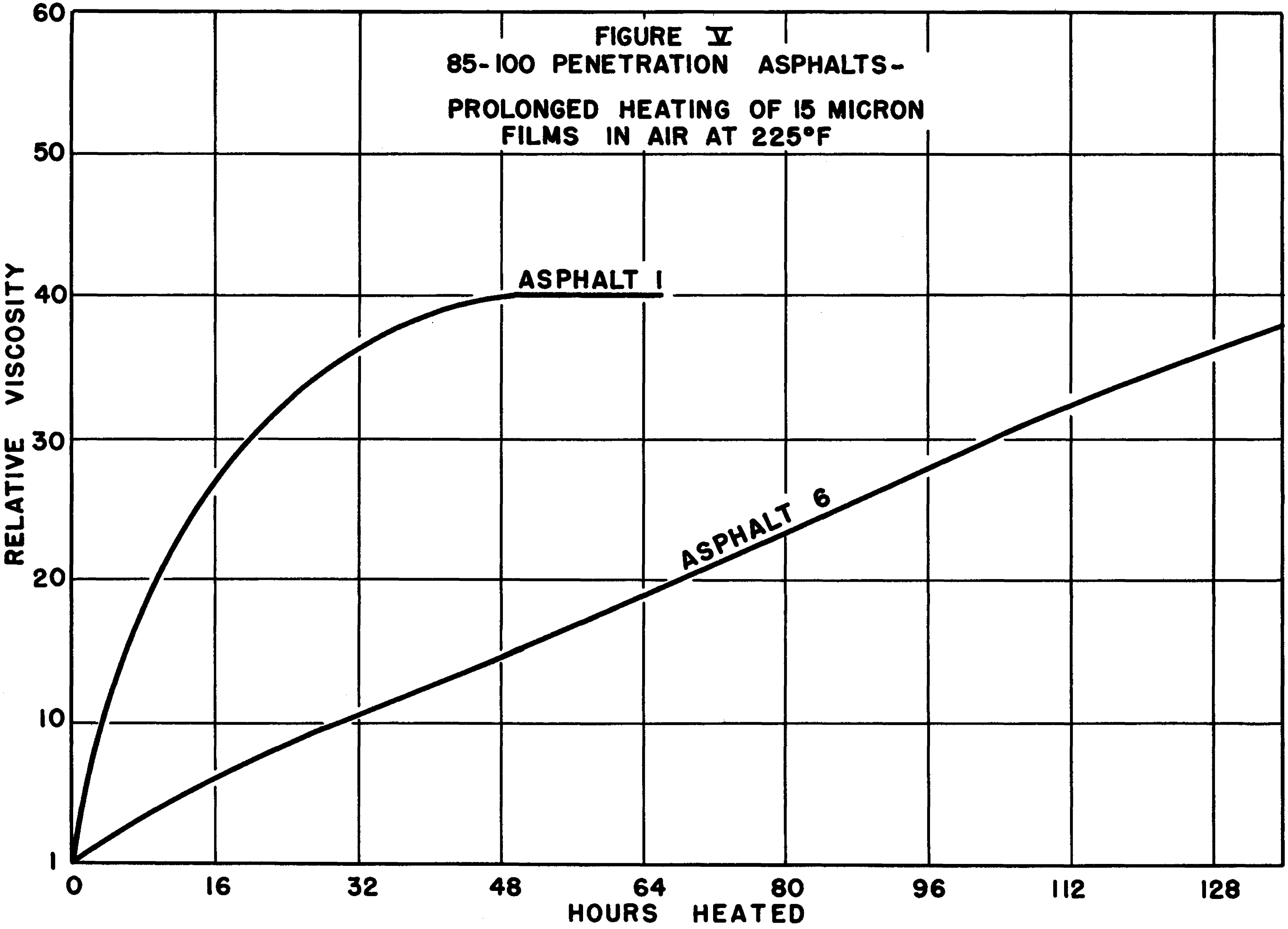


FIGURE V
85-100 PENETRATION ASPHALTS-
PROLONGED HEATING OF 15 MICRON FILMS IN AIR AT 225°F

6. Effect of Prolonged Heating in Air at 225°F

Upon completion of the tests discussed above, the question arose concerning the effect of heating the asphalt films for more than 4 hours. Asphalts 1, 1A, 1B, 6, 6A and 6B were selected for further investigation because these two sources represent the extremes of resistance to hardening found by the previous tests. The remaining 19 asphalts have not been subjected to prolonged heating tests because of the time required and the urgency of other work. Also, it is safe to assume that the 19 asphalts are intermediate to the extremes selected for this investigation.

The time-viscosity curves tend to become asymptotic to the time axis as illustrated in Figure V, facing. Data on the 6 asphalts studied are recorded in Table A-4 of the Appendix. It is obvious that 15 micron films, exposed to air at 225°F for long periods of time, harden excessively, and that some harden more rapidly than others.

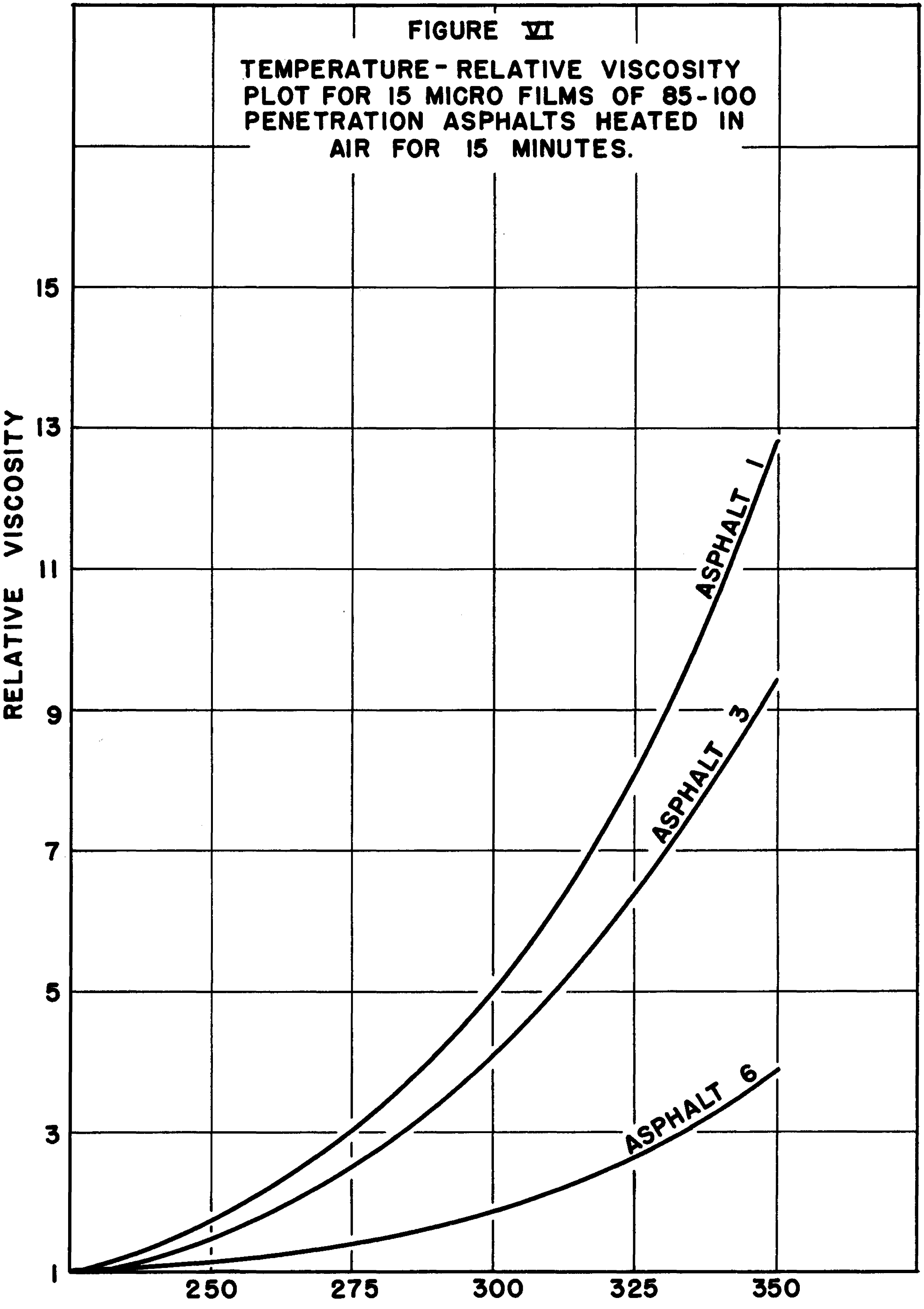


FIGURE VI

TEMPERATURE - RELATIVE VISCOSITY PLOT FOR 15 MICRO FILMS OF 85-100 PENETRATION ASPHALTS HEATED IN AIR FOR 15 MINUTES.

7. Effect of Temperature and Time on Rate of Hardening of Asphalts Heated in Air

After general trends had been established by the preceding experiments, attention was turned to an investigation of the hardening of representative asphalt films at temperatures in the range 225 to 350°F and times from 15 to 120 minutes. These temperatures encompass those to which a hot asphalt mixture may be exposed. High temperatures in the uncompacted asphaltic mixtures may be retained up to 30 minutes or more. Viscosity and relative viscosity data are given in Table A-5 of the Appendix. Figure VI, facing, shows the temperature-relative viscosity data obtained by heating 15 micron films of Asphalts 1, 3 and 6 in air for 15 minutes.

As an example of how the data in Figure VI can be used, let us assume that the temperature of the asphalt in a hot mix plant attains a temperature of 350°F and that the mass of loose asphaltic mixture remains at this temperature for 15 minutes and then drops to 325°F and 15 minutes later to 300°F. This is not an impossible situation since frequently 45 minutes elapse before a hot paving mixture is laid and properly compacted. From Figure VI it will be noted the conditions described above would result in a 26 fold hardening of Asphalt 1 over a 45 minute period. For Asphalt 3, the hardening would be 19.5 fold and for Asphalt 6 this severe temperature-time combination would result in 8.5 fold increase in viscosity. The data given in Table A-5 make possible the calculation of the hardening effect of numerous temperature-time combinations for these three representative asphalts.

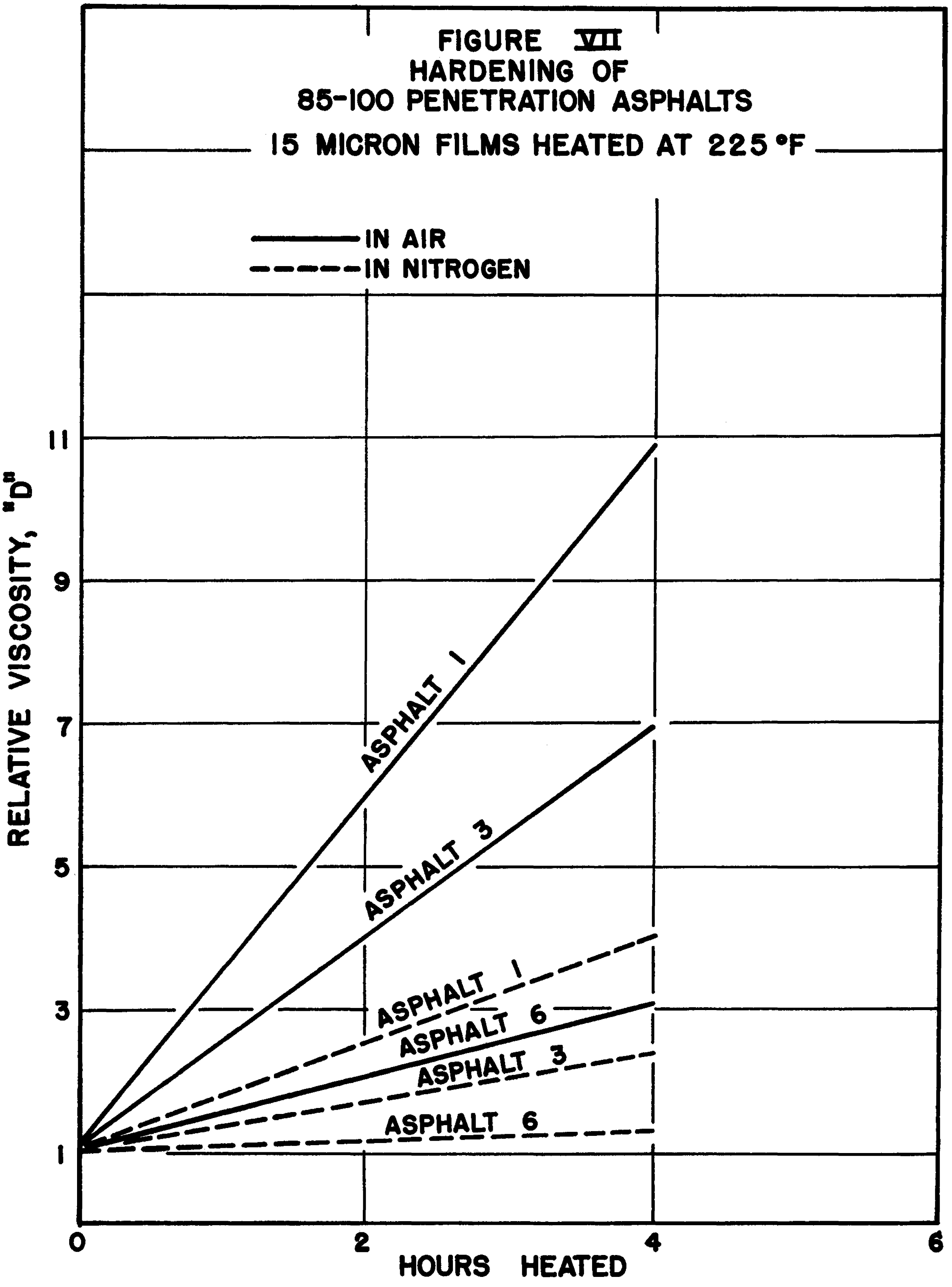


FIGURE VII
HARDENING OF
85-100 PENETRATION ASPHALTS
15 MICRON FILMS HEATED AT 225 °F

8. Hardening by Heating in Nitrogen at 225°F

The earlier investigators attributed much of the hardening of asphalt, heated in air, to volatilization of the lighter components. Subsequently, the pendulum swung in the other direction and the hardening was thought to be caused chiefly by oxidation.

Some experiments were conducted to obtain preliminary, quantitative data concerning the relative effects of volatilization and oxidation at similar conditions of time and temperature. In this phase of the work the 25 asphalts listed in Table 1 facing page 6 were heated on glass plates in nitrogen at one atmosphere for 4 hours at 225°F. The film was 15 microns thick. Additional information, which could be obtained by conducting the experiments also at 2 hours (as was the case in the tests in air) would not be commensurate with the work involved. This study will be expanded later to include higher temperatures and shorter times.

A. Relative Effect of Oxidation and Volatilization

Table A-6, in the Appendix, gives data on the 25 asphalts when heated in air and in nitrogen for 4 hours at 225°F. Figure VII, facing, illustrates the difference in rate of hardening obtained by heating films of asphalt in air and nitrogen. Asphalts 1, 3 and 6 were again selected for illustration because they represent the spread of data obtained. Rates of hardening caused by volatilization (measured in an atmosphere of nitrogen) are shown by the broken lines. The solid lines represent the rate of hardening caused by volatilization plus oxidation (measured in an atmosphere of air). These solid line curves are the same as those shown in Figure IV.

TABLE 2

Relative Effect of Oxidation and Volatilization of OA-90 Asphalts Heated in 15 Micron Films 4 Hours at 225°F

Asphalt No.	Relative Viscosity after Heating in Air	Relative Viscosity after Heating in Nitrogen	Percent Total Hardening Caused by Oxidation	Percent Asphaltene
3	7.5	2.6	65	24.6
7	10.5	4.2	60	14.9
1	10.9	3.8	65	17.8
8	7.3	2.7	63	1.0
2	9.1	3.7	59	19.0
		Average	63	15.5
10	5.8	2.8	52	11.6
4	4.8	2.0	58	9.3
5	4.0	2.0	50	8.1
6	3.0	1.25	58	1.0
11	5.5	2.85	48	11.0
9	6.4	2.9	55	17.0
		Average	53	9.7

The data on the eleven OA-90 asphalts summarized in Table 2, facing, indicate that oxidation usually is responsible for a major portion of the hardening of asphalts exposed to heated air. The percentage of hardening caused by oxidation alone varies from 48 to 65 percent of the total caused by heating in air at 225°F. It is interesting that the asphalts showing the most rapid hardening when heated in air (Asphalts 3, 7, 1,8 and 2) possess the greatest susceptibility to the effects of oxygen. Also, in general, their asphaltene content is higher than for the 6 asphalts with less susceptibility to oxidation. There is one exception to the general trend. Asphalt 8 although showing considerable susceptibility to oxidation has only one percent asphaltenes. It is evident that reliance cannot always be placed on the asphaltene content as a criterion of susceptibility to oxidation.

TABLE 3

Effect of Heat on Confined Films of OA-90 Asphalts for 4 Hours in Absence of Light

Temperature °F	Viscosity @ 77°F Megapoises	Relative Viscosity
	Asphalt 6	
225	0.70	1.00
325	0.86	1.20
350	0.90	1.30
375	1.10	1.55
	Asphalt 3	
225	1.8	1.50
325	2.4	2.00
350	4.8	4.00
375	2.1	1.75
	Asphalt 1	
225	1.3	1.20
325	4.2	3.80
350	1.9	1.70
375	1.7	1.55

9. Effect of Heat on Confined Films of Asphalt

Films of representative OA-90 asphalts (Asphalts 1, 3 and 6) were heated between glass plates in the dark for 4 hours at temperatures ranging from 225° to 375°F. Viscosity of the heated asphalt was determined at 77°F and its relative viscosity calculated. Table 3, facing, shows the results of these experiments.

The sensitivities of the asphalts to elevated temperatures are somewhat different. As the temperature is raised the confined films of Asphalt 6 slowly increase in viscosity. This is the result of condensation polymerization which can occur in the absence of oxygen or sunlight. Viscosities of the Asphalt 3 samples increased rapidly with rising temperatures through 350°F. This behavior indicates that condensation polymerization is more rapid and pronounced than for Asphalt 6. However, when the Asphalt 3 asphalt is heated to 375°F a sharp decrease in viscosity occurs. The presence of solid particles and gas bubbles in the heated film indicates that the effect of condensation polymerization is to a large extent destroyed by cracking (depolymerization) at the elevated temperature.

Asphalt 1 shows an increase in viscosity (polymerization) at temperatures through 325°F. Thermal decomposition (cracking) of this asphalt is severe at 350°F and increases somewhat at 375°F. Thus, Asphalt 1 is subject to cracking at a lower temperature than is Asphalt 3. Asphalt 6 is resistant to thermal decomposition at temperatures through 375°F, but this asphalt would be expected to crack at a higher temperature.

10. Effect of Actinic Light on Asphalts

It is known that short wave lengths of light have a measurable hardening and deteriorating action on most asphalts. Actinic light induces free radical initiated polymerization in unsaturated compounds. Experiments are planned which will evaluate the effect of light on the 25 asphalts used in this project. Such measurements are necessary to expand our understanding of the factors contributing to the hardening and loss of durability of asphalts during service.

It appears likely that the causes of hardening of most asphalts, in decreasing order of importance, are:

Oxidation

Volatilization

Action of Actinic Light

Condensation Polymerization

11. Composition of Asphalt

The variations in hardening of asphalts by heat and oxygen, discussed in the preceding pages, have their origin in differences of chemical composition. Although the chemistry of asphalt is now being vigorously investigated by various agencies, no simple and entirely satisfactory method of evaluation has been developed. A simple method is a necessity. And, because it fulfills that requirement, the so called "component analyses" method has been used. In addition, the Asphaltene content (that portion insoluble in n-pentane) of each asphalt has been determined.

A brief description of the component analysis procedure follows:

A sample of the asphalt is digested in hot n-butanol. The residue is separated from the solution by filtration and then weighed. This is Fraction I, which at one time was called Asphaltics. Solvent is stripped from the butanol solution and the residue is dissolved in hot acetone. This solution is then chilled to -10°F for a number of hours which results in the precipitation of an oily material. The cold acetone solution is decanted from the material which has become insoluble in acetone at the low temperature. The decanted acetone solution is stripped of solvent and the residue weighed. This is Fraction II, which at one time was called Cyclics. The solvent free material precipitated from the cold acetone is weighed as Fraction III. In the past, this material has been called Paraffinics or Saturates. With the improved techniques that have become available for the analysis of asphaltic fractions, it is evident that the terms Asphaltics, Cyclics and Paraffinics or Saturates may become misleading and confusing. However, in the discussions below the old descriptive terms will be used to some extent. In a further elaboration of the component analysis method, Fraction I (Asphaltics) minus Asphaltenes is called Fraction IV. This material has been called Resins, but in all honesty this is an unsatisfactory name. It will be used, however, at certain times when referring to Fraction IV.

Table A-7, of the Appendix, gives data on the composition of the 25 asphalts listed in Table 1, facing page 6. Figure VIII, following, is a plot, on triangular coordinates, of the component analyses of seven representative 85-100 penetration asphalts used by THD. Six of these asphalts fall within the confines of a parallelogram drawn on the chart.

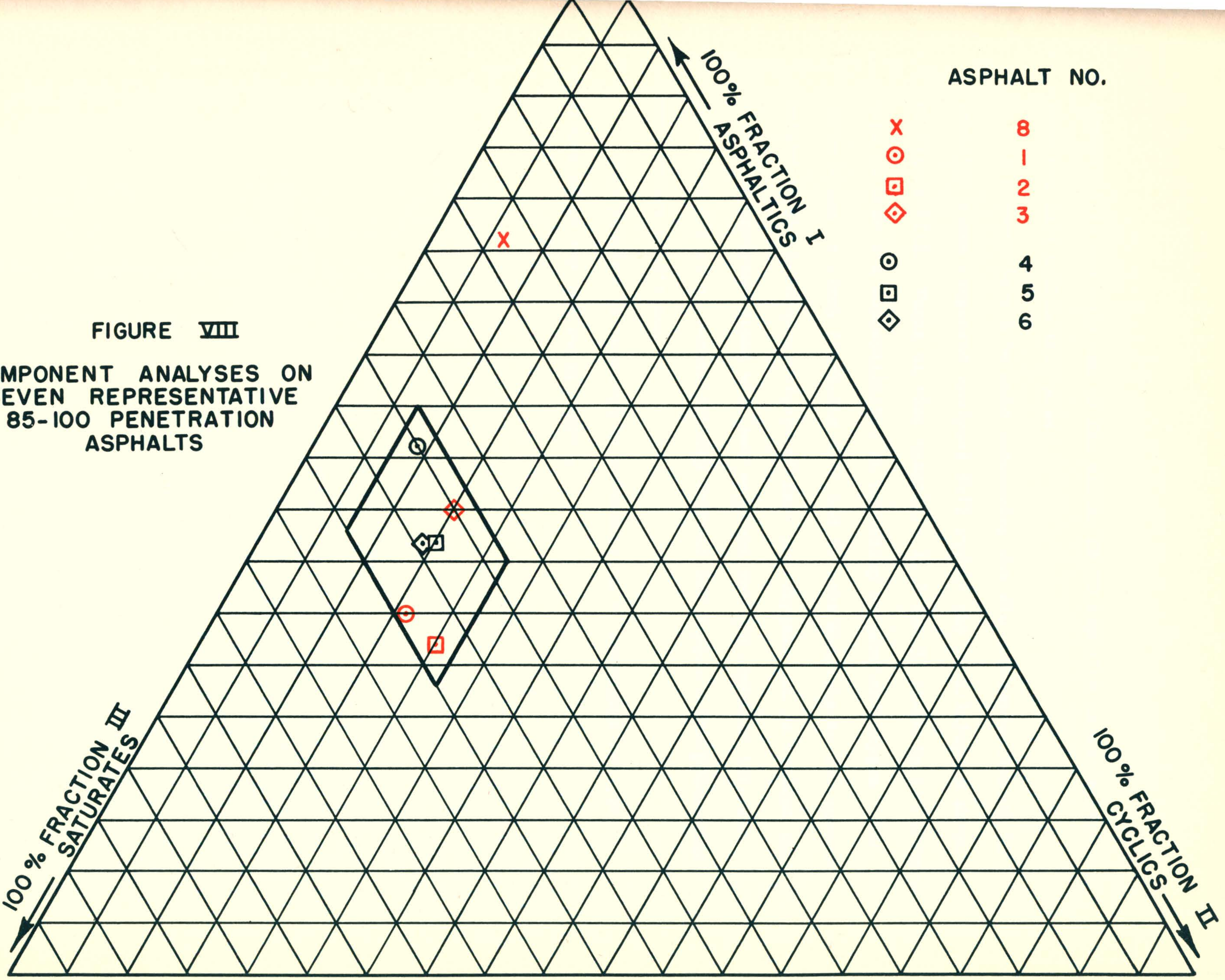


FIGURE VIII

COMPONENT ANALYSES ON
SEVEN REPRESENTATIVE
85-100 PENETRATION
ASPHALTS

Asphalt 8 is the only one of the eleven OA-90 asphalts investigated that does not fall within this area.

A comment should be made concerning the six representative OA-90 asphalts whose component analyses fall within the parallelogram shown on Figure VIII. Three of them (Asphalts 1, 2 and 3) shown in red possess high to moderate susceptibility to hardening by heat and oxygen. The three shown in black (asphalts 4, 5 and 6) have moderate to low susceptibility to the hardening effects of heat and oxygen. It is evident that component analyses alone will not separate the six asphalts into two groups of differing susceptibility to heat and oxygen under processing and service conditions.

This problem is resolved by an extension to component analyses discussed in the following section.

TABLE 4

Analyses on 85-100 Penetration Asphalts

Asphalt No.	Asphaltenes, A	Fraction IV, R	Fraction III, S	Fraction II, C	Coefficient of Dispersion "X" = $\frac{R+C}{A+S}$
1	17.8	17.2	49.0	16.0	0.50
2	9.0	13.0	48.0	20.0	0.49
3	24.6	20.4	40.0	15.0	0.55
4	9.3	41.7	40.0	9.0	1.03
5	8.1	33.9	43.0	15.0	0.96
6	1.0	41.0	44.0	14.0	1.22
8	1.0	70.0	23.0	6.0	3.16

12. Correlation of Composition with Hardening of Asphalt

As pointed out above the asphaltene content of an asphalt can be subtracted from Fraction I (Asphaltics) to yield Fraction IV (Resins). For any asphalt, the sum of Fraction IV plus Fraction II divided by the sum of the asphaltenes plus Fraction III gives a number which has been called Dispersion Coefficient X. This coefficient correlates with the relative viscosity developed by the action of heat and oxygen.

Table 4, facing, gives compositions and the calculated Dispersion Coefficients for the seven asphalts shown on Figure VIII.

Table 5, following, shows the correlation obtained between the Dispersion Coefficient and the extent of hardening indicated by the relative viscosity of each asphalt after heating for four hours at 225°F in nitrogen or air. The correlation is satisfactory except for Asphalt 8. For this asphalt the Coefficient of Dispersion indicates excellent resistance to hardening but the relative viscosities of the treated samples show relatively high susceptibilities to heat and oxygen.

What is the significance of the Dispersion Coefficient? It is an evaluation of the colloidal nature of the asphalt. The asphaltenes comprise the component of the asphalt which is dispersed in the lower molecular weight materials. Fraction III (Saturates) contains compounds that are poor dispersing agents and in some cases may cause aggregation or floculation of the asphaltenes. Thus, the denominator of the expression $\frac{R+C}{A+S}$ represents the amount of material that must be dispersed plus the compounds present that hinder or prevent dispersion.

Now let us turn to the numerator of the expression $\frac{R+C}{A+S}$. Fraction II (Cyclics) contains compounds that have powerful dispersing action on

TABLE 5

Relationship Between Composition and Resistance to Hardening for 85-100 Penetration Asphalts

Asphalt No.	Relative Viscosity 15 Micron Film heated for 4 hours @ 225°F in Nitrogen	Air	Coefficient of Dispersion $"X" = \frac{R+C}{A+S}$ (Table 4)
	Poor Resistance to Heat and Oxygen		
1	3.8	10.9	0.50
2	3.7	9.1	0.49
3	2.2	6.9	0.55
Average	2.2	9.0	0.51
8	2.7	7.3	3.61
	Good Resistance to Heat and Oxygen		
4	2.0	4.8	1.03
5	2.0	4.0	0.96
6	1.25	3.0	1.22
Average	1.75	3.9	1.07

asphaltenes. They may be considered to counteract the flocculating or aggregating action of Fraction III (Saturates). Also, Fraction IV (Resins) contains compounds that protect and stabilize the asphaltenes dispersed in the oily phase of the asphalt. Thus, the numerator represents the amount of dispersing agent in the asphalt. As the numerator becomes larger, and the value of X increases, the asphalt becomes a better dispersed system. This is reflected in its "sol" characteristics and rheological properties. When the numerator becomes smaller and the value of X decreases, the asphalt is not so well dispersed and manifests more "gel" properties, which are associated with non-Newtonian flow and other characteristics indicating the presence of internal structure. The results of these studies on 25 asphalts used by THD disclose that a well dispersed or sol like bitumen is not as susceptible to hardening as a poorly dispersed material.

VII. APPENDIX

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Table A-1

Standard Tests on 25 Paving Asphalts

OA-90 Asphalts

Asphalt No.	Penetration 77°	Ductility 77°	R&B °F	Sp.Gr. 77°	Loss on Heating %	Pen. of Residue	Residue, % of orig.	Oliensis Spot	Solubility in CCl_4	Flash, COC °F
3	90	100+	117	1.028	0.000	81	90.0	N	99.9+	545
10	92	141+	119	0.998	0.040	82	89.0	N	99.9+	600+
4	93	100+	115	1.003	0.014	78	84.0	N	99.7+	600+
7	94	100+	117	1.030	0.008	76	81.0	N	99.9+	555
1	92	100+	117	1.003	0.006	76	82.5	N	99.7+	580
5	90	100+	115	1.014	0.052	77	85.5	N	99.7+	600+
6	89	100+	118	0.990	0.000	81	91.0	N	99.7+	600+
8	98	115+	116	0.987	0.036	83	85.0	N	99.7+	600+
2	92	141+	111	1.024	0.028	78	80.5	N	99.7+	565
11	93	100+	117	1.018	0.016	83	89.0	N	99.9+	570
9	90	141+	117	0.994	0.008	79	88.0	N	99.7+	590
OA-135 Asphalts										
3A	142	100+	111	1.024	0.042	118	83.0	N	99.9+	540
7A	144	100+	111	1.026	0.128	116	80.5	Mod. N	99.9+	550
1A	132	100+	111	0.999	0.040	116	88.0	N	99.7+	560
6A	133	100+	111	0.985	0.008	121	91.0	N	99.7+	600+
11A	133	100+	111	1.011	0.012	119	89.5	N	99.9+	570
OA-175 Asphalts										
10B	160	141+	109	0.993	0.002	144	90.0	N	99.7+	600+
7B	172	100+	108	1.022	0.024	140	81.5	Mod. N	99.9+	540
1B	163	119	108	0.997	0.084	139	85.0	N	99.7+	575
5B	150	141+	109	1.010	0.010	137	91.5	N	99.7+	600
12B	168	100+	104	1.010	0.004	138	82.0	N	99.7+	600+
6B	170	100+	104	0.981	0.000	156	92.0	N	99.7+	600+
8B	188	141+	106	0.979	0.004	148	79.0	N	99.7+	600+
2B	185	141+	103	1.014	0.004	149	80.5	N	99.7+	560
11B	177	100+	107	1.011	0.008	153	86.5	N	99.9+	575

Table A-2

Data on OA-90 and OA-135 Asphalts Obtained by Bureau of Public Roads Film Test at 325°F

Asphalt No.	Original Viscosity, Megapoises at 77°F	Heated for 5 Hours		Heated for 10 Hours		Heated for 15 Hours	
		Viscosity, Megapoises at 77°F	Relative Viscosity	Viscosity, Megapoises at 77°F	Relative Viscosity	Viscosity, Megapoises at 77°F	Relative Viscosity
				OA-90 Asphalts			
6	0.70	1.5	2.1	3.1	4.4	4.0	5.7
5	0.85	1.9	2.2	3.7	4.3	5.8	6.8
11	1.30	4.7	3.6	7.2	5.5	11.0	8.5
4	0.80	2.9	3.6	4.5	5.6	6.5	8.1
3	1.20	4.9	4.0	8.7	6.6	12.0	9.3
8	0.90	3.6	4.0	8.5	9.4	13.0	14.5
10	1.00	4.1	4.1	6.2	6.2	9.0	9.0
9	0.90	3.8	4.2	6.2	6.9	10.0	11.2
2	0.90	4.8	5.3	7.1	8.0	11.0	12.2
7	0.80	4.6	5.8	11.0	13.5	17.0	21.0
1	1.10	9.1	8.2	15.0	13.5	21.0	19.1
				OA-135 Asphalts			
6A	0.36	1.1	3.1	2.0	5.5	-	-
7A	0.40	4.0	10.0	7.0	17.5	-	-
11A	0.49	1.6	3.2	2.7	5.5	-	-
3A	0.54	2.5	4.6	5.0	9.3	-	-
1A	0.59	4.0	6.8	7.5	13.1	-	-

Table A-3

Data on 25 Paving Asphalts Obtained by a Modified Shell Thin Film Test

Asphalt No.	Viscosity of Original Asphalts Megapoises at 77°F	Viscosity of 15 Micron Film after 2 hours at 225°F Megapoises at 77°F	Relative Viscosity	Viscosity of 15 Micron Film after 4 hours at 225°F Megapoises at 77°F	Relative Viscosity
OA-90 Asphalts					
3	1.2	5.2	4.3	9.0	7.5
10	1.0	3.3	3.3	5.8	5.8
4	0.8	2.0	2.5	3.8	4.8
7	0.8	5.0	6.2	8.5	10.5
1	1.1	6.6	6.0	12.0	10.9
5	0.85	2.4	2.8	3.4	4.0
6	0.7	1.5	2.1	2.1	3.0
8	0.9	3.6	4.4	6.6	7.3
2	0.9	4.1	4.5	8.2	9.1
11	1.3	4.3	3.3	6.8	5.5
9	0.9	3.2	3.5	5.8	6.4
OA-135 Asphalts					
3A	0.54	2.2	4.0	3.8	7.0
7A	0.40	1.9	4.8	3.4	8.5
1A	0.59	2.5	4.2	4.4	7.5
6A	0.36	0.9	2.5	1.3	3.6
11A	0.49	1.3	2.6	2.1	4.3
OA-175 Asphalts					
10B	0.27	0.9	3.4	1.5	5.6
7B	0.30	1.4	4.7	2.5	8.3
1B	0.30	1.4	4.7	2.8	9.3
5B	0.29	0.85	2.9	1.0	3.5
12B	0.24	0.6	2.5	0.98	4.1
6B	0.21	0.7	3.3	0.8	3.8
8B	0.21	0.8	3.7	1.1	5.2
2B	0.22	0.8	3.6	1.3	5.9
11B	0.23	0.9	3.8	1.4	6.1

Table A-4

Data on Prolonged Heating of 15 Micron Films in Air at 225°F

	Viscosity, Megapoises at 77°F and (Relative Viscosity) after heating for							
Asphalt No.	**4 hrs.**	**10 hrs.**	**16 hrs.**	**32 hrs.**	**48 hrs.**	**64 hrs.**	**128 hrs.**	**164 hrs.**
1	12.0 (10.9	17 (15.5)	30 (27)	42 (37)	-	44 (40)	-	-
1A	4.3 (7.3)	-	13 (22)	31 (52)	44 (75)	50 (85)	-	-
1B	2.8 (9.3)	-	12 (40)	-	-	50 (165)	-	-
6	2.1 (3.0)	-	4.4 (6.3)	7.2 (10.3)	-	13 (18.5)	-	30 (43)
6A	1.3 (3.6)	-	4.0 (11)	7.8 (22)	16 (40)	20 (56)	47 (235)	-
6B	0.8 (3.8)	-	1.9 (9)	5.0 (24)	-	10 (48)	25 (120)	-

Table A-5

Hardening of 15 Micron Films of Asphalt
Heated in Air at Various Temperatures and Times

Asphalt 1

Temperature °F	Viscosity at 77°F Megapoises	Relative Viscosity
	15 Minutes	
275	3.5	3.2
300	5.5	5.0
325	9.0	8.2
350	14.0	12.7
	30 Minutes	
275	6.6	6.0
300	12.0	10.9
325	22.0	20.0
350	50.0	45.0
	60 Minutes	
275	12.5	11.4
300	21.0	19.1
325	43.0	39.0
	120 Minutes	
225	6.6	6.0
250	12.0	10.9
275	22.0	20.0
300	44.0	40.0

Table A-5 (cont'd)

Asphalt 3

Temperature °F	Viscosity at 77°F Megapoises	Relative Viscosity
	15 Minutes	
275	3.0	2.5
300	4.8	4.0
325	8.0	6.6
350	11.0	9.2
	30 Minutes	
275	4.4	3.7
300	9.0	7.5
325	15.0	12.5
350	37.0	31.0
	60 Minutes	
275	8.6	7.2
300	16.0	13.3
325	30.0	25.0
	120 Minutes	
225	5.2	4.3
250	9.0	7.5
275	15.5	12.9
300	35.0	29.0

Table A-5 (cont'd)

Asphalt 6

Temperature °F	Viscosity at 77°F Megapoises	Relative Viscosity
	15 Minutes	
275	1.3	1.85 (high)
300	1.3	1.85
325	1.9	2.7
350	2.7	3.9
	30 Minutes	
275	1.5	2.2
300	2.3	3.3
325	4.3	6.1
350	12.0	17.2
	60 Minutes	
275	2.3	3.3
300	3.5	5.0
325	10.1 (average 2 runs)	14.4
	120 Minutes	
225	1.5	2.1
250	2.2	3.1
275	4.2	6.0
300	6.6	9.5

Table A-6

Data on the Effect of Heating 25 Asphalts in Air and in Nitrogen for 4 Hours at 225°F

		15 Micron Film Heated in Air for 4 Hours at 225°F		15 Micron Film Heated in Nitrogen 4 Hours at 225°F			
Asphalt No.	**Viscosity Original Asphalt Megapoises at 77°F**	**Viscosity Megapoises at 77°F**	**Relative Viscosity**	**Viscosity Megapoises at 77°F**	**Relative Viscosity**	**Percent of Total Hardening Caused by Oxidation**	**Asphaltene Content**
			OA-90 Asphalts				
3	1.2	9.0	7.5	3.1	2.6	65	24.6
10	1.0	5.8	5.8	2.8	2.8	52	11.6
4	0.8	3.8	4.8	1.6	2.0	58	9.3
7	0.8	8.5	10.5	3.4	4.2	60	14.9
1	1.1	12.0	10.9	4.2	3.8	65	17.8
5	0.85	3.4	4.0	1.7	2.0	50	8.1
6	0.7	2.1	3.0	0.88	1.25	58	1.0
8	0.9	6.6	7.3	2.4	2.7	63	1.0
2	0.9	8.2	9.1	3.3	3.7	59	19.0
11	1.3	6.8	5.5	3.7	2.85	48	11.0
9	0.9	5.8	6.4	2.6	2.9	55	17.0
			OA-135 Asphalts				
3A	0.54	3.8	7.0	2.1	3.9	44	17.5
7A	0.40	3.4	8.5	1.6	4.0	53	12.5
1A	0.59	4.4	7.5	2.3	3.9	48	11.0
6A	0.36	1.3	3.6	0.82	2.3	36	1.0
11A	0.49	2.1	4.3	1.2	2.5	42	11.0
			OA-175 Asphalts				
10B	0.27	1.5	5.6	1.0	3.7	34	9.5
7B	0.30	2.5	8.3	1.35	4.5	46	13.0
1B	0.30	2.8	9.3	1.6	5.3	43	16.0
5B	0.29	1.0	3.5	0.8	2.65	24	8.5
12B	0.24	0.98	4.1	0.7	2.9	32	7.0
6B	0.21	0.8	3.8	0.6	2.85	25	1.0
8B	0.21	1.1	5.2	0.75	3.6	31	0.65
2B	0.22	1.3	5.9	0.84	3.8	36	14.5
11B	0.23	1.4	6.1	0.9	3.9	36	15.0

Table A-7

Composition of 25 Paving Asphalts

Asphalt No.	"A" % Asphaltenes	"As" % Asphaltics	"R" % Resins As-A	R/A	Saturates "S" %	Saturates "S" Density 70/70°	Saturates "S" RI 158°F	Cyclics "C" %	Cyclics "C" Density 70/70°	Cyclics "C" RI 158°F
OA-90 Asphalts										
3	24.6	45	20.4	0.84	40	0.9429	1.520	15	1.0770	1.592
10	11.6	49	37.4	3.2	40	0.9157	1.516	11	1.0480	1.602
4	9.3	51	41.7	4.5	40	0.9662	1.523	9	1.0040	1.582
7	14.9	31	16.1	1.08	48	0.9538	1.530	21	1.0432	1.602
1	17.8	35	17.2	0.97	49	0.9782	1.520	16	1.0433	1.607
5	8.1	42	33.9	4.2	43	0.9500	1.528	15	1.0200	1.570
6	1.0	42	41.0	41.0	44	0.9631	1.528	14	1.0513	1.587
8	1.0	71	70.0	70.0	23	0.9716	1.532	6	1.0500	1.576
2	19.0	32	13.0	0.68	48	0.9500	1.524	20	1.0200	1.563
11	11.0	31.5	20.5	1.85	49	0.9506	1.516	19.5	0.9730	1.572
9	17.0	33	16.0	0.94	50	0.9500	1.518	17	1.0200	1.561
OA-135 Asphalts										
3A	17.5	43	25.5	1.45	43	0.9540	1.512	14	1.0350	1.560
7A	12.5	31	18.5	1.48	47	0.9623	1.510	22	0.9854	1.585
1A	11.0	32	21.0	1.9	51	0.9479	1.511	17	1.0573	1.585
6A	1.0	56	55.0	55.0	35	0.9591	1.514	9	1.1114	1.748
11A	11.0	38	27.0	2.45	45	0.9540	1.511	17	1.0579	1.585
OA-175 Asphalts						Used Avg.				
10B	9.5	43	33.5	3.95	50	0.9500	1.510	7		
7B	13.0	31	18.0	1.38	49	"	1.521	20		
1B	16.0	30	14.0	0.87	50	"	-	20		
5B	8.5	40	31.5	3.7	44	"	1.524	16		
12B	7.0	30	23.0	3.3	50	"	-	20		
6B	1.0	52	51.0	51.0	39	"	1.528	9		
8B	0.65	69	68.35	105.0	25	"	1.528	6		
2B	14.5	28	13.5	0.93	50	"	1.518	22		
11B	15.0	40	25.0	1.67	43	"	1.511	17		