

MICHIGAN
STATE HIGHWAY DEPARTMENT
Murray D. Van Wagoner
State Highway Commissioner

CHANGES IN CHARACTERISTICS
OF
SLOW-CURING ASPHALTIC OILS

By

E.A. Finney and Thaddeus Wolczynski

Research Project 36 C-1

Research Laboratory
Testing and Research Division
Report No. 6
November 25, 1940

CHANGES IN CHARACTERISTICS OF SLOW-CURING ASPHALTIC OILS

During the past few years, considerable research has been performed on different types of asphaltic materials and bituminous mixtures to develop a laboratory procedure whereby the durability and service behavior of a bituminous material may be predicted with some degree of accuracy.

Several important factors have made the problem, relative to slow curing asphalts, difficult to solve; first, the fact that although certain chemical and weathering tests will show comparatively that one product will withstand a certain laboratory treatment better than another, these tests are not indicative that the product which fails in the laboratory will fail in service; second, insufficient data is available on the change in characteristics of asphaltic materials after incorporation in bituminous mixtures and third, the definition as to what constitutes an undesirable property of slow curing asphaltic materials has not been definitely established.

Published research reports pertaining to the durability and service behavior of slow-curing asphaltic oils are comparatively recent and few in number. The work done by the Public Roads Administration and reported by Lewis and Hillman ^{1,2,3} includes a comparative study of the changes in physical and chemical characteristics of slow-curing asphalts produced in the various laboratory tests and when the same materials are exposed to sunlight, heat and air. Also their work has included a more recent study where they have attempted to correlate changes in physical and chemical

properties of liquid asphalts present as binder in road surface mixtures and subjected to similar service conditions with the results of conventional laboratory tests and with the results of exposure tests. The asphalts were exposed in thin films to the action of solar light, heat and air; the amount of volatile matter lost was determined and the residues were tested for consistency, ductility and solubility. Mixtures of the liquid asphalts with aggregates were tested for stability and toughness. The mixtures were also tested on a circular track exposed to weather conditions and subjected to controlled traffic of rubber-tired wheels.

More recently a comprehensive study on the subject has been completed jointly by the University of Wisconsin and the Wisconsin Highway Department and reported by Holberg, Hougen and Zapata.⁴ The purpose of their investigation was to find an explanation for the differences in service behavior of slow curing asphalts meeting the same specifications; to determine the value of the requirements of current specifications and to ascertain their relation to behavior and durability in service; to determine the influence of chemical and physical properties of slow-curing asphalts upon their adhesion and resistance to stripping by water from aggregates and to study the effect of composition on the properties of the slow-curing asphalts. Slow-curing asphalts were separated into their asphaltene, resin and oily constituents, recombined using predetermined proportions of the three constituents and subjected to laboratory analyses and weathering tests. Bituminous materials were recovered from bituminous mixtures subjected to road service and studied to determine changes in properties and characteristics.

In 1935, the Michigan State Highway Department initiated a large bituminous program involving the construction of several hundred miles of oil

aggregate surfacing per year. A program such as this would naturally require a considerable amount of slow-curing asphaltic material of the SC-6 type. Realizing the failure of current specifications to furnish the necessary information enabling engineers to predict the durability and behavior of this type of material under service conditions, the Highway Department, in June 1936, authorized an extensive investigation on asphaltic materials of the SC-6 type. The purpose of the investigation was to determine the changes in characteristics of slow-curing asphalts before and after weathering with the idea of perfecting a laboratory test whereby it would be possible to distinguish between bituminous materials possessing good or undesirable weathering qualities before they are incorporated in the bituminous mixture.

It is a well established fact that bituminous materials harden with age, either in a container or in a road surface. In the case of a road surface the change in consistency of a bituminous material may be due chiefly to the loss of oil constituents by evaporation, absorption, and weathering. This being true there should be some kind of relationship between change in consistency and length of service whereby if the characteristics of an asphaltic material which has undergone excessive change in service were known, a laboratory test could be devised to duplicate these characteristics on the original material. Consequently, the investigation was developed with that thought in mind.

As originally planned, the scope of the investigation included three important phases of the subject of durability, namely, the viscosity-temperature relationship of bituminous materials before and after weathering, physical and chemical surface phenomena, and the effect of change in constituents upon durability. This work was to be augmented by field studies

relative to the service behavior of existing bituminous surfaces constructed with materials of the SC-6 type.

This report presents a review of the work completed at the present time and will include the following subjects: the viscosity-temperature relationship of sixteen different SC-6 asphaltic materials before and after being subjected to various laboratory tests; a method for recovering asphaltic materials of the slow-curing type; and the change in some characteristics of slow-curing asphalts recovered from existing road surfaces.

VISCOSITY-TEMPERATURE RELATIONSHIP STUDY

It was desired to study the change in viscosity with temperature because it was considered to be the most advantageous method of evaluating the change in characteristics of a bituminous material upon weathering. Because of the limitations of present standard methods for determining viscosity, a type of viscosimeter was chosen whereby the viscosity of all the asphaltic oils at different consistencies and temperatures could be determined in absolute units, thus obtaining a definite basis for comparison of the consistency by a common measure.

Bituminous Materials

The asphaltic materials used in the investigation were of the SC-6 type used in low cost bituminous road construction. The materials were selected as follows: first, the manufacturer who would be in a position to furnish materials to the Michigan bituminous program; second, the type of crude from which the material was made and third, the method of manufacture. The materials include the residue of topping, cracking and straight run processes, the blending of one type of residue with another and the residue obtained

73

by cutting back heavy residues with lighter distillates. According to the manufacturers of these materials they were produced from the following crudes, Mid-Continental, Urbana, Smackover, Mexican, Oregon Basin, California, Kansas, and Wyoming. The various materials together with their source, manufacture and physical characteristics are summarized in tables 1 and 2.

Viscosimeter

A viscosimeter suitable for the viscosity-temperature relationship study had to meet the following requirements; (1) sufficiently accurate within ± 2.0 percent, (2) the time required for test not to exceed 2,000 seconds, (3) must operate on not more than 5 cc of material, (4) capable of measuring the viscosity of any product regardless of its viscous characteristics, providing true fluid flow is obtained, (5) usefulness of the viscosimeter should not be limited by temperature, (6) must be capable of making several determinations on the same sample at different temperatures, (7) applicable to opaque liquids, and (8) the determination of viscosity must be in absolute units.

After careful consideration and study, the Koppers Viscosimeter based upon the capillary rise method and developed by Rhodes, Volkman and Barker was selected as the best instrument available. With this instrument, viscosity is determined by timing the flow of the material under test through a capillary tube. The material is made to ascend through the capillary tube. This is accomplished by immersing the lower end of a capillary tube into the sample of material to be tested, the upper end of the capillary tube being connected with a partly evacuated reservoir. Two fixed points are chosen on the capillary tube and the time required for the passage of the air-sample interface between these two points is noted. From the time, vacuum applied, the distance between the points, and the radius of the bore of the capillary tube, the viscosity of the sample can be calculated. The viscosi-

TABLE NO. 1

SOURCE OF ASPHALTIC MATERIALS USED IN THE INVESTIGATION

Lab. Ident.	Field	Crude	Process
A	Mixed	Mid-Continent	Cracked Residue
B	Mixed	Mid-Continent	Blend of cracked and uncracked residues
C	Mixed	Mid-Continent	Cut-back, heavy residue with gas oil
D	Urbana	Urbana	Residue from topped crude
E	Urbana	Urbana	Blend of cracked and uncracked residues
F	Smackover	Smackover	Cut-back, topped crude with gas oil
G	Mexico	Mexican	Straight run residue
H	Mixed	Mid-Continent	Blend of cracked residues
I	Oregon Basin	Oregon	Straight run residue
J	Mixed	California	Blend of steam distilled residues
K	Mixed	Kansas	Straight run residue
L	Mixed	Kansas	Blend of cracked and uncracked residues
M	Mixed	Wyoming	Straight run residue
N	Mixed	Wyoming	Blend of cracked residues
O	Mixed	Mid-Continent	Cracked residue
P	Mixed	California	Residue from topped crude

TABLE NO. 2

LABORATORY ANALYSES OF SLOW CURING ASPHALTIC MATERIALS

LABORATORY IDENTIFICATION	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Specific Gravity, 25°C/25°C	1.082	0.992	0.979	0.980	0.995	0.976	0.984	1.052	0.993	0.972	1.009	1.025	0.996	0.999	1.055	0.978
Water and Sediment, per cent	0.0	0.3	0.4	0.05	0.0	0.0	0.05	0.02	0.05	0.0	0.2	0.0	0.05	0.0	0.4	0.0
Flash Point, (Cleve. Open Cup) °C	152	130	148	214	145	150	140	155	140	156	150	154	174	170	210	205
Viscosity Saybolt Furol, 60°C, Sec.	480	446	465	420	649	552	593	467	498	522	435	472	683	637	458	532
Heterogeneity Test	Posi- tive	Sl.Pos- itive	Nega- tive	Nega- tive	Sl.Pos- itive	Nega- tive	Nega- tive	Posi- tive	Nega- tive	Nega- tive	Nega- tive	Posi- tive	Nega- tive	Posi- tive	Posi- tive	Nega- tive
Asphaltenes, per cent	26.00	8.95	12.66	6.46	8.80	8.61	20.41	19.05	13.14	10.00	11.78	14.66	14.07	13.04	13.29	5.08
DISTILLATION																
0 to 225° C, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0 to 315° C, %	0.0	1.5	0.2	0.0	0.0	trace	3.0	trace	trace	0.0	trace	trace	0.0	trace	0.0	0.0
0 to 360° C, %	1.8	7.0	7.0	0.5	0.5	3.0	12.0	3.5	2.5	1.5	1.2	1.0	trace	0.5	0.0	0.5
TESTS ON DISTILLATION RESIDUE																
Bitumen Soluble in CCl ₄ , %	99.96	99.93	99.99	99.94	99.97	99.98	99.91	99.85	99.93	99.94	99.95	99.89	99.93	99.94	99.52	99.80
TESTS ON 100 PENETRATION RESIDUE																
Actual Penetration or Residue	95	105	93	90	93	107	107	94	99	95	98	100	98	91	107	90
Heating time to above Residue, hrs.	1-1/2	11	6	22	11-1/2	9-1/2	3	2-1/2	9	7	4-3/4	3	6	4-1/2	7	---
Total Residue, %	84.0	79.1	78.8	75.5	80.1	82.3	75.3	81.8	76.2	79.7	77.4	80.1	76.3	81.2	84.6	70.0
Ductility, 25° C, 5 cm/min, cms.	105	100	111	148	110	140	125	133	108	95	150+	148	94	150+	70	117
Ductility, 4° C, 5 cm/min, cms.	0	5.5	6.5	7.0	6.5	9.5	9.5	1.0	9.5	7.0	7.0	7.0	9.0	5.5	4.5	9.4

meter is illustrated by the diagrammatic sketch in figure 1. At the present time, the Koppers Viscosimeter is so well known that no further explanation of its operation is deemed necessary. Its use as an instrument for measuring the consistency of tars has been illustrated by Messrs. Rhodes, Volkmann and Barker. Recently, Lewis and Halstead⁶ have shown that it is equally adaptable to measuring the consistency of asphalts especially of the liquid type.

THE KOPPERS VISCOSIMETER AND ITS USE WITH
SLOW-CURING ASPHALTS

At the time of purchase of the Koppers Viscosimeter we had no knowledge that it was ever used for measuring the viscosity of liquid asphaltic materials. Consequently, a study was made to determine the suitability of the Koppers Viscosimeter for our work.

In order to check the accuracy of the instrument as it would be used under ordinary laboratory conditions, a sample of heavy oil of known viscosity was obtained from the United States Bureau of Standards. This oil had an absolute viscosity of 31.3 poises at 25°C. The twelve capillary tubes purchased with the instrument were marked and an independent determination was made with each tube. The average results from these tests are to be found in table 3.

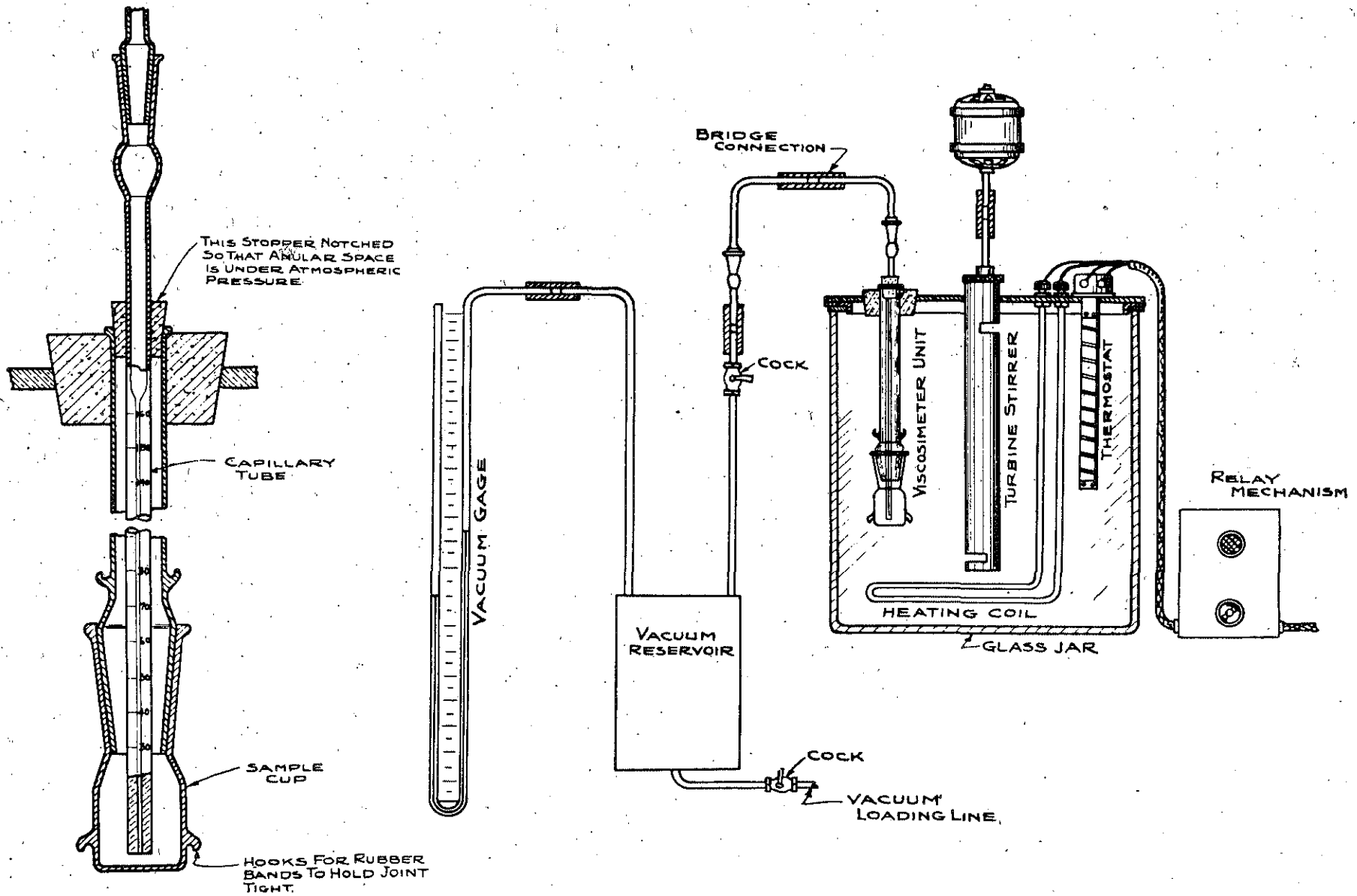


Figure 1

TABLE 3

Viscosity Determinations by Kopper Viscosimeter				
U.S.E.S. Sample 7				
Capillary Tube	Viscosity at 25° C		Poises	Percent Diff.
	Centistokes			
1	3423		31.4	0.3
2	3392		31.2	0.3
3	3444		31.6	0.9
4	3449		31.7	1.2
5	3439		31.6	0.9
6	3371		31.0	0.9
7	3360		30.9	1.2
8	3375		31.1	0.6
9	3370		31.0	0.9
10	3444		31.6	0.9
11	3386		31.2	0.3
12	3417		31.4	0.3

At the 25° C. determination, the value for all capillary tubes was equal to, or well under the accuracy specified for this viscosimeter.

The Pressure-Time Relationship for Capillary Tubes.

7

Bingham states that the quantity of liquid which transpires through a capillary in a given time and at a given temperature is directly proportional to the pressure, or in other words, the same liquid flowing through the same capillary at different pressures should give a constant value for pressure times the time of flow. Grueisen showed that this condition is by no means rigidly fulfilled by viscosimeters of the Ostwald type in which the liquid flows under its own hydrostatic pressure.

8

To determine if this law is fulfilled by the Koppers viscosimeter, tests were made using three different grades of materials. The data from these tests will be found in tables 4, 5 and 6. The results show that in the case of the three materials chosen, this law is in general true.

TABLE 4

Reproducibility of the Kopper Viscosimeter on a Low Viscosity
Material, U. S. B. S. Sample No. 7

Temp. of Test	Driving Forces P cm H ₂ O	Time of Flow t sec.	Rate of Flow cm/sec.	P x t	Viscosity Centis- tokes	Deviation from Average
20° C	15.75	42.3	.1892	666.23	5,837	1.71%
20° C.	11.70	55.0	.1454	643.50	5,720	0.33%
20° C.	10.00	65.0	.1231	650.00	5,720	0.33%
20° C.	8.10	81.0	.0988	656.10	5,670	1.20%
20° C.	6.50	104.8	.0763	681.20	5,764	0.43%
20° C.	5.60	121.8	.0657	682.08	<u>5,725</u>	<u>0.24%</u>
				Average	5,739	0.70%

TABLE NO. 5
 REPRODUCIBILITY OF KOPPER'S VISCOSIMETER
 FOR
 SLOW-CURING ASPHALT MATERIAL "A"

Temp. of Test	Pressure or Driving Force Cm.Hg.	Time Secs.	Rate of Flow Cm/Sec	PXT	Viscosity Centistokes	Diff. From Average	Percent Diff.
25°C	42.0	38.5	.0520	162	136,675	3,877	2.76
"	38.2	42.8	.0466	163	136,900	3,652	2.59
"	33.5	50.8	.0394	169	142,740	2,188	1.55
"	26.1	65.0	.0308	169	141,000	448	.32
"	19.0	90.2	.0222	171	143,000	2,448	1.73
"	14.8	115.2	.0174	170	143,000	2,448	1.73
					Av. 140,552		Av. 1.78%
40°C	41.5	34.2	.2340	1420	10,930	134	1.24
"	35.3	39.4	.2030	1390	10,800	4	.04
"	28.6	49.6	.1615	1410	10,900	104	.96
"	23.1	61.0	.1310	1410	10,750	46	.43
"	17.4	81.4	.0985	1415	10,680	116	1.07
"	13.4	107.2	.0748	1430	10,720	76	.71
					Av. 10,796		Av. .74%
50°C	11.80	33.5	.2388	3995	2,940	10	.34
"	10.20	37.7	.2122	385	2,860	70	2.38
"	8.10	50.4	.1587	407	2,970	40	1.36
"	6.20	67.1	.1194	416	2,880	50	1.70
"	4.20	103.4	.0773	435	2,930	0	.00
"	3.37	137.3	.0583	462	2,950	20	.68
					Av. 2,930		Av. .91%
60°C	4.10	37.0	.2160	152	1,020	26	2.62
"	3.25	47.1	.1695	153	990	4	.40
"	2.54	66.1	.1215	168	1,000	6	.60
"	2.01	88.2	.0910	176	988	6	.60
"	1.76	107.2	.0749	189	986	8	.81
"	1.42	153.0	.0522	217	979	15	1.52
					Av. 994		Av. 1.09%
70°C	2.05	35.8	.2240	73	415	2	.5
"	1.82	43.2	.1850	79	423	6	1.4
"	1.34	69.1	.1160	93	401	16	3.8
"	1.24	88.4	.0905	109	425	8	1.9
"	1.13	102.8	.0780	116	422	5	1.2
"	.98	143.8	.0555	140	418	1	.9
					Av. 417		Av. 1.61%

TABLE NO. 6
 REPRODUCIBILITY OF KOPPER'S VISCOSIMETER
 FOR
 SLOW-CURING ASPHALT MATERIAL "D"

Temp. of Test	Pressure or Driving Force Cm.	Time Secs.	Rate of Flow Cm/Sec.	PXT= k	Viscosity Centistokes	Diff. From Average	Percent Diff.
30°C	42.3	44.6	.1793	1886	16,056	2	.01
"	35.8	52.6	.1520	1883	15,990	68	.42
"	30.3	62.8	.1273	1902	16,077	19	.12
"	25.3	75.5	.1006	1910	16,082	24	.15
"	19.8	84.9	.0843	1879	15,943	115	.71
"	14.8	132.8	.0753	1965	16,202	144	.90
					Av. 16,058		Av. 0.38%
40°C	22.1	29.0	.2759	641	5,394	8	.15
"	17.5	36.5	.2191	639	5,329	73	1.35
"	13.3	49.8	.1606	662	5,478	76	1.40
"	11.7	56.7	.1410	663	5,443	41	.76
"	7.3	92.8	.0862	677	5,382	20	.37
"	6.4	105.6	.0763	676	5,386	16	.29
					Av. 5,402		Av. 0.72%
50°C	7.10	36.5	.2191	259	2,081	16	.77
"	5.40	49.2	.1626	266	2,066	1	.05
"	4.20	62.2	.1286	261	2,052	13	.63
"	3.00	97.3	.0822	292	2,084	19	.92
"	2.52	120.6	.0663	304	2,063	2	.09
"	1.65	215.0	.0372	354	2,043	22	1.06
					Av. 2,065		Av. 0.59%
60°C	4.20	30.2	.2649	127	972	5	.50
"	2.90	46.6	.1716	135	979	2	.20
"	2.33	61.0	.1311	142	970	7	.71
"	1.72	94.4	.0847	162	982	5	.50
"	1.69	97.6	.0819	165	976	1	.10
"	1.33	140.0	.0571	186	980	3	.30
					Av. 977		Av. 0.38%
70°C	2.36	31.2	.2564	120	505	7	1.31
"	1.97	40.8	.1960	80	518	6	1.17
"	1.73	49.0	.1632	85	519	7	1.31
"	1.46	60.4	.1324	88	518	6	1.17
"	1.32	73.1	.1094	96	504	8	1.56
"	1.06	113.0	.0708	120	509	3	0.58
					Av. 512		Av. 1.18%

For a viscous material, the rate of flow is proportional to the pressure and flow should start no matter how small a pressure is applied. The plotting of pressure versus rate of flow for the three materials is shown in figure 2.

The results obtained with the Koppers Viscosimeter and illustrated in tables 4, 5, and 6 show that the instrument is suitable for liquid asphalts and may be expected to check within ± 2.0 per cent or better.

It is interesting to note that cracked material showed a greater deviation from the mean than the uncracked materials.

R. H. Lewis and W. J. Halstead⁶ have shown recently that this instrument is also applicable to semi-solid asphalts when certain refinements are observed.

Viscosity Determinations.

Since the changes in consistency of slow-curing asphalts caused by weathering were to be measured in viscosity units, it was necessary first to determine the viscosity of the sixteen different materials at two or more temperatures. The following temperatures, 20, 25, 30, 40, 50, 60 and 70° C, were selected for three reasons; first, to determine the susceptibility of the various materials over a wide range and second, to establish a viscosity temperature relationship for comparative purposes, and third, this range of temperature was the most ideal from the standpoint of material and equipment.

The viscosities determined, shown in table 7, are the average of at least three determinations.

It is interesting to note that at 20° C. the maximum viscosity for all

of the asphaltic materials was 335,179 centistokes and the minimum 52,156 centistokes, while at 70° C. the maximum and minimum viscosities were 692 and 413 centistokes respectively. Or, in other words, at elevated temperatures the various asphaltic oils will approach to approximately the same viscosity while at low temperatures there is a wide variation in viscosity values. This will no doubt reflect upon the characteristic behavior of the different materials at depressed temperatures.

Viscosity-Temperature Relationship

In order to obtain a better understanding of the viscosity-temperature relationship of the various materials, the viscosity of each asphaltic oil as shown in table 7, was plotted on a specially prepared log graph paper and was found to lie on a straight line in accordance with the A.S.T.M. equation.

$$\log \log (VK + 0.8) = b + \log T \tag{1}$$

The ordinate is the log log of the viscosity in centistokes, and the abscissa is the log of absolute temperature in centigrade. Early in the investigation it was found that the constant 0.8 appearing in the A.S.T.M. equation could be dropped in the case of liquid asphaltic materials of the slow-curing type without affecting materially the accuracy of the plotting or the viscosity value obtained by using the above equation.

Figure 3 shows the viscosity temperature relationship of several asphaltic materials. These curves not only verify the usefulness of the A. S. T. M. equation but they also reveal the susceptibility of slow-curing asphalts to temperature change.

RELATION BETWEEN
PRESSURE AND RATE OF FLOW
IN CAPILLARY TUBES

RATE OF FLOW CM./SEC.

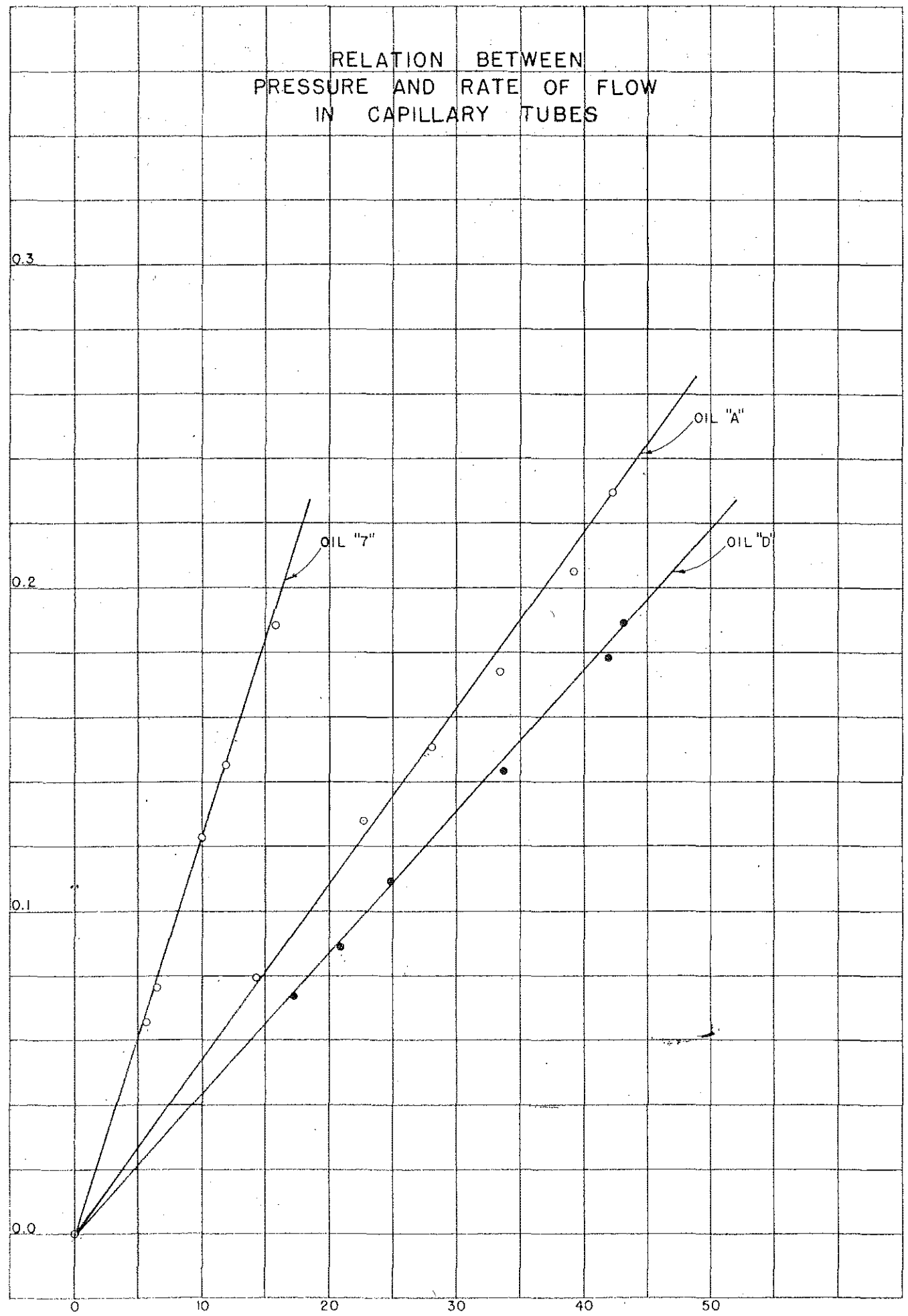


FIG. 2

VISCOSITY - TEMPERATURE RELATIONSHIP FOR ASPHALTIC OILS

LOG. LOG VISCOSITY VS. LOG. ABSOLUTE TEMP.

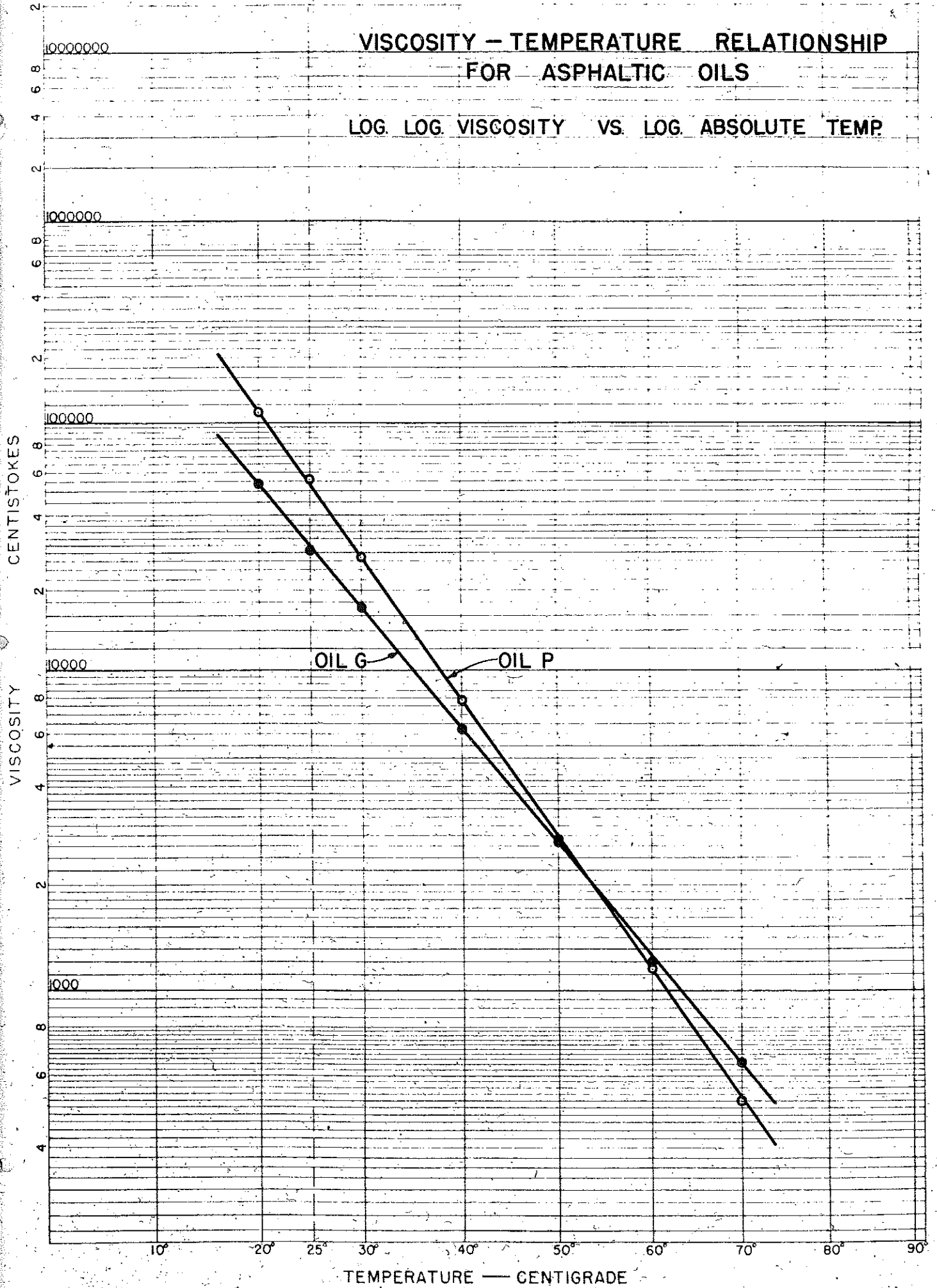


TABLE NO. 7

VISCOSITY OF SLOW-CURING ASPHALTS
AT
DIFFERENT TEMPERATURES

Sample No.	DEGREES CENTIGRADE						
	20	25	30	40	50	60	70
A	335,179	120,476	51,427	10,818	2,811	1,003	413
B	47,695	25,723	14,414	5,724	2,181	1,031	534
C	43,964	24,798	13,554	4,688	1,925	909	479
D	52,156	26,293	15,321	5,253	2,066	954	498
E	89,525	41,810	23,306	7,211	2,714	1,179	573
F	80,311	40,281	23,209	7,801	3,028	1,403	691
G	53,840	28,125	17,370	6,232	2,649	1,173	644
H	168,234	63,918	31,616	7,850	2,443	976	417
I	74,853	35,385	19,907	6,405	2,501	1,115	552
J	155,200	63,363	32,610	9,313	2,814	1,160	536
K	58,857	25,759	14,692	5,121	2,009	948	474
L	113,935	46,407	24,430	6,879	2,347	1,004	469
M	114,271	51,128	29,459	8,121	3,111	1,386	662
N	143,389	67,071	34,884	9,727	3,384	1,397	656
O	211,795	78,839	34,846	7,348	3,080	900	413
P	112,285	55,105	26,812	7,906	2,671	1,152	433

Viscosity Values in Centistokes

TABLE NO. 8

MAXIMUM, MINIMUM AND AVERAGE VISCOSITY FOR ALL MATERIALS

Temp.	Maximum	Minimum	Average
20°C	335,179	43,964	115,968
25°C	120,476	20,190	49,367
30°C	51,427	13,555	24,199
40°C	10,818	4,688	7,275
50°C	3,385	2,010	2,609
60°C	1,403	900	1,106
70°C	692	413	528

Viscosity values in centistokes

The Susceptibility Factor

Adopting the A. S. T. M. chart for the viscosity range covered, and assuming that viscosity plotted against temperature on the chart will result in a straight line, a very simple evaluation of the viscosity-temperature characteristics or susceptibility is possible. The viscosity at a known temperature and the slope of the viscosity-temperature curve will define the viscosity of the material at any other temperature.

The tangent of the angle of slope of the viscosity-temperature curve on the A.S.T.M. graph was chosen as the indicator of the susceptibility factor. The slope "b" of the V-T curve may be calculated from equation (1) when the viscosity at two temperatures is known. The equation for slope may be expressed as follows:

$$-b = \frac{\log \log V_1 - \log \log V_2}{\log T_2 - \log T_1}$$

The use of the slope of the V-T curve as a temperature susceptibility index was first proposed by H. G. Nevitt⁹ in his study on lubricating oils.

In some instances, it may be more practicable to handle the susceptibility factor graphically than by the above formula. This may be done by plotting the V-T curve on a proper chart and scaling the X and Y ordinates between the points V_1 and V_2 . In order to obtain a numerical value for "b" equal to the value determined by the equation, it will be necessary to apply a correction factor. This correction factor will be different for every chart. By plotting the V-T curves of the different materials used in the investigation on a chart based on the A.S.T.M. scale, a constant of 4.5348 was obtained.

When the various bituminous materials were tabulated according to their degree of susceptibility, the results, in general, show that the susceptibility of a material varies with the source of the crude and the method of manufacture. The results in table 9 show the cracked products to have the highest susceptibility factor of 4.74 and the steam refined materials to have the lowest of 3.34. The various blends and cut-backs fall in between the two extremes.

When the maximum and minimum viscosity values for the sixteen different materials were plotted on the A.S.T.M. graph and the average susceptibility curve established, it is significant that perhaps further study should be given to the possibility of establishing viscosity limitations for liquid asphalts at two temperatures and including the susceptibility factor.

This change would necessitate the adoption of a standard method of determining viscosities in absolute units, a method which we believe is becoming more and more to be recognized in both commercial testing and research work.

CHANGES IN CHARACTERISTICS OF SLOW-CURING ASPHALTS WHEN SUBJECTED TO DIFFERENT LABORATORY TREATMENTS

The purpose of this study was to determine if the changes which occur in the characteristics of slow-curing asphaltic materials when subjected to laboratory treatments could be correlated with the changes occurring when the materials are incorporated into bituminous mixtures.

The asphaltic materials were subjected to four different treatments, an oven volatilization test, the A. S. T. M. distillation test; blowing with air, and ultra-violet radiations by a modified weatherometer test.

TABLE NO. 9

RELATION BETWEEN SUSCEPTIBILITY
FACTOR, PROCESS AND SOURCE OF MATERIAL

Lab. No.	Process	Source	Susceptibility Factor
A	Cracking	Mid. Cont. Crudes	4.74
O	Cracking	Mid. Cont. Crudes	4.55
H	Cracking	Mid. Cont. Crudes	4.27
J	Steam Residues	California Crude	4.04
L	Cracking & Straight Blend	Kansas Crudes	3.95
P	Steam Distillation Blend	California Crude	3.94
N	Cracked Residues Blend	Wyoming Crude	3.86
E	Cracked & Straight	Urbana Crude	3.68
M	Steam Distillation Blend	Wyoming Crude	3.64
I	Steam Refined	Wyoming Crude	3.63
C	Vacuum Residue + Gas Oil Blend	Kansas Crude	3.56
D	Topped Crude Cut Back	Urbana Crude	3.55
K	Vacuum. & Steam Dist. Blend	Kansas Crudes	3.54
F	Topped Crude + Gas Oil	Smackover Crude	3.43
B	Cracked & uncracked	Mid. Cont. Crudes	3.43
G	Steam Refined	Mexican Crude	3.34

After these treatments the viscosity was determined at 25° C and 60° C., and the susceptibility was computed.

Oven Volatilization Test

The oven volatilization test was conducted in the following manner; the oil was weighed out in tared tins and then placed into an ordinary laboratory drying oven at a constant temperature for a definite period of time. The tins, after removal from the oven were cooled and weighed and the percent loss was computed.

Four materials, B, D, G, J, of varying degrees of volatility as shown by the A. S. T. M. distillation tests to be 7, 5, 12.0, and 1.5 percent respectively, were chosen to study the effect of time on the loss of volatile matter and consequent change in viscosity.

35

The data shown in table 10 and illustrated in figures 5 and 6 show that there is a marked difference between the rates of hardening of the two materials D and G.

In addition to the above volatility test on materials B, D, G, and J, a five hour oven test at 163° C. - 50 gram was performed on the balance of the sixteen materials as a matter of comparison between loss of volatile matter and increase in viscosity to determine to what degree the change in consistency of the residues would be comparable to gain in viscosity of a material in service.

Distillation Test

The sixteen materials were also subjected to the A.S.T.M. distillation test. The viscosity and susceptibility of the residue was determined upon completion of the test.

Air Blowing

The third treatment involved blowing air through a 75 gram sample of each asphaltic material at 180° C. for two hours at a rate of 500 cubic centimeters per minute. Air was introduced into the sample through a copper tube similar to that used in the Abson recovery method. The compressed air was bubbled through NaOH to remove carbon dioxide and then H_2SO_4 to remove moisture before passing through a calibrated flowmeter which was regulated to maintain a flow of 500 cubic centimeters per minute.

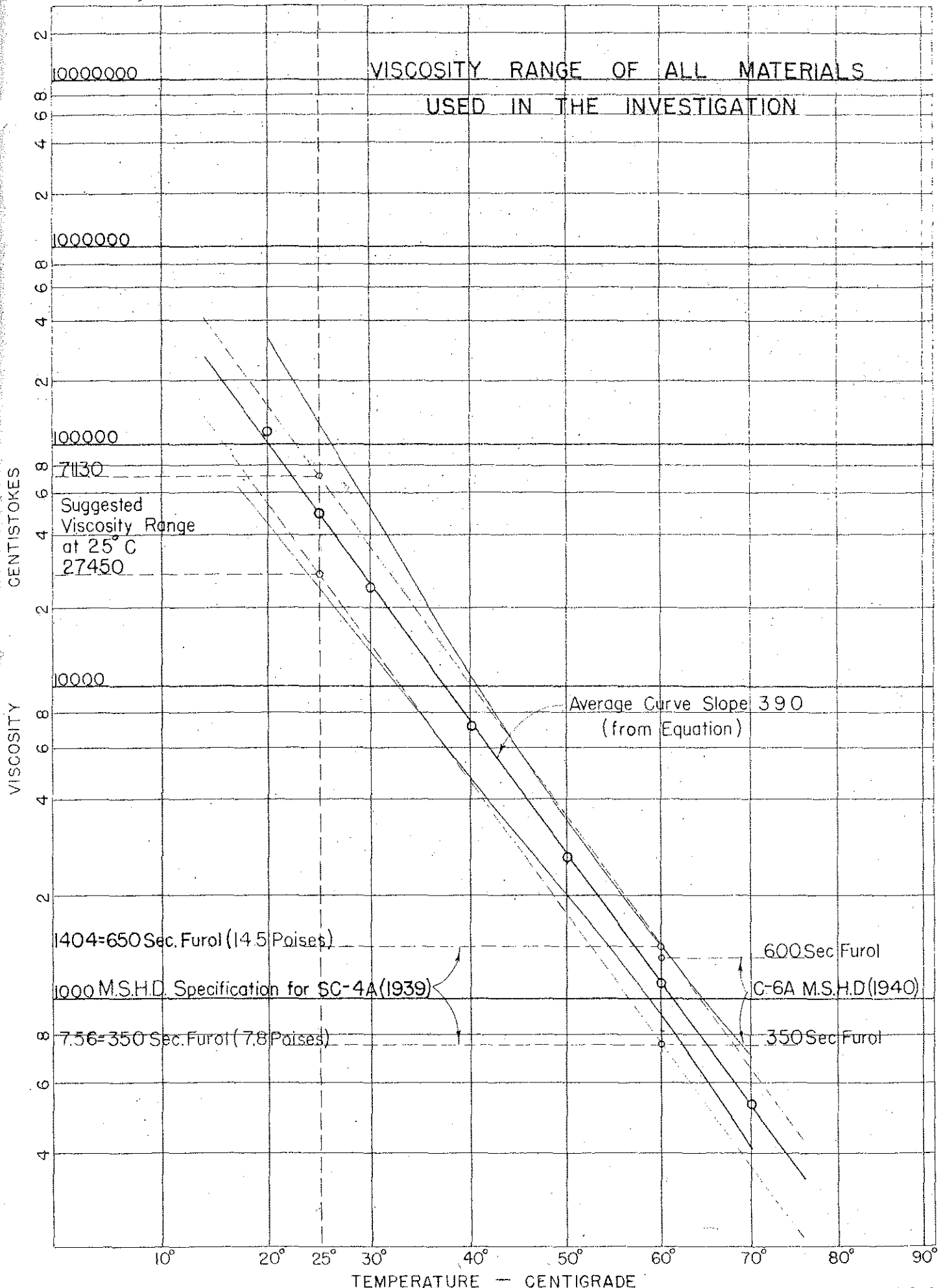


FIGURE 4

EFFECT OF HEATING ON CHANGE OF VISCOSITY

MATERIAL "D"

50 G. - 163°C - HOURS AS SHOWN

CENTISTOKES

VISCOSITY

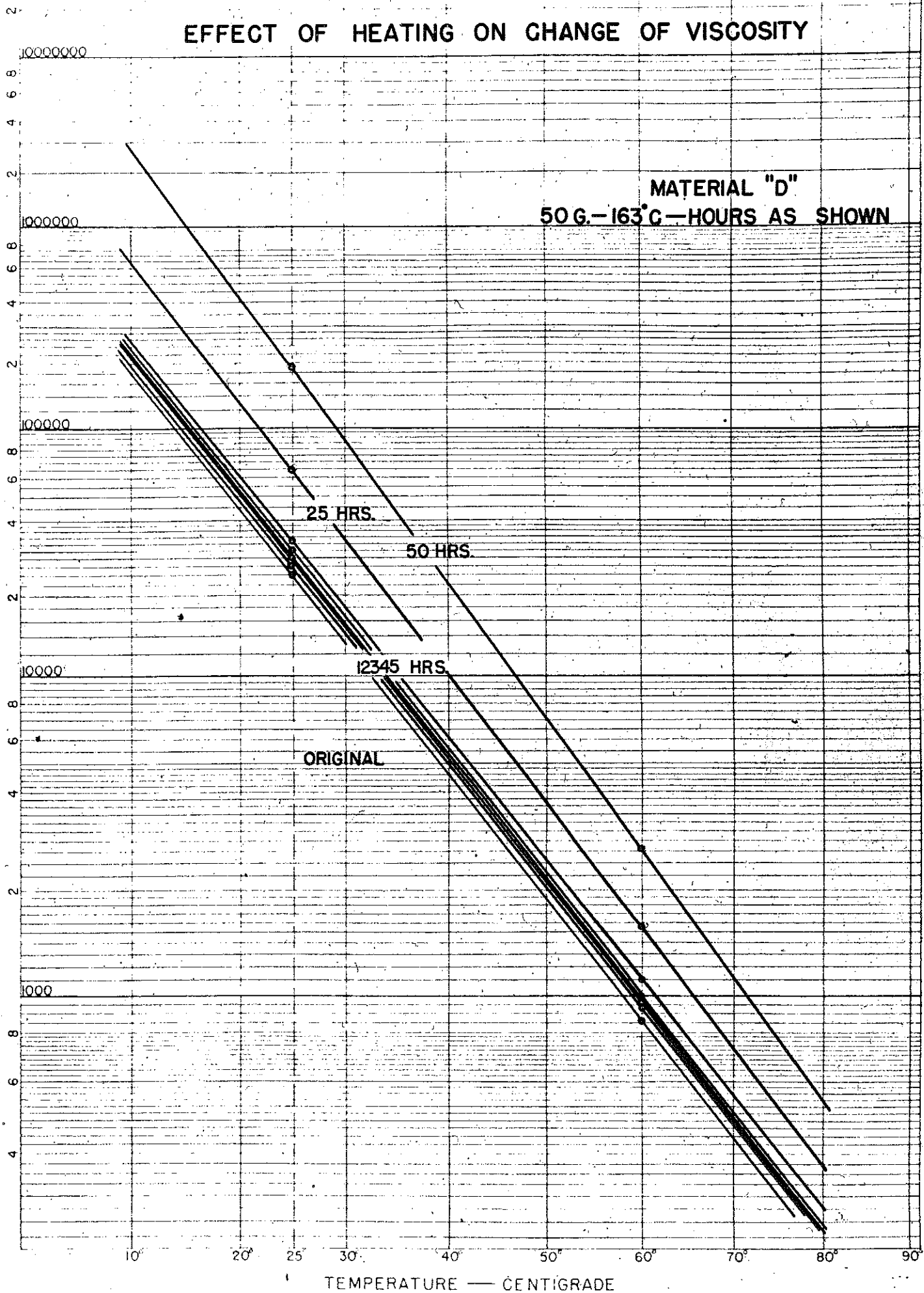


FIG 5

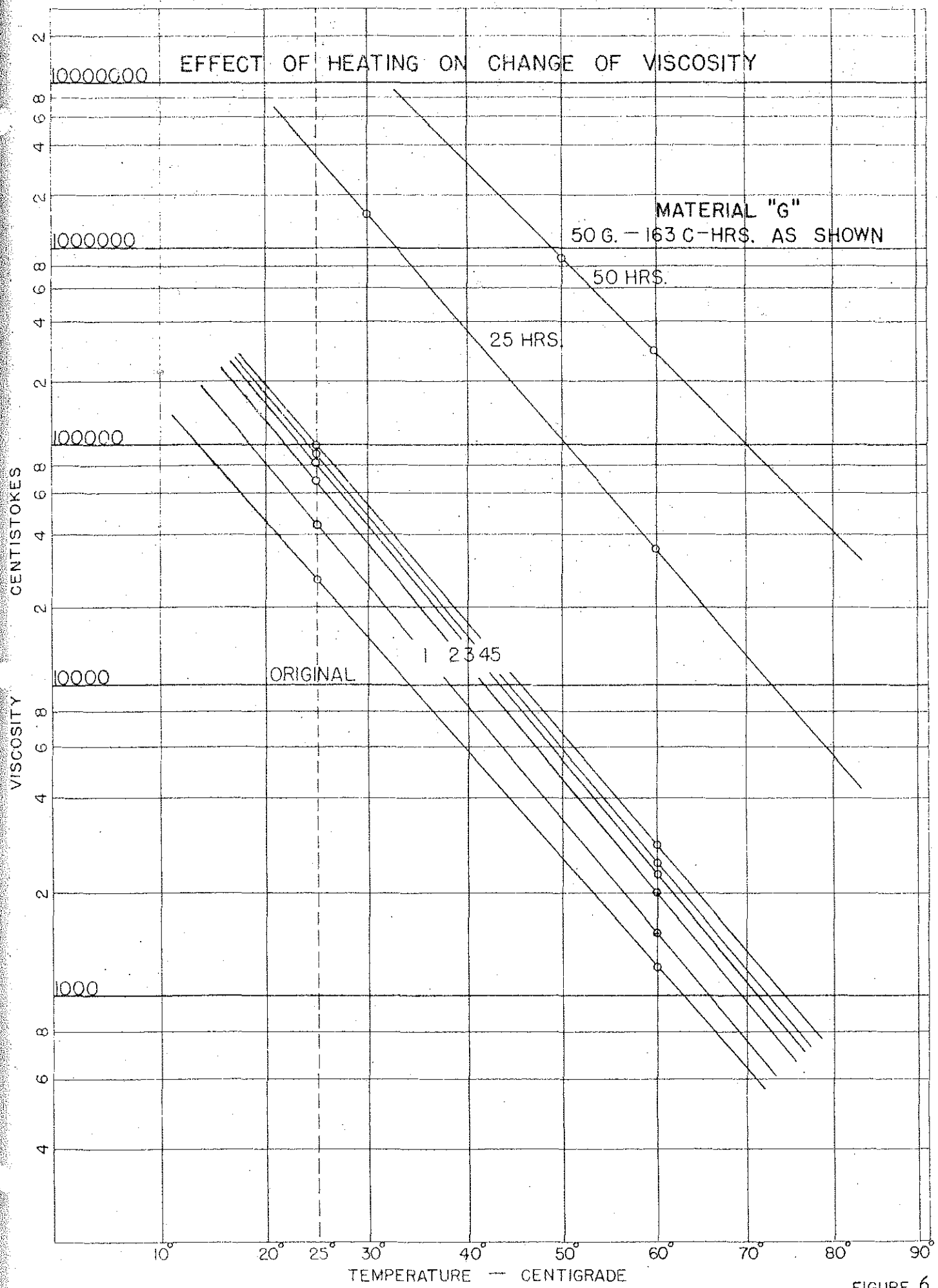


FIGURE 6

TABLE NO. 10

VISCOSITY DETERMINATIONS ON RESIDUES FROM
OVEN VOLATILIZATION TEST

50 grams ± at 163°C - Time as given - Viscosity in centistokes

Hrs. in Oven	B		D		G		J	
	% Loss	Viscosity	% Loss	Viscosity	% Loss	Viscosity	% Loss	Viscosity
				Temperature at 25°C				
0	0	25,723	0	26,294	0	28,126	0	63,364
1	2.053	44,420	0.110	28,791	1.836	44,633	0.761	122,462
2	2.348	52,270	0.305	28,936	2.893	66,048	1.392	129,837
3	3.234	63,533	0.395	29,215	4.110	81,343	1.621	136,576
4	4.123	75,526	0.401	30,160	4.185	85,195	1.890	169,944
5	5.074	112,095	0.437	32,022	5.078	108,725	2.308	257,555
25	10.181	791,628	2.520	62,487	13.673	1,940,705	6.082	1,307,108
50	15.500		3.220	118,870	16.805		10.421	
				Temperature at 60°C				
0	0	1,031	0	954	0	1,174	0	1,161
1	2.053	1,271	0.110	898	1.836	1,507	0.761	1,268
2	2.348	1,590	0.305	977	2.893	2,020	1.392	1,444
3	3.234	1,646	0.395	1,018	4.110	2,269	1.621	1,573
4	4.123	1,898	0.401	1,034	4.185	2,525	1,890	1,615
5	5.074	2,316	0.437	1,087	5.078	2,821	2.308	1,849
25	10.181	7,546	2.520	1,544	13.673	34,632	6.082	5,159
50	15.500	40,911	3.220	2,613	16.805	277,300	10.421	37,596

Weatherometer Tests

The fourth treatment involved mixing 15 grams of asphaltic oil with 485 grams of clean 20-30 grade Ottawa sand and exposing the mixture for 168 hours on a weatherometer. The weatherometer was manufactured by the Atlas Electric Device Company of Chicago, Illinois, and consisted of two arc lamps, one acting from the center and one from the side of the apparatus. The weatherometer has a turntable for supporting the samples. The rotation of the turntable was one revolution in 17 minutes and 35 seconds.

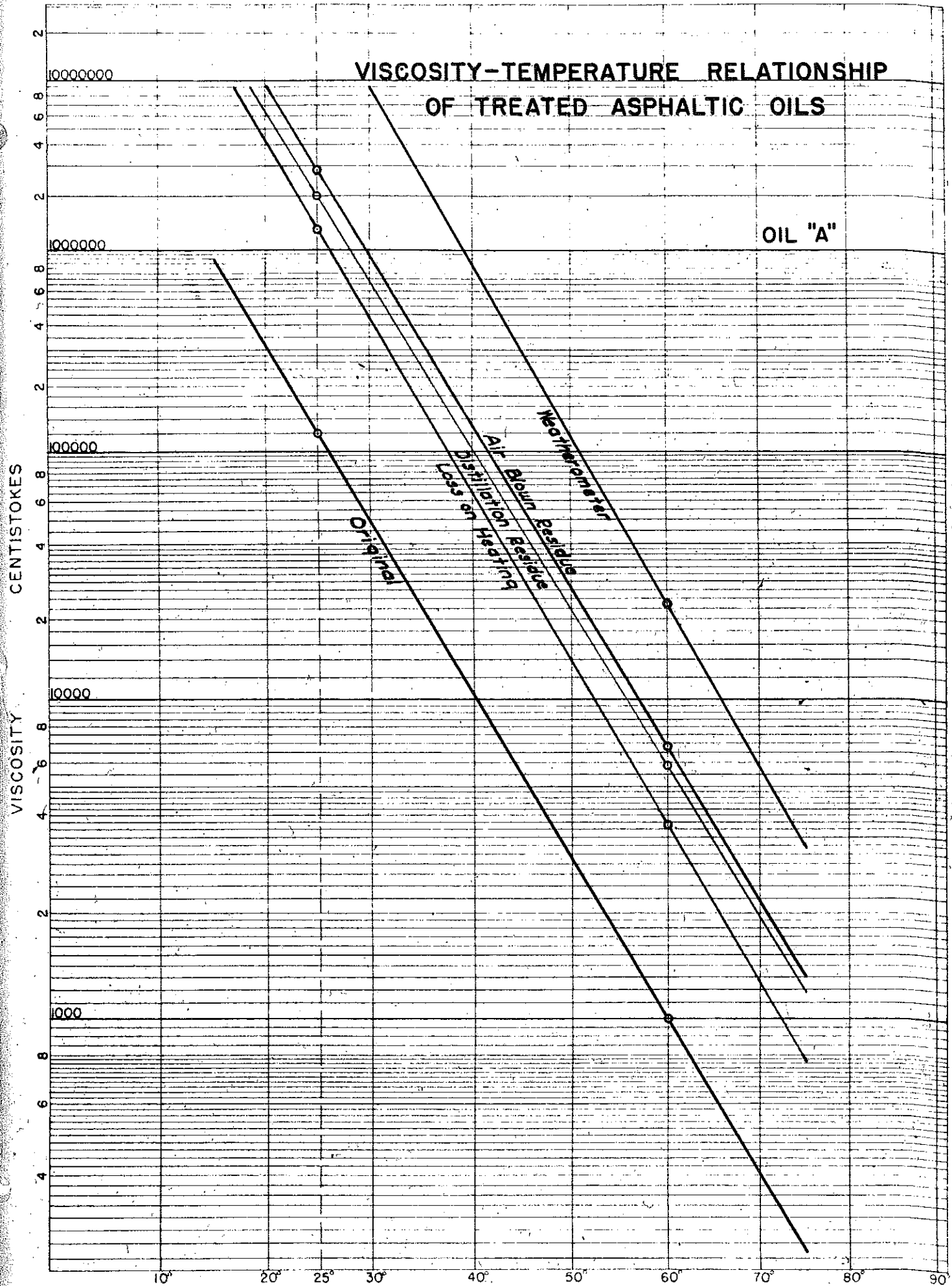
The bituminous mixtures were placed in tins giving an exposed area of 48 square inches. The mixtures were stirred twice daily to insure uniform exposure of all surfaces. The temperature of test was maintained at 140° F. by circulating air over the samples. The tests were performed in a dust-free room. The results from the various treatments are presented for comparative study in table 11. Two materials "A" and "O" were selected as typical samples for representing graphically the V-T curves obtained when the data in table 11 is plotted. These curves are illustrated in figures 7 and 8.

Effect of Continued Weathering with Weatherometer

Further weathering tests were concluded on material "O" to determine the rate of hardening which might be obtained on the weatherometer. "O" was chosen because it appeared to be affected most by the weatherometer test. The material was mixed with Ottawa sand and subjected to the same test procedure as defined above for oils "A", "G", and "D", with the exception of time which was varied to give residues at 1 day, 7 days, and 12 days. Upon recovery the viscosity and susceptibility was determined.

VISCOSITY-TEMPERATURE RELATIONSHIP OF TREATED ASPHALTIC OILS

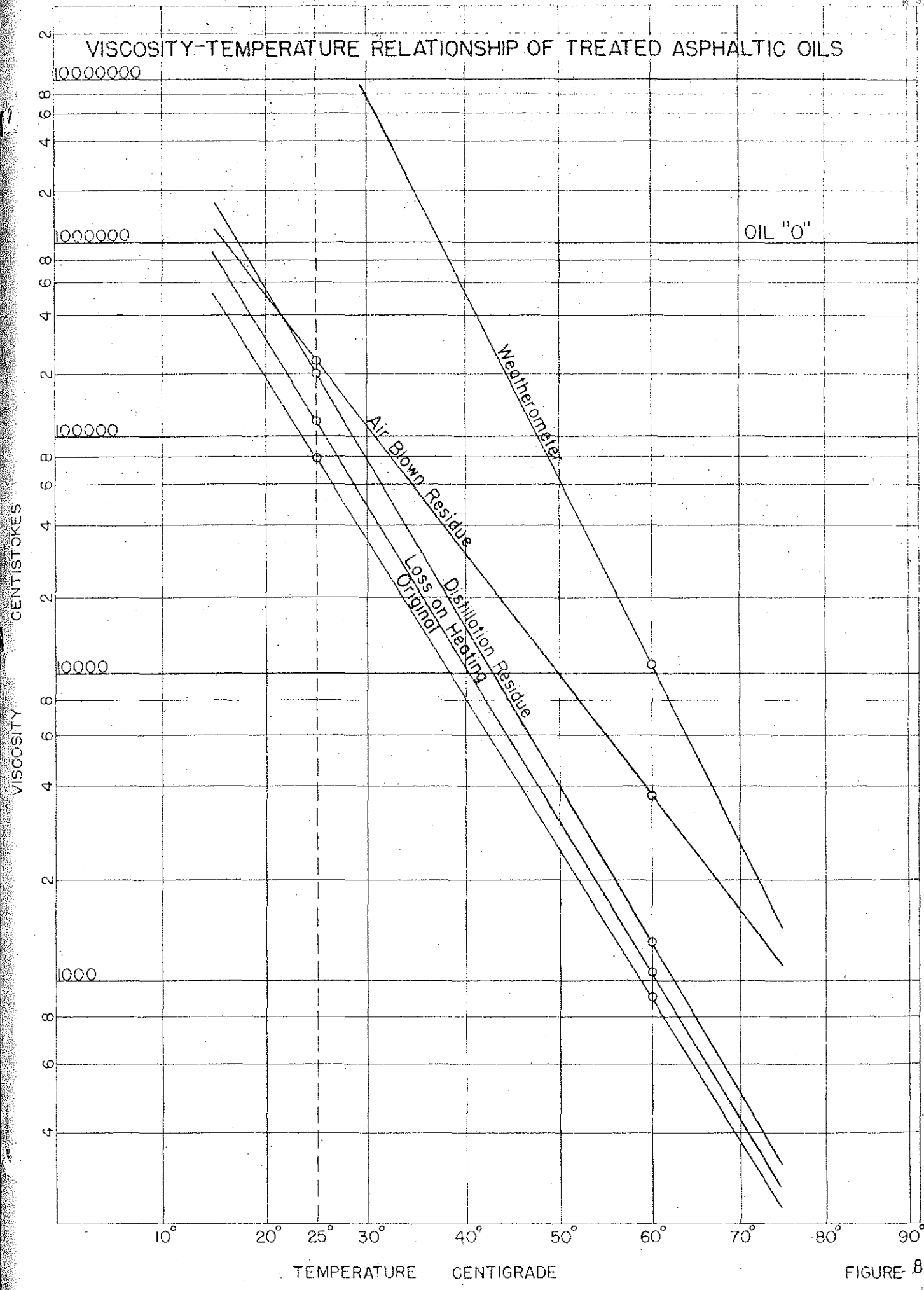
OIL "A"



TEMPERATURE — CENTIGRADE

FIGURE 7

VISCOSITY-TEMPERATURE RELATIONSHIP OF TREATED ASPHALTIC OILS



OIL "O"

TEMPERATURE CENTIGRADE

FIGURE 8

TABLE NO. 11

VISCOSITY AND SUSCEPTIBILITY OF SLOW-CURING ASPHALTS
AFTER SUBJECTION TO LABORATORY TREATMENTS

Viscosity in Centistokes

Oil	Original Asphaltic Oil			Oven Volatilization Residue		Distillation Residue		Air Blown Residue		Residue Modified Weatherometer	
	Viscosity 25° C	Viscosity 60° C	Susc.	Viscosity 60° C	Susc.	Viscosity 60° C	Susc.	Viscosity 60° C	Susc.	Viscosity 60° C	Susc.
A	120,480	1,003	4.741	3,671	4.898	5,810	4.919	6,884	4.719	22,847	4.927
B	25,720	1,032	3.429	2,316	3.656	4,195	3.664	5,945	3.798	51,274	3.915
C	24,800	909	3.562	2,104	3.640	3,016	3.682	8,335	3.657	30,208	3.362
D	26,290	954	3.551	1,001	3.661	1,060	3.520	1,628	3.584	10,841	3.815
E	41,810	1,179	3.679	2,390	3.956	2,130	3.768	4,535	4.014	28,650	4.451
F	40,280	1,403	3.434	3,392	3.415	4,335	3.497	8,183	3.652	18,851	3.730
G	28,130	1,174	3.343	2,821	3.406	11,440	3.440	22,104	3.476	5,207,400	3.357
H	63,920	976	4.275	3,301	4.329	3,116	4.381	13,344	3.494	314,885	4.234
I	35,390	1,115	3.629	2,821	3.662	2,342	3.789	5,080	3.585	58,059	3.833
J	63,360	1,161	4.043	2,316	4.295	2,209	4.439	2,943	3.901	96,876	4.041
K	25,760	949	3.540	2,182	3.721	2,848	3.843	6,750	3.970	12,250	4.086
L	46,410	1,005	3.952	3,685	4.044	2,590	4.048	12,556	4.030	77,224	3.242
M	51,130	1,386	3.644	2,292	3.583	1,695	3.636	5,475	3.842	50,966	4.252
N	67,070	1,398	3.855	3,298	3.936	3,958	3.772	17,923	3.889	165,620	4.415
O	78,840	900	4.551	1,043	4.289	1,287	4.799	3,652	3.687	10,682	5.691
P	55,110	1,152	3.939	1,403	3.944	1,551	3.917	2,127	4.130	10,276	3.939

The results of this study show that the viscosity temperature curves when plotted indicate the rate of hardening of the residue. At the end of 7 days test the residue of material "O" had lost its adhesive properties and appeared to be completely dried out. The V-T curves are illustrated in figure 9.

From the data obtained from the oven test, the distillation test, air blowing, and the weatherometer tests, it may be concluded that the oven volatilization test will give residues comparable to those obtained from the other three tests if given the proper length of exposure at 163°C. The weatherometer test produces the greatest change in consistency of the residue. A presentation of these data in graph form seems to indicate that the major increase in consistencies of the various residues was caused by evaporation of the volatile materials present in the original asphalt. The slope of the V-T curves also indicates that some materials undergo other changes in their characteristics due to conditions imposed by the test.

CHANGES IN CHARACTERISTICS OF SLOW-CURING MATERIALS INCORPORATED INTO BITUMINOUS MIXTURES

This phase of the investigation was to correlate the changes in characteristics of recovered asphaltic materials with those changes occurring from laboratory tests previously described or to be developed.

With this end in view, test sections were established in November 1937, and every year thereafter on certain asphaltic oil aggregate projects. The projects were selected for location and type of asphaltic

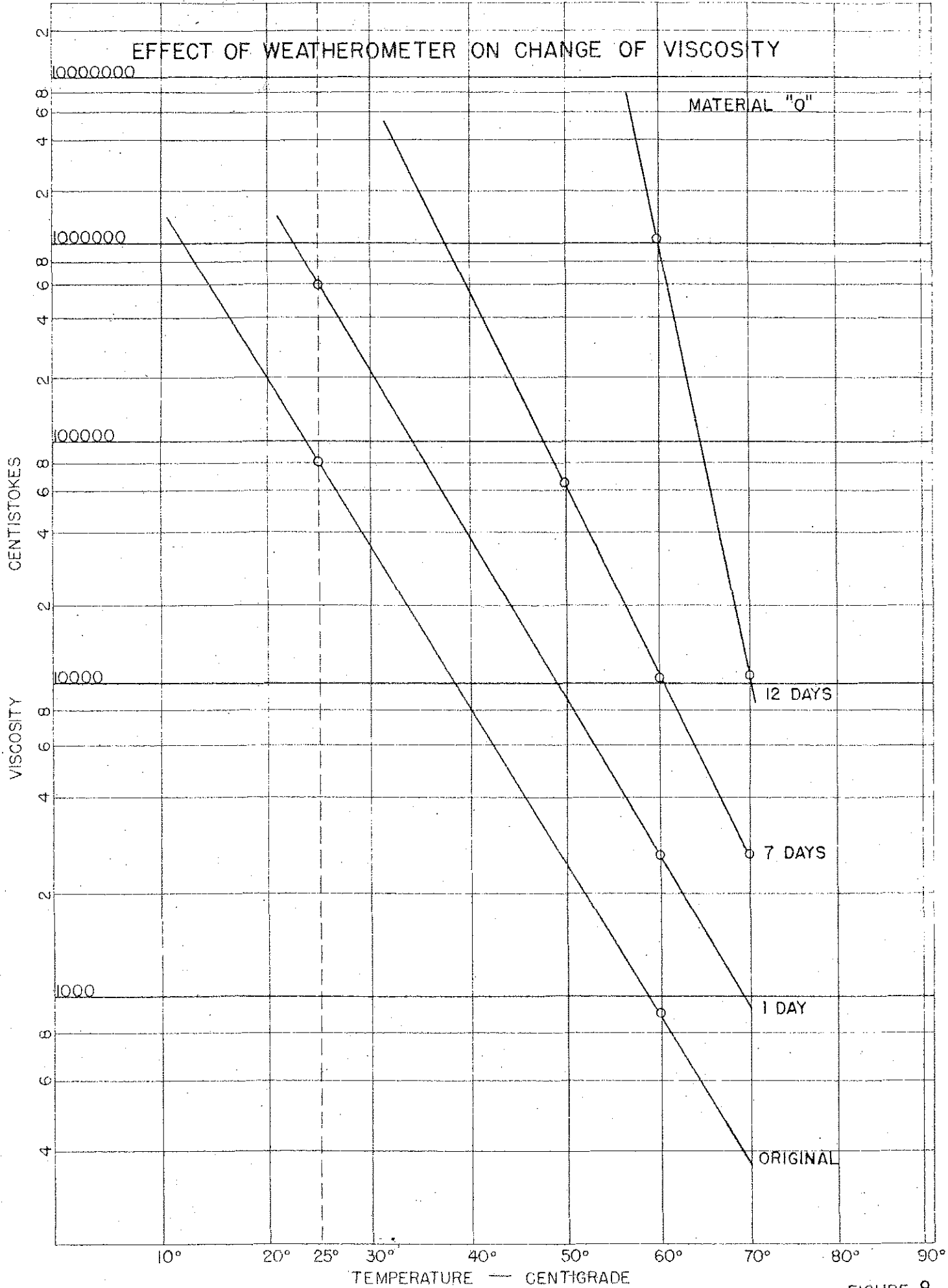


FIGURE 9.

material used as a binder. At the time the test section was established, samples were obtained of the original bituminous material going into the mixture. A sample of the bituminous mixture was also obtained and an analysis made to determine the change in consistency of the asphaltic material after incorporation into the mixture. Also, a check was made on the percentage of asphalt present.

Yearly thereafter samples of the road surface in the test area were obtained and analyzed in the laboratory.

In addition to the establishment of test sections, a survey was made this year of all bituminous surface of the SC type with special consideration given to those which were showing signs of disintegration and those which were in need of surface treatment. Samples were obtained for laboratory study to determine the present characteristics of the bituminous binder as compared with the original material. It is hoped that the data from these two field studies will throw some light on the limitation requirements for an accelerated durability test and perhaps furnish desirable information pertinent to writing future specifications for materials of this type.

The Recovery of Slow-Curing Asphaltic Materials.

Because of the presence of considerable amounts of volatile matter and light distillates in slow-curing asphalts, it was believed that the recovery methods employed for recovering paving asphalts would not be desirable for this work. This was verified by the erratic results which were obtained when they were tried. Consequently, after considerable trial and experimentation, the following recovery method was developed which has proven quite satisfactory for materials of this character.

111

In general, the recovery method consists of removing the asphaltic material from the aggregate by means of a solvent; the removal of fine particles and foreign colloidal matter in the asphalt-solvent solution by filtration and the separation of the asphaltic material from the solvent by means of vacuum-distillation with an inert gas as an aid.

Solvent

Benzol (Thiophene free C_6-H_6) was used throughout the investigation for all recovery tests. After considerable experimentation with other solvents it was found that Benzol gave the most consistent results.

Extraction

All extractions were performed by the Dulin Rotarex Extractor in accordance with A.A.S.H.O. method (T-58-37). Each extraction consisted of a charge of bituminous material sufficient to give approximately 50 grams of recovered asphaltic material.

Filtration

It was found that the quantity of fine particles passing the filter in the extractor varied from one percent to eight percent of the weight of the recovered asphaltic material. Such quantities of fine material if allowed to remain in the recovered asphalt will naturally affect the viscosity and other characteristics of the recovered material.

For the removal of fine particles from asphalt-benzol solutions sedimentation, filtration, and super-centrifuge methods have been used by various investigators. However, a study of the characteristics of the asphalt-benzol solution and the mineral matter contained therein revealed the possibility of removing the fine material by filtration.

A method of filtration suggested by the John-Mansville Company and modified somewhat for this work is illustrated in figure 10, and described as

follows. A slurry consisting of clean benzol and one to two ounces of Standard Super-Cel filter aid is prepared and poured onto a filter paper in the Buchner funnel "W" and vacuum applied. The filter aid forms a cake on the filter paper and any filter aid going through the paper will go into flask "c". Just before the cake on the paper becomes dry, the asphalt-benzol extract is poured onto the mat in the Buchner funnel and a small amount of the solution is allowed to run into flask "c" to insure clarity of the filtrate. The stop cock "j" is then turned to divert the filtrate into flask "b". After all of the asphalt-benzol solution has been filtered, successive washes of 50 cc portions of Benzol are poured upon the mat until the washes show a filtrate that is only slightly discolored. The filtrate is now ready for distillation.

To prevent clogging of the filter mat due to the presence of water in the solution, one percent of filter aid by weight of solution is added to the solution upon extraction and thoroughly shaken. The solution is allowed to stand about 15 minutes before filtering.

Distillation

A vacuum-distillation method for asphalt recovery originated by Suida, Benigni, and Janisch¹⁰ and later modified by Greutert¹¹ was adapted for use in recovering the slow-curing asphalts. In order to make the procedure applicable to slow-curing asphalts, considerable experimentation was necessary to determine the correct time for complete distillation, rate and temperature of distillation, the quantity of material to recover at one time, the amount of vacuum necessary, and the method and rate of applying the inert gas. The recovery apparatus is illustrated in figure 10 and the recovery technique is described as follows:

The asphalt-benzol solution is fed into the distillation flask at a rate equal to the amount of solvent being distilled off, keeping a constant level of approximately one-half the depth of the flask. During this distillation period the temperature of the water bath surrounding the distillation flask is maintained at a constant temperature of 65°C, by thermostatic control. The vacuum is maintained by means of a water pump at 22 inches of mercury during the entire distillation period.

When the bulk of the solvent has been distilled off and the rate of distillation becomes slow, the temperature of the water bath is gradually increased from 65°C. to 100°C and maintained at that temperature for the balance of the distillation period. When the temperature of the water bath becomes 100°C., carbon dioxide is introduced into the residue, slowly at first and gradually increased to a rate of 150 cc per minute as measured by a flow meter. The rate of gas flow is maintained at 150 cc/minute for a period of thirty minutes from the time distillation ceases. The recovered asphaltic material is poured into a container where it is allowed to remain at room temperature for one hour before viscosity determinations are made.

The Recovery Procedure

The asphalt-benzol solution from the extractor is introduced into the apparatus via the Buchner funnel "W" containing filter paper covered by a mat of filter aid which removes dust in the manner described previously. (See Fig.10). The solution free of mineral dust passes down into flask "b". When filtration is complete, stop cock "p" is turned into distillation position and a vacuum of 22 inches of mercury on the mano-

115

meter "V" is maintained. The filtrate in flask "b" is admitted into distillation flask "J" by simply opening stop cock "p" which controls the feed line into "J". It is thus possible to control the rate of feed to maintain a constant level in the distillation flask. The distillation flask "J" is surrounded by a thermostatically controlled water bath "G". The apparatus is so arranged that when the great bulk of solvent has distilled off, carbon dioxide in tank "A" can be admitted into bottle "B" then through flow meter "C" into distillation flask "J" by means of stop cock "O" and capillary tube "I". The use of carbon dioxide gas is necessary to insure removal of the last traces of solvent. The benzol vapors on leaving the distillation flask rise into reflux column "R" which being packed with 1/2 inch length glass tubes aids in fractionating the heavier from the lighter vapors. The rate of distillation is controlled by the rate of reflux and the temperature of the vapor as it passes the thermometer "Q" located in the top of the column. Condensation of benzol vapors is brought about by a pair of efficient cold water condensers "S" and "T". The liquid distillate of benzol is caught in reservoir "X" which is arranged so that it can be emptied by siphoning. The vacuum is furnished by an ordinary water pump. The distillation flask is fitted with ground glass joints and the whole system is completely sealed and at no time during the recovery process does the asphalt-benzol solution come in contact with air. All solution movements after filtering are actuated by vacuum. It is possible to control the vacuum in the system within very narrow limits, insuring quite uniform distillation. Temperatures cannot get out of control, and fire hazards are

at a minimum. The complete recovery from filtration to recovered asphalt will average from three to four hours.

The outstanding features of the method are that all manual operations have been reduced to a minimum; very little attention is necessary on the part of the operator, and it is possible to operate all recoveries under practically the same conditions. Excellent correlation was obtained between the physical properties of the original and those of the recovered bitumens. Results of check determinations before and after recovery are shown in table 12.

EFFECT OF RECOVERY PROCEDURE ON PHYSICAL AND CHEMICAL PROPERTIES OF SOME MATERIALS

Filter Process

Check tests were made to determine whether or not the filter process materially changed the characteristics of the recovered material. Results of these tests are shown in table 13. Fifty gram samples of eight slow-curing asphalts were split and dissolved in benzol to proper concentration comparable to actual recovery. Half of the samples were passed through the filter and recovered. The other half was recovered without filtering. The results in table 13 show close agreement in most cases.

Presence of Benzol in Recovered Material

The following test procedure was developed to detect the presence of benzol in the recovered material. This method was used to determine limitations in the recovery procedure.

Recovery Procedure and the Detection of Benzene

The procedure used in the recovery of asphaltic oils was at first

TABLE NO. 12

VISCOSITY DETERMINATION ON SLOW-CURING ASPHALTS
BEFORE AND AFTER RECOVERY

Viscosity in centistokes

	25°C Original Viscosity	25°C Recovered Viscosity	60°C Original Viscosity	60°C Recovered Viscosity
A	135,228	130,968	1,004	1,019
B	27,559	27,523	973	980
C	24,228	23,816	954	927
D	26,294	26,718	954	954
E	41,911	40,832	1,165	1,133
F	44,640	38,194	1,446	1,368
G	31,067	30,976	1,243	1,227
H	78,632	78,539	1,124	1,113
I	40,030	37,882	1,130	1,159
J	75,960	80,458	1,240	1,248
K	30,493	35,183	989	1,040
L	51,585	56,712	1,099	1,110
M	58,515	46,020	1,517	1,414
N	76,115	73,800	1,409	1,444
O	84,995	86,920	846	852
P	42,562	37,811	1,161	1,010

TABLE NO. 13

SHOWING COMPARISON OF FILTERED AND RECOVERED
VERSUS
UNFILTERED AND RECOVERED SAMPLES

Sample Number	Vis. in Centistokes at 25°C		Vis. Centistokes at 60°C		Asphaltene Content		Sp. Gr. at 25°C	
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
1	28,300	28,100	990	980	6.68	6.46	.974	.974
2	25,200	25,100	1,020	991	6.58	6.69	.977	.975
3	45,500	40,800	1,280	1,310	8.96	8.88	.998	.990
4	36,700	35,100	1,300	1,210	9.04	8.96	.991	.986
5	46,180	49,190	1,590	1,590	17.70	18.22	.988	.987
6	39,100	35,450	1,600	1,470	17.52	17.76	.986	.988
7	29,020	29,130	1,170	1,180	9.60	9.54	.974	.974
8	31,370	31,800	1,210	1,340	9.36	9.20	.977	.978

established empirically by trial; and the criteria of good procedure being the degree of success attained in matching viscosity determinations before and after recovery. With the development of a sensitive chemical test for the detection of benzene in bituminous substances, it was now possible to check the procedure in a totally different way.

In this study one asphaltic oil was used, solutions of 1000 cc of benzol to 50 g of asphaltic oil were recovered. It was attempted to keep all conditions of recovery constant except to vary the time of final flow of gas when distillation had ceased. The data as presented in table 14 shows the relation of time to complete removal of benzol.

Description of Test

A solution is prepared consisting of approximately 10 cc of carbon tetrachloride benzene free and 40 cc of bitumen. The carbon tetrachloride is then distilled off; if benzene was present in the bitumen the carbon tetrachloride distillate will be contaminated with benzene. Hence it is then possible to convert the benzene to nitrobenzene by adding a specially prepared 50-50 mixture of nitric and sulphuric acids (HNO_3) (H_2SO_4) in the presence of carbon tetrachloride and shaking well. The carbon tetrachloride is not affected by these acids. The acids are removed by adding water and separating the water layer from the carbon tetrachloride layer in a separatory funnel. If the carbon tetrachloride layer contains any nitro-benzene, evaporation of carbon tetrachloride should leave nitro-benzene which can be identified by its characteristic odor.

However, to make this test more effective, due to the masking effect of conflicting odors, it was found necessary to use a chemical test,

TABLE NO. 14

EFFECT OF THE TIME OF GAS FLOW
ON RECOVERY PROCEDURE

Time of Gas Flow at 100°C	Quantity of Gas	Vacuum	Viscosity 25°C	Presence of Benzene	Viscosity 25°C Unrecovered
15 min.	150 cc/min.	22 in. hg.	31,400	Present	33,800
25 min.	"	"	34,350	Trace	"
30 min.	"	"	34,500	None	"
40 min.	"	"	35,950	None	"

that is the addition of stannous chloride SnCl_2 plus concentrated hydrochloric acid to produce aniline hydrochloride which on the addition of excess of 5 normal sodium hydroxide and subsequent steam distillation, produces traces of aniline. Aniline can be conveniently tested for by addition of a few drops of freshly prepared and filtered bleaching powder solution. A violet red coloration is obtained if aniline is present.

Sensitivity Range of Test

- 1 part benzene per 20,000 CCl_4 positive test .005% by volume
- 1 " " " 100,000 no test obtained .001% by volume

Effect of Recovery on Some Physical and Chemical Properties

In this study four different asphaltic oils from widely different sources and processing were recovered. The effect of the method of recovery was ascertained by testing the asphaltic oil before and after recovery in several ways; by viscosity, photometer or light transmission of like concentrations in benzene, and chemical means, that is by the bromine absorption test. The data was tabulated and results indicate that the greatest variance exists in viscosity, and is the best criteria of success of recovery. Results of tests are shown in table 15.

CHANGE IN CHARACTERISTICS OF SLOW-CURING ASPHALTS AFTER WEATHERING UNDER SERVICE CONDITION

The purpose of this phase of the investigation was to ascertain what changes in viscosity and susceptibility occur in slow-curing asphaltic oils when they are incorporated into a bituminous mixture and subjected to service conditions. It was thought that the results from this study might be helpful in establishing certain definite relationships and to

TABLE NO. 15

SHOWING THE EFFECT OF RECOVERY OPERATION ON SOME
PHYSICAL AND CHEMICAL PROPERTIES

TYPE OF ASPHALTIC OIL	-	-	"F"		"I"		"H"		"J"	
			Original	Recovered	Original	Recovered	Original	Recovered	Original	Recovered
Absolute Viscosity 25°C (Poise)	-	-	583	599	587	561	1186	1250	1110	1090
Bromine Absorption	-	-	23.6	24.0	36.8	37.7	41.6	41.6	30.8	30.9
Light Transmission of .1% Conc. Benzene Sol.	No Filter	-	33.9	32.1	24.5	24.1	19.0	18.9	33.3	33.1
" " "	Red Filter	Max. Transmission 700 m	48.1	46.8	38.8	38.0	32.0	31.0	47.3	46.5
" " "	Green Filter	Max Transmission 525 m	23.9	22.7	16.9	16.2	12.3	12.0	24.1	24.0
" " "	Blue Filter	Max. Transmission 400 m	2.9	2.8	1.9	1.9	.9	.9	3.3	3.1

predict the normal rate of hardening of bituminous materials occurring under actual service condition.

To pursue this study, test sections were established on newly constructed bituminous surfaces using asphaltic binders of the SC-6 type and from different sources. These test sections were essential to facilitate future sampling and to insure that the same source of bituminous material would be obtained throughout the study.

At present there have been 15 test projects established embracing six different types of SC-6 asphaltic oil all meeting Michigan State Highway specifications. Two test projects were established in November 1937, eight test projects were established in July 1939 and five test projects were established in July 1940. The test projects are located throughout the entire state where they will be subjected to varying traffic and climatic conditions.

On each test project a definite sampling area, approximately 50 feet long was definitely located where the source of bituminous material going into the mixture could be ascertained.

Each year samples representing the top half of the road surface will be removed from the sampling area of each test project. The bituminous material will be recovered by the method previously described. It is contemplated to analyze samples from these test projects over an indefinite period of years.

Analyses for Changes in Characteristics

At the present time insufficient data has been obtained to warrant drawing any definite conclusions. However, the data presented in table 16

TABLE NO. 16

TEST SECTIONS NO. 1 AND NO. 2
SHOWING THE CHANGE OF VISCOSITY WITH AGING

	Test Section No. 1	Test Section No. 2
Asphaltic Oil in Mix		
Viscosity 25°C	37,786 C.S.	34,529 C.S.
" 60°C	1,135 C.S.	1,074 C.S.
Susceptibility	3.635	3.635
Sp. Gr. 25°C/25°C	.981	.987
Recovered Oil After 1 Year		
Viscosity 25°C	46,631 C.S.	57,927 C.S.
" 60°C	1,539 C.S.	1,703 C.S.
Susceptibility	3.427	3.474
Sp. Gr. 25°C/25°C	.982	.989
Recovered Oil After 2 Years		
Viscosity 25°C	76,212	93,702
" 60°C	1,752	2,393
Susceptibility	3.682	3.477
Sp. Gr. 25°C/25°C	.987	.994
Recovered Oil After 3 Years		
Viscosity 25°C	164,395	129,276
" 60°C	2,928	3,089
Susceptibility	3.679	3.437
Sp. Gr. 25°C/25°C	.990	1.005

and illustrated by figures 11 and 12 show very clearly that there is a continuous hardening taking place comparable in some respects to the hardening obtained when asphaltic materials of the SC-6 type are subjected to laboratory procedures explained previously.

The V-T curves in figures 11 and 12 also show that the rate of hardening of the two recovered bituminous materials after three years is practically the same.

The characteristics of the original bituminous materials discussed are given in table 17.

Figure 13 represents in another way the rate of hardening of the bituminous materials from the test projects when the viscosity of the recovered asphalt at 60°C. is plotted against time in years.

CONDITION SURVEY OF EXISTING BITUMINOUS SURFACES USING SC-6 ASPHALTIC MATERIALS AS BINDER

During the summer of 1940, an extensive survey was made, including a greater portion of the slow-curing bituminous pavements in the state. The purpose was to study the characteristics of recovered bitumen from surfaces showing normal changes. Particular attention was paid to the source of asphalt, age of road, and physical condition of the surface. From this survey, 28 bituminous surfaces were selected for laboratory study. Samples of the mixture were taken from the top course of each project and subjected to laboratory analysis.

In judging the criteria of the complete failure of the bituminous substance in the pavement, the following factors were kept in mind:

1. Conditions must be general, not localized to a few isolated spots as at edges or on hills,

VISCOSITY - TEMPERATURE RELATIONSHIP OF WEATHERED ASPHALTIC OILS

TEST PROJECT NO. I

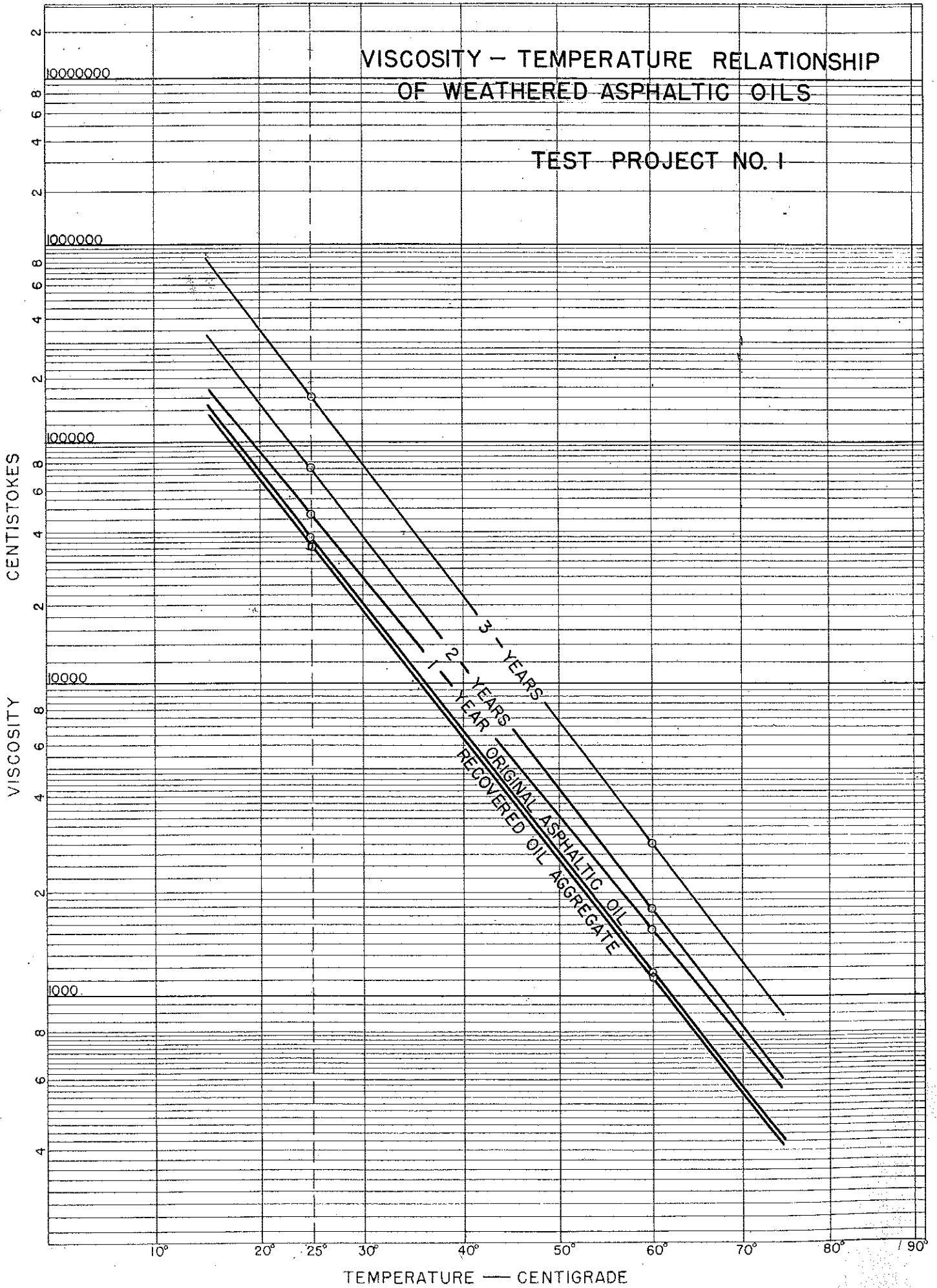


FIG. II

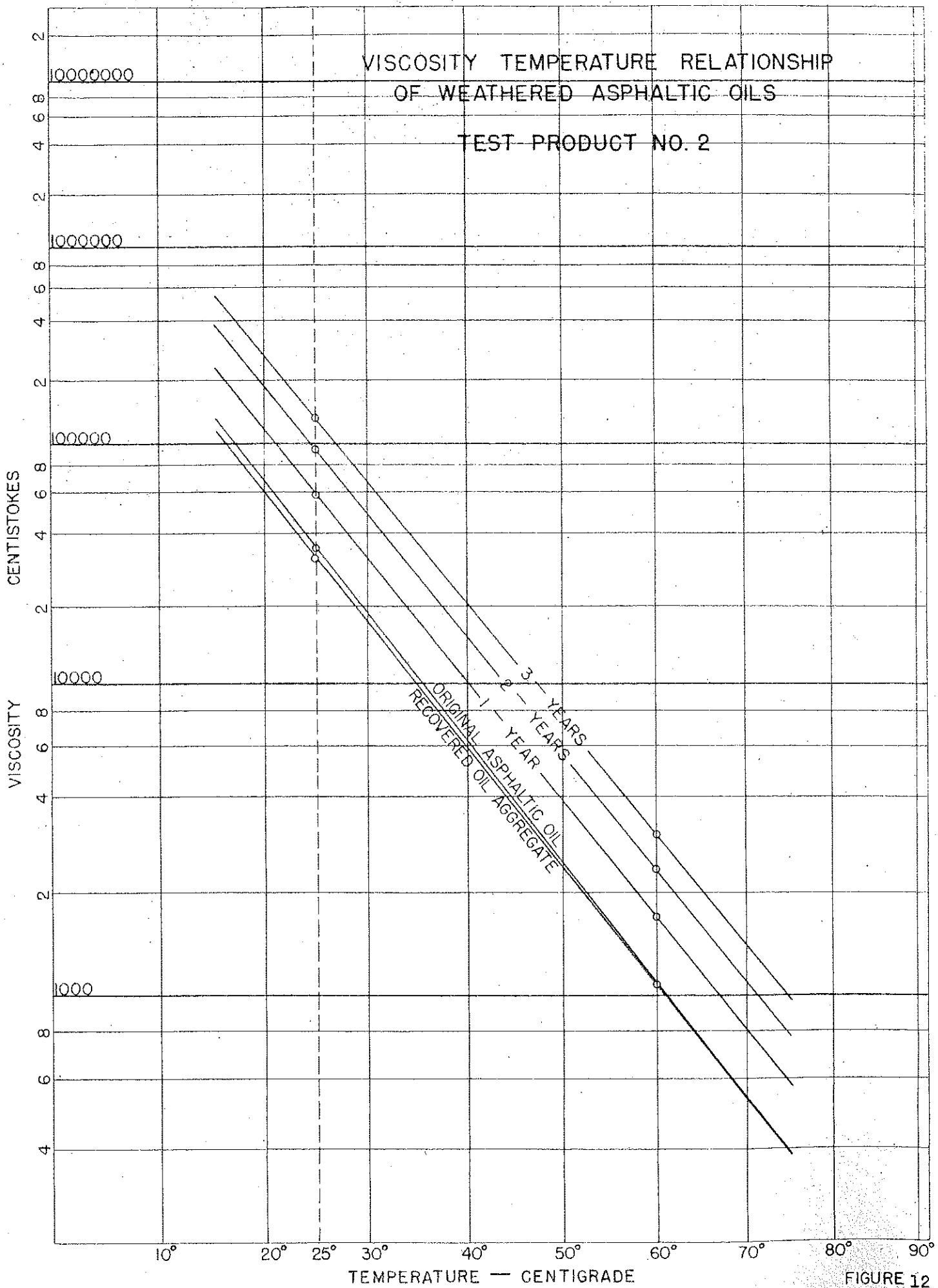


FIGURE 12

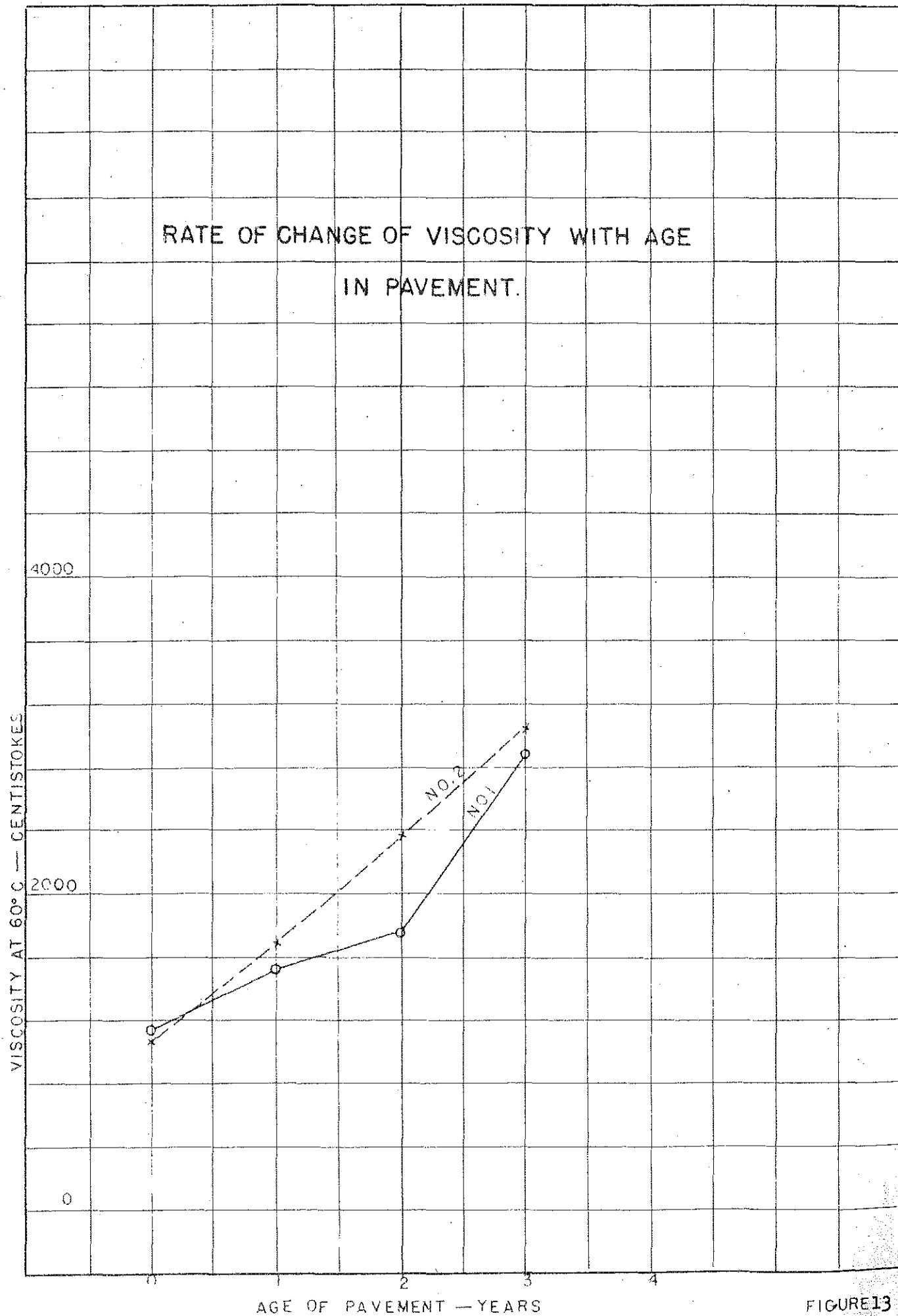


FIGURE 13

TABLE NO. 17

LABORATORY ANALYSIS OF BITUMINOUS MATERIALS
USED IN TEST PROJECTS NO. 1 AND NO. 2

Remarks	Material	Material
Identification	Test Project No. 1	Test Project No. 2
Sp. Gr. 25°C/25°C	.981	.987
Furol Vis. 60°C	544	531
Flash Point	210°C	160°C
% 100 Pen. Res.	75.0	75.2
Duct. Res. at 25°C	100+	100+
Duct. Res. at 4°C	8.5	9
% Sol. in CCL ₄	99.92	99.96
Distillation		
0-225°C	0	0
0-315°C	0	0
0-360°C	Trace	2.5
Loss on Heating		
50 g. 5 hr. 163°C	1.76%	2.93%

2. That subgrade failures can cause raveling, alligating and cracking of the surface.

This survey revealed that no bituminous surface had failed completely, although a few showed considerable signs of wear and excessive alligating, requiring a seal coat or surface treatment to place them in good condition. The alligating was caused by poor subgrade conditions which were known to exist prior to laying of the pavement.

However, the most important result of this survey is the realization that many of the surfaces examined have given fair service behavior to date, yet they reveal that abnormal hardening of the bituminous binder has taken place and that the original flexible mat has changed entirely to a rigid type of pavement similar to bituminous concrete. The bituminous^{mat} when once disturbed or broken up cannot be recompacted without additional bituminous material, flux or application of heat. The recovered bitumen from bituminous surfaces of this nature had viscosity values of 4200 centistokes or higher at 60°C., thus indicating a 300 to 400 percent increase over the original value. The pavements possessing abnormal hardness were between three and four years old.

The fact that this premature change in bituminous surfaces of the slow-curing type is caused by abnormal hardening of the bituminous binder, is brought out by further tests which show that the recovered bitumens from a majority of pavements one to five years of age, irrespective of the source of bitumen, had viscosity values at 60°C. ranging from 1400 to 3200 centistokes. At 60°C. the viscosity of slow-curing asphaltic materials of the SC-6 type is in the neighborhood of 1000 centistokes. To further

TABLE NO. 18

SURVEY OF EXISTING SLOW-CURING ASPHALTIC PAVEMENTS

Laboratory Designation	Source of Bit.Mat.	Age in Years	Grade of Bit.Mat.	Original Viscosity 60° C Centistokes	Recovered Viscosity 60° C Centistokes	Bitumen Content Recovered Sample	Susc.	Surface Condition	Subgrade Condition	Richness of Surface Mixture	Deterioration	Observation on Removing Sample From Pavement
40 BR-14	V	3	SC-4A	1068	1410	2.69%	3.587	Excellent	Good	Normal	Sound	Live
40 BR-4	V	4	"	892	1465	2.53%	3.348	"	"	"	"	"
40 BR-25	V	1	"	1138	1506	2.62%	3.489	"	"	"	"	"
40 BR-39	VIII	1	"	1112	1856	3.01%	3.358	"	"	"	"	"
40 BR-26	VI	1	"	974	2034	3.47%	3.333	"	"	"	"	"
40 BR-40	VIII	1	"	1112	2116	3.15%	3.391	Bad Spot	Poor	"	Alligatored	"
40 BR-1	II	5	SC-3A	486	2131	2.05%	3.422	Fair	Good	"	Slightly Worn	"
40 BR-15	V	3	SC-4A	1068	2140	3.35%	3.414	Bad Spot	Poor	"	Alligatored	"
40 BR-22	VII	1	"	1112	2156	2.40%	3.464	"	"	"	"	"
40 BR-3	III	5	"	873	2236	3.59%	3.649	Excellent	Good	Sl. Rich	Sound	"
40 BR-23	V	1	SC-7	1780	2309	3.05%	3.585	Fair	"	Normal	"	"
40 BR-10	V	3	SC-4A	984	2323	3.33%	3.558	Excellent	"	"	"	"
40 BR-24	VI	1	"	1289	2365	2.63%	3.440	"	"	"	"	"
40 BR-17	V	3	"	1079	2428	2.65%	3.534	"	"	"	"	"
40 BR-21	VII	1	"	1112	2553	2.49%	3.507	Fair	"	"	"	"
40 BR-12	V	3	"	1062	2708	3.93%	3.504	Bad Spot	Poor	"	Alligatored	"
40 BR-16	I	3	"	1030	2804	2.98%	3.724	Fair	Good	"	Slightly Worn	"
40 BR-18	V	3	"	1065	2928	3.14%	3.679	"	"	"	Sound	"
40 BR-19	IV	3	"	1055	3089	2.68%	3.437	"	"	"	"	"
40 BR-2	V	5	"	1062	3161	2.33%	3.493	"	"	"	"	"
40 BR-9	IV	4	"	1190	3352	2.91%	3.566	Excellent	"	"	"	"
40 BR-20	IV	3	"	1055	4268	2.56%	3.810	Bad Spot	Poor	Sl. Dry	Alligatored	Hard, brittle top
40 BR-8	IV	4	"	985	4540	2.44%	3.583	Excellent	Good	"	Sound	Hard, top very live base
40 BR-5	V	4	"	942	4594	3.05%	3.676	Fair	"	"	"	" " " " "
40 BR-13	V	3	"	1233	4672	2.37%	3.455	Poor	"	"	Worn	" " " " "
40 BR-11	V	3	"	1082	54,384	3.70%	3.587	Excellent	"	"	Sound	" " " " "
40 BR-7	V	4	"	952	1,059,542	1.77%	4.113	Bad Cond.	"	"	Badly Worn	Top brit., " " "
40 BR-6	V	4	"	961	1,630,848	3.58%	4.722	Fair	"	Normal	Sl. Cracked	Hard brittle, both courses

101

illustrate the variation in hardening which might be expected, four pavements were found from which the recovered bitumen showed a viscosity greater than 54, 000 centistokes at 60°C. Also it was observed that in some cases the bituminous material derived from the same processing and source, became abnormally hard in one surface while in another it remained soft and flexible over the same period of time.

The degree of hardening throughout the bituminous mat is another factor to be considered. In general, it was found that the bituminous mat consisted of a hard crust at the exposed surface varying in thickness as much as 1 inch and the mixture under the crust was live and workable. It is evident that the progressive hardening of the mat which is characteristic of this type of bituminous road may develop in two ways, either by a slow rate of hardening from the exposed surface of the mat towards the base, or by a gradual and uniform progress throughout the entire mat.

These facts bring out the importance of considering other factors affecting the relative rate of hardening of asphaltic materials in bituminous surfaces such as the permeability of the mat surface, the density of the mixture, the composition of the mineral filler and to some extent the petrogenic characteristics of the aggregates.

CONCLUSIONS

While the primary purpose of the investigation has not been completely accomplished, we believe that from the information presented, the following conclusions can be drawn.

Since it would be advantageous to the highway industry that a recognized method be established for determining the viscosity of all grades of bituminous materials over a wide range of temperatures in absolute units and since an instrument is available for the determination of absolute viscosity of liquid bituminous materials, it is evident that a standard method for determining the consistency of bituminous materials in absolute units should be adopted.

The plotting of the double log of viscosity against the log of absolute temperature is a satisfactory method for studying the change in viscosity of a bituminous material due to weathering or from other causes. The relative position and slope of the viscosity-temperature lines as plotted on the graph are indicative to some extent of the physical and chemical changes taking place in the bituminous material. A parallel relationship of the viscosity-temperature lines seems to indicate a change in consistency due to loss of volatile oily constituents; the spacing of the viscosity-temperature lines relative to one another illustrates the rate at which hardening of the bitumen or "setting" of the mixture is progressing and a marked divergence of the viscosity-temperature lines denotes that in addition to the physical changes some chemical change has occurred or it may mean that the susceptibility of the volatile oily constituents is not the same as that of the residue.

It is evident that during the early life of a bituminous surface the gradual hardening of the binder is caused primarily by the loss of oily constituents due to evaporation, absorption, and weathering.

It has been shown that the rate of change in the consistency of a bituminous material when subjected to certain laboratory heat tests is comparable to a similar change occurring when the bituminous material is used as a binder in a road mixture. It is evident that some kind of an evaporation test would aid in the selection of suitable liquid asphaltic materials of the slow-curing type. It is a concensus of opinion that a bituminous binder with a low rate of hardening is more desirable for asphaltic oil aggregate surfaces than one with a high rate of hardening.

Abnormal hardening of the asphaltic binder does not necessarily mean that the bituminous surface will not endure under service conditions, nor does it necessarily mean that the binder is an inferior product. However, if we consider the initial purpose and design of asphaltic oil aggregate surfaces, abnormal and excessive hardening of the binder is objectionable. From the standpoint of present Michigan practice, excessive hardening is objectionable because of the maintenance problem. Stock piles of the bituminous mixture are established at strategic points during the construction of the road. It is desirable that the material in the stock piles remain live and workable over a period of years to serve as patching material. Also, it is desirable in cases of total or partial failure of the surface to be able to scarify and reconsolidate the existing materials into a serviceable road surface.

It is evident that an asphaltic oil aggregate surface may change gradually from a flexible to a semi-rigid or rigid state over a period

of years. The rate of transformation is dependent upon the inherent properties and constituents of the mixture. It was found that at the rigid state the pavement had lost at least 25 percent of its original bituminous content and in most cases the inherent binding and cementing properties of the binder had practically disappeared. Thus, in establishing criteria for judging bituminous materials on the basis of their service behavior and durability, it is evident that the following factors must be taken into consideration, namely, the amount of oily constituents and their rate of dissipation, the cohesive and adhesive properties of the bitumen when aged, the petrogenic characteristics of the mineral aggregates and the inherent properties of the bituminous mixture.

It is believed that before any successful laboratory test can be recognized, it will be necessary to establish, to the satisfaction of all concerned, definite criteria as to what constitutes undesirable qualities in a slow-curing asphaltic material and what the characteristics of the binder should be when the surface is judged to be unsatisfactory or has failed completely. To this end, we dedicate our future work.

LITERATURE CITED

- Bingham, E. C., Fluidity and Plasticity, McGraw-Hill Book Company, New York City, 1922.
- Dunstand and Thole, Viscosity of Liquids, Longmans' Green and Co., London 1914.
- Greutert, J., "Greutert's Modification of Suida's CO₂ Method," J. Inst. Pet. Tech. vol. 18, 846, 1932.
- Holberg, A. J., Hougen, O. A., and Zapata, Jos., "The Properties and Composition of Asphalts of the Slow Curing Type," University of Wisconsin, Bulletin No. 86, October 1939.
- Lewis, R. H., and Halstead, W. J., "Determination of the Kinematic Viscosity of Petroleum Asphalts with a Capillary Tube Viscosimeter," Public Roads, vol. 21, no. 7, September 1940.
- Lewis, R. H., and Hillman, W. O'B., "A Study of Some Liquid Asphaltic Materials of the Slow-Curing Type," Public Roads, vol. 15, no. 4, June 1934.
- Lewis, R. H., and Hillman W. O'B., "Further Studies of Liquid Asphaltic Road Materials," Public Roads, vol. 16, no. 6, August 1935.
- Lewis, R. H., and Hillman, W. O'B., "Laboratory Exposure, and Simulated Service Tests of Slow-Curing Liquid Asphalts," Public Roads, vol. 18, no. 5, July 1937.
- Mason, S., Loomis, R. J., Patterson, S. D., Nevitt, H. G. and Krchma, L. C., "Physical Properties of Asphalt - Viscosity Temperature Susceptibility," Industrial and Engineering Chemistry, Anal. Ed., vol. 9, no. 3, pp.138-139, 1937.
- Nevitt, H. G., "Viscosity Temperature Susceptibility Coefficient," Technical Bulletin, Socony-Vacuum Oil Co., RO-4510-A, 1933.
- Nevitt, H. G. and Krchma, L. C., "The Effect of Temperature on the Consistency of Asphalts - the Viscosity Temperature Susceptibility Coefficient as an Index," Industrial Engineering Chemistry, Anal. Ed. vol. 9, no. 3, pp. 119-122, (1937).
- Rhodes, E. O., Volkmann, E. W., and Barker, C. T., "Koppers Products Viscosimeter," Engineering News, vol. 115: 714-18, November 21, 1935.
- Suida, Benigni and Janisch, "Recovery of Extracted Bitumen CO₂ Method," Asphalt u Teer Z, vol. 31, 197, 1931.