

OXYGEN CONSUMPTION BY ASPHALT
FILMS AND RESULTING VISCOSITY CHANGES

by

R. N. Traxler
Research Chemist

and

Frank L. Carter, Jr.
Assistant Research Chemist
Texas Transportation Institute

Progress Report No. 10
Study No. 2-8-59-9
Research Area 8

Submitted to
Research Committee
of the Texas Highway Department

March 1, 1967

TEXAS TRANSPORTATION INSTITUTE
TEXAS A&M UNIVERSITY
COLLEGE STATION, TEXAS

Abstract

Report: Progress Report No. 10 - Study No. 2-8-59-9 of Research Area 8.

Title: Oxygen Consumption by Asphalt Films and Resulting Viscosity Changes

Period: April 1, 1964 to May 1, 1965

Objective: Determine the amount of oxygen consumed by thin films of different asphalts heated in a closed air cell for 3 hours at 225° F. and measure the increase in viscosity of each asphalt caused by this treatment.

Experimental: Pressure change in a sealed, constant volume system was used to measure oxygen consumption from air by asphalt microfilms. The films (14± microns thick) were formed on 4 cm. x 4 cm. glass plates which were then placed in the closed cell. Since the mass of the asphalt was known it was possible to calculate the amount of oxygen consumed per unit mass of asphalt. Viscosities of the asphalt before and after the heat treatment in air were determined at 77° F. and $5 \times 10^{-2} \text{ sec}^{-1}$ (rate of shear) in the thin film, sliding plate viscometer. The ratio of the viscosity of the hardened asphalt to that of the original asphalt was used as a measure of the tendency of the asphalt to harden under the test conditions.

Conclusions: The following conclusions are drawn from the data given in this report.

- (1) For a particular asphalt the moles of oxygen consumed per unit weight of asphalt usually decreases with increasing thickness of the asphalt film.
- (2) When essentially the same film thickness (14± 1 microns) is used, the consumption of oxygen by the seven asphalts investigated varied from 0.033 to 0.016 moles of oxygen per gram of asphalt.
- (3) Relative Viscosities (hardening) of the asphalt films, heated for 3 hours at 225° F. in an enclosed cell filled with air, did not correlate with the amount of oxygen consumed, because polymerization (by heat) which also results in hardening occurs simultaneously with oxygen consumption.
- (4) The hardening effect of heat alone on each asphalt when subtracted from the hardening obtained from the treatment in the air filled cell indicated that rather small amounts of hardening of the asphalts were caused by oxidation alone. In fact asphalts Nos. 5 and 6 appeared to be slightly softened by the consumption of oxygen.

Recommendations: No Recommendations are made.

Future Work: No further work is planned for the immediate future. However, these exploratory experiments point to the need for more precise measurements to clearly define the action of oxygen on asphalts. For example, combination of oxygen with the bitumen should be measured by activation analysis of the material hardened by heat in the presence of air. Also, CO₂ content of the residual air in the closed cell at the end of the experiment should be measured to determine how much of the carbon in the asphalt was converted to this gas.

CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
I.	OBJECTIVES OF STUDY NO. 2-8-59-9 Research Area 8	1
II.	HISTORY	1
III.	CONCLUSIONS	3
IV.	RECOMMENDATIONS	4
V.	FUTURE WORK	4
VI.	EXPERIMENTAL WORK	5
	1. Asphalts Investigated	5
	2. Oxygen Consumption	7
	(a) Introduction	7
	(b) Apparatus	7
	(c) Procedure	7
	3. Standard Oven Test at 225°F. and Three Hours	10
	4. Oxygen Consumption Data from Closed Cell Tests for Three Hours at 225°F.	12
	5. Hardening by Time and Temperature	15
	6. Hardening in Closed Air Cell Compared with Hardening in an Air Oven (3 Hours at 225°F.)	18
VII.	APPENDIX	19

TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1	Asphalts Used	5
2	Laboratory Hardening Tests on 14_{-1}^{+1} Micron Asphalt Films in Air Oven for Three Hours at 22°F .	9
3	Oxygen Consumption and Hardening of 14_{-1}^{+1} Micron Asphalt Films Enclosed in Air Cell for Three Hours at 225°F .	11
4	Effect of Film Thickness on Oxygen Consumption and Hardening in Enclosed Air Cell for Three Hours at 225°F .	13
5	Hardening Caused by Heating 28_{-2}^{+2} Micron Asphalt Films Between Glass Plates for Three Hours at 225°F .	14
6	Hardening of 14_{-1}^{+1} Micron Asphalt Films in Closed Air Cell for Three Hours at 225°F .	16
7	Comparison of Viscosities after Heating Three Hours at 225°F . in Dark Air Oven and Closed Cell	17

FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
I.	Diagram of Apparatus	6

OXYGEN CONSUMPTION BY ASPHALT FILMS AND RESULTING VISCOSITY CHANGES

I. OBJECTIVES OF STUDY NO. 2-8-59-9 OF RESEARCH AREA 8

The objectives of the project are:

- (1) Investigate the asphalt cements used by the Texas Highway Department.
- (2) Establish specifications to assure use of superior asphalts by the Department, and
- (3) Determine how the durability of paving asphalts can be improved.

The investigation discussed in this report is a part of the broad objective given under (1) above. It involved measurement of the moles of oxygen which reacted with a unit mass of several different asphalts. At the same time the Relative Viscosity of the treated asphalt was determined.

II. HISTORY

Progress Reports 1, 3, 4, 5 and 7 of this Research Study have described and given data on a thin film test for evaluating the susceptibility of asphalt cements to hardening by time, heat and oxidation. Films of asphalt ranging from 3 to 15 microns thick have been subjected to various environments and the resulting increases in viscosity determined. A simple evaluation test has been established which comprises heating 14 ± 1 micron films of asphalt for 2 hours in an air oven at 225°F . The viscosities of the original asphalt and of the hardened film are determined at 77°F . in the thin film, sliding plate (Hallikainen) type viscometer. The quotient obtained by dividing the viscosity of the hardened film by that of the original asphalt is called the Relative Viscosity and is considered a measure of the tendency of the asphalt to harden under the conditions of the test.

Although this test might be considered as a measure of the susceptibility of the asphalt to oxidation, a part of the increased viscosity is due to polymerization and volatilization both of which result in hardening and development of internal structure (thixotropy) within the asphalt.

N. W. West, J. C. Giffen and T. F. Ross presented a paper, "Experimental Oxidation Studies on Road Making Bitumen," at the Australian Road Research Board's Third Biennial Conference during September 1966. Their procedure was similar in many

respects to the one described in this report. Pure oxygen, air and nitrogen were used as the atmospheres bathing the asphalt surfaces. The procedure employed was a modification of the Bureau of Public Roads Thin Film Oven Test; 1/16 inch (1587 microns) film heated for 5 hours at 325°F. (162.8°C.). These authors stated "Experiments on the effect of heating bitumen in various atmospheres have revealed a close association between oxygen reactivity and the rate of change in properties, the bitumens of known poor service value showing the most change." They also concluded that viscosity ratio (Relative Viscosity) between the hardened (oxidized) asphalt and the original material is more useful than ductility for assessing changes in flow properties caused by heat and oxidation.

III. CONCLUSIONS

The following conclusions are drawn from the data given in this report.

1. For a particular asphalt the moles of oxygen consumed per unit weight of asphalt usually decrease with increasing thickness of the asphalt film.
2. When essentially the same film thickness (14 ± 1 microns) is used, the consumption of oxygen by the seven asphalts investigated varied from 0.033 to 0.016 moles of oxygen per gram of asphalt.
3. Relative Viscosities (hardening) of the asphalt films, heated for 3 hours at 225°F . in an enclosed cell filled with air, did not correlate with the amount of oxygen consumed, because polymerization (by heat) which also results in hardening occurs simultaneously with oxygen consumption.
4. The hardening effect of heat alone on each asphalt when subtracted from the hardening obtained from the treatment in the air filled cell indicated that rather small amounts of hardening of the asphalts were caused by oxidation alone. In fact asphalts Nos. 5 and 6 appeared to be slightly softened by the consumption of oxygen.

IV. RECOMMENDATIONS

No recommendations are made.

V. FUTURE WORK

No further work is planned for the immediate future. However, these exploratory experiments point to the need for more precise measurements to clearly define the action of oxygen on asphalts. For example, combination of oxygen with the bitumen should be measured by activation analysis of the material hardened by heat in the presence of air. Also, CO₂ content of the residual air in the closed cell at the end of the experiment should be measured to determine how much of the carbon in the asphalt was converted to this gas.

VI. EXPERIMENTAL

1. Asphalts Investigated

The seven asphalts used in this study are identified in Table 1 below. Five of these were asphalts sold to the Texas Highway Department during 1963 and are currently being used in an investigation of the hardening of 85-100 penetration asphalt cements during preparation and service of bituminous pavements. This work has been described in Progress Reports 8 and 9 of Research Study 2-8-59-9.

Asphalts 13 and 16 were included in the study of oxygen consumption because they were found to harden considerably in the laboratory test described under History above.

TABLE 1

ASPHALTS USED

<u>Producer</u>	<u>From Lot No.</u>	<u>District No. and Location</u>
5	13	20 - Beaumont
6	14	14 - Austin
7	6	5 - Lubbock
8	3	4 - Amarillo
11	4	11 - Lufkin
13	--	--
16	--	--

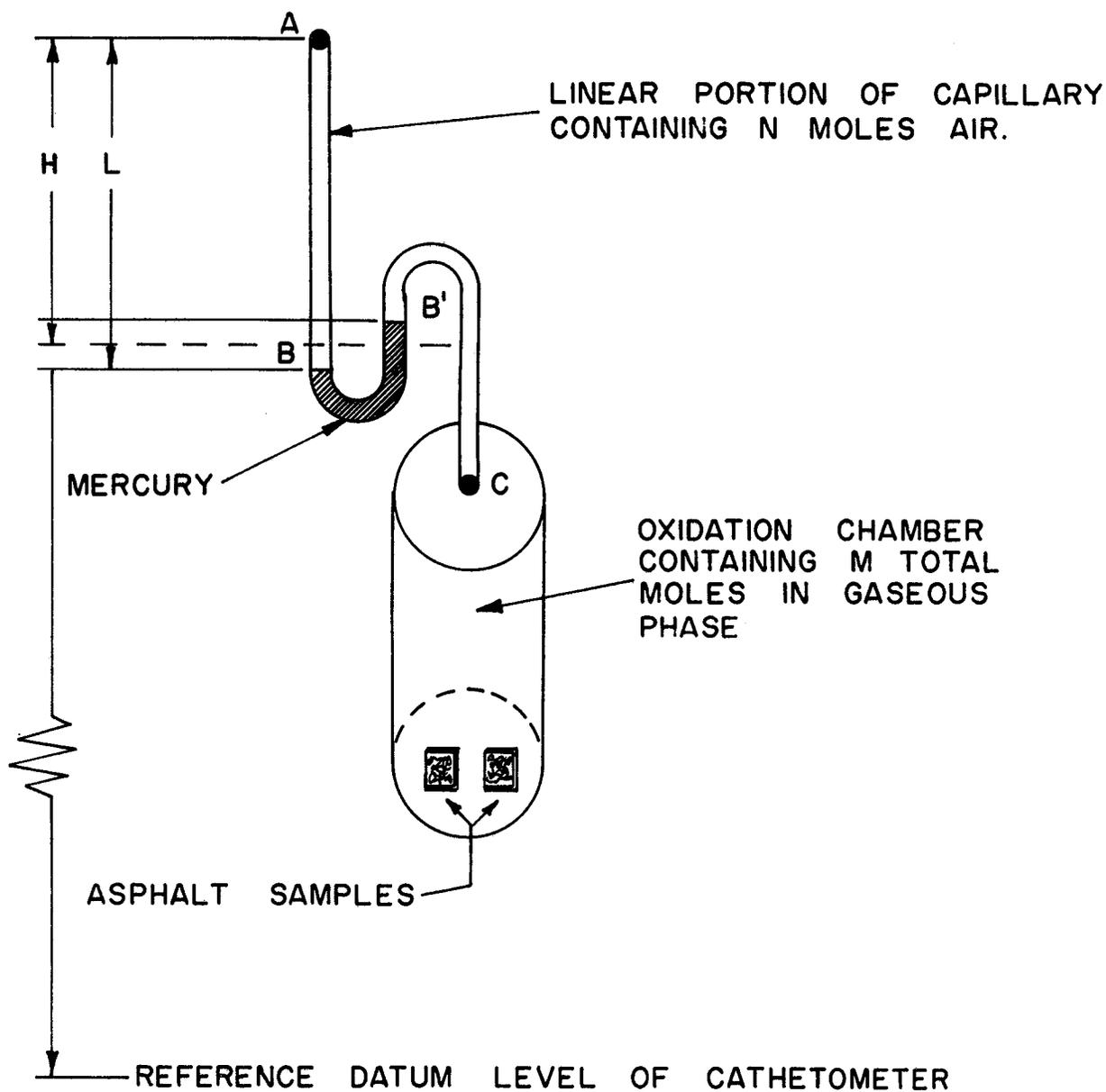


DIAGRAM OF APPARATUS
FIGURE 1

2. Oxygen Consumption

(a) Introduction

Pressure change in a sealed, constant volume system was used to measure oxygen consumption from air by asphalt microfilms. Since the mass of the asphalt film was known, it was possible to calculate the moles of oxygen consumed by unit weight of asphalt.

(b) Apparatus

Figure I, facing, illustrates schematically the apparatus devised to make the oxygen consumption measurements. The detachable capillary-manometer ABB'C was used to measure the pressure in the air chamber as a function of the length AB and the pressure difference observed on segment BB' which served as a manometer.

The capillary ABB'C was sealed permanently at A, had air trapped in the linear portion AB, contained the mercury manometer BB', and could be attached to the sealed container at C. During the oxygen consumption measurements, a ground glass male and female joint (at point C) sealed the oxidation chamber and capillary-manometer ABB'C into one continuous system whose total volume was constant. The length AB and the pressure difference (B'-B) were measured with a cathetometer while the system was immersed in a constant temperature oil bath maintained at 225°F.

(c) Procedure

If the length AB and pressure difference (B'-B) are measured at room temperature with C open to the atmospheric pressure, the moles of air, N, trapped in section AB can be calculated. Bernoulli's equation and the gas law provide the relationship

$$(NRT)/(LA) = P + (B'-B)$$

where: N = moles of air in section AB

R = gas law constant

L = length of section AB, mm

A = capillary cross-sectional area, mm²

P = atmospheric pressure, mm Hg

T = room temperature, $^{\circ}\text{Rankine}$

$(B'-B)$ = pressure difference, mm Hg

Determination of N made oxygen consumption measurements possible.

Two 4 cm. x 4 cm. glass plates covered with a thin film of asphalt of known weight were placed in the oxidation chamber and the chamber then partially immersed, for a 10-minute preheating period, in an oil bath maintained at 225°F . At the end of the preheating period, the capillary-manometer ABB'C was joined to the oxidation (air) chamber and the entire system immersed completely in the bath. At specified intervals, readings were taken of the length AB and the pressure difference $(B'-B)$. The oxygen consumption was calculated using these values observed after heating at 225°F for 3 hours.

For this system it may be shown that

$$(NRT)/(LA) - 2(L-H) = (MRT)/V$$

where: H = length L when $(B'-B) = 0$

M = moles air in oxidation chamber

T = bath temperature, $^{\circ}\text{Rankine}$, and

V = volume oxidation chamber, mm^3

with previous notation applicable. This equation expresses M , the moles of air in the oxidation chamber, in terms of the length L and appropriate experimental constants. The gas law gives the initial value of M . The final length gives the value of M after 3 hours oxidation. The difference was the moles of oxygen consumed by the asphalt samples.

TABLE 2

Laboratory Hardening Tests on 14+1 Micron Asphalt Films in Air Oven for 3 Hours at 225°F.

Asphalt No.	Viscosity, megapoises at 77°F. (1)		Relative Viscosity (2)
	Original	Hardened	
16	1.06	8.80	8.30
7	1.11	7.31	6.60
13	1.23	7.82	6.36
5	0.77	2.74	3.56
8	1.05	3.65	3.47
6	0.65	1.98	3.05
11	1.13	3.25	2.88

(1) Viscosities calculated at $5 \times 10^{-2} \text{ sec}^{-1}$ rate of shear.

(2) Viscosity of hardened film divided by viscosity of original asphalt.

3. Standard Dark Oven Test at 225°F. for Three Hours

A considerable number of exploratory runs were made to determine satisfactory conditions of time and temperature for conducting the measurement of oxygen consumption. It was mentioned on page 5 that considerable research had already been done on 5 of the 7 asphalts discussed in this report. Among the evaluations used was a quality test which measured the tendency of an asphalt to harden (increase in viscosity) when a 14+1 micron film was subjected to heat and air in a dark air oven for 2 hours at 225°F. By dividing the viscosity of the hardened asphalt at 77°F. by the viscosity of the original asphalt at the same temperature, the quotient obtained indicated how many fold the asphalt hardened at the time and temperature used in the experiment.

The exploratory experiments indicated that although 225°F. was a convenient temperature to use in the oxygen consumption experiments a time of 2 hours was not adequate. Three hours were found to be the shortest time for obtaining good repeatable data.

Thus, the laboratory test described above for the susceptibility of the seven asphalts to hardening by heat and air in a dark oven was run on each asphalt using the standard conditions except that the time was changed from two to three hours to give data comparable with the other measurements discussed in this report.

Data are shown in Table 2, facing. It should be remembered that viscosities obtained after 3 hours in the oven test at 225°F. are greater than those obtained after treatment by the standard procedure (2 hours) commonly used in TTI laboratories.

TABLE 3

Oxygen Consumption and Hardening of 14+1 Micron Asphalt Films Enclosed in Air Cell for 3 Hours at 225°F.

Asphalt No.	Oxygen Consumption Moles/gram of asphalt	<u>Viscosity, megapoises at 77°F. (1)</u>		Relative Viscosity (2)
		Original	Hardened	
13	0.033	1.23	3.15	2.56
8	0.031	1.05	1.77	1.68
7	0.026	1.11	1.57	1.42
16	0.023	1.06	3.45	3.26
6	0.023	0.65	0.69	1.06
5	0.022	0.77	1.03	1.33
11	0.016	1.13	1.57	1.39

(1) Viscosities calculated at $5 \times 10^{-2} \text{ sec}^{-1}$ rate of shear.

(2) Viscosity of hardened film divided by viscosity of original asphalt.

4. Oxygen Consumption Data From Closed Air Cell Tests for Three Hours at 225°F.

Oxygen consumption (moles/gram of asphalt) are listed in descending order in Table 3, facing. The thickness of asphalt film used in these experiments was 14 ± 1 microns. The consumption of oxygen by asphalt No. 13 is about twice that of asphalt No. 11 and the hardening of No. 13 is about twice that found for No. 11. Asphalt No. 16 which consumes only 70 per cent as much oxygen as asphalt No. 13 shows 27 per cent greater hardening as measured by the Relative Viscosity.

The consumption of oxygen per unit mass of asphalt is dependent on the thickness of asphalt film used. For the data given in Table 3, the film thickness is quite uniform and this variable is not very important. Table 4, following, gives the data obtained on two asphalts by using films of varying thickness. For the thinner film the moles of oxygen consumed per gram of asphalt is larger and the hardening (Relative Viscosity) is greater.

TABLE 4

Effect of Film Thickness on Oxygen Consumption and Hardening in Enclosed Air Cell for Three Hours at 225°F.

Asphalt No.	Film Thickness, Microns	Oxygen Consumption Moles/gram of Asphalt	Viscosity, megapoises @ 77°F. (1)		Relative Viscosity (2)
			Original	Hardened	
7	15.22	0.021	1.11	1.46	1.32
7	13.50	0.030	1.11	1.68	1.51
8	18.25	0.017	1.05	1.61	1.53
8	14.10	0.031	1.05	1.77	1.68

13

(1) Viscosity calculated at $5 \times 10^{-2} \text{ sec}^{-1}$ rate of shear.

(2) Viscosity of hardened film divided by viscosity of original asphalt.

TABLE 5

Hardening Caused by Heating 28 ± 2 Micron Asphalt Films Between Glass Plates for Three Hours at 225°F .

Asphalt No.	Viscosity at 77°F ., megapoises (1)		Relative Viscosity (2)
	Original	Hardened	
5	0.77	1.47	1.91
6	0.65	0.95	1.46
7	1.11	1.47	1.32
16	1.06	1.32	1.24
8	1.05	1.27	1.21
11	1.13	1.32	1.17
13	1.23	1.43	1.16

(1) Viscosities calculated at $5 \times 10^{-2} \text{ sec}^{-1}$ rate of shear.

(2) Viscosity of hardened film divided by viscosity of original asphalt.

5. Hardening by Time and Heat (Polymerization)

Some of the hardening occurring in an asphalt film, enclosed in the air cell and shown in Table 3, may be caused by polymerization (inter-molecular association) as well as oxidation. Thus, additional experiments were conducted as follows:

Films of each asphalt 28 ± 2 microns thick were heated between 4 cm. x 4 cm. glass plates for 3 hours in an air oven at 225°F . and the viscosities of the hardened films determined. Since oxidation and volatilization were held to a minimum by this procedure, the hardening which took place was considered as caused by polymerization. Table 5, facing, shows the results on the seven asphalts which are arranged in descending order of susceptibility to hardening by this test. Asphalt 5 shows the greatest hardening in this test and asphalts 8, 11, and 13 the least.

From these data it becomes evident that the increased viscosity of an asphalt heated in the closed air cell is not due entirely to oxygen consumption. If the hardening caused when films are heated between glass plates (no substantial amount of oxygen in contact with the bitumen) is subtracted from the hardening which results from heating in the closed cell small values are obtained for hardening by oxidation. The increases in viscosity (Relative Viscosities) calculated as due to oxygen consumption are shown in Table 6, following. The negative values shown for asphalts Nos. 5 and 6 appear to indicate that the action of small amounts of consumed oxygen cause a softening of these asphalts. This situation suggests the need for extended and more precise evaluations.

TABLE 6

Hardening of 14±1 Micron Asphalt Films in Closed Air Cell for Three Hours at 225°F.

Asphalt No.	Relative Viscosity Caused By		
	Oxygen Consumption plus Polymerization	Polymerization	Oxygen Consumption (calculated)
16	3.26	1.24	2.02
13	2.56	1.16	1.40
8	1.68	1.21	0.47
11	1.39	1.17	0.22
7	1.42	1.32	0.10
6	1.06	1.46	-0.40
5	1.33	1.91	-0.58

TABLE 7

Comparison of Viscosities after Heating
Three Hours at 225°F. in Dark Air Oven
and Closed Cell.

Asphalt No.	Viscosity, megapoises at 77°F.		Ratio (1)/(2)
	After Oven Test (1)	After Closed Cell Test (2)	
8	3.65	1.77	2.06
11	3.25	1.57	2.06
13	7.82	3.15	2.50
16	8.80	3.45	2.55
5	2.74	1.03	2.66
6	1.98	0.69	2.87
7	7.31	1.57	4.65

6. Hardening in Closed Air Cell Compared With Hardening in Air Oven
(3 Hours at 225°F.)

Because of the greater flow of warm air moving past the asphalt surfaces in the dark air oven as compared to the more static conditions in the closed cell, we would expect the hardening in the oven to be the greater. Viscosity data shown in Tables 2 and 3 indicate this to be true. Table 7, facing, indicates that the ratio between the viscosity of the asphalt taken from the oven and that hardened in the closed cell varies to a certain extent among the seven asphalts studied. Viscosities of asphalts No. 8 and 11 from the oven are about twice those from the closed cell. Asphalt No. 7 shows an unusually high viscosity from the oven test as compared with the closed cell test. This result may be significant because Asphalt 7 has shown an excessive increase in viscosity during service in the pavement.

VII. APPENDIX

A. Tables

INDEX

<u>Table</u>	<u>Title</u>	<u>Page</u>
A-1	Capillary Calibration Data	20
A-2	Oxygen Consumption Data	21
A-3	Calculated Results from Data Taken During the Air-Cell Operation	22

B. Calculations

	Calculation of Oxygen Consumption	23
--	-----------------------------------	----

TABLE A-1

Capillary Calibration Data

Asphalt	Text.	Datum Levels			Temperature	Pressure
		A, mm	B, mm	B', mm	T, °Rankine.	P, mm Hg
5	A	868.60	799.28	771.86	549.0	750.57
5	B	868.10	797.85	771.67	549.0	751.57
13	A	865.55	799.15	765.40	548.0	752.85
13	B	867.00	802.10	765.65	537.5	750.82
16	A	872.55	807.45	771.50	537.0	747.01
16	B	872.82	808.47	781.05	546.0	752.86
7	A	872.55	807.45	771.50	537.0	747.01
7	B	872.55	807.45	771.50	537.0	747.01
11	A	872.55	807.45	771.50	537.0	747.01
11	B	872.55	807.45	771.50	537.0	747.01
8	A	871.37	806.10	780.36	546.0	753.11
8	B	868.60	801.95	768.70	545.0	756.16
6	A	867.05	797.60	771.90	535.0	758.86
6	B	865.65	796.40	770.35	533.0	759.21

TABLE A-2

Oxygen Consumption Data

Asphalt	Test	Weight Grams	Datum Levels			Pressure P, mm Hg
			A, mm	B, mm	1/2(B'+B), mm	
5	A	0.0483	926.60	835.65	843.85	750.57
5	B	0.0454	926.40	835.30	843.45	751.57
13	A	0.0497	932.90	841.30	850.20	752.85
13	B	0.0479	931.10	841.00	848.58	750.82
16	A	0.0463	923.75	837.50	841.80	750.12
16	B	0.0456	919.05	834.00	841.95	752.86
7	A	0.0492	921.18	835.80	841.40	754.66
7	B	0.0436	922.90	834.50	840.49	751.33
11	A	0.0459	922.70	839.65	840.39	754.46
11	B	0.0450	923.30	838.70	840.98	750.82
8	A	0.0590	919.25	833.74	842.00	753.11
8	B	0.0456	930.97	840.46	848.33	756.16
6	A	0.0499	922.75	831.60	840.65	758.86
6	B	0.0437	932.45	838.05	850.65	759.21

TABLE A-3

Calculated Results from Data Taken During the Air-Cell Operation

<u>Asphalt</u>	<u>Test</u>	<u>Viscosity, megapoises @ 77°F.</u>		<u>Relative Viscosity</u>	<u>Oxygen Consumption Moles/Gram</u>	<u>Thickness Microns</u>
		<u>Original</u>	<u>Hardened</u>			
5	A	0.77	0.95	1.23	0.023	14.95
5	B	0.77	1.10	1.43	0.021	14.05
13	A	1.23	2.39	1.94	0.033	15.38
13	B	1.23	3.92	3.18	0.032	14.82
16	A	1.06	3.23	3.05	0.022	14.33
16	B	1.06	3.68	3.47	0.024	14.11
7	A	1.11	1.46	1.32	0.021	15.23
7	B	1.11	1.68	1.51	0.030	13.49
11	A	1.13	1.55	1.37	0.014	14.20
11	B	1.13	1.59	1.41	0.018	13.93
8	A	1.05	1.61	1.53	0.017	18.26
8	B	1.05	1.77	1.68	0.031	14.11
6	A	0.65	0.71	1.09	0.017	15.44
6	B	0.65	0.67	1.03	0.029	13.52

B. Calculation of Oxygen Consumption

The method of calculation used to determine the oxygen consumption will be dealt with herein. Let M designate the total moles of air in the oxidation chamber of the system shown in Figure I. From Bernoulli's equation and the gas law, it may be shown that

$$(1) \quad (NRT)/(LA) - 2(L-H) = (MRT)/V$$

with previous notation applicable (see pages 7-8). For a given value of M, the length L is fixed, and conversely a given value of L fixes M. Thus M may be calculated from a measurement of L and the respective values of T, A, V, R, H, and N. Values of T, A, V, and R were constant for all tests, whereas N and H were constants which differed for all tests, whereas N and H were constants which differed for each individual test.

The basis of calculation involves the calculation of the initial value of M using the gas law, and the calculation of the final value of M using the length, L, observed after 3 hours at 225°F and the additional constants and experimental values called for by the above equation. The moles of oxygen consumed during testing equals M-initial minus M-final. Oxygen consumption equals the moles of oxygen consumed divided by the weight of asphalt tested.

Throughout calculations of M-initial and M-final, T, A, V, and R were constant. Values used for calculative purposes were

$$T = 685 \text{ }^{\circ}\text{Rankine}$$

$$A = 6.58 \text{ (mm)}^2$$

$$V = 322,500 \text{ (mm)}^3$$

$$R = 34,650,000 \text{ (mm Hg) (mm)}^3/\text{(mole) (}^{\circ}\text{R)}.$$

In addition to these constants, experimental values of N and H were required to calculate M-final. These were determined separately for each test.

The following assumptions were made in the calculation of M-initial:

- (a) The temperature of the oxidation chamber was equal to the oil bath temperature, T.

(b) The initial pressure of the oxidation chamber was atmospheric pressure, P.

(c) The volume of capillary segment B'C was negligible compared to the volume of the oxidation chamber, V.

The value of the M-initial was calculated using data of Table A-2 for values of P according to the gas law.

$$(2) \quad (M\text{-initial}) (RT)/V = P.$$

The value of M-final had to be calculated before calculating the moles of oxygen consumed.

To calculate M-final using equation (1), values of N and H were first determined. Table A-1 gives the data required to calculate N. At room temperature and with capillary end C open to atmospheric pressure, it may be shown that

$$(3) \quad (NRT)/(LA) = P + (B'-B).$$

In the above relationship A is the capillary cross-sectional area with $L = (A-B)$ and $(B'-B)$ using the respective datum levels A, B, and B' given in Table A-1. Note that N was determined prior to testing.

Values of H were determined for each test with the relationship

$$(4) \quad H = A - (B'+B)/2$$

where A, B, and B' were observed datum levels. Since H was a constant once it had been found one could find pressure difference $(B'-B)$ using the relationship

$$(5) \quad (B'-B) = 2(L-H).$$

Use of $2(L-H)$ was preferred since it involved measuring one datum level which was slowly moving, B, while $(B'-B)$ involved measuring simultaneously two datum levels, B and B', which were slowly moving. Values of $(B'+B)/2$ given in Table A-2 were determined after three hours when the relative motion of B' and B was a minimum. From these data H was calculated.

With the arguments of equation (1) now having either assigned or calculated values, the data of Table A-2 were then used to calculate M-final. The final length was $L = (A-B)$, where A and B were the respective datum levels of Table A-2. With the value of H from data of Table A-2 and the value of N calculated from data of Table A-1 substitution into equation (1) gave the value of M-final. Thus M-final was calculated from

$$(6) \quad (NRT)/(LA) - 2(L-H) = (M\text{-final}) (RT)/V$$

with previous notation and assigned values applicable.

The difference between M-initial and M-final was the moles of oxygen consumed during the test. Thus we have that

$$(7) \quad M\text{-initial} - M\text{-final} = \text{Oxygen Consumed.}$$

The oxygen consumption equaled the moles of oxygen consumed per gram asphalt or

$$(8) \quad (M\text{-initial} - M\text{-final})/\text{Weight} = \text{Oxygen Consumption}$$

where Table A-2 gave the weight of asphalt for each test. The calculated values of oxygen consumption are given in Table A-3 along with viscosity data for each test.