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THE CHEMICAL CHANGES OCCURRING DURING THE DEGRADATION OF TWO COATING ASPHALTS

by

Sidney H. Greenfeld

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Jointly Sponsored by
Asphalt Roofing Industry Bureau
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ABSTRACT

Some of the changes that occurred in the components of two asphalts and their water-soluble degradation products were followed through exposures of 3500 hours in an accelerated durability machine (22-1 cycle) and 18 months out-of-doors. Although the general overall trends in the two asphalts were similar, there were differences in their rates of degradation, the migration of the sulfur and nitrogen compounds among their components and into their degradation products, the changes of the molecular weights of their components and the relative amounts of volatile and non-volatile degradation products formed. Because of the complexity of the system, these data are insufficient to establish the actual mechanism of degradation of asphalt.

1. INTRODUCTION

On April 16, 1956, N.B.S. Report No. 4621, "The Degradation of Two Coating Asphalts", was issued. It covered the percentage changes that took place in the components of two asphalts exposed to several combinations of heat, light and water. The

components of Asphalts I and II recovered from specimens removed after various periods of exposure to the 22-1 cycle were subjected to further analysis, as follows: Molecular weight, unsaturation and carbon, hydrogen, oxygen, sulfur and nitrogen content were determined. The water-soluble and ethanol-soluble degradation products were also analyzed chemically. The results of these analyses are covered in this report.

2. EXPERIMENTAL

2.1 Materials

The characteristics of the asphalts investigated are reported in Table 1.

2.2 Methods

The exposure specimens were prepared by the hydraulic-press method (1)[1] and exposed to the 22-1[2] cycle in an accelerated durability machine within 24 hours (2). At exposure periods of 200, 400, 600, 900, 1200, 1700, 2500 and 3500 hours, all of the specimens were weighed and three were removed for component and chemical analysis. Each specimen was separated into asphaltenes, resins, dark oils and white oils by the method of Kleinschmidt (3). The components of the three specimens

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[1] The numbers in parentheses indicate references listed at the end of this report.

[2] 22 hours of dry light at 140 ±5°F followed by one hour of soaking.

TABLE 1.
CHARACTERISTICS OF ASPHALTS

CHARACTERISTIC	ASPHALT I	ASPHALT II
Softening Point,[a] °F	223	224
Penetration[b] at 32°F	10	11
Penetration at 77°F	17	17
Penetration at 115°F	30	26
Susceptibility[c]	1.16	0.87
Loss on Heating,[d] %	0.22	0.03
Pen. after Heating at 77°F	17	17
Specific Gravity at 77°F	1.015	0.999
Durability,[e] days	43	75
Component Analysis (4)		
Asphaltenes, %	39.0	38.4
Resins, %	10.3	9.9
Dark Oils, %	18.2	23.3
White Oils, %	27.4	24.4
Ethanol Extract, %	2.8	0.7
Recovery, %	97.7	96.7

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[a] ASTM D36-26.

[b] ASTM D5-52.

[c] $S = \frac{P_{115} - P_{32}}{P_{77}}$

[d] ASTM D6-39T

[e] 51-9C - 22 hours a day exposure to 51 minutes of light followed by 9 minutes of light + cold (40°F) water spray.

were combined and the ethanol extract, the molecular weight, unsaturation and carbon, hydrogen, oxygen, sulfur and nitrogen content determined on each of the components. The water in which the specimens were soaked daily was filtered and evaporated to dryness in a vacuum evaporator at 120-135°F. The solids were analyzed chemically.

The methods of analysis have been reported previously (4) and are outlined below for information:

Molecular Weight - This is an empirical, ebullioscopic procedure of Matteson (5), in which the boiling point rise of benzene produced by the unknown is compared with that produced by materials of known molecular weights at a definite concentration.

Unsaturation - The material is dissolved in chloroform and treated with a Wijs solution in the dark (6). Iodine adds to the double bonds.

Carbon and Hydrogen - The specimen is oxidized to CO_2 and H_2O in a stream of oxygen in the presence of copper oxide (7) and the CO_2 and H_2O are collected in absorption tubes and weighed.

Oxygen - The specimen is pyrolysed in a stream of nitrogen and passed over hot carbon, where all of the oxygen is converted to CO. The CO is converted to CO_2 by iodine

pentoxide and absorbed in ascarite in an absorption tube and weighed. The procedure is that of Unterzaucher (8), as modified by Aluise (9), Hinkel and Raymond (10), and Dundy and Stehr (11).

Sulfur - The material is oxidized in a Parr bomb at 450 psi and the sulfur, as sulfate, is titrated with a barium chloride solution to the monopotassium rhodizonate endpoint (12).

Nitrogen - The specimen is burned in oxygen and the gases passed over hot copper to remove the excess oxygen and over hot copper oxide to convert all of the carbon and hydrogen to CO_2 and water. The CO_2 and water are absorbed in a 50% aqueous potassium hydroxide solution and the nitrogen measured volumetrically. This method was developed by Alford (13).

3. RESULTS

The analyses of the components of asphalts I and II at various periods of weathering are presented in Tables 2 and 3, respectively. At each period of exposure the proportion of each component, expressed as a percentage of the original coating, is reported. The unsaturation is expressed as the number

TABLE 2. ASPHALT I
(22-1 CYCLE)

COMPONENT Asphaltenes	%	Mol. Wt.	Unsat. D.B. / g	Unsat. D.B. / Molecule	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %	Total %
Exposure, hr.											
0	41.8	3700	1.65	6.11	83.53	8.58	0.818	2.98	2.38	2.39	99.86
200	46.9	3000	1.55	4.65	----	----	----	4.17	2.77	----	----
400	48.5	2700	1.61	4.50	81.60	8.35	0.821	4.65	2.88	2.31	99.79
600	48.7	3050	1.66	5.06	----	----	----	4.68	3.01	----	----
900	48.7	----	1.65	----	----	----	----	----	2.93	----	----
1200	48.9	3020	1.65	4.98	----	----	----	----	2.99	----	----
1700	48.7	2300	1.71	3.94	80.72	8.40	0.808	4.71	2.92	1.97	98.72
2500	47.6	2250	1.96	4.41	81.30	8.28	0.826	4.95	2.90	----	----
3500	47.0	----	1.86	----	79.22	8.34	0.799	5.35	2.67	1.86	97.44
Resins											
Exposure, hr.											
0	10.3	930	1.74	1.62	82.17	9.93	0.695	2.72	3.32	1.34	99.48
200	11.4	965	1.51	1.46	----	----	----	3.90	3.28	----	----
400	11.4	990	1.52	1.50	80.77	10.29	0.660	4.18	3.22	1.15	99.61
600	10.6	965	1.41	1.39	----	----	----	4.70	3.22	----	----
900	9.6	---	1.44	----	----	----	----	----	2.96	----	----
1200	8.1	920	1.37	1.26	----	----	----	----	2.96	----	----
1700	7.3	---	1.34	----	79.70	10.63	0.630	5.11	2.88	0.75	99.07
2500	5.6	950	1.43	1.36	79.41	10.53	0.633	6.18	2.71	----	----
3500	5.6	---	1.33	----	80.40	10.55	0.641	5.95	2.59	0.6 1	100.10

TABLE 2. ASPHALT I (CONTINUED)
(22-1 CYCLE)

COMPONENT Dark Oils	%	Mol. Wt.	Unsat. D.B. g	Unsat. D.B. Molecule	Refractive Index at 50°C	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %	Total %
Exposure, hr.												
0	18.2	745	1.57	1.17	1.554	84.40	10.77	0.658	1.15	2.65	0.57	99.54
200	13.6	720	1.58	1.14	1.554	-----	-----	-----	1.25	2.45	----	-----
400	11.3	760	1.50	1.14	1.548	85.11	10.33	0.692	1.50	1.99	0.48	99.41
600	10.0	750	1.50	1.12	1.537	-----	-----	-----	1.39	1.80	----	-----
900	8.9	---	1.51	----	1.535	-----	-----	-----	----	1.67	----	-----
1200	8.1	720	1.41	1.02	1.533	-----	-----	-----	----	1.76	----	-----
1700	7.0	---	1.34	----	1.527	84.90	10.25	0.696	1.87	1.40	0.49	98.91
2500	6.9	730	1.26	0.92	1.523	83.72	11.02	0.640	2.58	1.43	----	-----
3500	5.6	---	1.18	----	1.516	83.82	10.93	0.642	2.42	1.05	0.20	98.42
White Oils					at 25°C							
Exposure, hr.												
0	27.4	450	0.84	0.38	1.4982	85.77	12.92	0.557	0.05	0.94	0.00	99.68
200	24.5	520	0.64	0.33	1.4969	-----	-----	-----	0.16	0.58	----	-----
400	22.9	560	0.44	0.25	1.4952	85.90	12.67	0.570	0.05	0.44	0.42	99.48
600	21.6	540	0.46	0.25	1.4940	-----	-----	-----	0.06	0.32	----	-----
900	20.3	---	0.45	----	1.4932	-----	-----	-----	----	0.34	----	-----
1200	18.5	520	0.39	0.20	1.4924	-----	-----	-----	----	0.29	----	-----
1700	17.9	---	0.35	----	1.4912	86.28	13.30	0.545	0.00	0.14	0.33	100.05
2500	17.8	530	0.36	0.19	1.4892	85.71	12.95	0.557	0.24	0.20	----	-----
3500	15.7	---	0.26	----	1.4888	85.48	12.66	0.577	0.10	0.13	0.26	98.63

TABLE 3. ASPHALT II
(22-1 CYCLE)

COMPONENT Asphaltenes	%	Mol. Wt.	Unsat. D.B. g	Unsat. D.B. Molecule	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %	Total %
Exposure, hr.											
0	39.1	4400	1.52	6.71	86.61	8.54	0.853	1.73	1.90	1.11	99.89
200	43.3	3600	1.48	5.33	-----	----	-----	3.19	1.70	----	-----
400	44.5	3575	1.35	4.83	84.25	8.30	0.853	3.23	1.78	1.11	98.67
600	45.0	2750	----	----	84.55	8.67	0.819	3.52	1.76	----	-----
900	45.3	3250	1.42	4.62	-----	----	-----	3.59	1.72	----	-----
1200	46.3	----	1.46	----	-----	----	-----	----	1.71	----	-----
1700	47.5	2850	1.40	4.00	84.45	8.54	0.831	3.61	1.66	1.10	99.36
2500	47.4	2825	1.40	3.96	-----	----	-----	----	1.66	----	-----
3500	47.2	2550	1.38	3.52	82.53	8.25	0.841	4.60	1.67	0.99	98.04
4100	47.5	----	1.23	----	-----	----	-----	----	1.61	----	-----
Resins											
Exposure, hr.											
0	9.9	1100	1.25	1.37	84.85	10.38	0.687	1.81	1.51	1.01	99.56
200	10.9	975	1.38	1.35	-----	-----	-----	2.65	1.47	----	-----
400	10.7	980	1.24	1.20	84.09	10.60	0.666	3.00	1.42	0.78	99.89
600	10.6	1060	1.20	1.28	83.64	10.91	0.644	3.21	1.45	----	-----
900	10.0	----	1.13	----	-----	-----	-----	3.36	1.46	----	-----
1200	9.0	1250	1.07	1.33	-----	-----	-----	----	1.43	----	-----
1700	8.1	1260	1.07	1.35	83.38	10.93	0.641	3.90	1.41	0.58	100.20
2500	8.1	1190	1.05	1.25	-----	-----	-----	----	1.32	----	-----
3500	8.0	1200	0.98	1.18	82.10	11.15	0.619	4.64	1.07	0.48	99.44
4100	7.3	----	0.80	----	-----	-----	-----	----	----	----	-----

TABLE 3. ASPHALT II (CONTINUED)
(22-1 CYCLE)

COMPONENT Dark Oils	%	Mol. Wt.	Unsat. D.B./g	Unsat. D.B./Molecule	Refractive Index at 50°C	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %	Total %
Exposure, hr.												
0	23.3	900	1.12	1.01	1.533	86.10	11.36	0.630	0.54	1.37	0.35	99.72
200	18.3	860	1.13	0.93	1.530	86.37	11.35	0.630	0.72	0.95	----	-----
400	16.9	880	1.10	0.97	1.530	86.55	11.62	0.626	0.76	0.85	0.41	100.19
600	15.7	930	1.04	0.98	1.524	85.97	11.81	0.611	0.72	0.78	----	-----
900	14.4	---	0.99	----	1.522	-----	-----	-----	0.87	0.72	----	-----
1200	13.3	1010	1.00	1.01	1.518	-----	-----	-----	----	0.85	----	-----
1700	11.3	1050	0.83	0.87	1.513	85.54	12.04	0.597	1.28	0.76	0.40	100.02
2500	10.2	1030	0.75	0.77	1.506	-----	-----	-----	----	0.82	----	-----
3500	9.0	1030	0.59	0.61	1.536[a]	84.75	12.50	0.569	1.18	0.67	0.21	99.31
4100	9.4	----	0.51	----	-----	-----	-----	-----	----	----	----	-----
White Oils					at 25°C							
Exposure, hr.												
0	24.4	500	0.41	0.21	1.4871	86.29	13.31	0.544	0.00	0.35	0.20	100.15
200	23.6	560	0.33	0.18	1.4870	-----	-----	-----	0.03	0.37	----	-----
400	23.0	560	0.29	0.17	1.4868	86.15	13.39	0.541	0.06	0.14	0.33	100.07
600	23.0	675	0.27	0.18	1.4860	85.94	13.80	0.523	0.12	0.15	----	-----
900	21.3	885	0.22	0.19	1.4858	-----	-----	-----	0.18	0.19	----	-----
1200	20.5	920	0.28	0.26	1.4858	-----	-----	-----	----	0.11	----	-----
1700	19.7	920	0.23	0.20	1.4852	85.78	13.53	0.532	0.24	0.08	0.30	99.93
2500	18.7	920	0.21	0.19	1.4834	-----	-----	-----	----	0.15	----	-----
3500	16.7	880	0.20	0.18	1.4828	85.82	13.21	0.545	0.08	0.06	0.11	99.28
4100	17.1	---	0.17	----	1.4820	-----	-----	-----	----	0.09	----	-----

[a] Fuzzy.

of double bonds per gram and per molecule to facilitate the interpretation of the data. The elemental analyses are expressed as percentages of the components.

The asphaltenes were analyzed before they were extracted with ethanol and, therefore, include the contributions of the relatively small proportion of the ethanol extract.

Table 4 contains the determinations made on the water-soluble degradation products. Because these products were not quantitatively recovered the weight losses of the asphalts are reported instead of the quantities of water-soluble materials collected.

Table 5 contains the analytical data on the ethanol-soluble degradation products. Because of the small portions of these materials, very little work was done on them, particularly on those from asphalt II.

Tables 6 and 7 contain the analyses of the components of these two asphalts made periodically during the first 18 months of exposure out-of-doors. The results are based on separations of individual specimans and, therefore, have more variation than the previous analyses. Because of the limitations of time and sample size, it was not possible to obtain complete analyses on all of the components of the specimens exposed out-of-doors.

TABLE 4. WATER-SOLUBLE DEGRADATION PRODUCTS
(22-1 CYCLE)

Exposure, hr.	Asphalt Loss %	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %	Ash %	Total %	Titration Mol. Wt.[a]
Asphalt I										
200	1.1	47.39	5.32	0.748	35.53	4.43	1.79	3.59	98.05	340
400	3.1	47.60	5.45	0.734	33.11	4.48	1.79	----	-----	---
600	5.9	-----	----	-----	-----	4.30	----	----	-----	330
900	9.7	51.49	4.99	0.867	36.30	4.02	----	2.39	-----	---
1200	12.9	-----	----	-----	-----	3.67	----	----	-----	382
1700	17.5	50.35	4.88	0.868	33.51	3.56	2.63	4.62	99.55	382
2500	20.7	47.99	4.73	0.849	33.87	3.75	----	7.92	-----	408
3500	24.4	47.30	5.01	0.792	33.05	3.25	3.40	5.81	97.82	---
Asphalt II										
200	0.7	-----	----	-----	-----	----	----	----	-----	---
400	2.2	52.26	4.68	0.938	34.97	1.91	1.54	----	-----	388
600	3.9	55.94	4.82	0.975	33.65	2.00	----	----	-----	---
900	6.3	-----	----	-----	36.01	1.97	----	----	-----	356
1200	8.4	-----	----	-----	-----	----	----	----	-----	390
1700	10.6	51.78	4.73	0.918	33.54	1.94	2.17	5.93	100.09	410
2500	13.2	-----	----	-----	-----	2.19	----	----	-----	430
3500	16.6	45.77	4.77	0.806	33.84	2.18	3.01	9.28	98.85	---
4150	17.4	-----	----	-----	-----	----	----	----	-----	---

[a] Assuming two carboxyl groups per molecule.

TABLE 5. ETHANOL-SOLUBLE DEGRADATION PRODUCTS (22-1 CYCLE)

Exposure, hr.	% of Original Asphalt	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur[a] %	Nitrogen %
Asphalt I							
0	2.80	79.49	9.68	0.690	4.80		1.45
200	3.59	66.68	9.10	0.735	----		----
400	----	-----	----	-----	----		1.65
600	4.87	-----	----	-----	----		----
900	----	-----	----	-----	----		----
1200	5.21	69.26	9.54	0.610	----		----
1700	4.87	73.95	9.32	0.666	11.15		0.77
2500	3.93	-----	----	-----	-----		----
3500	3.52	73.20	9.26	0.665	11.65[b]		0.78
Asphalt II							
0	0.68	-----	----	-----	-----		----
200	----	-----	----	-----	-----		----
400	1.56	-----	----	-----	10.7		----
600	----	-----	----	-----	-----		----
900	2.02	-----	----	-----	-----		----
1200	1.99	-----	----	-----	13.00[b]		0.60
1700	2.24	-----	----	-----	-----		----
2500	1.96	-----	----	-----	-----		----
3500	1.36	-----	----	-----	14.17[b]		0.61
4150	1.31	-----	----	-----	-----		----

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[a] Insufficient sample for sulfur determination.

[b] Single determination.

TABLE 6.

OUT-OF-DOOR EXPOSURES

ASPHALT I

Exposure, Mo.	%	Mol. Wt.	Unsat. DB g	Unsat. DB Molecule	Carbon %	Hydrogen %	C/H	Oxygen %	Sulfur %	Nitrogen %
Asphaltenes										
0	41.8	3700	1.65	6.11	83.53	8.58	0.818	2.98	2.38	2.39
3	44.0	----	1.74	----	------	------	------	3.44	2.54	----
6	45.3	1950	1.58	3.08	82.79	8.62	0.808	4.20	2.54	2.19
12	45.8	----	1.59	----	81.12	8.46	0.806	4.28	2.71	2.08
18	43.0	----	1.64	----	81.88	8.52	0.806	4.61	2.54	----
Resins										
0	10.3	930	1.74	1.62	82.17	9.93	0.695	2.72	2.65	1.34
3	10.9	----	1.62	----	------	------	------	3.25	2.94	----
6	11.6	770	1.42	1.10	81.40	10.35	0.661	3.79	2.91	1.08
12	11.2	----	1.40	----	80.09	10.79	0.630	3.06	3.09	1.13
18	9.8	----	----	----	79.25	10.61	0.627	2.87	3.20	----
Dark Oils										
0	18.2	745	1.57	1.17	85.40	10.77	0.658	1.15	3.32	0.57
3	15.1	----	1.82	----	------	------	------	1.08	3.02	----
6	12.6	540	1.61	0.87	85.68	10.69	0.674	1.06	2.23	0.53
12	12.4	----	1.53	----	83.24	10.55	0.662	1.71	1.96	0.69
18	11.5	----	----	----	84.16	10.66	0.663	2.16	2.08	----
White Oils										
0	27.4	450	0.84	0.38	85.77	12.92	0.557	0.05	0.94	0.18
3	24.8	----	0.81	----	------	------	------	0.25	0.72	----
6	22.2	320	0.42	0.13	85.92	12.91	0.558	0.29	0.46	0.45
12	21.5	----	0.40	----	85.82	12.50	0.576	0.15	0.36	0.60
18	23.2	----	0.43	----	85.62	12.60	0.572	0.02	0.44	----

TABLE 7.
OUT-OF-DOOR EXPOSURES
ASPHALT II

Exposure, Mo.	%	Mol. Wt.	Unsat. DB/g	Unsat. DB/Molecule	Carbon %	Hydrogen %	O/H	Oxygen %	Sulfur %	Nitrogen %
<u>Asphaltenes</u>[a/]										
0	39.1	4400	1.52	6.71	86.61	8.54	0.853	1.73	1.90	1.11
3	40.3	4200	1.55	6.51	------	----	------	2.26	1.98	----
6	40.9	2850	1.71	4.88	85.21	8.42	0.850	2.80	1.86	1.20
12	42.2	----	1.28	----	84.48	8.45	0.844	2.52	1.78	1.07
18	41.8	----	1.38	----	84.18	8.38	0.844	2.87	1.79	----
<u>Resins</u>										
0	9.9	1100	1.25	1.37	84.85	10.38	0.687	1.81	1.51	1.01
3	11.8	1180	1.40	1.65	------	------	------	2.07	1.68	----
6	11.0	1160	1.49	1.73	84.00	10.44	0.675	2.52	1.68	1.13
12	12.1	----	1.22	----	83.60	10.66	0.658	2.97	1.52	0.76
18	9.2	----	1.18	----	82.12	10.28	0.671	4.12	1.68	----
<u>Dark Oils</u>										
0	23.3	900	1.12	1.01	86.10	11.36	0.630	0.54	1.37	0.25
3	21.4	1030	1.30	1.34	------	------	------	0.59	1.26	----
6	20.5	940	1.41	1.32	86.08	11.38	0.636	1.07	1.16	0.40
12	17.9	----	0.96	----	86.26	11.00	0.658	0.94	1.01	0.41
18	14.6	----	1.09	----	84.37	11.34	0.625	1.55	1.26	----
<u>White Oils</u>										
0	24.4	500	0.41	0.21	86.29	13.31	0.544	0.00	0.35	0.20
3	23.7	940	0.40	0.38	------	------	------	0.09	0.29	----
6	24.3	800	0.39	0.32	85.33	13.37	0.536	0.21	0.25	0.56
12	20.5	----	0.21	----	84.33	12.79	0.553	0.50	0.12	0.49
18	23.4	----	0.23	----	84.37	12.11	0.584	0.64	0.11	----

4. DISCUSSION OF RESULTS

4.1 General

The origin of petroleum and the changes that occur during the conversion of petroleum and petroleum products to carbon dioxide and water are only vaguely understood. Some of the changes that occur during the conversion of the organic source materials to crude petroleum have been studied by numerous investigators (14), and several hypotheses of the conversion exist, but the evidence is insufficient to enable any of them to be considered more than an hypothesis.

The chemical constituents of the lighter fractions of petroleum have been studied more arduously than those in asphalt and considerable information has been accumulated on their compositions and properties. As the size of the molecules increases, less is known of them; almost nothing is known of the individual molecules in asphalt and very little has been reported on the chemical nature of asphalt.

4.2 Asphalt Flux

During the normal refining process of petroleum the more volatile constituents of the petroleum are removed by distillation. Because the process is conducted in the absence of oxygen and at temperatures at which cracking does not occur, few changes to individual molecules take place. When the lubricating

oils have been removed, a heavy, viscous residuum remains in the still pot. The residuum is the raw material, or flux, from which the coating-grade asphalt is made by means of a high-temperature oxidation process called "blowing". The component and chemical analyses of the fluxes of the two asphalts and the two coating-grade asphalts are shown in Table 8.

While both of the fluxes were semi-solids at room temperature, the viscosity-temperature coefficients were very different and the flux of asphalt I was much more fluid at 210°F than was that of asphalt II. The average molecular weight of the flux of asphalt I was 880, and that of asphalt II was 1150. The range of molecular weights in flux I was much greater. In separating flux I into its components, a relatively large amount of material could not be removed from the fuller's earth column (7.8%). This probably was similar to, but more polar than the resins. Flux II had significantly more dark oils and less white oils than flux I. Flux I contained more sulfur and oxygen than flux II.

During the blowing process, the fluxes were oxidized at about 450°F for varying periods of time and products were removed from the still when the charge had the desired softening point. At a softening point of approximately 225°F, the

TABLE 8.

RESIDUA AND ASPHALTS

	ASPHALT I		ASPHALT II	
PROPERTY	FLUX	ASPHALT	FLUX	ASPHALT
Softening Pt., °F	----	223	----	224
Viscosity at 210, F.S.	84	---	286	---
Asphaltenes, %**	13.2 (1850)*	41.8 (3700)*	13.2 (2200)*	39.1 (4400)*
Resins, %	16.8 (1000)*	10.3 (930)*	16.5 (1250)*	9.9 (1100)*
Dark Oils, %	29.8 (670)*	18.2 (745)*	37.6 (1020)*	23.3 (900)*
White Oils, %	32.4 (470)*	27.4 (450)*	29.0 (950)*	24.4 (500)*
Recovery, %	92.2	97.7	96.3	96.7
Ethanol Extract, %	1.28	2.80	0.25	0.68
<u>CHEMICAL ANALYSES</u>				
Carbon, %	84.64	83.89	86.51	85.51
Hydrogen, %	10.89	10.29	10.71	10.29
C/H	0.65	0.69	0.68	0.70
Oxygen, %	0.70	1.79	0.26	1.27
Sulfur, %	2.18	2.27	1.15	1.24
Nitrogen, %	1.11	1.23	0.90	0.79
Total, %	99.52	99.47	99.53	99.10

*Numbers in parentheses are number average molecular weights.

**Includes ethanol extract.

molecular weights of both asphalts had increased and had approximately doubled (1970 and 2230, respectively). The asphaltenes had increased, primarily at the expense of the resins and dark oils, both in quantity and molecular size. The white oil fraction of asphalt II was the only other portion that had changed significantly in molecular weight, having decreased appreciably.

During the blowing process there was a 1% increase in the oxygen content of the asphalts, but no other significant chemical changes occurred. Thus, in summary, the blowing process seems to have oxidized the asphalt and increased its molecular weight, producing n-pentane-insoluble material of high molecular weight at the expense of some portions of the n-pentane-soluble fraction of the asphalt.

4.3 Molecular Weight Changes During Exposure

When the two asphalts were exposed to both natural weathering and light, heat and water in the laboratory, further changes took place. Because many of the changes are complex and tend to counterbalance other changes, the asphalts were separated into simpler groups [reported in (15)] and the chemical changes occurring in each group were followed.

The molecular weight of each of the asphalts, which had increased during the blowing operation, began to decrease on exposure to the forces of degradation--light, heat, and water. In

asphalt I, the molecular weight of the asphaltenes increased during blowing from 1850 to 3700, decreased to 2250 (Table 2) during 3500 hr of exposure to the 22-1 cycle and to 1950 (Table 6) after 6 months out of doors. Similarly, in asphalt II, the molecular weight of the asphaltenes increased from 2200 to 4400 during blowing and decreased to 2550 (Table 3) and 2850 (Table 7) for the corresponding two exposures. Although the molecular weight decreased appreciably, the quantity of asphaltenes increased during exposure. The lowering of the average molecular weight was accompanied by a sharp increase in oxygen content, which served to maintain their poor solubility in n-pentane.

In asphalt I, the molecular weight of each of the pentane-soluble fractions did not change appreciably during the blowing operation and, also, changed little during exposure to the 22-1 cycle. However, in asphalt II, the molecular weight of the white oils was almost halved during blowing, but increased progressively during exposure to the 22-1 cycle. Those of the resins and dark oils decreased slightly during blowing and continued to decrease during the early periods of exposure, but soon increased to their values in the residuum. Thus, during exposure, in both asphalts the molecules seemed to have returned to the size they were before the high-temperature oxidation process. Quite possibly, those molecules which were changed by blowing were most susceptible to change during exposure.

Of course, chemically and physically the asphalt that remained after 3500 hours of exposure was very different from that which came from the still pot.

4.4 Chemical Changes

The chemical changes that have taken place may be stated as follows:

The unsaturation decreased during exposure as the asphalts were oxidized (Table 9). But, under the assumption that one oxygen molecule reacted with each double bond, it was found that the decrease in unsaturation was much greater than that required by the increase in the oxygen content of the asphalts. In asphalt I this decrease was about eight times as great and in asphalt II about five times. The loss of the other double bonds may have been the result of more complete oxidation of the components of the asphalt into products that were actually removed from the asphalt. These weight losses, which amounted to 24.4% and 17.4% for asphalts I and II, respectively, will be discussed later.

In asphalt I, the carbon-hydrogen ratios of the components remained relatively unchanged during exposure, which in combination with the constancy of molecular weights and relatively small melting range tend to indicate a uniformity of molecular species. The decrease in refractive indices of the oil fractions during exposure (Table 2) may then be attributed to a decrease in branching and a loss of double bonds. In asphalt II, however, the carbon-hydrogen ratio tended to decrease (Table 3) for all but the white

TABLE 9.

CHANGES IN OXUGEN AND UNSATURATION OF ASPHALTS DURING 3500 HOURS OF EXPOSURE

COMPONENT	EXPOSURE Hrs.	%	OXYGEN %	OXYGEN WT., g	OXYGEN CHANGE	UNSATURATION DB/g	UNSATURATION DB	UNSATURATION CHANGE
(ASPHALT I)								
Asphaltenes	0	41.8	2.98	1.25	0	1.65	0.690	0
"	3500	47.0	5.35	2.51	+1.26	1.86	0.875	+0.185
Resins	0	10.3	2.72	0.28	0	1.74	0.179	0
"	3500	5.6	5.95	0.33	+0.05	1.33	0.074	-0.105
Dark Oils	0	18.2	1.15	0.21	0	1.57	0.286	0
" "	3500	5.6	2.42	0.14	-0.07	1.18	0.066	-0.220
White Oils	0	27.4	0.016	----	0	0.84	0.230	0
" "	3500	15.7	0.016	----	0	0.26	0.041	-0.189
Asphalt	----	----	-----	----	+1.24 (0.08 mols)	----	-----	-0.33
(ASPHALT II)								
Asphaltenes	0	39.1	1.73	0.68	0	1.52	0.595	0
"	3500	47.2	4.60	2.17	+1.49	1.38	0.652	+0.057
Resins	0	9.9	1.81	0.18	0	1.25	0.124	0
"	3500	8.0	4.64	0.37	+0.19	0.98	0.079	-0.045
Dark Oils	0	23.3	0.54	0.13	0	1.12	0.261	0
" "	3500	9.0	1.18	0.11	-0.02	0.59	0.053	-0.208
White Oils	0	24.4	0.00	0.00	0	0.41	0.100	0
" "	3500	16.7	0.08	0.013	+0.01	0.20	0.033	-0.067
Asphalt	----	----	----	-----	+1.67 (0.105 mols)	----	-----	-0.263

oils (which are already very close to paraffinic in nature), indicating that the material remaining behind is more paraffinic than that being removed. The refractive index decrease was somewhat more restricted because the materials remaining in each component of the asphalt as degradation progressed were of increasingly higher molecular weight.

The sulfur and nitrogen contents of both asphalts decreased progressively during exposure; both of these materials were present in some of the molecules that became water soluble. Apparently, however, the reaction that made the molecules water soluble did not take place at the sulfur or nitrogen bonds (16), for no oxidized forms of sulfur or nitrogen were found in the degradation products.

Some of the sulfur compounds migrated into the aslphltenes during the early stages of exposure. In asphalt I this migration (probably a polymerization of some of the maltenes) actually increased the concentration of sulfur in the asphaltenes, while in asphalt II the concentration remained the same. In both cases, an appreciable amount of the sulfur in the asphalt moved into the asphaltenes.

In asphalt I the nitrogen compounds seemed to weather from the resins and dark oils, while in asphalt II, only the resins lost an appreciable amount of nitrogen compounds. The early increases in asphaltenes in both asphalts carried sufficient nitrogen into that fraction to maintain its nitrogen content almost constant for about 400 hours of exposure.

The material that was weathered from the asphalts went into water-soluble and volatile degradation products. Only the former were collected for analysis. The magnitude and probable composition of the latter will be discussed later. The water solubles (Table 4) were highly oxidized, acid materials having appreciable nitrogen and sulfur. Although in a general way these products were similar during the entire exposure period, specifically there were many differences present in the products collected during the various exposure intervals. These differences will be discussed in a later report. Chemically, the nitrogen content of the degradation products of asphalt I increased and the sulfur content decreased progressively as degradation proceeded. In those of asphalt II, both nitrogen and sulfur increased.

The ash is composed primarily of contaminating materials introduced by the reaction of the degradation products with the aluminum alloy specimen backings and supports and with dust that has fallen into the collecting jars while they were uncovered.

4.5 Ethanol Extract

Very little has been said concerning the ethanol extract of the asphaltenes. This material was not discovered until most of the chemical analyses had been completed and it is included in the data reported on the asphaltenes. However, it was extracted from the asphaltenes and analysed where sufficient material could be recovered. Physically, this extract is the portion of the film

that forms on the surface of asphalt as it weathers and is not soluble in water or n-pentane; hence, it remains with the asphaltenes after the asphalt has been extracted with n-pentane.

Before exposure, about one to three percent of a material soluble in hot ethanol was present in the asphaltenes. This material had about four percent oxygen. After 400 hours of exposure, the material extracted from the asphaltenes with hot ethanol contained over 10% oxygen. At other exposure periods its oxygen content was in the range of 11 to 14% for both asphalts. Only asphalt I yielded sufficient ethanol extract for further analysis. The nitrogen content dropped from about 1.5% before exposure to about 0.8% after 1700 hours of exposure. The carbon-hydrogen ratio dropped slightly along with the small decreases in both carbon and hydrogen. Insufficient material was available for sulfur analysis. This material seems to be an intermediate degradation product.

4.6 Quantitative Considerations

The above qualitative discussion of the changes that occurred in the two asphalts has shed some light on what transpires during exposure, but for a better understanding, the data must be examined quantitatively.

All of the complete chemical analyses accounted for between 98 and 100% of the material being analysed, introducing a maximum of two percent uncertainty in any particular analysis. In the component analyses there was usually about two to three percent of

material that remained on the fullers earth and was not included in the material that was collected for analysis. This loss was composed of a material of the same molecular weight as the resins and, when removed, was found to be similar to the resins in many other respects. As an approximation, it has been included in all calculations as so much additional resin.

Further examination of the mechanics of collecting the degradation products reveals that these materials were not recovered quantitatively. As a first approximation, based on previous quantitative recovery, it can be assumed that the formation of degradation products is equal to the weight losses of the asphalts. Because the water-soluble degradation products are about 35% oxygen, it would be required that about two-thirds of the loss go into the water-soluble products and one-third would go elsewhere; namely, into volatile losses. However, from the dry-light and oven exposures (15) it was known that no appreciable volatilization occurred, even at 200°F. Therefore, these volatile losses resulted directly from the reactions that took place in the presence of water, as well as light and heat. Because the products varied as degradation progressed, it is logical to believe that the proportions of volatile and non-volatile products varied as well.

Thurston and Knowles (17) reported that for each mol of oxygen absorbed by the asphalt, a mol of oxygen went into CO_2 and H_2O formation. No other volatile products were reported there or in

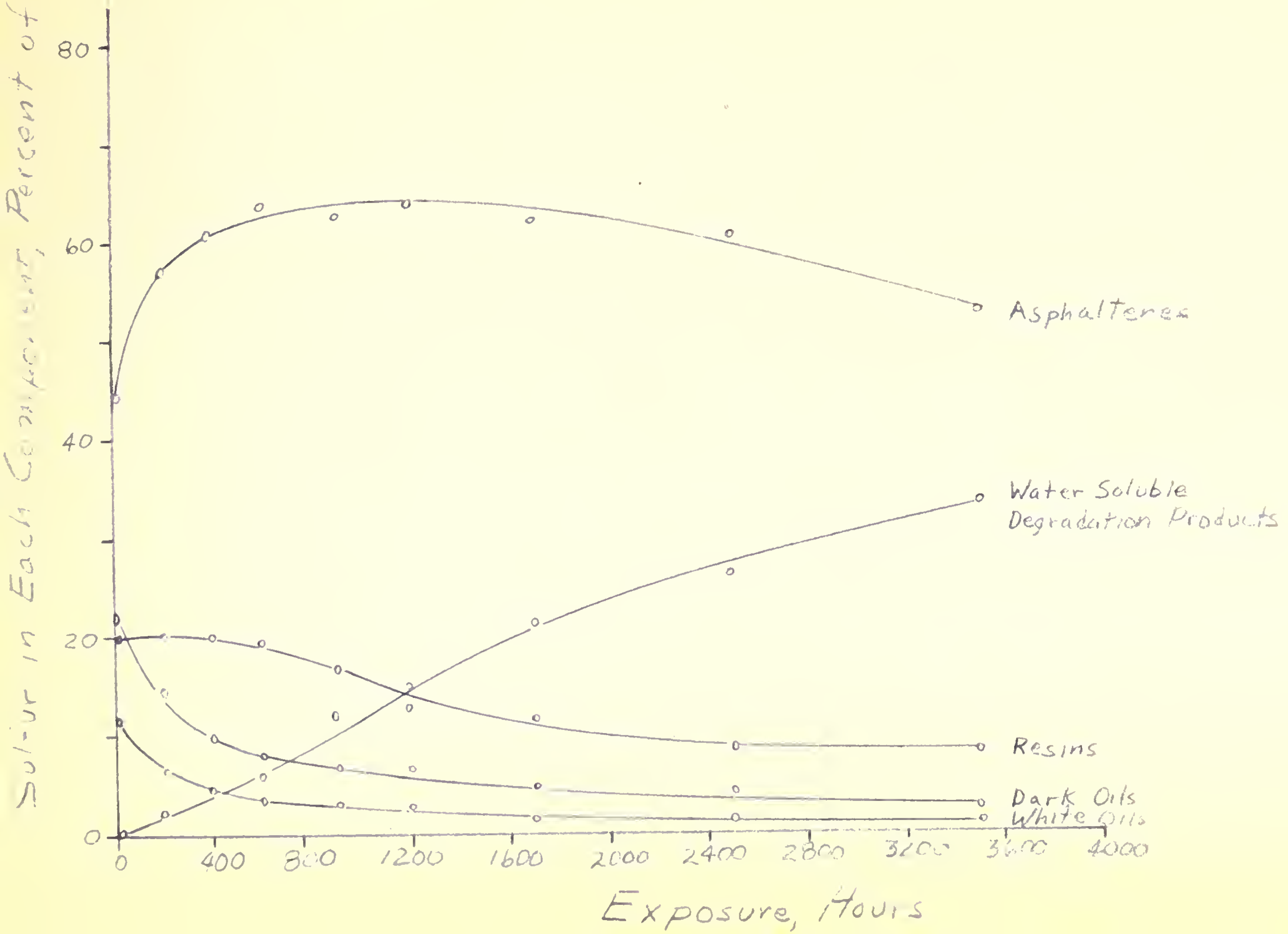
any other reference. Therefore, all volatile loss in the following discussion will be considered to be CO_2 and H_2O. Logically, then, all of the sulfur losses must have gone into the non-volatile, water-soluble degradation products, offering a convenient tracer for determining the exact amount of these products that have been formed. Then the carbon and hydrogen losses can be properly distributed between the volatile and non-volatile degradation products. Because nitrogen can be introduced into the system by direct reaction with some of its oxides always present in the atmosphere (18), it will be considered separately.

The sulfur distributions in the asphalts and water-soluble degradation products are shown in Figures 1 and 2. These curves closely parallel those of the change in the components themselves (15). The migration of the sulfur into the asphaltenes during the period in which the asphaltenes were increasing is readily apparent as is the gradual progressive transfer of sulfur-containing materials from the maltene fractions to the water-soluble degradation products.

Figures 3 and 4 contain the oxygen distributions for the two asphalts, considering the asphalts as entities, and the degradation products. All of the data are expressed as percentages of the original asphalt in order to have a common basis for comparison. A number of very interesting observations may be made from these curves. Both asphalts continuously increased in oxygen

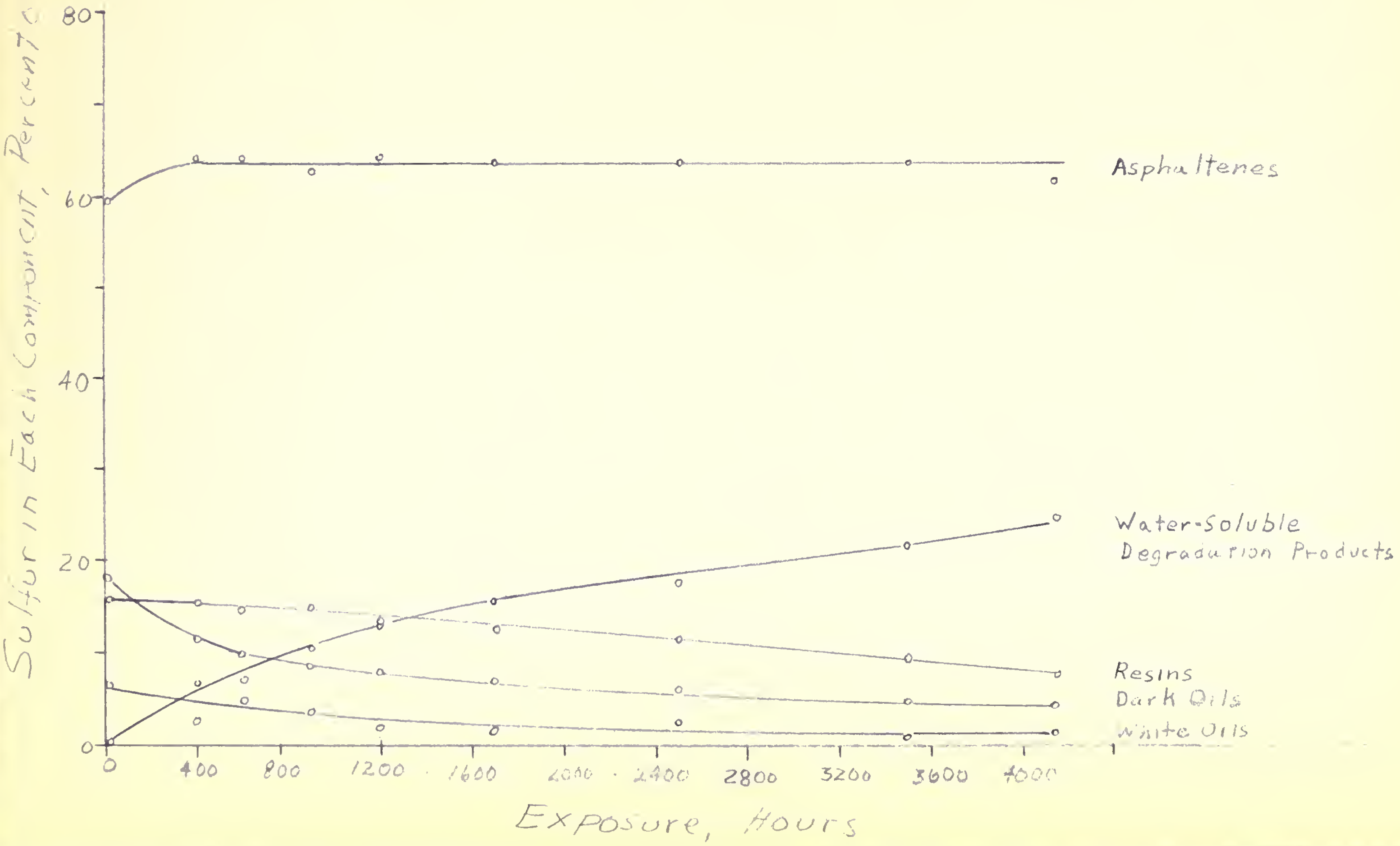
Sulfur Distribution
Asphalt I
22-1 Cycle

Figure 1



Sulfur Distribution

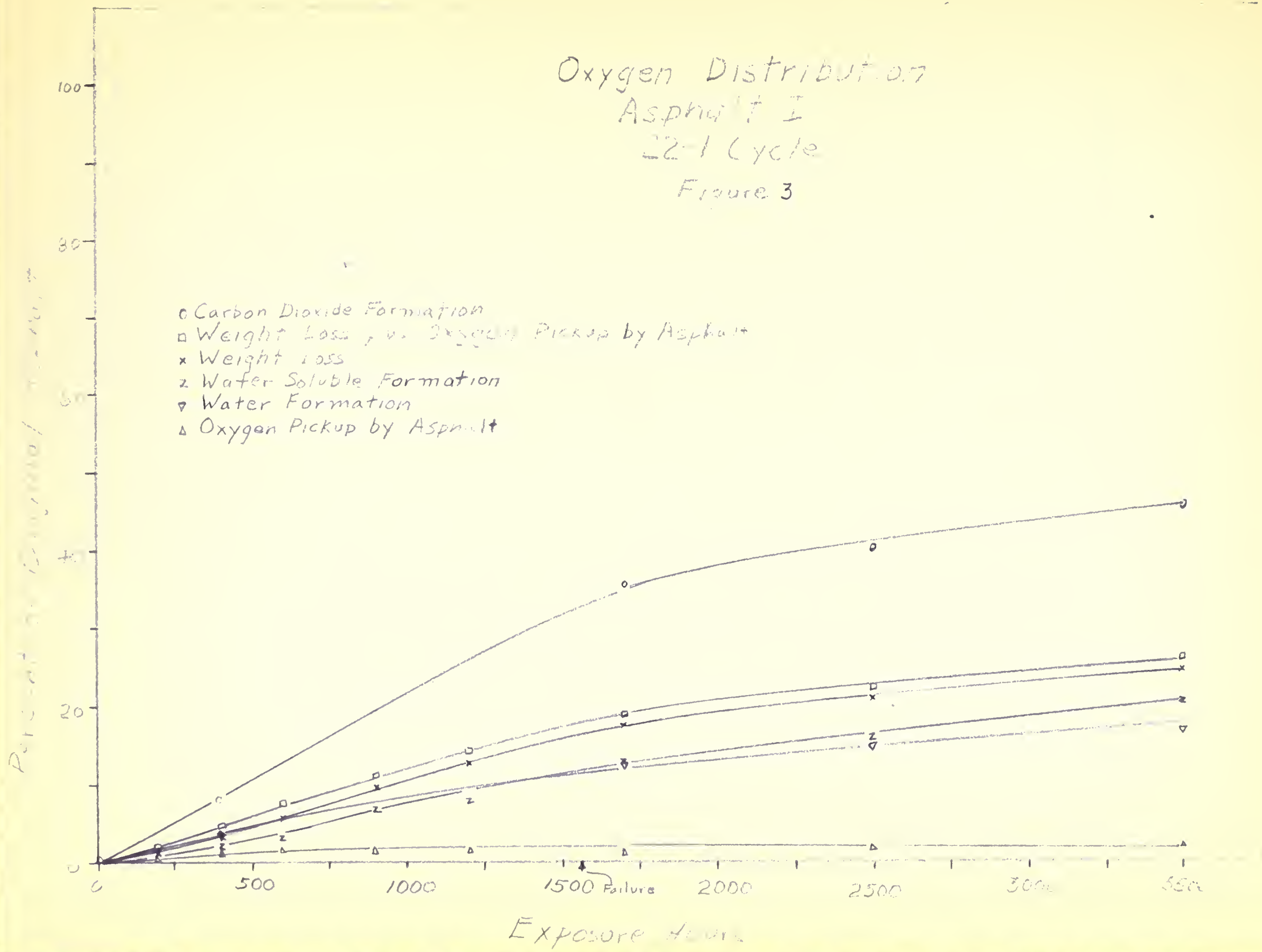
Asphalt II
22-1 Cycle
Figure 2



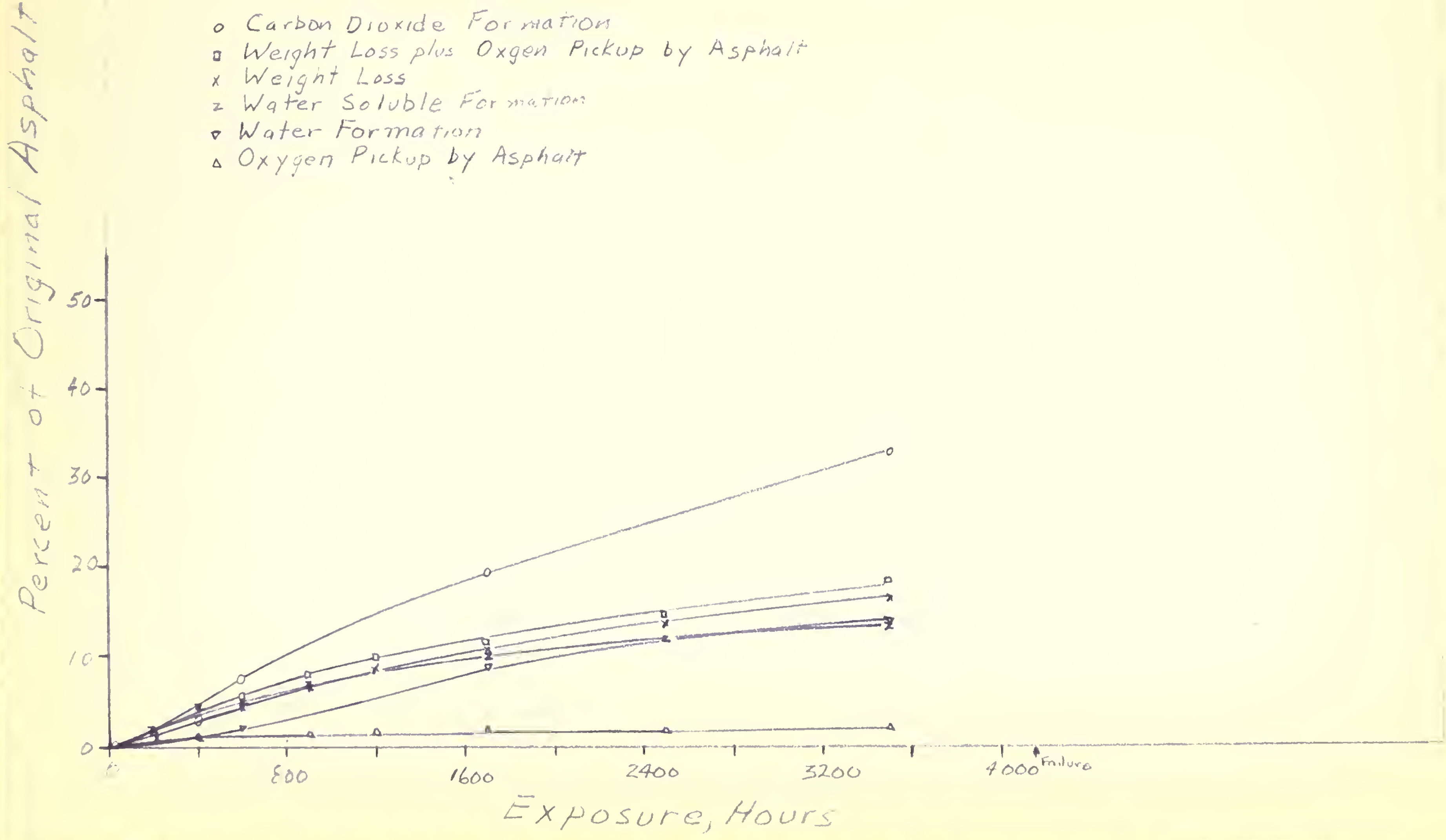
content despite the fact that they were losing considerable weight. At 3500 hours each had picked up just under two percent of oxygen. This oxygen pickup must be added to the actual weight losses to determine the net losses of the asphalts. The curves representing these figures are shown in Figures 3 and 4, also.

The curves labeled "water-solubles formation" were calculated from the quantity of sulfur lost from the asphalt and the percentage of sulfur found in the water-soluble degradation products. These curves are always lower than the weight-loss curves.

The carbon and hydrogen lost from the asphalt and not present in the non-volatile degradation products was assumed to have gone into the volatile products as CO_2 and H_2O. Each hydrogen molecule picked up roughly eight times its weight of oxygen and each carbon atom two and two-thirds times its weight. Thus very large quantities of CO_2 and H_2O were formed, as indicated in Figures 3 and 4. While the data during the early part of the exposure are in agreement with the previously mentioned results reported by Thurston and Knowles, as degradation progressed the proportions of CO_2 and water formed became significantly larger.


Oxygen Distribution
Asphalt I
22-1 Cycle
Figure 3

Oxygen Distribution
Asphalt II
22-1 Cycle
Figure 4



In the cases of both asphalts the nitrogen contents increased slightly and then leveled off as degradation progressed. The nitrogen increase may have come from the oxides of nitrogen in the atmosphere reacting with the unsaturated portions of the asphalt (18). However, the effect is small and of about the same order of magnitude as the errors involved in the nitrogen determination.

4.7 Outdoor Exposures

The results of the first 18 months of out-of-door exposures are reported in tables 6 and 7. The data* are incomplete, primarily in molecular weight and nitrogen measurements, and show less tendency toward specific trends than the more closely controlled laboratory exposures. However, there seemed to be a tendency of the molecular weights of the components of asphalt I to decrease while in asphalt II, those of only the asphaltenes decreased; those of the white oils increased (as in the laboratory exposures). Except for the resins in asphalt I, the carbon-hydrogen ratios of all of the components have remained fairly constant. All of the components have increased in oxygen content. The migrations of the sulfur and nitrogen

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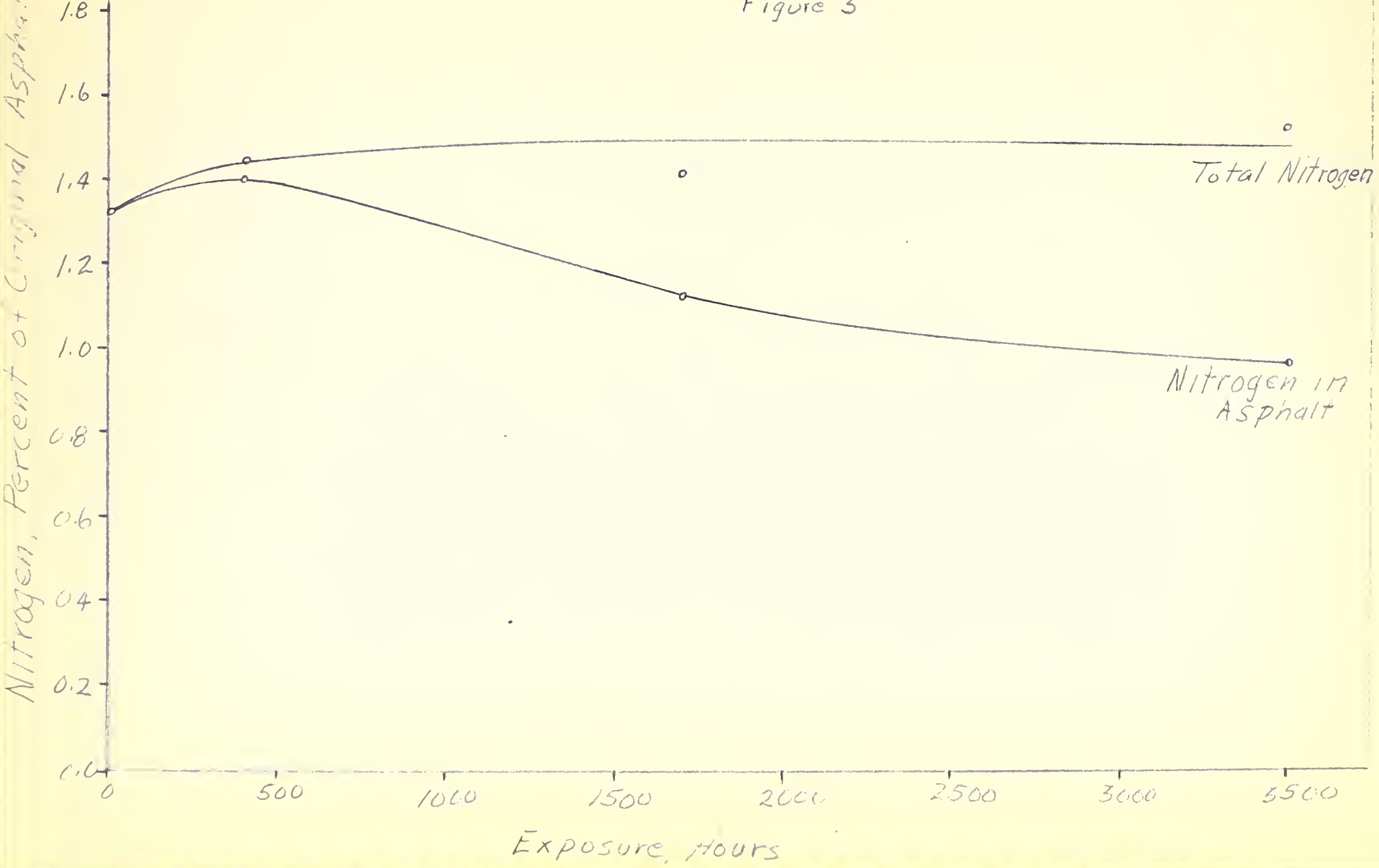
*These results are based on the analyses of individual specimens.

Nitrogen Content
Asphalt I
22-1 Cycle
Figure 5

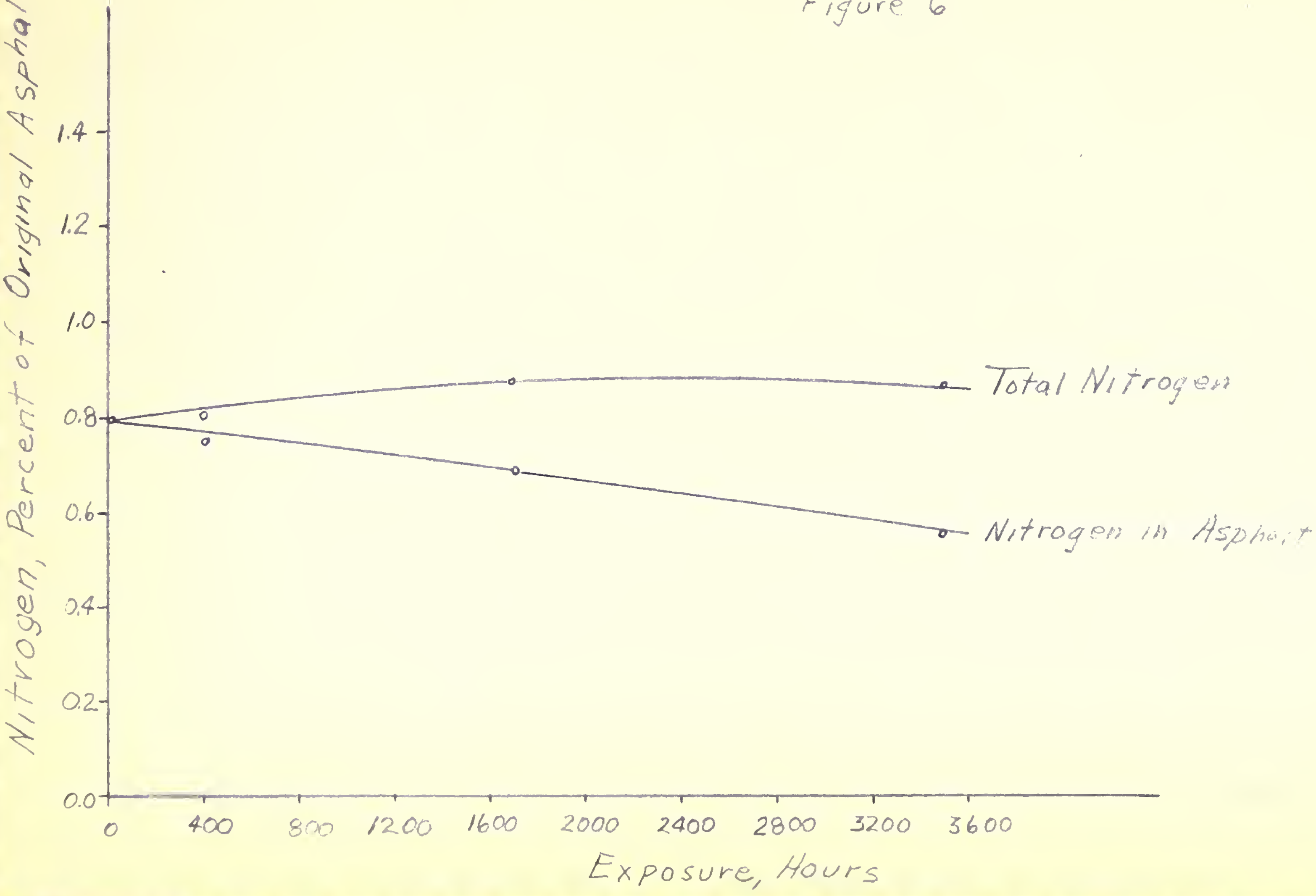


Nitrogen Content

Asphalt II

22-1 Cycle

Figure 6



compounds were erratic and little can be said about them. In general, possibly because individual specimens were involved, the results of the out-of-door exposures have not yielded significant trends.

5. SUMMARY AND CONCLUSIONS

When asphalts are exposed to light, heat and water numerous and complex chemical changes take place. Oxidation occurs and results in the formation of volatile and non-volatile degradation products. Over a third of the weight losses occur from the formation of CO_2 and H_2O. Two-thirds of the losses go into a water-soluble material that is highly acidic. A third product that is insoluble in water and n-pentane remains on the surface of the coatings.

Sulfur and nitrogen are in the molecules that polymerize during the early periods of exposure to form asphaltenes and resins and are also present in the water-soluble degradation products. Based on the constancy of sulfur, the water-soluble degradation products that are formed are almost equal in weight to the measured weight losses, and the volatile products are about two and one-half times the weight losses. A small increase in total nitrogen in the system during the early stages of degradation may indicate reaction of the asphalt with the oxides of nitrogen always present in the atmosphere.

Differences existed between the two asphalts and the manner in which they degraded. The principal differences were in the rate of degradation and in the molecular weight changes. Secondary differences were obvious in the way the sulfur- and nitrogen-containing molecules migrated through the asphalt and into the degradation products.

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