NATIONAL BUREAU OF STANDARDS REPORT

4732

REPORT ON THE EVALUATION OF TWENTY-ONE

COATING-GRADE ROOFING ASPHALTS

by

Sidney H. Greenfeld

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Jointly Sponsored by
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ABSTRACT

The properties and weathering characteristics (accelerated durability machines) of 21 coating-grade roofing asphalts were determined. Although the chemical and physical properties of these asphalts all fall within narrow ranges, their weathering characteristics were very different and their durabilities covered a six-fold range (51-9C cycle). Their weight losses at failure in the 51-9C cycle or at periods of exposure of 200, 400, 600 and 900 hours to the 22-1 cycle varied widely and were not related to any of the measured characteristics of the asphalts. Degradation, as determined by weight loss and change in components, is more rapid in the 22-1 cycle than in the 51-9C cycle, even though the latter results in a more rapid mechanical failure of the asphalt coatings.

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1. INTRODUCTION

Asphalt is not a single substance, but a complex mixture of high-molecular-weight organic compounds. Both the nature of the compounds and the proportions in which they are present determine the physical characteristics by which asphalts are known. Thus, by suitable processing of a single residuum, a large number of different asphalt products can be obtained from the same asphalt source. On the other hand, products of the same physical characteristics can be made from residua from different sources. However, there are always some basic differences in the degradation characteristics of these products, differences that can be related to the source.

Most of the early attempts to study the degradation of asphalts were limited to the examination of physical changes. Crack formation was by and large the most frequently used criterion, but "rust" formation [1]*, weight loss [2], decrease in solubility [3] and embrittlement [4] have also been used. All of these are merely physical manifestations of chemical changes that occur as degradation progresses. A number of investigators, however, have made efforts to measure the

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*The numbers in parentheses indicate references listed at the end of this report.

chemical changes directly by oxygen absorption (5) and composition of the degradation products (6). In all of these investigations it was indicated that asphalts from the various sources degraded differently.

As part of the study of the degradation of asphalts, samples of coating-grade asphalts were obtained from the major sources supplying asphalt in the United States. Nine asphalt producers and five roofing manufacturers contributed 21 samples. Eight samples were from west coast sources, seven were from the central part of the country and six were imported. With two exceptions, these asphalts were reported to be in commercial production.

2. MATERIALS AND METHODS

The 21 asphalts studied are described in Table 1. The physical data are those provided by the supplier, except where indicated. The chemical and component (7) analyses were determined by methods described in the appendix. The components are those described by Kleinschmidt (7) according to the method by which they are separated, as follows:

Asphaltenes - That fraction of the asphalt insoluble in n-pentane at room temperature.

White oils - That fraction of the n-pentane—soluble material in asphalt that is eluted from fuller's earth with n-pentane.

Dark oils - That fraction of the n-pentane-soluble material
in asphalt that is eluted from fuller's earth with methylene
chloride after the white oils have been removed with
n-pentane.

Asphaltic resins - That fraction of the n-pentane-soluble
material in asphalt that is eluted from fuller's earth with
methyl ethyl ketone after the dark oils have been removed
with methylene chloride. (The methyl ethyl ketone is saturated
with water.)

Cleanup - The material that is removed from the fuller's
earth with chloroform after the fuller's earth has been
deactivated by the water in the methyl ethyl ketone.

The ethanol extract, as its name implies, contains the mate-
rial extracted from the asphaltenes with 100 volumes/gram of hot
ethanol.

Each of the asphalts was melted in a 16-ounce, seamless
ointment can on a hot plate and maintained at about 420°F until
all entrained air and moisture were eliminated. Then ten ex-
posure specimens, 25 ±1 mil thick, were prepared by the hydraulic-
press method (8). The following day, four were exposed in accel-
erated durability machines to the 22-1* cycle, four to the

*22-1 cycle - 22 hours per day of arc light followed by one
 hour of soaking.

51-9C* cycle and two outdoors on the roof of the Industrial Building, National Bureau of Standards, facing due south at an inclination of 45°. The accelerated durability machines have been described previously (9).

Those specimens exposed outdoors were examined semi-annually and those exposed to the 51-9C cycle weekly with a high-voltage electric probe (8). Specimens were considered "failed" when failures occurred on a minimum of 50% of the surface of the coating, as determined through a 60-square grid on the spark photograph. The 22-1 cycle was used primarily to follow changes occurring in the components of the asphalts; hence, specimens were removed at 200, 400, 600 and 900 hours for analysis. The specimens exposed to the 51-9C cycle were analyzed at failure. None of the roof exposures has failed and, consequently, none has been analyzed.

3. RESULTS

The component changes occurring in each asphalt during exposure to the 22-1 and 51-9C cycles are reported in Table 2. For each asphalt the original analysis has been repeated for reference.

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*51-9C cycle - 22 hours per day of a sequence of 51 minutes of light followed by 9 minutes of cold (40°F) water spray.

TABLE 1. ASPHALT CHARACTERISTICS

(a) Central United States Asphalts

Asphalt	M200	Kansas	Kansas	Shallow Water	Oklahoma Illinois	Louisiana	Talco R-1240
Description	Illinois	Sweet Kansas	Sweet Kansas	Kansas	Okl-Ill Blend	Natchitoches	NE Texas
Soft. Pt., °F.	224	229	208	222	215	216	223
Pen., 32°F	11.2	7	11.5	17	14	10	11
Pen., 77°F	17.0	14.5	20.5	26	22	12	18
Pen., 115°F	26	21.5	36.9	41	46	22	28
Sp. Gr.	0.999	1.015[a]	1.008[a]	1.010	0.998[a]	1.007[a]	1.035
Duct., cm.	---	2.4	2.5	---	2.8	1.8	---
Loss on Heating, %	0.03	---	0	---	---	---	---
Flash, C.O.C., °F	600[a]	615[a]	600	615[a]	600[a]	575[a]	565
Oxygen, %	1.27	1.01	1.21	1.22	1.26	1.50	1.04
Sulfur, %	1.90	1.42	1.18	1.24	0.98	1.00	4.62
Nitrogen, %	0.53	0.73	0.89	0.79	0.62	0.61	0.38
Carbon, %	85.51	86.15	85.42	86.06	85.83	86.08	83.98
Hydrogen, %	10.29	10.00	10.33	10.61	10.04	10.52	9.83
Total, %	99.50	99.31	99.03	99.92	98.73	99.71	99.85
Asphaltenes,[b] %	38.4	37.5	36.7	36.4	36.9	38.2	43.2
Eth. Ext., %	0.7	0.3	0.3	0.8	0.5	0.3	0.4
Resins, %	9.9	11.9	9.4	9.7	12.8	10.0	6.9
Dark Oils, %	23.3	28.0	27.5	25.9	24.6	27.0	25.3
White Oils, %	24.4	19.5	22.5	24.8	21.0	22.4	20.2
Cleanup, %	---	1.3	1.3	0.6	2.5	0.7	1.1
Recovery, %	96.7	98.5	97.7	99.2	98.3	98.6	97.1

[a] Determined at the N.B.S.

[b] Includes ethanol extract.

TABLE 1. ASPHALT CHARACTERISTICS

(b) Western United States Asphalts

Asphalt	C210	C1175	810	1342	Envoy	Shell	Union	Ambit
Description	Santa Maria plus Virgin Lube Stock *(Huntington Beach)*	Wilmington plus Reclaim Lube Stock	Blown from 20/30 Los Angeles Basin	Santa Maria	Wilmington	Santa Maria	Santa Maria	Catalytic Santa Maria
Soft. Pt., °F	223	231	216	234a	216	230	230	216
Pen., 32°F	10	15a	1a	11a	10	11	14	9
Pen., 77°F	17	18	4	16	16	18	18	20
Pen., 115°F	30	36a	5a	19a	32	35	36	36
Sp. Gr.	1.015	1.023	1.047a	1.026a	1.035	1.028a	1.026a	1.030
Duct., cm.	---	1.5	0	---	4+	2.2	---	3.5
Loss on Heating, %	0.22	---	---	---	0.57	---	---	0.10
Flash, C.O.C., °F	495a	515	595a	505a	450	445	460	500
Oxygen, %	1.79	1.56	1.48	1.31	1.66	1.22	1.55	1.55
Sulfur, %	2.38	2.21	2.82	4.44	3.18	5.45	4.94	4.67
Nitrogen, %	1.18	1.13	1.44	1.00	1.30	1.56	1.28	1.48
Carbon, %	83.89	83.28	83.86	83.19	84.10	81.77	82.29	82.10
Hydrogen, %	10.29	10.02	9.71	10.23	10.31	10.28	10.14	10.04
Total, %	99.53	98.20	99.31	100.17	100.55	100.28	100.20	99.84
Asphaltenes, b %	39.0	39.8	44.7	44.6	44.1	42.9	43.7	41.8
Eth. Ext., %	2.8	0.7	1.8	0.9	---	---	---	---
Resins, %	10.3	9.5	13.6	9.6	8.6	8.4	8.9	8.6
Dark Oils, %	18.2	20.0	23.5	21.9	19.8	22.8	21.8	23.6
White Oils, %	27.4	27.3	12.4	21.1	26.6	25.2	24.4	26.8
Cleanup, %	---	2.0	1.0	0.5	0.6	Trace	0.05	0.05
Recovery, %	97.7	99.3	97.0	98.6	99.7	99.3	98.9	100.9

a Determined at the N.B.S.
b Includes ethanol extract.

TABLE 1. ASPHALT CHARACTERISTICS

(c) Foreign Asphalts

Asphalt	Middle East	Columbia	East Ven.	Lagunillas	Catalytic	Mexico
	11239	Standard Oil	54-3383	54-3384	465790	#12
Description	Kuwait				Lagunillas 1/2% P_2O_5	
Soft. Pt., °F	228	205	226	220	221	196[a]
Pen., 32°F	8	14.5	8	8	11	8[a]
Pen., 77°F	11	20.7	13	13	19	18[a]
Pen., 115°F	20	34.6	20	22	31	34[a]
Sp. Gr.	1.031	1.003[a]	1.024	1.032	1.028	1.076[a]
Duct., cm.	1.5	2.8	2.3	2.5	----	----
Loss on Heating, %	----	0.006	0.01	Tr.	----	----
Flash, C.O.C., °F	565	540	560	550	565[a]	505[a]
Oxygen, %	1.14	1.39	1.19	1.25	1.31	0.71
Sulfur, %	4.78	1.09	1.53	2.98	2.89	5.49
Nitrogen, %	0.55	0.67	0.62	0.78	0.71	0.68
Carbon, %	82.21	84.21	85.63	84.22	83.14	81.97
Hydrogen, %	9.90	10.50	9.69	9.94	10.10	9.58
Total, %	98.58	100.06	98.66	99.17	98.30	98.56
Asphaltenes,[b] %	45.7	36.1	38.7	41.8	42.1	42.3
Eth. Ext., %	0.6	0.5	0.4	0.4	1.17	0.6
Resins, %	7.3	11.0	8.0	9.1	10.8	9.0
Dark Oils, %	25.5	21.7	22.8	25.2	22.9	25.2
White Oils, %	18.8	27.0	28.3	20.0	22.7	21.6
Cleanup, %	0.5	1.8	0.9	1.3	0.4	0.6
Recovery, %	98.4	98.1	99.1	97.8	98.9	99.3

[a] Determined at the N.B.S.
[b] Includes ethanol extract.

C1175 - 25 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	540
Asphaltenes[a], %	40.5	48.5	50.5	53.3	52.6	50.3[c]
Resins, %	9.5	9.6	8.7	9.1	7.3	10.1
Dark Oils, %	20.0	13.5	11.8	8.7	7.1	10.6
White Oils, %	27.3	27.0	23.3	22.6	20.0	21.4
Cleanup, %	2.0	0.9	2.3	1.3	1.2	Trace
Loss, %	0.0	0.9	3.0	5.9	9.6	5.8
Ethanol Ext., %	0.7	4.1	4.6	4.7	_[b]	_[b]
Recovery	99.3	100.4	99.6	100.9	97.8	98.2

Middle East - 38 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	832[d]
Asphaltenes[a], %	46.3	54.2	60.2	58.2	57.0	55.1
Resins, %	7.3	9.6	7.5	8.3	8.4	10.1
Dark Oils, %	25.5	16.3	14.1	12.1	11.6	13.4
White Oils, %	18.8	17.2	16.1	14.2	13.8	14.0
Cleanup, %	0.5	0.3	0.2	0.1	0.2	0.1
Loss, %	0.0	1.3	3.1	5.1	7.5	7.5
Ethanol Ext., %	0.6	_[b]	2.8	_[b]	2.2	2.4
Recovery	98.4	98.9	101.2	98.0	98.5	99.5

Talco - 43 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	940
Asphaltenes,[a] %	43.6	48.2	51.3	51.9	53.7	53.2[e]
Resins, %	6.9	8.8	8.1	8.0	8.9	8.7
Dark Oils, %	25.3	20.4	17.9	17.7	13.4	14.0
White Oils, %	20.2	19.1	19.3	18.5	16.3	15.0
Cleanup, %	1.1	0.6	0.9	0.7	1.3	0.4
Loss, %	0.0	0.7	1.8	3.0	5.4	8.2
Ethanol Ext., %	0.4	1.3	2.0	2.3	2.7	_[b]
Recovery	97.1	97.8	99.3	99.9	99.4	99.5

[a]Includes Ethanol Extract.
[b]Not determined.
[c]Based on analysis of two specimens.
[d]One specimen with premature failure excluded.
[e]Based on analysis of one specimen.

TABLE 2. CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-2)

C210 - 43 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	945
Asphaltenes,[a] %	41.8	46.9	48.5	48.7	48.7	56.5
Resins, %	10.3	11.4	11.4	10.6	9.6	10.4
Dark Oils, %	18.2	13.6	11.3	10.0	8.9	10.3
White Oils, %	27.4	24.5	22.9	21.6	20.3	22.2
Cleanup, %	-b	-b	-b	-b	-b	0.2
Loss, %	0.0	1.1	3.1	5.9	9.7	-b
Ethanol Ext., %	2.8	3.6	-b	4.9	-b	-b
Recovery	97.7	97.5	97.2	100.9	97.2	99.6

Envoy - 44 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	959
Asphaltenes,[a] %	44.1	47.0	48.2	52.6	52.4	50.2
Resins, %	8.6	10.4	10.8	9.1	7.6	9.1
Dark Oils, %	19.8	17.3	14.5	11.9	9.7	10.3
White Oils, %	26.6	24.6	23.4	21.8	22.1	22.1
Cleanup, %	0.6	Trace	0.2	0.03	Trace	0.2
Loss, %	0.0	0.5	2.3	4.3	8.0	7.7
Ethanol Ext., %	-b	-b	3.00	-b	4.81	-b
Recovery	99.7	99.8	99.4	99.7	99.8	99.6

Lagunillas - 47 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1030
Asphaltenes,[a] %	42.2	45.9	48.3	47.2	48.7	50.7
Resins, %	9.1	10.5	10.3	11.1	12.3	12.1
Dark Oils, %	25.2	19.6	18.4	17.8	14.0	16.1
White Oils, %	20.0	19.3	18.4	18.5	17.8	17.3
Cleanup, %	1.3	0.9	1.3	0.9	1.9	0.3
Loss, %	0.0	1.3	2.8	3.7	4.6	4.4
Ethanol Ext., %	0.4	1.3	1.3	1.4	1.7	-b
Recovery	97.8	97.5	99.5	99.2	99.3	100.9

[a]Includes Ethanol Extract.   [b]Not determined.

TABLE 2.   CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-3)

East Venezuelan - 47 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1033
Asphaltenes,[a] %	39.1	43.1	44.0	45.2	45.5	47.0
Resins, %	8.0	9.9	10.0	8.7	10.1	9.4
Dark Oils, %	22.8	17.7	16.0	14.9	12.9	14.9
White Oils, %	28.3	24.8	24.5	23.5	23.3	24.0
Cleanup, %	0.9	1.3	1.2	1.9	1.2	0.1
Loss, %	0.0	1.5	3.6	4.9	6.0	5.1
Ethanol Ext., %	0.4	1.5	1.8	1.7	1.7	_[b]
Recovery	99.1	98.3	99.3	100.1	99.0	100.5

Ambit - 53 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1170
Asphaltenes,[a] %	41.8	46.8	48.7	52.4	54.0	53.5
Resins, %	8.6	9.0	10.8	8.5	7.7	7.6
Dark Oils, %	23.6	21.0	18.2	13.9	10.6	10.4
White Oils, %	26.8	22.5	20.3	21.5	20.2	17.1
Cleanup, %	0.05	0.2	0.2	0.03	0.02	0.1
Loss, %	0.0	0.2	1.3	3.2	6.8	10.8
Ethanol Ext., %	_[b]	_[b]	3.75	_[b]	5.72	5.5
Recovery	100.9	99.7	99.5	99.5	99.3	99.5

C1342 - 57 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1257
Asphaltenes,[a] %	45.5	50.0	52.2	53.4	53.4	51.4[c]
Resins, %	9.6	11.4	11.3	10.1	8.9	9.7
Dark Oils, %	21.9	17.3	13.2	12.0	10.7	9.8
White Oils, %	21.1	16.4	16.4	16.8	16.6	15.4
Cleanup, %	0.5	0.5	0.2	0.3	0.1	Trace
Loss, %	0.0	0.9	4.3	5.6	9.8	12.5
Ethanol Ext., %	0.9	_[b]	5.2	_[b]	5.3	_[b]
Recovery	98.6	96.5	97.6	98.2	99.5	98.8

[a]Includes Ethanol Extract.   [c]Based on analysis of one specimen.
[b]Not determined.

TABLE 2. CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-4)

Catalytic - 68 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1493
Asphaltenes,[a] %	42.1	46.0	46.9	48.3	47.0	47.1
Resins, %	10.8	12.0	12.1	10.9	11.1	7.6
Dark Oils,	22.9	20.6	18.8	17.0	15.6	12.9
White Oils, %	22.7	20.6	19.8	19.0	19.5	22.4
Cleanup, %	0.4	0.3	0.2	0.4	0.3	0.2
Loss, %	0.0	0.5	2.8	4.2	7.0	9.7
Ethanol Ext., %	1.2	-[b]	3.9	-[b]	2.8	-[b]
Recovery	98.9	100.1	100.5	98.8	100.5	99.9

Shallow Water - 72 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1589
Asphaltenes,[a] %	37.2	40.8	42.6	44.5	44.5	42.6
Resins, %	9.7	13.4	13.6	11.4	10.7	8.4
Dark Oils, %	25.9	22.9	19.3	17.5	16.3	14.6
White Oils, %	24.8	22.0	20.3	19.6	19.3	21.5
Cleanup, %	0.6	0.3	0.5	0.7	0.7	0.7
Loss, %	0.0	0.5	2.4	3.9	6.9	11.9
Ethanol Ext., %	0.8	-[b]	2.8	-[b]	2.7	-[b]
Recovery	98.2	99.9	98.7	97.6	98.4	99.7

M200 - 75 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1650
Asphaltenes,[a] %	39.1	43.3	44.5	45.0	45.3	49.0
Resins, %	9.9	10.9	10.7	10.6	10.0	10.3
Dark Oils, %	23.3	18.3	16.9	15.7	14.4	15.9
White Oils, %	24.4	23.6	23.0	23.0	21.3	24.3
Cleanup, %	-[b]	-[b]	-[b]	-[b]	-[b]	0.9
Loss, %	0.0	0.7	2.2	3.9	6.3	-[b]
Ethanol Ext., %	0.7	-[b]	1.6	-[b]	2.0	-[b]
Recovery	96.7	96.8	98.3	98.2	97.3	100.4

[a]Includes Ethanol Extract.   [b]Not determined.

TABLE 2. CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-5)

C810 - 81 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1773
Asphaltenes,[a] %	46.5	50.6	52.9	52.5	53.8	52.1
Resins, %	13.6	15.9	15.2	16.8	16.2	16.8
Dark Oils, %	23.5	20.3	18.8	17.4	15.6	15.8
White Oils, %	12.4	11.9	11.8	11.2	10.9	11.0
Cleanup, %	1.0	0.2	0.3	0.2	0.2	0.1
Loss, %	0.0	0.7	1.3	1.7	2.4	4.0
Ethanol Ext., %	1.2	-[b]	3.5	-[b]	5.5	-[b]
Recovery	97.0	99.6	100.3	99.8	99.1	99.8

Louisiana - 84 Days

Components, %	22-1 Cycle Time, Hours					51-9C Cycle Final Failure
	0	200	400	600	900	1844
Asphaltenes,[a] %	38.5	42.1	42.6	43.7	45.3	43.1
Resins, %	10.0	13.0	12.4	10.5	11.0	9.5
Dark Oils, %	27.0	22.3	20.7	19.7	16.9	18.1
White Oils, %	22.4	20.3	20.3	20.5	20.2	19.5
Cleanup, %	0.7	0.8	0.3	0.4	0.3	0.6
Loss, %	0.0	0.9	2.4	3.9	5.7	8.6
Ethanol Ext., %	0.3	-[b]	1.2	-[b]	0.9	0.8
Recovery	98.6	99.4	98.3	98.5	99.4	99.4

Columbia - 86 Days

Components, %	22-1 Cycle Time, Hours					51-9C Cycle Final Failure
	0	200	400	600	900	1903
Asphaltenes,[a] %	36.6	41.4	41.2	44.5	43.5	42.8
Resins, %	11.0	12.1	12.8	10.3	11.4	9.4
Dark Oils, %	21.7	17.3	16.4	14.0	12.3	12.5
White Oils, %	27.0	27.5	24.6	23.9	25.8	23.2
Cleanup, %	1.8	0.4	0.5	0.3	0.1	0.1
Loss, %	0.0	1.1	3.5	5.4	6.1	12.2
Ethanol Ext., %	0.5	-[b]	1.5	-[b]	2.0	3.9
Recovery	98.1	99.8	99.0	98.4	99.2	100.2

[a]Includes Ethanol Extract.　　[b]Not determined.

TABLE 2. CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-6)

Kansas 1 - 87 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1912[c]
Asphaltenes,[a] %	37.8	44.0	46.7	45.4	49.0	47.1
Resins, %	11.9	12.8	11.7	12.1	11.4	11.0
Dark Oils, %	28.0	21.7	19.6	18.6	16.9	16.5
White Oils, %	19.5	18.9	17.4	16.3	15.0	15.4
Cleanup, %	1.3	0.6	0.2	0.5	0.3	0.6
Loss, %	0.0	0.6	2.4	3.9	6.5	8.9
Ethanol Ext., %	0.3	_b	1.2	_b	1.5	1.8
Recovery	98.5	98.6	98.0	97.6	99.1	99.5

Kansas 2 - 88 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1933
Asphaltenes,[a] %	37.0	43.2	46.2	46.3	47.0	44.5
Resins, %	9.4	12.2	11.0	12.0	11.2	9.7
Dark Oils, %	27.5	22.4	19.8	17.9	16.1	16.5
White Oils, %	22.5	19.9	18.1	18.0	17.3	16.4
Cleanup, %	1.3	0.7	0.4	0.1	0.3	0.7
Loss, %	0.0	0.7	2.7	4.2	7.3	11.3
Ethanol Ext., %	0.3	_b	_b	_b	1.7	1.8
Recovery	97.7	99.1	98.2	98.5	99.2	99.1

Union - 90 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	1966
Asphaltenes,[a] %	43.7	47.3	48.1	51.8	51.6	52.0
Resins, %	8.9	10.0	10.6	9.7	9.1	8.4
Dark Oils, %	21.8	19.2	17.8	12.9	12.0	9.7
White Oils, %	24.4	22.2	21.2	20.9	19.8	15.3
Cleanup, %	0.05	0.6	0.04	0.1	0.03	0.1
Loss, %	0.0	0.06	1.7	4.1	7.1	13.8
Ethanol Ext., %	_b	_b	2.97	_b	3.53	_b
Recovery	98.9	99.4	99.4	99.5	99.6	99.3

[a]Includes Ethanol Extract. [c]One specimen with premature failure
[b]Not determined. excluded.

TABLE 2. CHANGE IN ASPHALTS DURING EXPOSURE (CONTINUED-7)

Mexico #12 - 95 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	2186[c]
Asphaltenes,[a] %	42.9	48.5	50.4	52.2	53.2	54.6
Resins, %	9.0	10.0	10.3	9.9	10.0	7.9
Dark Oils, %	25.2	21.9	19.1	17.1	14.6	12.5
White Oils, %	21.6	17.5	16.7	15.3	14.8	13.8
Cleanup, %	0.6	0.8	0.4	0.7	0.0	0.2
Loss, %	0.0	0.6	2.1	3.9	8.0	10.3
Ethanol Ext., %	0.6	_[b]	1.8	_[b]	2.5	1.8
Recovery	99.3	99.3	100.0	99.1	100.6	99.3

Shell - 101 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	2218
Asphaltenes,[a] %	42.9	45.5	47.4	49.6	49.7	51.2
Resins, %	8.4	9.5	10.2	9.9	9.0	7.5
Dark Oils, %	22.8	20.3	17.3	13.7	12.1	9.5
White Oils, %	25.2	23.2	22.2	21.3	21.2	15.3
Cleanup, %	Trace	0.3	0.3	0.4	0.03	Trace
Loss, %	0.0	0.04	2.2	4.3	7.3	16.6
Ethanol Ext., %	_[b]	_[b]	3.11	_[b]	3.40	4.2
Recovery	99.3	98.8	99.6	99.2	99.3	100.1

Oklahoma - Illinois - 150 Days

Components, %	22-1 Cycle Time, hours					51-9C Cycle Final Failure
	0	200	400	600	900	3304
Asphaltenes,[a] %	37.4	43.5	42.5	45.5	46.0	43.4
Resins, %	12.8	12.4	12.4	12.1	11.2	9.3
Dark Oils, %	24.6	19.7	19.6	16.7	15.6	13.1
White Oils, %	21.0	22.5	19.7	18.9	19.2	16.3
Cleanup, %	2.5	0.5	0.8	0.9	0.7	1.0
Loss, %	0.0	0.3	2.5	4.3	6.8	15.4
Ethanol Ext., %	0.5	_[b]	1.4	_[b]	1.8	0.9
Recovery	98.3	98.7	97.5	98.4	99.5	98.5

[a]Includes Ethanol Extract.
[b]Not determined.
[c]One specimen with premature failure excluded.

4. DISCUSSION OF RESULTS

Variations in Properties and Composition

Of the 21 asphalts evaluated, only one (C810) was represented by its supplier as being other than a typical coating-grade roofing asphalt. However, C810 was included in the program because it was an asphalt low in white oils, but normal in dark oils. Its resins and asphaltenes, consequently, were higher than average. The Mexico #12 asphalt had a low softening point and a high penetration index.

Despite the fact that these 20 asphalts (excluding C810) came from over half the surface of the earth, their properties are not too dissimilar. The softening points, penetrations, specific gravities and ductilities fell within narrow ranges. The west coast asphalts had relatively low flash points and high losses-on-heating-at-325°F.

The sulfur contents of the Talco, Mexico #12, Middle East and west coast asphalts tended to be higher than the others and the nitrogen content of the west coast asphalts was high, as well; but the remainder of the elements were within rather narrow ranges. For example, the carbon-hydrogen ratios for all of the asphalts ranged from 0.66 to 0.74, but Kansas 1 and Kansas 2, asphalts from the same group of fields, were 0.74 and 0.69 respectively. Hence, the variations in carbon-hydrogen ratio

among all of the asphalts are not much wider than the varia-
tion in a single source. If the properties of all of the
asphalts, except C810 and Mexico #12, are averaged, the results
might be considered a typical asphalt, as shown in Table 3.

TABLE 3.   PROPERTIES OF A TYPICAL ASPHALT

Softening Point, °F	220
Penetration at 32°F	12
at 77°F	19
at 115°F	33
Specific Gravity	1.01
Ductility, cm.	2.8
Loss at 325°F, %	0.2
Flash Point (C.O.C.), °F	530
Chemical Analysis:	
Oxygen, %	1.34
Sulfur, %	3.21
Nitrogen, %	0.97
Carbon	84.00
Hydrogen, %	10.10
Total, %	99.62
Carbon/Hydrogen Ratio	0.69
Component Analyses:	
Asphaltenes, %	40.9[a]
Ethanol Extract, %	1.6
Resins, %	9.9
Dark Oils, %	23.1
White Oils, %	23.5
Cleanup, %	1.3
Recovery, %	100.3

[a] Includes Ethanol Extract.

Variations in Behavior

When an asphalt is exposed to light, heat and water, marked
changes take place (8). The light induces the absorption of
and reaction with oxygen, resulting in the formation of more

polar molecules. Some of these products are water soluble and
result in weight losses when the asphalt is washed. Some are
volatile and escape into the atmosphere as the reaction progresses.
Others become pentane-insoluble and remain with the asphaltenes
when the asphalt is separated into its components. Some of
these can be extracted from the asphaltenes with hot ethanol.
The rates of the reactions are increased as the temperature is
elevated, as is that of a polymerization of some of the lighter
components to form asphaltenes. The loss of the pentane-soluble
components as water-solubles and volatiles and through polymer-
ization tends to harden and embrittle the asphalt to the point
where even small temperature changes will make it crack.

The changes taking place during exposure were followed
very closely in asphalts C210 and M200 and will be reported in
detail in two other reports. The changes taking place during
the first 900 hours of exposure to the 22-1 cycle of all 21
asphalts are reported here. Again, as in the physical and
chemical characteristics of the asphalts, there were differ-
ences among the 21 asphalts, but the trends were all nearly the
same. The asphaltenes increased rather rapidly during the first
200 to 400 hours and then remained almost constant. The
ethanol extract increased progressively and tended to level
off or start decreasing by 900 hours. The dark oils decreased
to about one-half to two-thirds of their original value in

900 hours, while the white oils decreased less rapidly. The
resins increased during the first 200 to 400 hours and then re-
mained constant or decreased slightly. Water-solubles formed
slowly during the first 200 hours, but more rapidly afterward.
It seems that in all instances, the asphaltenes, ethanol extract
and water-solubles increased at the expense of the oils. Be-
cause the determinations at each exposure interval were made
on individual specimens, irregularities in the results of as
much as 1% must be ignored.

Specimens of these 21 asphalts were also exposed to the
51-9C cycle until crack failures occurred. The time to failure
and composition and weight loss at failure are recorded with
each asphalt in Table 2. The time to failure and loss at
failure are again tabulated in Table 4 along with the weight
losses at the various intervals of exposure in the 22-1 cycle.

A number of interesting comparisons can be made among the
data in Tables 2 and 4. These are best considered when the
conditions of exposure are kept in mind. In the 22-1 cycle, the
specimens are exposed to the arc light for 22 hours daily,
about 21.5 of which are at 140 ±5°F. Then the specimens are
removed from the machines and soaked for 45 minutes in one
water bath at room temperature. A mild thermal shock results
during the immersion. The specimens are transferred to another

TABLE 4. COMPARISON OF THE DURABILITY AND WEIGHT LOSS
AT FAILURE IN THE 51-9C CYCLE WITH WEIGHT
LOSS IN THE 22-1 CYCLE.

Asphalt	Final Failure[a] 51-9C Cycle		Weight Loss in 22-1 Cycle		
	Days	Wt. Loss, %	10 Days %	20 Days %	40 Days %
C1175	25	5.8	0.9	3.0	9.6
Middle East	38	6.8	1.3	3.1	7.5
Talco	43	8.2	0.7	1.8	5.4
C210	43	---[b]	1.1	3.1	9.7
Envoy	44	7.7	0.5	2.3	8.0
E. Ven.	47	5.1	1.5	3.6	6.0
Lagunillas	47	4.4	1.3	2.8	4.6
Ambit	53	10.8	0.2	1.3	6.8
C1342	57	12.5	0.9	4.3	9.8
Catalytic	68	9.7	0.5	2.8	7.0
Shallow Water	72	11.9	0.5	2.4	6.9
M200	75	---[b]	0.7	2.2	6.3
C810	81	4.0	0.7	1.3	2.4
Louisiana	84	8.6	0.9	2.4	5.7
Columbia	86	12.2	1.1	3.5	6.1
Kansas - 1	87	9.3	0.6	2.4	6.5
Kansas - 2	88	11.3	0.7	2.7	7.3
Union	90	13.8	0.6	1.7	7.1
Mexico - 12	95	10.3	0.6	2.2	7.3
Shell	101	16.6	0.4	2.2	7.3
Oklahoma	150	15.4	0.3	2.5	6.8

[a] 50% Failure.   [b] Not Determined.

water bath for 15 minutes and then replaced in the accelerated durability machines, where the arc is turned on after about an hour. This cycle may be characterized as one having a long period of exposure at elevated temperature and one thorough washing period. In the 51-9C cycle, the specimens are exposed for 22 hours to a sequence of 51 minutes of dry light followed by nine minutes of light and cold ($40°F$) water spray. The specimens are at $140 \pm 5°F$ for only about 20 minutes each hour. The nine minutes of cold-water spray each hour do not provide sufficiently thorough washing to remove all of the water-soluble degradation products formed. This cycle may be characterized as one providing frequent thermal shocks and incomplete removal of the degradation products. The average operating temperature is lower than in the 22-1 cycle.

With these characteristics in mind, an examination of Table 2 yields some interesting facts: 1) In general, the increase in asphaltenes is less rapid in the 51-9C cycle at failure than would have been predicted from the changes observed in the 22-1 cycle. Since this increase is generally considered to be a bulk, thermal reaction, i.e., polymerization, the higher average temperature of the 22-1 cycle would be expected to yield a more rapid increase in asphaltenes. 2) The weight losses at failure in the 51-9C cycle are generally less than would have been predicted from the losses in the 22-1 cycle. The cold-water spray

is insufficient to remove all of the water-soluble products that form during the 51 minutes of dry light exposure. Those that are not removed tend to screen the asphalt and protect it from the light. The lower average temperature of the specimens also tends to slow the reactions. 3) The resins, dark and white oils in the specimens at failure in the 51-9C cycle tend to be higher than would be predicted from the 22-1 cycle data. This condition, of course, follows from the previous two, for these three components are the sources for the increase in asphaltenes and the formation of the water-soluble degradation products.

While the above discussion applies qualitatively to the data, no quantitative correlation seems to exist between the time to failure in the 51-9C cycle and the weight losses in either the 51-9C or the 22-1 cycles. If such a correlation existed at one period of exposure, it would not necessarily exist at others, for the weight-loss vs. exposure curves for the various asphalts had different slopes.

The 21 asphalts varied widely in durability in the 51-9C cycle, there being exactly a sixfold difference between the most and least durable. However, if the most durable and two least durable asphalts are not considered, the other 18 differ by little more than a factor of two. There is a gradual change in durability from a minimum of 25 days to a maximum of 150

days, with the only sharp break occurring between the two most durable asphalts. Those asphalts produced from crudes in the Mid-Continent basin are consistently among the more durable. But west coast asphalts varied widely in durability. The four South American asphalts were in the middle-durability range, with Venezuelan at the lower end and Columbian near the upper. The addition of the P_2O_5 catalyst to the Lagunillas stock before blowing increased somewhat the durability of that asphalt.

The four replicate specimens of only eight of the asphalts failed simultaneously, but for seven of the asphalts the failure was spread over an interval of 200 hours. For the others, failures occurred over a 100-hour interval. The uniformity of failure seems to be a characteristic of the asphalt, the cycle, and the arbitrary failure point, and is related to the nature of the strains and the relative ability of the asphalts to relieve the stresses set up during weathering.

5. SUMMARY AND CONCLUSIONS

Twenty-one coating-grade roofing asphalts from the United States, Mexico, South America, and the Middle East were exposed in accelerated durability machines to the 22-1 and 51-90 cycles, and the changes in components occurring during exposure determined. The compositions of the asphalts varied within narrow limits, and the changes in components on exposure differed only

in degree. The weight losses varied widely and the durability
in the 51-9C cycle varied over a six-fold range, from 25 to 150
days. There was no correlation between durability and any of the
properties of the asphalts that were measured.

5. APPENDIX

Methods of Analysis

(1) <u>Oxygen</u>

The physical changes that occur during weathering have been observed for many years and the physical breaking of the coating has been used as a criterion of failure. However, little work has been done on the chemical changes that are simultaneously occurring. A number of publications have appeared on the absorption of oxygen by asphalt during weathering (10, 11, 12) with sufficiently interesting results to indicate that oxidation is one of the processes involved in the degradation of asphalt. Accordingly, a method for the direct determination of oxygen was developed, based on the Aluise (13) modification of the Unterzaucher (14) method. The apparatus was modified by the addition of a low-temperature trap (15) to remove the non-acidic sulfur compounds that were formed during the combustion. Because pyrolytic hydrogen, as well as carbon monoxide, liberated iodine from the iodine pentoxide the results were invariably high. Therefore, a modification of the method published by Dundy and Stehr (16) was adopted. The iodine was absorbed in a tube of sodium thiosulfate followed by anhydrone and P_2O_5 and the carbon dioxide was absorbed in an ascarite filled tube and weighed. Thus, the final apparatus consisted of a cylinder of Linde High Purety nitrogen followed by a purefication system, bubble

counter, drying tube, combustion tube and reaction furnace as published by Aluise (13), a low-temperature trap and ascarite tube as in Hinkel's (15) apparatus, an iodine pentoxide furnace as in Aluise's (13) apparatus and a sodium thiosulfate tube and ascarite tube as proposed by Dundy (16). The particular type of ascarite tube used was developed by Corwin (17). It consisted of a stainless steel tube with teflon valves on each end, thus reducing the opportunity for ambient gases to diffuse through the tube while it was being weighed.

Because the details of the apparatus and procedure must be given rather meticulously in order to have any significance, they will not be reported here. The interested reader is referred to the references for this information. However, in order to permit evaluation of the data, results on pure compounds are reported in Table A-I and reproducibility figures are presented in Table A-II.

TABLE A-I. ACCURACY OF OXYGEN DETERMINATIONS

	Percent Oxygen	
Compound	Found	Theory
Benzoic Acid	26.2	26.2
Sucrose	51.0	51.4
Cystine	26.87	26.62
Acetanilide	11.78	11.83

TABLE A-II. REPRODUCIBILITY OF RESULTS

Material	Oxygen Control Percent		
	1	2	Ave.
Middle East Asphalt	1.15	1.13	1.14
C-3500 - Asphaltenes	5.36	5.34	5.35
C-3500 - Resins	5.97	5.93	5.95
C-3500 - Dark Oils	2.42	2.42	2.42
C-3500 - White Oils	0.11	0.09	0.10
C-3500 - Water Soluble	33.08	33.02	33.05

(2) Carbon and Hydrogen

The principal element in all of the compounds in asphalt is carbon. In combination with hydrogen it represents more than 90% of the asphalt. The ratio of carbon to hydrogen has proved to be a satisfactory means of characterizing the various homologous series of compounds in petroleum; and carries its significance into the heavy asphalt fractions. For example, the following ratios represent the important classes of petroleum compounds.

TABLE A-III. CARBON-HYDROGEN RATIOS

Ratio	Compounds
0.5	paraffins
0.5	naphthenes, olefins
0.5 - 0.6	polyolefins
0.8 - 0.9	porphyrins
1.0	monocyclic aromatics
1.0	polycyclic aromatics
1.5	condensed aromatics

The determination of carbon and hydrogen was essential to following the changes that take place during weathering. As in the oxygen determination, a micro-method was sought, but unlike the former, little difficulty was encountered. The method has been in use for a relatively long time and is reported in great detail by Niederl and Niederl (18) and Steyermark (19). The compound is burned in an atmosphere of oxygen and the combustion products are passed over hot platinum and copper oxide to insure complete conversion of the carbon and hydrogen to CO_2 and H_2O, respectively. Contaminating elements are removed by means of hot silver ribbon (sulfur) and lead peroxide (nitrogen). The water is absorbed in a tube filled with magnesium perchlorate and the carbon dioxide is absorbed in an ascarite tube, as described above. Results on standard materials are reported in Table A-IV and the reproducibility on unknown samples is shown in Table A-V.

TABLE A-IV. CARBON AND HYDROGEN ANALYSES

Compound	Carbon		Hydrogen	
	Found	Theory	Found	Theory
Acetanilid	70.93	71.1	6.77	6.70
Benzoic Acid*	68.92	68.84	5.05	4.95
Benzoic Acid	68.85	68.84	4.96	4.95
Benzoid Acid	68.78	68.84	4.98	4.95

*Benzoic acid is used as a standard and every time a new combustion or absorption tube filling is used, a sample is analyzed before any determination on unknowns are made.

TABLE A-V. REPRODUCIBILITY OF CARBON AND
HYDROGEN DETERMINATIONS

| Material | Analyses | | | | | |
| | Carbon | | | Hydrogen | | |
	1	2	Ave.	1	2	Ave.
Mid East Asphalt	82.25	82.17	82.21	9.91	9.89	9.00
C 2500 Asphaltenes	81.53	81.07	81.30	8.18	8.38	8.28
C 2500 Resins	79.71	79.11	79.31	10.53	10.53	10.53
C 2500 Dark Oils	84.25	83.73	83.99	11.05	10.98	11.02
C 2500 White Oils	85.79	85.63	85.71	13.14	12.75	12.95

(3) Sulfur

There are numerous methods for determining sulfur in
organic materials, differing primarily in the method by which
the sulfur is converted to the sulfate. The Parr Bomb was
selected arbitrarily because of its rapid, simple and efficient
operation. The reliability of the method is attested by its
acceptance in standard procedures of the A.S.T.M. (20), A.S.A.
(21), and A.P.I. (22).

After approximately 0.2 grams of material has been com-
busted with about 0.3 grams of sucrose (to increase the thermal
output and prevent the heat capacity of the bomb from quenching
the combustion) the bomb is cooled and its contents washed into
a 50 ml volumetric flask and diluted to 50 ml. An aliquot of
10 ml is removed to a 250 ml ehrlenmeyer flask, diluted with
10 ml of 95% ethanol (to lower the solubility of the $BaSO_4$) and

titrated with 0.01N barium chloride solution to the pink
endpoint of the monopotassium rhodizonate indicator (23). The
method is rapid and the last step is more reproducible than
the gravimetric procedure, once the operator has been trained
to recognize the endpoint. Table A-VI contains some data on
the reproducibility of the method.

TABLE A-VI. REPRODUCIBILITY OF SULFUR DETERMINATIONS

Material	Percent Sulfur		
	1	2	Ave.
C-2500 Asphaltenes	2.91	2.89	2.90
C-2500 Resins	2.69	2.73	2.71
C-2500 Dark Oils	1.43	1.42	1.42
C-2500 White Oils	0.197	0.201	0.199
C-2500 Water Solubles	3.72	3.78	3.75

(4) Nitrogen

Because of the extremely inert nature of some of the com-
ponents of asphalt, the conventional methods for determining
nitrogen did not yield accurate results. The Kjeldahl proce-
dures do not completely decompose the nitrogen compounds and,
thus, produce low results. Considerable time and effort were
expended on the micro Dumas procedure (18) as modified by
Hershberg and Wellwood (24), and others (19), but the results
were always high on materials similar to asphalts.

A new method was sought and the idea of converting all of the nitrogen to the nitrate form by combustion under oxygen pressure in a Parr Bomb was investigated. Once in the nitrate form, a colorimetric procedure based on the reaction of aqueous nitrates with 2,4 - phenoldisulfonic acid can be used. This procedure has been standard practice in the testing for nitrates in drinking water for many years (25). However, the nitrogen was not converted entirely to nitrate, even with a subsequent oxidation with bromine. While the ratio between the nitrogen found and the nitrogen present was fairly constant for any particular material, it was very different for different materials, and therefore, the method could not be used.

Finally, communication with W. C. Alford, of the National Institutes of Health, resulted in making about a dozen analyses on his apparatus, which has been modified somewhat from that reported in the literature (26). The results were entirely satisfactory and an apparatus was built similar to his, but incorporating some of Alford's suggestions for improvement. The apparatus yielded its first satisfactory results at the close of 1954. Table A-VII contains data on the reproducibility of this method. The accuracy of this procedure has been covered rather thoroughly by Alford with many more products than are available to this apparatus.

TABLE A-VII. REPRODUCIBILITY OF NITROGEN DETERMINATIONS

Material	Percent Nitrogen				Theory
	1	2	3	Ave.	
Cystine	11.65	11.71	-	11.68	11.66
Acetanilid	10.49	10.55	10.36	10.47	10.36 (Kjeldahl)
Shale Oil	3.94	3.87	-	3.90	4.00 (Alford)

(5) Unsaturation

There is considerable unsaturation in asphalts and it has
long been believed that the unsaturation may play an important
part in the way it weathers. Numerous procedures have been
developed for determining unsaturation, including direct
addition of bromine and iodine, selective oxidation and ozona-
tion and reduction with hydrogen. The type of double bonds
measured and the nature of conflicting reactions vary with the
types of compounds being evaluated. After investigating many
methods, theoretically and a few experimentally, it was found
that an iodine number technique proved satisfactory. It is
based on the Federal Specification TT-P-141b, Method 506-1,
varying primarily in quantities of reagents used. Because
the method was originally developed for relatively low molecular
weight materials, the quantity of Wijs solution was reduced
from 25 to 5 ml and the quantity of solvent increased from
10 to 20 ml. The method detects only bouble bonds in linear

molecules, i.e., styrene (vinyl benzene) has one double bond
per molecule by this method. Results on reproducibility appear
in Table A-VIII.

TABLE A-VIII. REPRODUCIBILITY OF IODINE NUMBER

| Material | Unsaturation, Double Bonds/gram | | |
	1	2	Ave.
C210 - 2500 Asphaltenes	1.94	1.97	1.96
C210 - 2500 Resins	1.45	1.40	1.42
C210 - 2500 Dark Oils	1.28	1.24	1.26
C210 - 2500 White Oils	0.363	0.358	0.360

(6) Molecular Weight

The molecular weight is extremely important in the ulti-
mate identification of compounds and much effort has been ex-
pended in developing numerous methods for its determination.
For materials of molecular weight below 1000, such methods as
vapor density, boiling point elevation and freezing point
depression and viscosity change have proved successful, while
in the range above 30,000, viscosities in dilute solution,
osmotic pressure effects, isothermal distillation, light
scattering and sedimentation analyses have worked, but between
1000 and 30,000 is a region in which no method is very reliable,
even on pure compounds. Since asphalts are complex mixtures of
molecules ranging from about 400 to 4,000 in molecular weight,
interpretation of a determination by any method would involve

considerable speculation. When measuring non-uniform materials some average molecular weight is obtained and because the average is different for each type of measurement, results are not directly comparable. It is extremely desirable to make measurements on a material that is as uniform as possible.

The asphalts were separated into five groups of components and their degradation products into two types of materials (section 7). While these each had many molecular species, their molecular weight ranges were relatively small and readily lent themselves to analysis. It was desirable to use one procedure for the molecular weight determination on all of the components, if possible, in order that the figures might be readily comparable. Since all of the materials were not volatile, vapor density measurements were excluded and since there is a strong tendency toward aggregation of some of the components as the temperature is lowered, the cryoscopic method cannot be used. Eckert and Weetman (27) have reported difficulties in attempting to measure the molecular weight of the asphaltenes by the viscosity method. Thus, the ebullioscopic method, offering the most promise, was extended by means of sensitive instruments to cover the range of 100 to 5000. Because the ebullioscopic constant varies with molecular weight it was decided to use an empirical method, with the ebulliometer calibrated directly with materials of known molecular weight.

The ebulliometer used was that described by Matteson (28),
but by careful evacuation of the vapor pressure thermometer
and by using benzene instead of chloroform, an apparatus capable
of measurement to molecular weights of 5000 was obtained. A
second ebulliometer, using methyl ethyl ketone as solvent and
working on 5, instead of 10, ml of solution was also con-
structed. (The degradation products are soluble in methyl
ethyl ketone, but not in benzene.)   The manisci in both
instruments are read by a traveling telescope, which reads to
0.001 mm.

The instrument was calibrated with the following materials
of known molecular weight:

TABLE A-IX. MOLECULAR WEIGHT STANDARDS

Benzene	Naphthalene	128
	1, 2, 4, 5-Tetrachlorobenzene	216
	1, 2, 4, 5-Tetrabromobenzene	
	Tristearin	891
	Tritrityl Pentacetyl Sucrose	1280
	α- Methyl Styrene	2200
	α- Methyl Styrene	3750
	α- Methyl Styrene	5400
	Inulin Acetate	11000
Methyl ethyl ketone	Indole	117
	Sebacic acid	202
	Phenolphthalein	318
	Triiodophenol	472

While in the conventional ebullioscopic method the results
are extrapolated to zero concentration to determine the ebulli-
oscopic constant, in this procedure the deflection of the man-
iscus in the vapor pressure thermometer at some finite concen-
tration is plotted against the molecular weight on semi-
logarithmic paper; the molecular weight of the unknown is read
directly from this graph.

In practice a constant volume of solvent is put into the
ebulliometer and boilded until equilibrium conditions are ob-
tained. Then small increments of solute are added one at a
time through the condenser and the deflection produced by each
is recorded. The deflection where the straight portion of
the curve of deflection vs. weight added intersects the
particular reference weight chosen is the point at which the
molecular weight is obtained from the calibration curve. Table
A-X shows the reproducibility of this method.

TABLE A-X. REPRODUCIBILITY OF MOLECULAR WEIGHTS

Material	Determination		
	1	2	Ave.
Cal. Flux Dark Oils	670	670	670
Cal. Flux Resin	990	1020	1005
C2500 Asphaltenes	2250	2250	2250
M2500 Resins	1160	1210	1185
C210-3Mo-D. O.	575	630	603

(7) <u>Separations</u>

As emphasized previously, it is extremely difficult to make many of the necessary determinations on materials as complex as asphalt. It was also desired to see if there were internal changes taking place in the asphalts during weathering that were not apparent from studying the degradation products. Methods for separating asphalts into a number of component groups were investigated, primarily by N.B.S. staff members. Because there are many methods of fractionating asphalts available (29), all depending on either selective solvents or adsorbents, or both, and each method having its particular applications, only the final method selected will be discussed. This method was developed by Kleinschmidt (7) and has been reported to the Asphalt Roofing Industry Bureau Research Committee.

Essentially the method comprises the following steps:

(1) Solution of the maltenes in n-pentane - asphaltenes are removed by filtration.

(2) Adsorption of the resins and dark oils on Fuller's earth - white oils are washed from the column with an excess of pentane.

(3) Elution of the dark oils with methylene chloride.

(4) Elution of the resins with methyl ethyl ketone (saturated with water).

(5) Cleaning up the column with chloroform.

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