Characteristics of Fifteen Coating-Grade Asphalts

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A survey of asphalts used in coatings on asphalt prepared roofing was made and their characteristics measured. Despite the fact that all of the asphalts were similar in the characteristics by which they are normally specified, they varied over a sixfold range in durability in accelerated weathering machines. They were also different in component and chemical in accelerated weathering machines. While no quantitative relation was found between durability and any of the analyses. measured characteristics, it was found that the more durable and less durable asphalts could be identified with certain ranges of flash point, specific gravity, percent carbon plus hydrogen, percent sulfur, percent asphaltenes, and percent resins.

1. Introduction

The refining of oil from worldwide sources, with few exceptions, results in residua that can properly be designated asphalts. These residua vary tremendously in composition and quality; hence, many are never used for roofing purposes. However, with further processing, a select few residua eventually are marketed as roofing asphalts. Further segregation and processnig produces the relatively few coating-grade asphalts used by the American roofing industry.

Because of the special requirements of coatinggrade asphalts, those available are all similar in the normally measured characteristics and properties. However, despite their physical and chemical similarities, some differ widely in durability.

This article is a summary of some of the characteristics of 15 coating-grade asphalts and their behavior under accelerated weathering conditions.

2. Materials and Methods

2.1. Asphalts

The 15 asphalts studied were produced from widely distributed crudes. They included six from the central United States, four from the west coast, and five from overseas. These five represented three different countries and four different producing areas. Eight of the asphalts were unmodified, three were blends, two were fluxed with oils, and two were blown with catalysts (ferric chloride and phosphorus pentoxide). These asphalts and their measured physical characteristics are listed in table 1 in order of decreasing durability.

2.2. Analytical Procedures

All of the asphalts were analyzed by recognized chemical procedures. However, because of the complex nature of asphalt, several of the techniques had to be modified in order to yield reproducible and realistic analyses.

					Sec. Alter					
No.	Description	Soft	Penetration ^b at—			Sp. Gr.	Duct.d	Flash	Dura-	Rating
		point a	32° F	$77^{\circ} \mathrm{F}$	$115^{\circ} \mathrm{F}$	at 77° F		point e	bility f	
		$^{\circ}F$	dmm	dmm	dmm		cm	$COC \circ F$	Days	
1	Blend	215	14	22	46	0.998	2.8	600	150	Excellent.
2	do	208	12	20	37	1.008	2.5	600	88	Good.
3	do	229	7	14	22	1.015	2.4	615	87	Do.
4	Unmodified	205	14	21	35	1.003	2.8	540	86	Do.
5	do	216	10	12	22	1.007	1.8	575	84	Do.
6	do	222	17	26	41	1.010		615	72	Do.
7	0.5% P ₂ O ₅	221	11	19	31	1.028		565	68	Do.
8	Unmodified	234	11	16	19	1.026		505	57	Fair.
9	0.35% FeCl ₃	216	9	20	36	1.030	3.5	500	53	Do.
10	Unmodified	226	8	13	20	1.024	2.3	560	47	Do.
11	do	220	8	13	22	1.032	2.5	550	47	Do.
12	Fluxed	216	10	16	32	1.035	4.1	450	44	Do.
13	Unmodified	223	11	18	28	1.035		565	43	Do.
14	do.	228	8	11	20	1.031	1.5	565	38	Poor.
15	Fluxed	231	15	18	36	1.023	1.5	515	25	Do.
		201	10	10	00					

TABLE 1. Characteristics of asphalts

ASTM D36-26—Test for softening point of bituminous materials.
 ASTM D5-59T—Penetration of bituminous materials.
 ASTM D71-52—Test for specific gravity of asphalts and tar pitches.
 ASTM D113-44—Test for ductility of bituminous materials.
 ASTM D92-57—Test for fash and fire points by Cleveland Open Cup.
 f 51-9C cycle—50% failure point. Probable standard deviation=6% [1].

a. Carbon-Hydrogen

Carbon and hydrogen were determined by the microcombustion technique described by Niederl and Niederl [2] ¹ and Stevermark [3].

b. Oxygen

Oxygen was determined by a modified Unterzaucher [4] method. The principal modifications were those of Aluise et al. [5], plus the addition of a low-temperature trap to remove the nonacidic sulfur compounds formed during combustion [6]. Because some pyrolytic hydrogen liberated iodine, as did the carbon monoxide (resulting in high-oxygen figures), a modification developed by Dundy and Stehr [7] was also used. The liberated iodine was absorbed in an absorption tube containing sodium thiosulfate, followed by Anhydrone and phosphorus pentoxide. The carbon dioxide was absorbed in a microabsorption tube and weighed, as in the carbonhydrogen determination. Thus, the final apparatus consisted of a cylinder of high-purity Linde nitrogen followed in turn by a purification system, bubble counter, drying tube, and reaction furnace, as described by Aluise [5], a low-temperature trap and absorption tube, as described by Hinkel [6], an iodine pentoxide furnace [5], a sodium thiosulfate absorption tube [7], and an ascarite microabsorption tube, as developed by Corwin [8]. This apparatus produced determinations which checked the specified values of standard samples (NBS 140 benzoic acid, NBS 141 acetanilide, NBS 143 cystine, and thiamine hydrochloride) within 1 percent of their reported values.

c. Sulfur

Sulfur was determined as sulfate by means of the titration of an oxidized sample of material in alcoholwater solution. The sample (0.2 g) was oxidized in a Parr Bomb over 10 ml of water with 0.3 g of sucrose in oxygen at 300-psi pressure. The bomb contents were diluted to 50 ml. A 10-ml aliquot was further diluted with 10 ml of 95 percent ethanol and titrated with a 0.01 N barium chloride solution. Monopotassium rhodizonate was used as the internal indicator [9]. The results were reproducible to ± 0.02 percent.

d. Nitrogen

The determination of nitrogen was the most difficult of the elemental analyses. The Kjeldahl procedure produced low results, and the conventional micro-Dumas [2] procedure as modified by Hershberg and Wellwood [10] and others [3] gave high results on a standard sample of shale oil. The procedure of Alford [11], modified by the addition of an electrolysis apparatus for the generation of pure oxygen, was found to be satisfactory for asphalt. Alford [11] discussed its accuracy thoroughly. The repeatability of the results reported in this paper was of the order of ± 0.04 percent.

2.3. Component Analysis

The asphalts were separated into component groups by the procedure of Kleinschmidt [12]. The asphaltenes were precipitated with n-pentane. The maltenes (material soluble in n-pentane) were adsorbed on a column of Fuller's earth and successively treated with n-pentane, methylene chloride, and methyl ethyl ketone (water-saturated). These solvents desorbed the white oils, dark oils, and resins, respectively. A final product, called "cleanup" in table 3, desorbed with chloroform was combined with the resins because it was found to be similar to the resins.

2.4. Specimen Preparation, Exposure, and Inspection

The asphalts were exposed as films $2\frac{1}{4}$ by $5\frac{1}{2}$ in. by 25-mils thick on 2³/₄ by 6 by ¹/₁₆ in. aluminum sheets. The exposure panels were made by the hydraulicpress method [13].² Teflon sheet was used in place of the specified dextrin-coated paper to prevent the adhesion of the asphalt to the upper platen of the press.

Within 24 hr after they were made, the panels were exposed in one of two accelerated weathering machines [14]. Four panels were subjected to the 22-1 cycle, which consisted of 22 hr of light followed by 1 hr of soaking in distilled water each day 5 days a week [15]. The panels were at ambient conditions for the remaining hour each day and on weekends. This set of panels was used primarily for the determination of the weight losses and the changes in components during exposure. Specimens were removed after 9, 18, 27, and 41 days of exposure (approximately 200, 400, 600, and 900 hr of exposure to arc light).

Another set of four panels was exposed to the 51-9C cycle ³ [15] for 22 hr each day, 5 days a week. In both cycles the specimens were at 77 $\pm 2^{\circ}$ F at times other than those specified. During exposure the specimens and specimen holders were rotated on alternate days to increase the uniformity of exposure of all specimens.

The specimens exposed to the 51-9C cycle were examined with a high-voltage probe⁴ [16] after 20 min of exposure (to dry them completely) following a spray period and removed when failures occurred in 50 percent of their surface area. The failures were counted on spark photographs [17] through a 60-square grid.

When asphalts are exposed to the 51-9C cycle under these conditions, the standard deviation of the durability should be of the order of 6 percent [1].

 ² ASTM D1669–59T—Preparation of test panels for accelerated and outdoor weathering of bituminous coatings.
 ³ ASTM D529–59T—Accelerated weathering test of bituminous materials.
 ⁴ ASTM D1670–59T—Failure end point in accelerated and outdoor weathering

of bituminous materials.

¹ Figures in brackets indicate the literature references at the end of this paper.

3. Results

The chemical analyses of the 15 asphalts before exposure are tabulated in table 2.

The component analyses, changes in components, and weight losses during 900 hr of exposure to the 22-1 cycle and the durability of the asphalts in the 51-9C cycle are in table 3.

No.	Durability	Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen	Recovery	$\rm C/H$	C+H
1 2 3 4	Days a 150 88 87 83		$\frac{\%}{10.04} \\ 10.32 \\ 10.00 \\ 10.50 \\ 10.52 $	$\% \\ 1.23 \\ 1.21 \\ 1.01 \\ 1.39 \\ 1.50 \\ 1.5$		$\% \\ 0.62 \\ .89 \\ .73 \\ .67 \\ .61$	% 98.73 99.03 99.31 97.85 90.71	0.718 .694 .724 .674	$\begin{array}{c} -\% \\ 95.87 \\ 95.75 \\ 96.15 \\ 94.71 \\ 96.60 \end{array}$
	72 68 57 53 47	86.03 83.14 83.19 82.10 85.63	$10.61 \\ 10.10 \\ 10.23 \\ 10.04 \\ 9.69$	$1.30 \\ 1.22 \\ 1.31 \\ 1.31 \\ 1.55 \\ 1.19 $	$ 1.24 \\ 2.89 \\ 4.44 \\ 4.67 \\ 1.53 $.61 .79 .71 1.00 1.48 0.62	$\begin{array}{c} 99.\ 71\\ 99.\ 92\\ 98.\ 15\\ 100.\ 17\\ 99.\ 84\\ 98.\ 66\end{array}$. 681 . 681 . 683 . 687 . 742	$\begin{array}{c} 96.\ 60\\ 96.\ 67\\ 93.\ 24\\ 93.\ 41\\ 92.\ 14\\ 95.\ 32\\ \end{array}$
$11 \\ 12 \\ 13 \\ 14 \\ 15$	$47 \\ 44 \\ 43 \\ 38 \\ 25$	84. 22 84. 10 83. 98 82. 21 83. 28	$9, 94 \\10, 31 \\9, 83 \\9, 90 \\10, 02$	$1.25 \\ 1.66 \\ 1.04 \\ 1.14 \\ 1.56$	$\begin{array}{c} 2.98\\ 3.18\\ 4.62\\ 4.78\\ 2.21 \end{array}$.78 1.30 0.38 .55 1.13	$\begin{array}{c} 99.17\\ 100.55\\ 99.85\\ 98.58\\ 98.20 \end{array}$.712 .685 .717 .696 .696	94.16 94.41 93.81 92.11 93.30

TABLE	2.	Chemical	analyses	of	asphalts	before	exposure
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a 51-9C cycle-50% failure level.

TABLE 3. Composition and durability of asphalts exposed to accelerated weathering a

		Asph	alt 1						Aspł	alt 4			
		22–1 Cy	vele; time	e, hours		51–9C Cycle final failure, days			22–1 C	vcle; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	150	Components%	0	200	400	600	900	84
Asphaltenes%- Resins%- Dark oils%- Uhite oils%- Cleanup%- Weight loss%- Recovery%-	$\begin{array}{c} 37.\ 4\\ 12.\ 8\\ 24.\ 6\\ 21.\ 0\\ 2.\ 5\\ 0.\ 0\\ 98.\ 3\end{array}$	$\begin{array}{c} 43.5\\12.4\\19.7\\22.5\\0.5\\.3\\98.7\end{array}$	$\begin{array}{c} 42.\ 5\\ 12.\ 4\\ 19.\ 6\\ 19.\ 7\\ 0.\ 8\\ 2.\ 5\\ 97.\ 5\end{array}$	$\begin{array}{c} 45.5\\ 12.1\\ 16.7\\ 18.9\\ 0.9\\ 4.3\\ 98.4 \end{array}$	$\begin{array}{c} 46.\ 0\\ 11.\ 2\\ 15.\ 6\\ 19.\ 2\\ 0.\ 7\\ 6.\ 8\\ 99.\ 5\end{array}$	$\begin{array}{c} 43.4\\ 9.3\\ 13.1\\ 16.3\\ 1.0\\ 15.4\\ 98.5 \end{array}$	Asphaltenes% Resins% Dark oils% White oils% Cleanup% Weight loss% Recovery%	$\begin{array}{c} 36.\ 6\\ 11.\ 0\\ 21.\ 7\\ 27.\ 0\\ 1.\ 8\\ 0.\ 0\\ 98.\ 1\end{array}$	$\begin{array}{c} 41.\ 4\\ 12.\ 1\\ 17.\ 3\\ 27.\ 5\\ 0.\ 4\\ 1.\ 1\\ 99.\ 8\end{array}$	$\begin{array}{c} 41.\ 2\\ 12.\ 8\\ 16.\ 4\\ 24.\ 6\\ 0.\ 5\\ 3.\ 5\\ 99.\ 0 \end{array}$	$\begin{array}{c} 44.\ 5\\ 10.\ 3\\ 14.\ 0\\ 23.\ 9\\ 0.\ 3\\ 5.\ 4\\ 98.\ 4\end{array}$	$\begin{array}{c} 43.\ 5\\11.\ 4\\12.\ 3\\25.\ 8\\0.\ 1\\6.\ 1\\99.\ 2\end{array}$	$\begin{array}{c} 42.8\\ 9.4\\ 12.5\\ 23.2\\ 0.1\\ 12.2\\ 100.2 \end{array}$
		Aspł	nalt 2						Aspl	nalt 5			·
		22-1 Cy	vele; time	e, hours		51–9C Cycle final failure, days			22–1 Cy	zcle; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	88	Components%	0	200	400	600	900	86)
Asphaltenes%- Resins%- Dark oils%- Cleanup%- Recovery%-	$\begin{array}{r} 37.\ 0\\ 9.\ 4\\ 27.\ 5\\ 22.\ 5\\ 1.\ 3\\ 0.\ 0\\ 97.\ 7\end{array}$	$\begin{array}{c} 43.2\\12.2\\22.4\\19.9\\0.7\\.7\\99.1 \end{array}$	$\begin{array}{c} 46.\ 2\\ 11.\ 0\\ 19.\ 8\\ 18.\ 1\\ 0.\ 4\\ 2.\ 7\\ 98.\ 2 \end{array}$	$\begin{array}{r} 46.3\\ 12.0\\ 17.9\\ 18.0\\ 0.1\\ 4.2\\ 98.5 \end{array}$	$\begin{array}{r} 47.\ 0\\ 11.\ 2\\ 16.\ 1\\ 17.\ 3\\ 0.\ 3\\ 7.\ 3\\ 99.\ 2\end{array}$	$\begin{array}{c} 44.5\\ 9.7\\ 16.5\\ 16.4\\ 0.7\\ 11.3\\ 99.1 \end{array}$	Asphaltenes% Resins% Dark oils% White oils% Cleanup% Recovery%	38.510.027.022.40.7.098.6	$\begin{array}{r} 42.1\\ 13.0\\ 22.3\\ 20.3\\ 0.8\\ .9\\ 99.4 \end{array}$	$\begin{array}{c} 42.\ 6\\ 12.\ 4\\ 20.\ 7\\ 20.\ 3\\ 0.\ 3\\ 2.\ 4\\ 98.\ 3\end{array}$	$\begin{array}{r} 43.\ 7\\ 10.\ 5\\ 19.\ 7\\ 20.\ 5\\ 0.\ 4\\ 3.\ 9\\ 98.\ 5\end{array}$	$\begin{array}{c} 45.3\\ 11.0\\ 16.9\\ 20.2\\ 0.3\\ 5.7\\ 99.4 \end{array}$	$\begin{array}{c} 43.1\\ 9.5\\ 18.1\\ 19.5\\ 0.6\\ 8.6\\ 99.4\end{array}$
		Aspł	nalt 3						Aspł	alt 6			
		22-1 Cy	vcle; time	e, hours		51–9C Cycle final failure, days			22–1 Cy	zcle; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	87 b	Components%	0	200	400	600	900	72
Asphaltenes% Resins% Dark oils%- White oils%- Cleanup% Recovery%-	$\begin{array}{c} 37.8 \\ 11.9 \\ 28.0 \\ 19.5 \\ 1.3 \\ 0.0 \\ 98.5 \end{array}$	$\begin{array}{c} 44.\ 0\\ 12.\ 8\\ 21.\ 7\\ 18.\ 9\\ 0.\ 6\\ .\ 6\\ 98.\ 6\end{array}$	$\begin{array}{r} 46.\ 7\\ 11.\ 7\\ 19.\ 6\\ 17.\ 4\\ 0.\ 2\\ 2.\ 4\\ 98.\ 0\end{array}$	$\begin{array}{c} 45.\ 4\\ 12.\ 1\\ 18.\ 6\\ 16.\ 3\\ 0.\ 5\\ 3.\ 9\\ 97.\ 6\end{array}$	$\begin{array}{c} 49.\ 0\\ 11.\ 4\\ 16.\ 9\\ 15.\ 0\\ 0.\ 3\\ 6.\ 5\\ 99.\ 1\end{array}$	$\begin{array}{c} 47.1\\ 11.0\\ 16.5\\ 15.4\\ 0.6\\ 8.9\\ 99.5\end{array}$	Asphaltenes% Resins% Dark oils% White oils% Cleanup% Weight loss% Recovery%	$\begin{array}{c} 37.2\\ 9.7\\ 25.9\\ 24.8\\ 0.6\\ .0\\ 98.2 \end{array}$	$\begin{array}{r} 40.8\\ 13.4\\ 22.9\\ 22.0\\ 0.3\\ .5\\ 99.9\end{array}$	$\begin{array}{r} 42.\ 6\\ 13.\ 6\\ 19.\ 3\\ 20.\ 3\\ 0.\ 5\\ 2.\ 4\\ 98.\ 7\end{array}$	$\begin{array}{r} 44.5\\11.4\\17.5\\19.6\\0.7\\3.9\\97.6\end{array}$	$\begin{array}{r} 44.5\\ 10.7\\ 16.3\\ 19.3\\ 0.7\\ 6.9\\ 98.4 \end{array}$	$\begin{array}{c} 42.\ 6\\ 8.\ 4\\ 14.\ 6\\ 21.\ 5\\ 0.\ 7\\ 11.\ 9\\ 99.\ 7\end{array}$

See footnotes at end of table.

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TABLE 3. Composition and durability of asphalts exposed to accelerated weathering a-Continued

		Asph	alt 7						Asph	alt 12			
		22–1 Су	cle; time	, hours		51–9C Cycle final failure, days			22-1 Cy	vele; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	609	900	68	Components%	0	200	400	690	900	44
Asphaltenes	$\begin{array}{c} 42.1 \\ 10.8 \\ 22.9 \\ 22.7 \\ 0.4 \\ .0 \\ 98.9 \end{array}$	$\begin{array}{c} 46.0\\ 12.0\\ 20.6\\ 20.6\\ 0.3\\ .5\\ 100.1 \end{array}$	$\begin{array}{r} 46.9\\ 12.1\\ 18.8\\ 19.8\\ 0.2\\ 2.8\\ 100.5 \end{array}$	$\begin{array}{c} 48.3\\ 10.9\\ 17.0\\ 19.0\\ 0.4\\ 4.2\\ 98.8 \end{array}$	$\begin{array}{c} 47.0\\ 11.1\\ 15.6\\ 19.5\\ 0.3\\ 7.0\\ 100.5 \end{array}$	$\begin{array}{c} 47.1\\ 7.6\\ 12.9\\ 22.4\\ 0.2\\ 9.7\\ 99.9 \end{array}$	Asphaltenes% Resins%- Dark oils%- White oils%- Cleanup%- Weight loss%- Recovery%-	$\begin{array}{c} 44.1\\ 8.6\\ 19.8\\ 26.6\\ 0.6\\ .0\\ 99.7 \end{array}$	47.0 10.4 17.3 24.6 Trace 0.5 99.8	$\begin{array}{c} 48.2 \\ 10.8 \\ 14.5 \\ 23.4 \\ 0.2 \\ 2.3 \\ 99.4 \end{array}$	52. 69. 111. 921. 80. 034. 399. 7	52. 4 7. 6 9. 7 22. 1 Trace 8. 0 99. 8	$50.2 \\ 9.1 \\ 10.3 \\ 22.1 \\ 0.2 \\ 7.7 \\ 99.6$
		Asph	alt 8						Asph	alt 13			
		22–1 Су	vele; time	, hours		51–9C Cycle final failure, days			22-1 Су	vele; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	57 b	Components%	0	200	400	600	900	43
A sphaltenes% Resins%- Dark oils%- White oils%- Cleanup%- Weight loss%- Recovery%-	$\begin{array}{c} 45.5\\ 9.6\\ 21.9\\ 21.1\\ 0.5\\ .0\\ 98.6 \end{array}$	$50.0 \\ 11.4 \\ 17.3 \\ 16.4 \\ 0.5 \\ .9 \\ 96.5$	$52. 2 \\11. 3 \\13. 2 \\16. 4 \\0. 2 \\4. 3 \\97. 6$	$53. \ 4 \\ 10. \ 1 \\ 12. \ 0 \\ 16. \ 8 \\ 0. \ 3 \\ 5. \ 6 \\ 98. \ 2$	53.4 8.9 10.7 16.6 0.1 9.8 99.5	51. 4 9. 7 9. 8 15. 4 Trace 12. 5 98. 8	Asphaltenes% Resins% Dark olls% White olls% Cleanup% Recovery%	$\begin{array}{r} 43.\ 6\\ 6.\ 9\\ 25.\ 3\\ 20.\ 2\\ 1.\ 1\\ 0.\ 0\\ 97.\ 1\end{array}$	$\begin{array}{r} 48.2\\ 8.8\\ 20.4\\ 19.1\\ 0.6\\ .7\\ 97.8 \end{array}$	51.3 8.1 17.9 19.3 0.9 1.8 99.3	$51.9\\8.0\\17.7\\18.5\\0.7\\3.0\\99.9$	53.7 8.9 13.4 16.3 1.3 5.4 99.4	$53. 2 \\ 8. 7 \\ 14. 0 \\ 15. 0 \\ 0. 4 \\ 8. 2 \\ 99. 5$
		Asph	alt 9						Asph	alt 14		1	
		22-1 Cy	cle; time	, hours		51–9C Cycle final failure, days			22–1 Cy	vcle; time	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	53	Components%	0	200	400	600	900	38 b
Asphaltenes	$\begin{array}{c} 41.8\\ 8.6\\ 23.6\\ 26.8\\ 0.05\\ .0\\ 100.9 \end{array}$	$\begin{array}{c} 46.8\\ 9.0\\ 21.0\\ 22.5\\ 0.2\\ .2\\ 99.7 \end{array}$	$\begin{array}{r} 48.7\\ 10.8\\ 18.2\\ 20.3\\ 0.2\\ 1.3\\ 99.5 \end{array}$	$52. \ 4 \\ 8. \ 5 \\ 13. \ 9 \\ 21. \ 5 \\ 0. \ 03 \\ 3. \ 2 \\ 99. \ 5$	$54.0 \\ 7.7 \\ 10.6 \\ 20.2 \\ 0.02 \\ 6.8 \\ 99.3$	$53.5 \\ 7.6 \\ 10.4 \\ 17.1 \\ 0.1 \\ 10.8 \\ 99.5$	Asphaltenes Resins Dark oils White oils Cleanup Weight loss Recovery%-	$\begin{array}{r} 46.3 \\ 7.3 \\ 25.5 \\ 18.8 \\ 0.5 \\ .0 \\ 98.4 \end{array}$	54. 29. 616. 317. 20. 31. 398. 9	$\begin{array}{c} 60.2 \\ 7.5 \\ 14.1 \\ 16.1 \\ 0.2 \\ 3.1 \\ 101.2 \end{array}$	58. 28. 312. 114. 20. 15. 198. 0	$57.0 \\ 8.4 \\ 11.6 \\ 13.8 \\ 0.2 \\ 7.5 \\ 98.5$	$55.1 \\ 10.1 \\ 13.4 \\ 14.0 \\ 0.1 \\ 7.5 \\ 99.5$
		Asph	alt 10			·			Asph	alt 15			
		22-1 Cy	zele; time	e, hours		51–9C Cycle final failure, days			22–1 Cy	zcle; tim	e, hours		51–9C Cycle final failure, days
Components%	0	200	400	600	900	47	Components%	0	200	400	600	900	25 b
Asphaltenes	$\begin{array}{c} 39.1 \\ 8.0 \\ 22.8 \\ 28.3 \\ 0.9 \\ .0 \\ 99.1 \end{array}$	$\begin{array}{r} 43.1\\ 9.9\\ 17.7\\ 24.8\\ 1.3\\ 1.5\\ 98.3 \end{array}$	$\begin{array}{c} 44.0\\ 10.0\\ 16.0\\ 24.5\\ 1.2\\ 3.6\\ 99.3 \end{array}$	$\begin{array}{r} 45.2\\ 8.7\\ 14.9\\ 23.5\\ 1.9\\ 4.9\\ 100.1 \end{array}$	$\begin{array}{c} 45.5\\ 10.1\\ 12.9\\ 23.3\\ 1.2\\ 6.0\\ 99.0 \end{array}$	$\begin{array}{c} 47.\ 0\\ 9.\ 4\\ 14.\ 9\\ 24.\ 0\\ 0.\ 1\\ 5.\ 1\\ 100.\ 5\end{array}$	Asphaltenes	$\begin{array}{c} 40.5 \\ 9.5 \\ 20.0 \\ 27.3 \\ 2.0 \\ 0.0 \\ 99.3 \end{array}$	$\begin{array}{c} 48.5\\ 9.6\\ 13.5\\ 27.0\\ 0.9\\ .9\\ 100.4 \end{array}$	$50.5 \\ 8.7 \\ 11.8 \\ 23.3 \\ 2.3 \\ 3.0 \\ 99.6$	$53.3 \\ 9.1 \\ 8.7 \\ 22.6 \\ 1.3 \\ 5.9 \\ 100.9$	52.67.37.120.01.29.697.8	50.3 10.1 10.6 21.4 Trace 5.8 98.2
		Asph	alt 11				^a Analyses are the av cycle and four specimen	verages on the	of determ 51–C cy	inations cle.	on three	e specim	ens in the 22–1
		22-1 Cy	ycle; tim	e, hours		51–9C Cycle final failure, days	^b One specimen with	premat	ure failur	e exclud	ed.		
Components%	0	200	400	600	900	47							
Asphaltenes	$\begin{array}{c} 42.2\\ 9.1\\ 25.2\\ 20.0\\ 1.3\\ 0.0\\ 97.8\end{array}$	$\begin{array}{c} 45.9\\ 10.5\\ 19.6\\ 19.3\\ 0.9\\ 1.3\\ 97.5 \end{array}$	$\begin{array}{c} 48.3\\ 10.3\\ 18.4\\ 18.4\\ 1.3\\ 2.8\\ 99.5 \end{array}$	$\begin{array}{c c} 47. \ 2\\ 11. \ 1\\ 17. \ 8\\ 18. \ 5\\ 0. \ 9\\ 3. \ 7\\ 99. \ 2\end{array}$	$\begin{array}{c} 48.7\\ 12.3\\ 14.0\\ 17.8\\ 1.9\\ 4.6\\ 99.3 \end{array}$	$50.7 \\ 12.1 \\ 16.1 \\ 17.3 \\ 0.3 \\ 4.4 \\ 100.9$							

4. Discussion of Results

While the 15 asphalts were produced from diverse crudes, they were refined in this country to meet specifications of various roofing manufacturers. These specifications served to limit the physical characteristics of these asphalts to rather narrow ranges.

The average values for the characteristics of the 15 asphalts are shown in table 4.

TABLE 4. A	verage	values	for	coating-grade	e a sph	alt
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Softening point	221
Penetration at 32° F	11
Penetration at 77° F	17
Penetration at 115° Fdmm	30
Flash point (COC)	555
Ductilityem	2.5
Specific gravity (77/39.2)	1.020

These characteristics are the ones to which values are usually assigned in purchase specifications and have a direct bearing on the manufacture and application of roofing. However, the values of these characteristics have little direct relation to the most important single requirement of coating-grade asphalts-durability. Durability itself is never specified quantitatively. It is controlled indirectly by roofing manufacturers through the specification of the source of the crude from which the asphalt is produced and control of its processing. The asphalts are used in service in combination with other ingredients, such as additives, granules, and felts, which greatly affect their weathering characteristics. The finished products exhibit a wide range of durability, depending largely on their application and service environment and secondarily on the statistical factors that enter into most aging processes. However, properly manufactured products made from even the poorest of these asphalts have appreciable durabilities, and evaluation of the finished products by service tests is impractical.

The evaluation process has been accelerated somewhat through the exposure of unsurfaced products, but even this type of exposure requires a number of years. Exposure of the coating-grade asphalts out-of-doors on aluminum panels has accelerated the process still further, but good-weathering asphalts still last more than 5 yr and poor ones last 18 to 24 months in the Washington, D.C., area. In all types of exposures out-of-doors, the durabilities vary among replicate specimens and on exposures made at different times of the year. Various factors of weather affect the various asphalts differently, and weather, itself, is fickle.

The need for a rapid and reliable means for evaluating the durability of normal coating-grade asphalts has led to the use of accelerated weathering equipment. With suitable precautions and adequate controls, durability figures can be obtained that are more reproducible than those for natural weathering. Sets of exposure conditions have been developed that will rank a series of asphalts in approximately the same order as outdoor exposures at a given time in a given place. However, primarily because of the great variations in weather from place to place and from one year to another in any one location, no general quantitative correlation has been obtained between the results from outdoor and accelerated weathering. This discussion will deal primarily with exposures to accelerated weathering because they produce rapid results that are more reproducible than those from outdoor exposures, yet they rank asphalts in approximately the same order of durability as outdoor exposures.

Wilkinson, Striker, and Traxler [18] have decried the use of accelerated weathering and have published criteria for establishing the quality of asphalts as related to durability. They have attempted to correlate a number of the characteristics of asphalts with a single determination of durability by exposure outdoors in Port Neches, Texas (see table 5).

TABLE 5. Criteria for Durability

Characteristics	Limits
Softening point°F	210 to 230
Penetration at $32 \circ F$ d mm	10 minimum.
Penetration at $77 \circ F$ dmm	18 to 25
Penetration at $115 \circ F$ dmm	25 to 40
Flash point (COC) °F	500 minimum.
Specific gravity (77/39.2)	0.990 to 1.040

Based on these criteria, the softening points (table 1) of asphalts 2 and 4 are too low and of 8 and 15 too high. Asphalts 3, 9, 10, 11, and 14 have penetrations that are too low at 32 °F. The penetrations of asphalts 3, 5, 8, 10, 11, 12, and 14 are too low at 77 °F and that of asphalt 6 is too high at 77 °F. Asphalts 3, 5, 8, 10, 11, 14, and 15 have 77 °F. Aspnants 3, 5, 6, 10, 11, 11, 11, performing penetrations that are too low at 115 °F. Only penetrations that are too low at flash point basis. All of the asphalts are within the specific gravity limits. An asphalt having the average characteristics listed in table 4 would meet all of the requirements except penetration at 77 °F, which is 1 decimillimeter low. Of the asphalts included in this study, only asphalt 1 would satisfy all of the requirements. Yet, all of these asphalts were being used commercially when this study was started and were considered satisfactory. The six more durable asphalts are considered to be among the best available, yet some of these fall outside the limits of several of these criteria.

While this lack of a general correlation of durability with physical characteristics is discouraging, it does not preclude the existence of some relations between durability and some physical properties. There are apparent relations between two of the properties reported in table 1 and the durabilities reported in table 3. The asphalts with specific gravities below 1.020 and those with flash points above 565 °F were the more durable. However, both asphalts 4 (flash point=540 °F) and 7 (sp gr= 1.028) are notable exceptions.

Examination of the chemical and component analyses in table 2 yields some interesting results as well. Carbon and hydrogen were the major elements present, comprising between 92 and 97 percent of the asphalt. Oxygen was present to between 1.0 and 1.7 percent, sulfur to between 1.0 and 4.8 percent, and nitrogen to between 0.4 and 1.5 percent. The relations between the elemental analyses and durability will be discussed later.

The asphaltene content varied from 36 to 46 percent, resin content from 8 to 15 percent, dark oil content from 20 to 28 percent, and white oil content from 19 to 28 percent. The normal coatinggrade asphalt was about half oil and half asphaltenes and resins. The exact proportions of the various components must be balanced in order to accommodate the differences in the molecular species and produce the desired characteristics of asphalt.

Thus, it is seen that asphalts used for the coating on prepared roofing are not very different in the physical properties by which they are described, but do vary considerably in both elemental and component analyses.

The durabilities of the asphalts in the 51-9C cycle covered a six-fold range, from 25 to 150 days. There was no quantitative correlation between the durability and the weight loss at failure in the 51-9C cycle. Nor was there a correlation between durability and weight loss or component changes in the 22-1 cycle.

Despite the fact that no quantitative correlation was apparent between durability and any of the reported characteristics of the asphalts, a number of trends are worthy of note. There was no correlation between carbon-hydrogen ratio and durability, but the sum of carbon and hydrogen seemed to bear some relation to durability. This sum exceeded 94.5 percent for 5 of the 6 more durable asphalts.

Similarly, without any real quantitative correlation, the asphalts of high-sulfur content were the less durable ones and those of low-sulfur content, under 1.5 percent, were the more durable.

Asphalt is currently believed to consist of a dispersion of asphaltenes in oils. The asphaltenes produce the structure of the asphalt through loose association, and the oils plasticize the structure. The resins help keep the system homogeneous by acting as dispersing agents.

When an asphalt is exposed to the weather, the asphaltenes increase, and the oils and resins decrease. Eventually there is insufficient material left in the oil phase to plasticize the asphaltene structure satisfactorily, and the asphalt fails by cracking.

When an asphalt is exposed to weather or to the elements of weather in an accelerated weathering machine, chemical changes occur which ultimately result in the failure of the asphalt [19]. Some of the changes taking place were followed during the course of 900 hr of exposure to the 22–1 cycle (table 2). While there were individual variations among the asphalts as to the magnitude of the changes, the trends were similar for all of them.

During the first few days of exposure all of the asphalts gained weight, but by the end of 200 hr, all had lost from 0.3 to 1.5 percent of their original

weight (table 3, column 3). The weight loss became progressively larger at a constant rate for nine of the asphalts, at a decreasing rate for two of them, and an increasing rate for one. Neither the length of the induction period (the time required for an asphalt to return to its initial weight), nor the rate of weight loss during this early exposure, was related to the durability of the asphalts.

During the first 200 to 400 hr of exposure the asphaltenes increased rather rapidly in all of the asphalts. For the next 500 hr they remained relatively constant for four of the asphalts, increased at a slower rate for 10 and decreased slightly for one.

Similarly, the resins increased at the expense of the oils, particularly the dark oils, during the early part of the exposure. From the very beginning, the dark oils decreased rapidly. At 900 hr, they were reduced by 30 to 50 percent. The white oils decreased more slowly. Later during the exposure period the oils and resins continued to decrease as the asphalts weathered and lost weight.

Wilkinson, Striker, and Traxler [18] reasoned that the fewer the asphaltenes present initially, the longer an asphalt should weather before failure. They recommended an upper limit of 40 percent asphaltenes. Examination of the data in table 6 reveals that truly the six more durable asphalts have less than 40 percent asphaltenes. However, asphalts 10 and 15 (within the tolerance of the determination) would also meet this requirement. Asphalts 7, 8, 9, and 11 have more than 40 percent asphaltenes, but are quite acceptable on a durability basis.

Similarly, a high-resin content may be regarded as conducive to good weathering. Knowles, McCoy, Weetman, and Eckert [20] recommended the addition of resins to asphalt to improve its durability. The resin contents of the asphalts in table 6 vary from 7.3 to 12.8 percent. If a minimum resin content is established, the logical value, based on these data, would be at about 9 percent. As in the case of the asphaltenes, the poorest asphalt would be admissible and three of the borderline asphalts would be excluded.

TABLE 6. Asphalt components

As- phalt	Dura- bility ª	Asphal- tenes	Resins	Dark oils	White oils	Resins Asphal- tenes	Total oils Asphal- tenes
	Days	%	%	%	%		
1	150	37.4	12.8	24.6	21.0	0.34	1. 22
2	88	37.0	9.4	27.5	22.5	. 25	1.35
3	87	37.8	11.9	28.0	19.5	. 31	1.26
4	86	36.6	11.0	21.7	27.0	. 30	1.33
5	84	38.5	10.0	27.0	22.4	. 26	1.28
6	72	37.2	9.7	25.9	24.8	. 26	1.36
7	68	42.1	10.8	22.9	22.7	. 26	1.08
8	57	45.5	9.6	21.9	21.1	. 23	0.95
9	53	41.8	8.6	23.6	26.8	. 21	1.21
10	47	39.1	8.0	22.8	28.3	. 21	1.31
11	47	42.2	9.1	25.2	20.0	. 22	1.08
12	44	44.1	8.6	19.8	26.6	. 19	1.05
13	43	43.6	6.9	25.3	20.2	.16	1.04
14	38	46.3	7.3	25.5	18.8	. 16	0.96
15	25	40.5	9.5	20.0	27.3	. 23	1.17

^a Fifty-percent failure level in the 51–9C cycle.

No such grouping exists that would relate the oil contents, either white or dark oil, alone or together, to durability. Since the failure of the asphalt results when there are insufficient oils to plasticize the asphaltenes, the initial ratio of oils to asphaltenes might have some relationship to durability. Examination of the data shows no such relationship to exist. However, when the ratios of resins to asphaltenes in the asphalts are compared with durabilities, and a minimum limit set at 0.25, the seven more durable asphalts are acceptable.

It is apparent that component analysis, either asphaltene content, resin content, or a ratio of the two, can be used to separate the better asphalts from the poorer ones. However, these criteria are subject to error, and they cannot be used as a basis for predicting quality until correlations have been obtained for many more asphalts.

5. Summary and Conclusions

Investigation of the characteristics of 15 coatinggrade asphalts indicated that through suitable processing all 15 had arrived at similar physical properties. All the asphalts lost weight on exposure to two different cycles in accelerated weathering machines. The asphalts ranged in durability from 25 to 150 days in the 51-9C cycle. Although there was no quantitative correlation between durability and any of the measured characteristics, there were groupings of the more and less durable asphalts based on specific gravity, flash point, carbon and hydrogen, sulfur, asphaltene, and resin contents.

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6. References

- [1] S. H. Greenfeld, E. W. Mertens, and P. W. M. John, A statistical study of weather-ometer data on coating-
- grade asphalts, to appear in ASTM Bull.[2] J. B. Niederl and V. Niederl, Micromethods of quanti-tative organic analyses (J. Wiley & Sons, Inc., New York, N.Y., 1952).
- [3] A. Stevermark, Quantitative organic microanalysis (The Blakiston Co., New York, N.Y., 1951). J. Unterzaucher, Ber. **73B**, 391 (1940). V. A. Aluise, R. T. Hall, F. C. Staats, and W. W. Becker,
- Oxvgen in organic compounds, Anal. Chem. 19, 347 (1947)
- [6] R. D. Hinkel and R. Raymond, Direct semimicrodeterminations of oxygen in organic substances, Anal. Chem. 25. 470 (1953)
- [7] M. Dundy and E. Stehr, Determinations of oxygen in organic materials by modified Schutze-Unterzaucher method, Anal. Chem. 23, 1408 (1951).
- [8] A. H. Corwin, Johns-Hopkins University (private communication).
- [9] O. E. Sundberg and G. L. Royer, Microdeterminations of halogen and sulfur, Anal. Chem. **18**, 719 (1946). [10] E. B. Hershberg and G. W. Wellwood, A carbon dioxide
- generator for the micro-dumas determination of nitro-
- gen, Ind. Eng. Chem. Anal. Ed. **9**, 303 (1937). [11] W. C. Alford, Microdetermination of nitrogen in organic compounds, Anal. Chem. 24, 881 (1952)
- [12] L. R. Kleinschmidt, Chromatographic method for the fractionation of asphalt into distinctive groups of components, J. Research NBS 54, 163 (1955) RP2577.
- [13] S. H. Greenfeld, A method for preparing uniform films of bituminous materials, ASTM Bull. 193, 50 (1953).
- [14] S. H. Greenfeld, The effects of thermal shock on the durability of asphalt coatings under accelerated test,
- ibid, 46-50 (1953). [15] L. R. Kleinschmidt and S. H. Greenfeld, Influence of exposure conditions on the accelerated durability test-ing of asphalts, ASTM Bull. **213** (1956).
- [16] A. H. Boenau and L. A. H. Baum, The design and application of a spark-gap instrument for detecting crack failures of asphalt coatings during weathering, symposium on accelerated durability testing of bituminous materials, ASTM (1949). [17] J. B. Hunter, F. C. Gzemski, and L. Laskaris, A new
- method for evaluating failure of bituminous materials
- due to weathering, ibid. [18] C. E. Wilkinson, L. Striker, and R. N. Traxler, Criterion for the evaluation of roof coating asphalts, ASTM Bull. 230, 42 (1958)
- [19] L. R. Kleinschmidt and H. R. Snoke, Effect of light and water on the degradation of asphalt, J. Research NBS **63C**, 31 (1959). [20] E. C. Knowles, F. C. McCoy, B. Weetman, and G. W.
- Eckert, Relation of asphalt composition to its durability in service, symposium on chemistry and composition of asphalts, Am. Chem. Soc. (Apr. 13-18, 1958).