NATIONAL BUREAU OF STANDARDS REPORT

8660

~~Not for publication or for reference.~~

MODIFIED BLOWING OF ASPHALTS

by

Sidney H. Greenfeld

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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NBS PROJECT		NBS REPORT
421.04-12-4210141	1 April 1965	8660

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ABSTRACT

The effects of blowing under reflux conditions or pressure and in the presence of oxygen, chlorine, or sulfur on the properties of coating-grade roofing asphalts were studied. Refluxing the volatilized and entrained oils tended to decrease the blowing losses and to improve the softening point-penetration relationships and the durabilities of asphalts produced from three fluxes. Pressure of 25 psig during blowing had mixed effects on the blowing times and physical properties of the asphalts, but increased their durabilities. The enrichment of the blowing air with 25 percent oxygen or 10 percent chlorine (without changing the total gas volume) greatly accelerated the blowing and improved the physical properties of the asphalts produced from four fluxes. Durabilities were also appreciably increased. On the other hand, five percent sulfur in conjunction with the blowing air or sulfur alone tended to decrease the durabilities of the asphalts and lower their penetrations. Sulfur did, however, accelerate the hardening reactions above 400°F (200°C). Only small percentages of the sulfur or chlorine used remained in the asphalts produced.

1. INTRODUCTION

Many methods exist for modifying the blowing process used to produce coating-grade roofing asphalts. This report will discuss two process variables and three oxidants in addition to air. The process variables were blowing under reflux conditions and under pressure; the oxidants were oxygen, chlorine, and sulfur.

In an earlier publication by Murayama (1)[1/], he reported that when all of the volatilized and entrained oils were refluxed during the blowing of an Arabian flux, the softening point-penetration relationships were independent of air rate, air volume, and reaction temperature. Although Arabian

1/ Numbers in parentheses refer to references tabulated in the bibliography.

asphalts are not used alone in this country for roofing purposes, they have been employed with some success as blending stocks. The differences encountered in their processing and weathering are related to their relatively paraffinic nature. The results reported by Murayama (1) may not be pertinent to the naphthenic and aromatic base stocks more customarily used.

Both Chelton, Traxler and Romberg (2) and Levinter and Galiakbarov (3) have reported that blowing under pressure reduced the blowing time and improved the rheological properties of asphalts. The former worked with both Louisiana and Texas fluxes; the latter, with a Tuimazy (Russia) flux. Chelton, et al, blew their fluxes to, and in some instances beyond, the coating-grade range. Levinter and Galiakbarov stopped short of coating-grade.

A number of investigators have reported on the use of oxygen, either alone or in addition to air, for blowing asphalt (4, 5, 6). Patents have been issued (7), in which its use to accelerate the blowing reaction alone and with catalysts has been claimed. Graham, et al (4) reported that irrespective of whether oxygen or air was used, only a small part of the oxygen used remained in the asphalt and the ratio of oxygen consumed to that supplied was constant. The apparatus, however, was very inefficient and only about one and a half percent of the oxygen was consumed. Campbell and Wright (6) reported that the softening point increase on blowing was much more rapid with oxygen than with air. Examination of their Figure 1 shows this increase to be of the order of seven fold. Graham, et al (4) reported in a similar vein that at normal blowing temperatures it required only one-third of the time to reach a given penetration when oxygen was used that it did with air.

Pfeiffer (8) reported on hardening of asphalt with chlorine or sulfur. Both of these agents performed in a manner similar to oxygen; that is, the asphalt hardened, only a small percentage of the additive remained in the asphalt and the major portion of the additive escaped from the asphalt as a reaction product with hydrogen. From the data presented, it appeared that the Venezuelan asphalt blown with chlorine was quite similar to the one blown with air. However, Pauer and Haruni (9) reported that when chlorine mixed with air was used to blow an asphalt flux from a mixed base Egyptian crude, the rate of reaction increased as the chlorine content increased (to 4 percent) and the softening point-penetration relationships were modified. Unfortunately the runs were made for periods of six hours. The products had widely different properties and were difficult to compare. In all instances where products had softening points in the vicinity of 220°F, less than one percent chlorine remained in the asphalts.

Sanderson (10) blew asphalt with dry chlorine at 300°F (150°C) (to favor addition instead of substitution reactions) until hydrochloric acid was evolved. Under these conditions the penetration decreased, the softening point increased and the resistance to hardening (on exposure to oxygen under pressure) increased. All of these asphalts were paving-grade materials.

A number of patents have been issued on the use of chlorine in conjunction with air to oxidize asphalts and oils (11). These claim chlorine improves the temperature susceptibility of asphalts when used in low concentrations.

Pfeiffer (8) reported that when 5-10 percent of sulfur was added to an asphalt flux at 350-400°F (180-200°C) perceptible reaction occurred, with the liberation of hydrogen sulfide. About a third of the sulfur used remained in the asphalt. The penetrations were lowered as the softening point was increased. However, the specific effects varied with the asphalt source. No information was presented on the use of sulfur in conjunction with air.

Sulfur was used rather extensively at one time to harden asphalts and improve their temperature susceptibility. The products were known as Dubbs asphalt, Ventura Flux or Pittsburgh Flux (12). The advent of air blowing has displaced these processes for economic reasons in the United States, but sulfur is still used in parts of Europe. A critical review and evaluation of the relative merits of sulfur in asphalts was made by Marten (13) in 1961. The reported results in the literature were rather inconclusive and highly speculative as far as durability was concerned. A literature review and bibliography of the use of sulfur in bitumens has been published by the Sulfur Institute (14). The most recent publication (15) on the use of sulfur to harden asphalts relates to its distribution in the asphalt components.

2. MATERIALS AND METHODS

The fluxes used in this study are described in Table I. The blowing characteristics of the soft fluxes were discussed earlier (16). The properties of asphalts produced from all of these fluxes both with and without blowing additives have also been reported (17).

TABLE I.

ASPHALT FLUXES

Flux	California Coastal	Kansas Soft	Kansas Hard	Talco Soft	Talco Hard	Tia Juana Soft[1/]	Tia Juana Hard
Softening Point, °F	122	101	120	104	120	104	111
Penetration at 32°F, 0.1 mm	20	42	18	44	27	44	25
Penetration at 77°F, 0.1 mm	64	249	80	190	92	152	91
Penetration at 115°F, 0.1 mm	TS[2/]	TS	TS	TS	TS	222	232
Specific Gravity at 77°F	1.030	0.994	1.004	1.020	1.022	1.004	1.011
Flash Point (C.O.C.), °F	460	635	645	555	560	575	620
Asphaltenes, %	30.7	19.3	24.9	26.7	28.1	23.4	20.8
Sulfur, %	5.6	1.4	1.4	4.6	4.8	2.9	3.1

1/ Partially blown.

2/ Too soft.

The blowing stills described in reference (16) were modified to accommodate the special requirements for each phase of this study.

For the refluxing work, a water-cooled, straight copper tube (7/16 in. inside diameter by 21-in. long) was used as a condenser on the vapor exhaust from the still. Substantially all of the condensable material in the exhaust gases was drained back into the still by this condenser.

When the asphalts were blown under pressure, a throttling valve was put on the exhaust from the still to control the back pressure at the desired level. The flow rate was corrected to provide the reported volume of gas at standard conditions.

Oxygen or chlorine gas was passed directly into the apparatus from its respective gas cylinder through a rotameter. It was blended with metered air before entering the still. When oxygen was used the exhaust gases were vented directly into the hood, but when chlorine was used they were percolated through a dilute sodium hydroxide solution to dispose of the hydrochloric acid generated and any unreacted chlorine. No noticeable odors of chlorine or hydrochloric acid were apparent in the exhaust of the absorber.

Flowers of sulfur were blended into the asphalt fluxes below 350°F (177°C) with the aid of a laboratory stirrer prior to adding the flux to the blowing still. In this temperature range, no evolution of gases was evident. However, at temperatures above 400°F (200°C) gas was exhausted from the still whether or not air was being introduced. The gases were percolated through a sodium hydroxide solution before being exhausted in a hood. A faint odor of hydrogen sulfide always persisted over the caustic solution.

In the determinations in which sulfur was used alone, a weighed quantity of flowers of sulfur was stirred slowly into about 300 grams of asphalt in a pint can on a thermostated hot plate. The first series was maintained at approximately 430°F (220°C) until a coating-grade softening point was obtained. At this temperature, the reaction was extremely violent and the softening point rise very rapid, as shown in Table II.

TABLE II.

EFFECT OF SULFUR ON ASPHALT AT 430°F (220°C)

Asphalt	Sulfur %	Final SP °F	Reaction Time Min.
California	5	217	83
California	7	219	81
California	9	219	80
California	10	222	80

Penetrations could not be determined on these asphalts because they were quite foamy and reaction continued whenever they were heated sufficiently to start breaking the foam. Consequently, nothing further was done with this set.

A second series of runs was made with the object of finding the concentration of sulfur required to harden each flux to a coating-grade softening point and no higher. The temperature was reduced to the 375-400°F (190-205°C) range to slow the reaction and reduce the foaming. At these lower temperatures the reactions were steady and the following results obtained (Table III).

TABLE III.

EFFECT OF SULFUR ON ASPHALTS AT 375-400°F (190-205°C)

Sulfur Concentration %	California S.P. °F	California Time Min.	Kansas (S) S.P. °F	Kansas (S) Time Min.	Talco (S) S.P. °F	Talco (S) Time Min.	Tia Juana (S) S.P. °F	Tia Juana (S) Time Min.
2	149	810	123	680				
3	180	1560	120	680	148	690		
4	---	---	142	1080	172	690		
5	196	1200	147	660	196	690	162	660
6			168	1410			203	660
8			196	1140			---	---
9							232	1140

From extrapolations and interpolations of these results, the concentrations of sulfur required to approximate coating-grade softening points were determined and the following asphalts produced (Table IV).

3. RESULTS AND DISCUSSION

(a) Total Reflux

When asphalts are blown under conditions of relatively poor contact between the blowing air and the asphalt flux, long periods of time are spent in the stills. During this residence at high temperature the part of the air that is not consumed tends to strip the more volatile components and reaction products from the flux and discharge them with the exhaust gases. This material is, quite frequently, burned along with the fuel to heat the stills in commercial installations. As reported earlier (16), fluxes with low molecular weight oils have the greatest losses; the California flux blown without agitation lost as much as 11%. This loss of oils is not only uneconomical, but it hardens the resulting asphalt unduly.

One way to reduce this type of blowing loss is to reflux the oils back into the charge by means of a condenser on the exhaust port. When this was done on one of the laboratory blowing stills, the results reported in Table V were obtained.

TABLE IV.

SULFUR HARDENED ASPHALTS

Flux	Sulfur %			Reaction Time Min.	S.P. °F	Penetrations at 32°F dmm	77°F dmm	115°F dmm	Durability (51-9C) Days
	In Flux	Added to Flux	In Asphalt						
California	5.6	5.5	6.7	2340	215	6	8	20	44
Kansas (Soft)	1.4	9.25	3.4	660	216	8	14	23	34
Talco (Soft)	4.6	8.7	6.7	870	217	7	13	22	26
Tia Juana (Soft)	2.9	7.9	4.8	600	219	8	13	26	36

TABLE V.

Air Blowing Under Reflux Conditions
475°F, No Agitation, 75ft^3/Ton-Min.

	California		Talco (Soft)		Talco (Hard)		Tia Juana (Soft)		Tia Juana (Hard)	
	Reflux	Normal	Reflux	Normal	Reflux	Normal	Reflux	Normal	Reflux	Normal
Softening Point, °F	219	223	217	219	219	219	217	217	219	217
Penetration										
at 32°F, 1/10 mm	6	4	13	11	9	12	14	14	10	9
at 77°F, 1/10 mm	10	9	20	17	15	17	23	21	16	16
at 115°F, 1/10 mm	23	17	35	33	28	32	38	38	29	30
Blowing Time, Min.	453	300	540	600	553	212 [2]	415	390	390	374
Blowing Loss, %	0.5	10.0	1.0 [1]	2.5	0.2	0.4	0.0	1.2	- [3]	- [3]
Durability(51-9c),Days	53	44	65	45	62	57	69	59	92	68

1/ A small, but undetermined, transfer loss is included in this figure.

2/ Blown with 150ft^3/Ton-Min Air Rate

3/ Not determined

The blowing losses were reduced for each flux, but most dramatically for the California one. Here, a prohibitively high loss of 10 percent was reduced to 0.5%, even though the blowing time was increased 50%. While the resultant asphalt was not improved sufficiently to meet coating-grade requirements, its penetrations were increased and its durability improved.

The losses for both the soft and hard Talco fluxes were also reduced, and the penetrations of the asphalt produced from the softer flux were increased. However, the blowing time was shortened by 10%. This decrease in blowing time may indicate that the oils returned to the asphalt were relatively more susceptible to the changes that are produced by blowing than those that normally remain in the residue (18). This speculation is given further credence by the fact that the asphalt produced under reflux conditions from the harder Talco flux required a longer blowing time than did the soft flux under the same conditions. The material lost during reduction from the soft flux (175/200 pen.) to the hard flux (85/100 pen.) were these same susceptible oils. Unfortunately, an arbitrary change in the air rate to permit the completion of runs in one day left no "normal" run for the hard Talco flux to be compared with the reflux run. The durability of the Talco asphalt produced from the soft flux under reflux was appreciably greater than that of the normally produced asphalt.

The Tia Juana asphalts produced under reflux were also appreciably more durable than their normally produced counterparts. However, little change in the penetrations and only slight increases in the blowing times were observed. The blowing losses were reduced to zero for the soft flux; loss determinations were not made for the hard flux.

In summary, it is apparent that refluxing the oils always improved the durability of the resultant coating-grade asphalts and usually improved the softening point-penetration relationships. The blowing time was usually increased, but where reactive oils were refluxed, it was decreased. The changes were most pronounced for asphalts that normally had appreciable blowing losses.

(b) Blowing Under Pressure

Because of the complexity of the reactions occurring during blowing, it would be difficult to anticipate the precise effects of increased pressure. There are a number of positive effects, such as increased solubility of oxygen in the charge, reduction of volume by oxygen combination with molecules in the asphalt and decreased bubble size, which should tend to increase the reaction rate. There are neutral effects, such as maintenance of the same proportions of nitrogen to oxygen and the formation of one molecule of carbon dioxide from one molecule of oxygen. And there are negative effects, such as the

formation of two molecules of water from each molecule of oxygen, the increased solubility of volatile reaction products in the charge and the smaller volume of unreacted gases sweeping the reaction products from the charge. The net effect would be the resultant of these and other unanticipated factors; the nature of the net effect should be related to both processing conditions and asphalt source.

Examination of the data in Table VI reveals that the effect of pressure on the processing and properties of the fluxes was quite variable. In one instance (soft Talco flux), the blowing time was reduced by 20%; in another, the hard flux from the same Talco source, it was increased 30%; and in the two other instances for which comparable data are available, the blowing time was unaffected. The penetrations of the asphalt produced from the California flux blown under pressure were increased appreciably, but those of asphalts produced from the other fluxes were changed only to a minor degree. The asphalts blown under 25 psig pressure were all appreciably more durable than their counterparts blown at atmospheric pressure. The improvements ranged from 10 to 17 days, averaging about 20%.

Chelton, Traxler and Romberg (2) had reported a decrease in blowing time and an increase in penetration at 77°F for Texas and Louisiana fluxes blown under pressure; the magnitudes of the effects were different for the two, however. This work shows that for some fluxes these improvements are valid; for others, little effect on penetration or blowing time was observed at 25 psig.

(c) <u>Blowing with Oxygen-Enriched Air</u>

Whenever air is used in a controlled oxidation process, enrichment with oxygen can be used to increase existing capacity at a relatively low initial investment cost. The proportion of oxygen that can be used is related to the economics and physical limitations of the process. In the case of air blowing of asphalts, the use of oxygen alone has been reported both at normal blowing temperatures (4) and at lower-than-normal blowing temperatures (6). The oxygen in both instances reduced the blowing times, but in neither were sufficient data reported to describe the products sufficiently well to determine if oxygen changed their properties appreciably.

The data in Table VII describe the asphalts produced with 25% oxygen enrichment of the blowing air without changing its volume flow rate. The entrance air was 40 percent oxygen. This enrichment shortened the blowing times for all four fluxes by from 30 to 50 percent. Greater enrichment would be expected to reduce it further. The exact acceleration would depend on the efficiency of contact, time of contact, nature of the flux and conditions of blowing. Graham, et al (4), working with a Lloydminster flux, found a 70% acceleration when 100% oxygen was used.

TABLE VI.

Air Blowing Under Pressure

475°F, No Agitation, 150ft^3/Ton-Min

	California		Talco (Soft)		Talco (Hard)		Tia Juana (Soft)		Tia Juana (Hard)	
	25 psig	Normal	25 psig	Normal	25 psig	Normal	25 psig	Normal	25 psig	Normal
Softening Point, °F	219	217	217	219	217	219	219	217	219	217
Penetration										
at 32°F, 1/10 mm	7	4	13	12	10	12	14	14	9	9
at 77°F, 1/10 mm	12	8	20	19	16	17	20	22	15	16
at 115°F, 1/10 mm	27	18	38	36	30	32	34	39	29	30
Blowing Time, Min	248	240	258	317	282	212	210	206	246	374 1/
Blowing Loss, %	0.4	0.3	0.8	0.9	0.1	0.4	0.8	0.4	0.2	-
Durability(51-9c), Days	61	44	66	56	74	57	70	60	80	68

1/ 75ft^3/Ton-Min Air Rate

TABLE VII.

Blowing with 25% Oxygen-Enriched Air

475°F, No Agitation, $150 ft^3$/Ton-Min

	California		Kansas (Soft)		Talco (Soft)		Tia Juana (Soft)	
	25% O_2	Normal	25% O_2	Normal	25% O_2	Normal	25% O_2	Normal
Softening Point, °F	217	217	217	221	219	219	217	217
Penetrations								
at 32°F, 1/10 mm	7	4	14	11	13	12	14	14
at 77°F, 1/10 mm	11	8	20	19	18	19	21	22
at 115°F, 1/10 mm	23	18	36	29	33	36	37	39
Susceptibility	1.45	1.75	1.10	0.95	1.11	1.26	1.10	1.14
Blowing Time, Min	169	240	160	330	178	317	129	206
Blowing Loss, %	0.9	5.0	0.2	0.0	1.1	0.9	0.6	0.4
Durability(51-9c),Days	71	44	108	65	66	56	80	60

The penetrations of the California and Kansas asphalts were higher than normal, but the former were not high enough to meet coating-grade specifications. The penetrations of the Talco and Tia Juana asphalts were essentially unchanged. The durabilities of all of the asphalts produced with the oxygen-enriched air were higher than their normally produced counterparts. The improvements ranged from 18 percent for the Talco asphalts to 66 percent for the Kansas asphalts.

Thus, the use of oxygen to enrich the blowing air always decreased the blowing time and increased the durabilities of asphalts from the four sources.

(d) Blowing with Chlorine-Enriched Air - (Table VIII)

The use of 5% or 10% chlorine in the blowing air greatly accelerated the hardening of all four fluxes. The accelerations were appreciably greater than those produced by the oxygen-enrichment. As blowing progressed, copious quantities of hydrochloric acid gas were produced, indicating that much of the chlorine was consumed in dehydrogenating the fluxes. Analyses of the blown asphalts revealed that only 8-11 percent of the chlorine used remained with the asphalts. These results are in agreement with Sanderson's (10), even though he used chlorine alone at temperatures at which addition was the principal reaction and he stopped when hydrochloric acid evolution began. These results would indicate that the chlorine addition products formed are relatively stable and once they have formed, the reactions become entirely dehydrogenations.

Because the literature reported chlorinated asphalts to have higher penetrations for a given softening point than normally blown asphalts, the hard fluxes were used for this series. In all instances, 10% chlorine in the blowing air significantly increased the penetrations of the blown asphalts; it even brought the California asphalt into normal coating-grade specifications (16).

Whereas blown asphalts normally have flash points very close to those of the fluxes from which they were produced, the California and Talco asphalts produced with chlorine had flash points significantly higher than their fluxes.

The chlorinated asphalts were all more durable than their corresponding normally produced asphalts. While the increases in durability were not great, they ranged from 14 percent for the Talco asphalts to 38 percent for the Tia Juana asphalts.

TABLE VIII.

Blowing with Chlorine-Enriched Air

475°F, No Agitation, 150ft^3/Ton-Min

	California			Kansas (Hard)			Talco (Hard)		Tia Juana (Hard)	
	5% Cl	10% Cl	Normal	5% Cl	10% Cl	Normal	10% Cl	Normal	10% Cl	Normal
Softening Point, °F	223	219	217	219	221	219	221	219	217	217
Penetrations										
at 32°F, 1/10 mm	9	10	4	13	18	9	14	12	13	9
at 77°F, 1/10 mm	15	17	8	24	29	18	20	17	22	16
at 115°F, 1/10 mm	29	32	18	39	48	36	37	32	40	30
Susceptibility	1.33	1.39	1.75	1.08	1.03	1.50	1.15	1.18	1.23	1.31
Blowing Time, Min	75	45	240	53	35	202	41	212	35	374
Blowing Loss, %	0.6	0.6	5.0	0.3	0.2	0.8	0.8	0.4	-	-
Chlorine Used, % of Asphalt	5.1	6.2	-	3.6	4.9	-	5.8	-	4.9	-
Chlorine Retained, % of Asphalt	-	0.61	-	-	0.53	-	0.37	-	0.45	-
Flash Point (COC) °F	490	480	460	625	630	635	600	560	615	620
Durability(51-9c),Days	-	60	44	89	93	81	65	57	94	68

1/ 75ft^3/Ton-Min Air Rate

(f) Blowing Asphalts in the Presence of Sulfur - (Table IX)

As discussed by Martin (13), the effect of sulfur on the oxidation of asphalts is not well understood. No work has been reported on the effect of blowing with sulfur and air on the durability of asphalts. However, Bencowitz and Boe (19) reported that asphalts hardened with 25% and 40% sulfur under conditions which did not involve the evolution of hydrogen sulfide tended to increase more slowly in softening point and decrease more rapidly in penetration during weathering than did normally produced asphalts.

Sulfur was very effective in decreasing the time required to blow each flux to a coating-grade softening point. Five percent sulfur reduced the time about 40% for three of the fluxes and 70% for the California flux. Ten percent sulfur reduced the time another 40% for the Kansas flux and another 27% for the California flux. The latter required only eight minutes; the asphalt product in the latter case was so reactive that it hardened too much on reheating to permit the determination of meaningful penetrations.

Sulfur generally reduced the durabilities of the asphalts. At the five percent level the reduction ranged from zero for the California asphalts to 40 percent for the Talco asphalts. The reduction was much greater when 10 percent sulfur was used, ranging to over 75 percent for the California asphalt. Even though chemical analyses showed that only small permanent increases in the concentration of sulfur occurred, all of the asphalts blown with sulfur continued to change faster than normal when heated to the vicinity of 400°F (200°C).

Because of the violence of the reaction between sulfur and asphalt flux in the absence of blowing air above about 425°F (218°C), the reactions were conducted between 375 and 400°F (190-205°C). Only sufficient sulfur was used to permit the reaction to be essentially complete at softening points near those of coating-grade asphalts. As seen in Table IV, the reaction times were extremely long at these temperatures and only 20 to 25 percent of the sulfur used remained in the asphalts. Very little additional hardening occurred during the preparation of exposure specimens. The penetrations were drastically lowered for all except the asphalt produced from the California flux, which were similar to those of the normally produced asphalt.

TABLE IX.

Blowing Asphalts in the Presence of Sulfur

	California			Kansas (Soft)			Talco (Soft)		Tia Juana (Soft)	
	5% S	10% S	Normal	5% S	10% S	Normal	5% S	Normal	5% S	Normal
Softening Point, °F	217	223	217	217	223	221	217	219	221	217
Penetrations										
at 32°F, 1/10 mm	6	1/	4	12	8	11	9	12	10	14
at 77°F, 1/10 mm	11	1/	8	18	15	19	14	19	14	22
at 115°F, 1/10 mm	23	1/	18	32	27	29	27	36	29	39
Blowing Time, Min	66	8	240	189	60	330	180	317	127	206
Blowing Loss, %	0.7	-	5.0	0.8	1.2	0.0	-	0.9	0.7	0.4
Sulfur, % of Asphalt	6.8	-	5.6	-	-	1.4	-	4.6	3.1	2.9
Durability(51-9c), Days	46	10	44	53	32	65	34	56	45	60

1/ Hardened upon reheating for penetration determinations

The durabilities of the normally produced asphalts generally varied inversely with the sulfur content of the fluxes from which they were produced (but were not necessarily related to sulfur content); there was no trend of durability with sulfur content of asphalts hardened with sulfur. The durabilities of all but the California asphalt were greatly reduced; that of the California asphalt was unchanged. From these data it would seem that sulfur can, at best, produce asphalts similar to those produced by air blowing and usually produces asphalts markedly inferior for roofing uses.

4. BIBLIOGRAPHY

(1) Murayama, K., T. Fukushima, Y. Fukuda, and A. Shimada, Bull. Jap. Pet. Inst. 2, 63-9 (1960).

(2) Chelton, A. M., R. N. Traxler, and J. W. Romberg, Ind. Eng. Chem. 51, 1353-4 (1959).

(3) Levinter, M. K. and M. F. Galiakbarov, Khim. i Teknol. Topliv. i Masel 9, 32-6 (1964).

(4) Graham, W., W. J. G. Cudmore, and R. D. Heyding, Can. J. Technol. 30, 143-52 (1952).

(5) Shearon, W. H., Jr. and A. J. Hoiberg, Ind. Eng. Chem. 45, 2122-32 (1953).

(6) Campbell, P. G. and J. R. Wright, Ind. Eng. Chem. Prod. Res. and Dev. 3, 186-194 (1964).

(7) Abraham, H., Asphalt and Allied Substances, D. Van Nostrand, Sixth Ed., II, 169 (1964).

(8) Pfeiffer, J. P., The Properties of Asphaltic Bitumen, Elsevier Publishing Co., 1950.

(9) Pauer, V. O. and M. M. Haruni, Erdol u Kohle 12, 771-773 (1952).

(10) Sanderson, F. C., Highway Res. Bd. Bull. 118, 1-11 (1956)

(11) (a) Douthett, O. R., U.S.P. 1,979,677, Nov. 6, 1934.

(b) Sparks, J. W., U.S.P. 2,059,051, Oct. 27, 1936.

(c) McConnell, E. B., U.S.P. 2,148,869, Feb. 28, 1939.

(d) Burk, R. E. and C. H. Whitacre, U.S.P. 2,200,914, May 14, 1940.

(e) Mauch, K. and O. Pauer, U.S.P. 2,348,832, May 16, 1944.

(12) Abraham, H., Asphalt and Allied Substances, D. Van Nostrand, Sixth Ed., II, 156, 178-179 (1964).

(13) Martin, K. G., J. Inst. Pet. 47, 321-328 (1961).

(14) Sulfur in Bitumens - A Literature Survey, The Sulfur Institute Tech. Bull. 7, (1963).

(15) Tucker, J. R. and H. E. Schweyer, Ind. Eng. Chem. Prod. Res. and Dev. 4, 51-57 (1965).

(16) Greenfeld, S. H. Ind. Eng. Chem. Prod. Res. and Dev. 3, 158-164 (1964).

(17) Greenfeld, S. H., NBS Report 8607, Air Blowing Asphalts in the Presence of Additive Oils, Catalysts and Polymers, Dec. 15, 1964.

(18) Greenfeld, S. H. and J. C. Weeks, NBS Report 8110, A Comparison of Thin-Film Oxidation with Conventional Weatherometer Exposures, Oct. 18, 1963.

(19) Bencowitz, I. and E. S. Boe, Effect of Sulfur on Some of the Properties of Asphalts, ASTM Preprint, 9 pp. (1938).

5. ACKNOWLEDGMENT

This work was sponsored by the Asphalt Roofing Industry Bureau at the National Bureau of Standards under the guidance of their Research Committee. The author gratefully acknowledges the advice of the members of the Research Committee, both individually and collectively, and the help of Messrs. T. R. Davis and J. C. Weeks, ARIB Research Associates, for their assistance in collecting the data reported here.

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