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NATIONAL BUREAU OF STANDARDS REPORT

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A COMPARISON OF THIN-FILM OXIDATION

WITH CONVENTIONAL WEATHEROMETER EXPOSURES

by

S. H. Greenfeld

and

J. C. Weeks

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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ABSTRACT

The thin-film oxidation characteristics of eleven asphalts blown in laboratory stills from four different fluxes were determined and compared with conventional durability data determined in weatherometers. The more volatile oils in the asphalts seemed to be the least resistant to oxidation, for asphalts produced from the fluxes that were reduced the most before blowing and the asphalts produced in the runs with the largest blowing losses were the most resistant to oxidation. However, some of the asphalts that had retained these oils were the more durable.

The time required to produce a carbonyl index of 0.080 for these asphalts correlated with durability and the correlations fit the curve reported by Wright and Campbell (3). However, these data did not fit the other correlations reported by these authors.

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1. INTRODUCTION

Exposure of asphalts in the form of films approximately twenty-five mils thick on aluminum panels (1)[1/] in weatherometers has been used for many years as a means for predicting the life expectancy of finished roofing products. Although this procedure has a number of deficiencies, a sufficient background of information has been developed to permit asphalt technologists to use the technique with confidence. Thus, a decision involving asphalt durability can be made in a matter of weeks instead of years.

As long as asphalt sources were relatively few in number and little was being done to change processing techniques, the few weeks required for weatherometer evaluations were not objectionable. However, as more sources of asphalt have become available and processing technology has advanced, more rapid methods for predicting durability have become desirable. Greenfeld and Wright (2) reported on a comparison of four such procedures. While all gave results that generally correlated with durability, there was always sufficient scatter to raise questions concerning the value of these correlations for predicting the durability of individual, unfamiliar asphalts. One of these four procedures consisted of the exposure of films of asphalt one mil thick to a carbon arc for seven hours and measuring the change in absorbance of the film in the 5.88μ region of the infrared spectrum. The data scattered as in the other procedures, but the method was developed further by Wright and Campbell (3) to yield improved correlations with durability. One of the principal reasons for the scatter was the nature of the oxidation of asphalts. Each asphalt, as it oxidizes, undergoes an induction period followed by a uniform rate period and a changing rate period and terminates with film rupture. As each of these periods is variable in length as well as in magnitude of oxidation, the selection of any arbitrary exposure time can lead only eventually to difficulty. The improved correlations, therefore, each involved some meaningful part of the oxidation-rate curve rather than some arbitrary oxidation time. Wright and Campbell, working with eight asphalts, reported correlations with durability (51-9c cycle) of the time to film failure, the time to deviation from the uniform rate period, the time to the end of the induction period, and the time to produce a given change in absorbance. (ΔA=0.080).

All of this work was based on commercial asphalts; their physical properties were within coating-grade roofing asphalt specifications and they were actually being used by roofing manufacturers when obtained.

[1/] The numbers in parentheses refer to references listed at the end of the report.

It appeared that this thin-film oxidation rate procedure might be used to yield data that would permit a better understanding of the behavior of the asphalts produced in the laboratory. Specimen asphalts were selected to represent the ranges of durability of the asphalts blown from each flux and the effects of some of the blowing variables on thin-film oxidation. This brief report covers the results of this study.

2. MATERIALS AND METHODS

The fluxes from which most of the asphalts used in this study were blown and the blowing apparatus and procedure have been described (4). The asphalts produced in runs B217, B213 and B81 were blown from harder fluxes than those previously described, but coming from the same corresponding batches of crude. These were produced by the refineries by continuing to reduce the crude after the softer fluxes had been withdrawn. These three harder fluxes are described in Table 1.

TABLE 1.

Properties of Hard Fluxes

Property	Source		
	Kansas L27	Talco 85/100	Tia Juana 611*
Softening Point, °F	120	120	111
Penetration @ 32°F, 1/10 mm	19	---	25
Penetration @ 77°F, 1/10 mm	83	92	91
Penetration @ 115°F, 1/10 mm	TS	TS	232
Flash Point (coc), °F	620	560	620
Specific Gravity @ 77°F	1.0077	---	---
Specific Gravity @ 60°F	---	1.032	---
Coating Asphalt Designation	B217	B213	B81

*Partially blown at the refinery.

The blowing conditions used to make the asphalts employed in this study and the properties of the asphalts are summarized in Table 2.

The conventional durability figures were obtained from the exposure of coatings 25 mils thick on aluminum panels in two weatherometers. The specimens were prepared as described in ASTM C 1669-59T,[2/] exposed to the 51-9c cycle (Cycle A of ASTM D 529-59T) and removed at the 50% failure level (ASTM D 1670-59T).

[2/] Teflon reinforced with glass was used in place of the dextrin-coated paper.

TABLE 2.

Description of Asphalts

Run No.	Flux	Blowing Conditions					S.P.	Penetrations		
		Time, Min.	Temp. °F	Agitation rpm	Air Rate ft^3/T.M.	Loss %	°F	@ 32°F 1/10 mm	@ 77°F 1/10 mm	@115°F 1/10 mm
B38	California	84	439	1400	75	0.5	221	7	15	28
B39	California	64	531	1400	75	1.0	223	6	10	22
B52	California	225	518	0	75	11.0	225	3	6	12
B85	Kansas L22	81	473	1400	150	1.0	219	12	21	36
B89	Kansas L22	330	475	0	75	0.0	221	11	19	29
B217	Kansas L27	62	474	1400	75	0.8	219	12	19	34
B16	Talco 175/200	65	478	1400	75	0.5	217	13	20	34
B111	Talco 175/200	452	526	0	75	1.0	223	10	16	26
B213	Talco 85/100	61	470	1400	150	0.5	217	11	18	35
B78	Tia Juana 612	64	475	1400	75	1.5	217	13	21	37
B81	Tia Juana 611	75	472	1400	75	1.0	217	11	16	31

The thin films were prepared in accordance with a modification described by Wright and Campbell (3) of the procedure reported by Greenfeld and Wright (2). A further modication in the film holders was made by Wright and Campbell (5); the new holders were used in this work. They were approximately 3/8 inch wide and 2 inches high and consisted of two 1/8-inch thick aluminum plates between which the asphalt film was clamped. A window 1/4-inch wide by 1-inch high with rounded corners permitted the asphalt to be exposed and scanned.

The thin films were exposed in a Model SMCR Weather-Ometer at 120±2°F and 40% R.H. The infrared scans were made in a Perkin-Elmer Infracord Spectrophotometer, Model 137. A special adapter plate was made to hold the specimens in the spectrophotometer.

The carbonyl index was calculated from the change in absorbance at 5.88μ produced during exposure. A baseline drawn between the 5.5 and 6.5μ shoulders was used as the reference as described in (3) and shown in Figure 1.

3. RESULTS

A typical pair of infrared spectra are shown in Figure 1. Only the portion of the spectra pertinent to this study were measured in order to save time.

Figure 2 contains oxidation rate curves at 120°F and 40% R.H. of three asphalts blown from the California flux. Figure 3 contains three oxidation rate curves of Kansas asphalts exposed under the same conditions. Figure 4 contains the oxidation rate curves of three Talco asphalts and Figure 5, two oxidation rate curves of Tia Juana asphalts.

Table 3 is a summary of the conventional durability of the 11 asphalts studied and a compilation of a number of parameters measured on the curves in Figures 2 to 5.

4. DISCUSSION OF RESULTS

Figure 1 contains typical infrared spectra of one thin film of asphalt before and after exposure for 22 hours to the radiant energy of a carbon arc at 120°F and 40% R.H. These conditions of exposure were selected to produce oxidation results that would be comparable to those reported earlier (3). In Table 3 are tabulated parameters that can be related directly to those Wright and Campbell (3) correlated with durability for eight asphalts. These results do not fit their correlations involving length of induction period, slope of the constant rate period, time to deviation from the constant rate or breaking point. However, except for

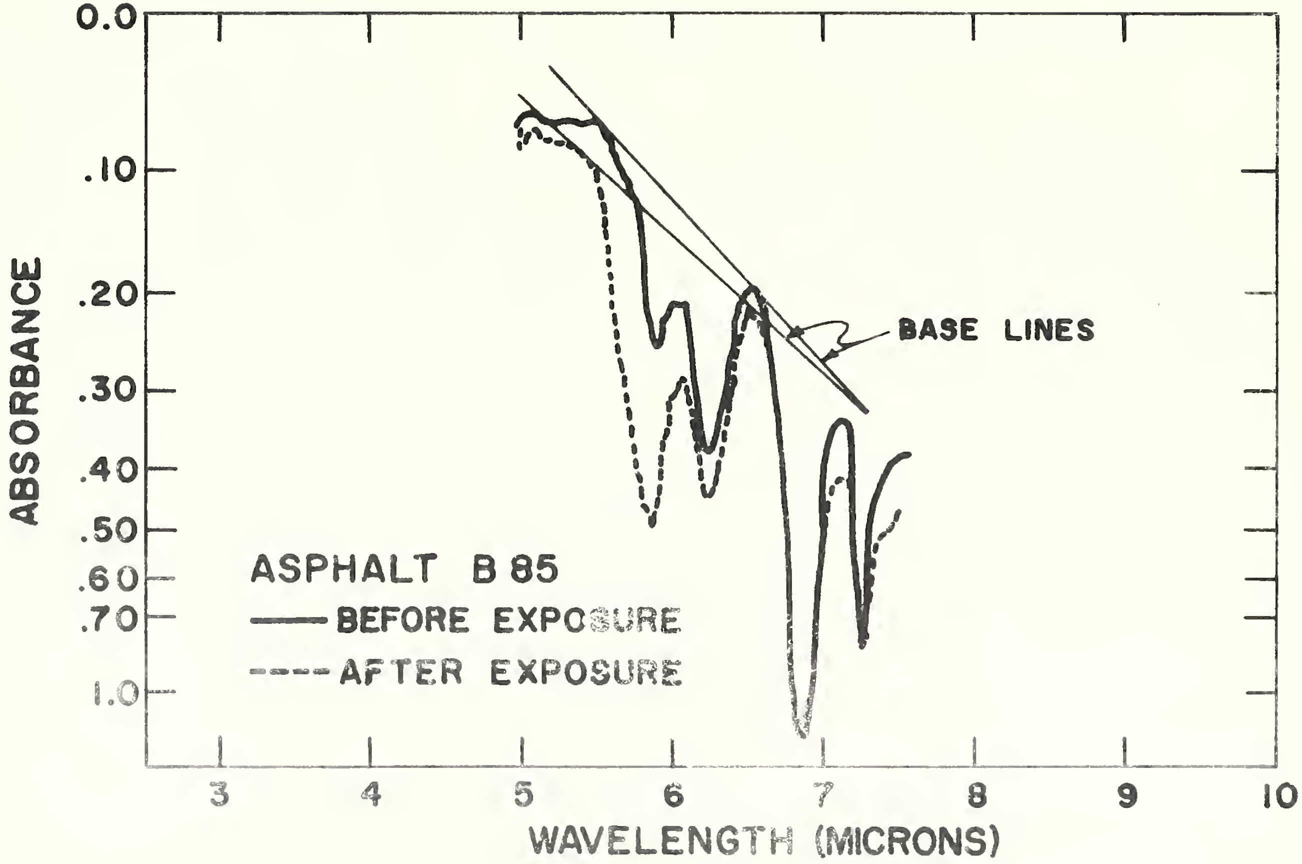

FIG. 1 - TYPICAL INFRA-RED SPECTRA.

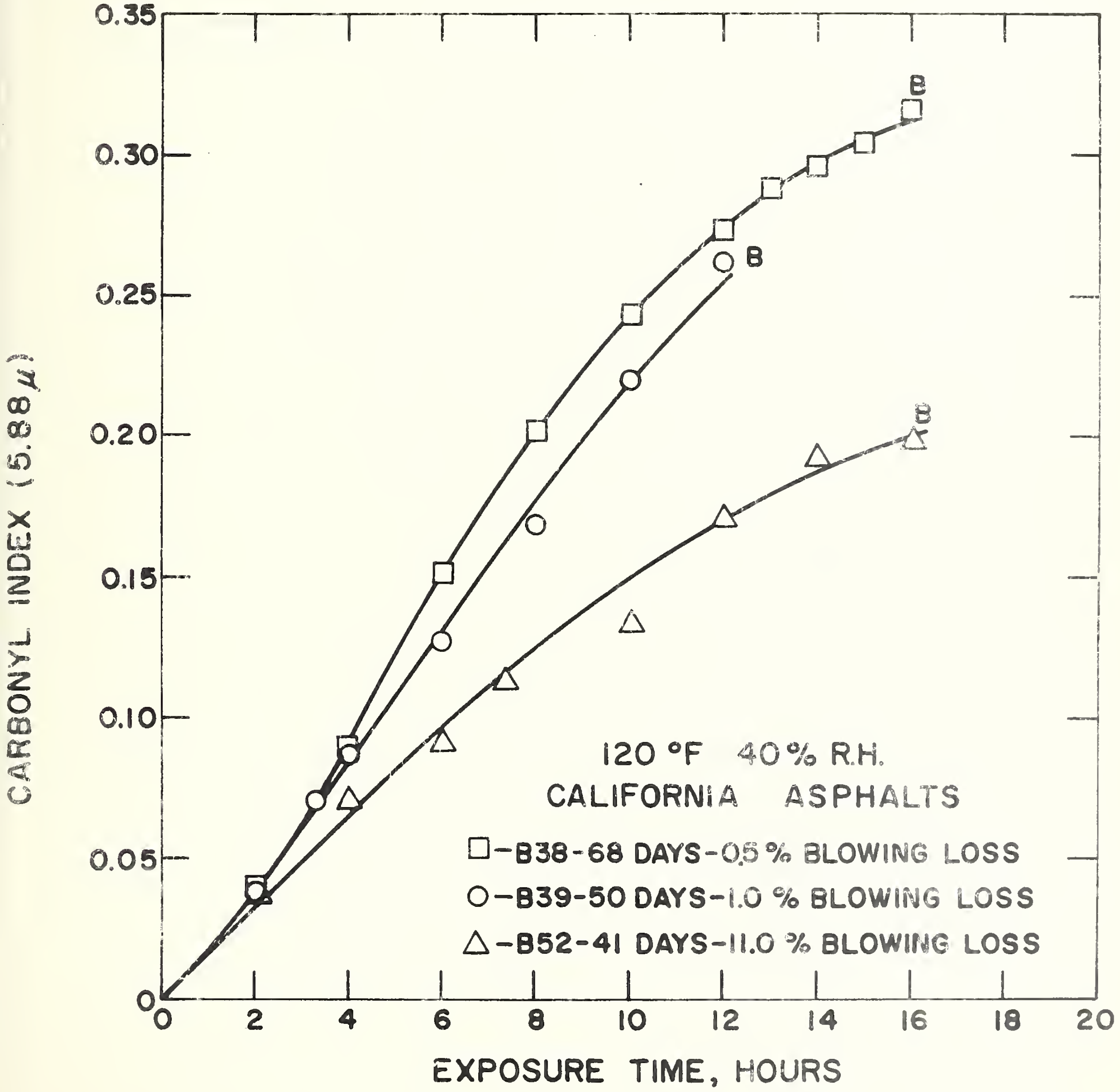

FIG. 2- CARBONYL INDEX VS EXPOSURE TIME.

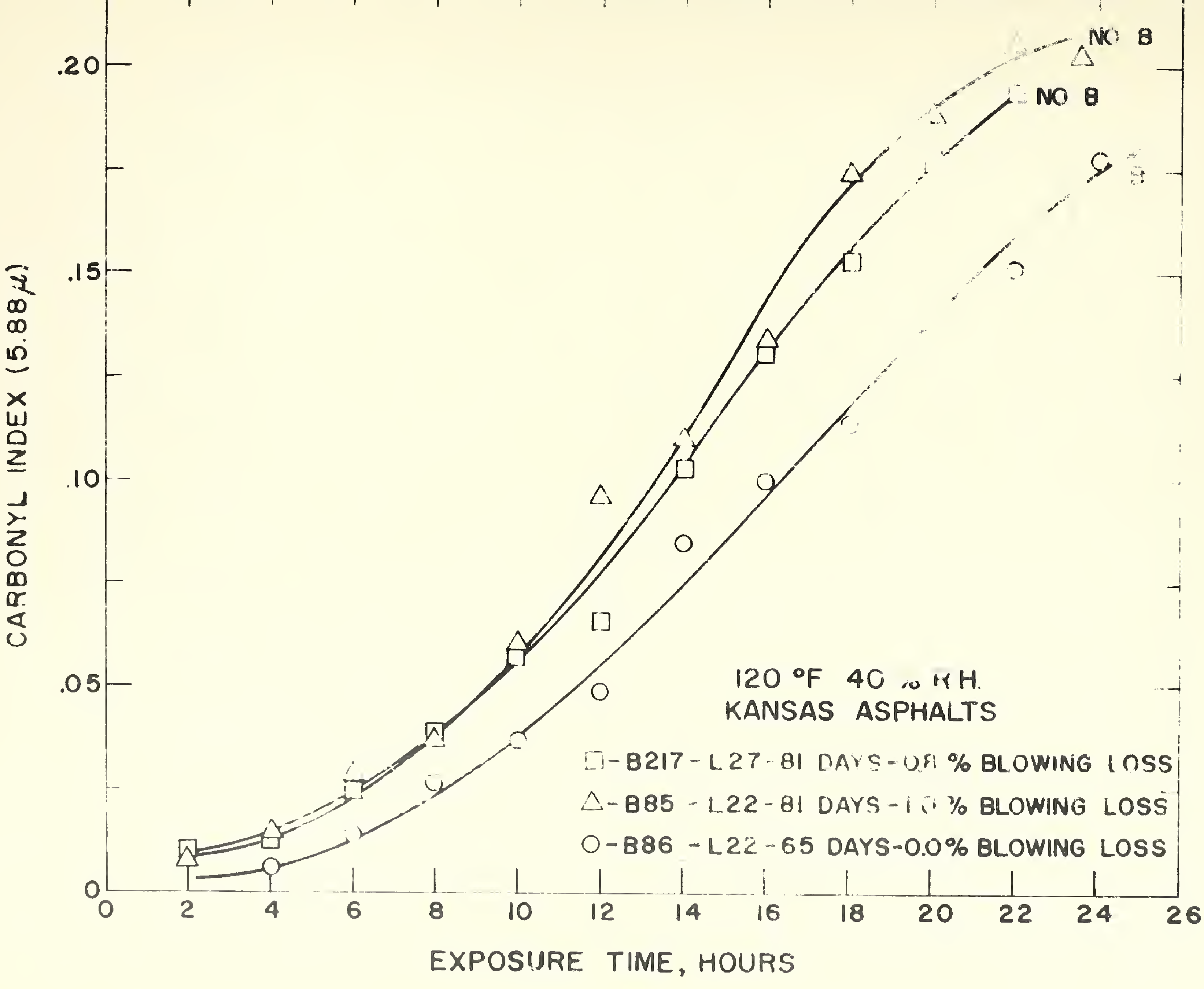

FIG. 3-CARBONYL INDEX VS EXPOSURE TIME.

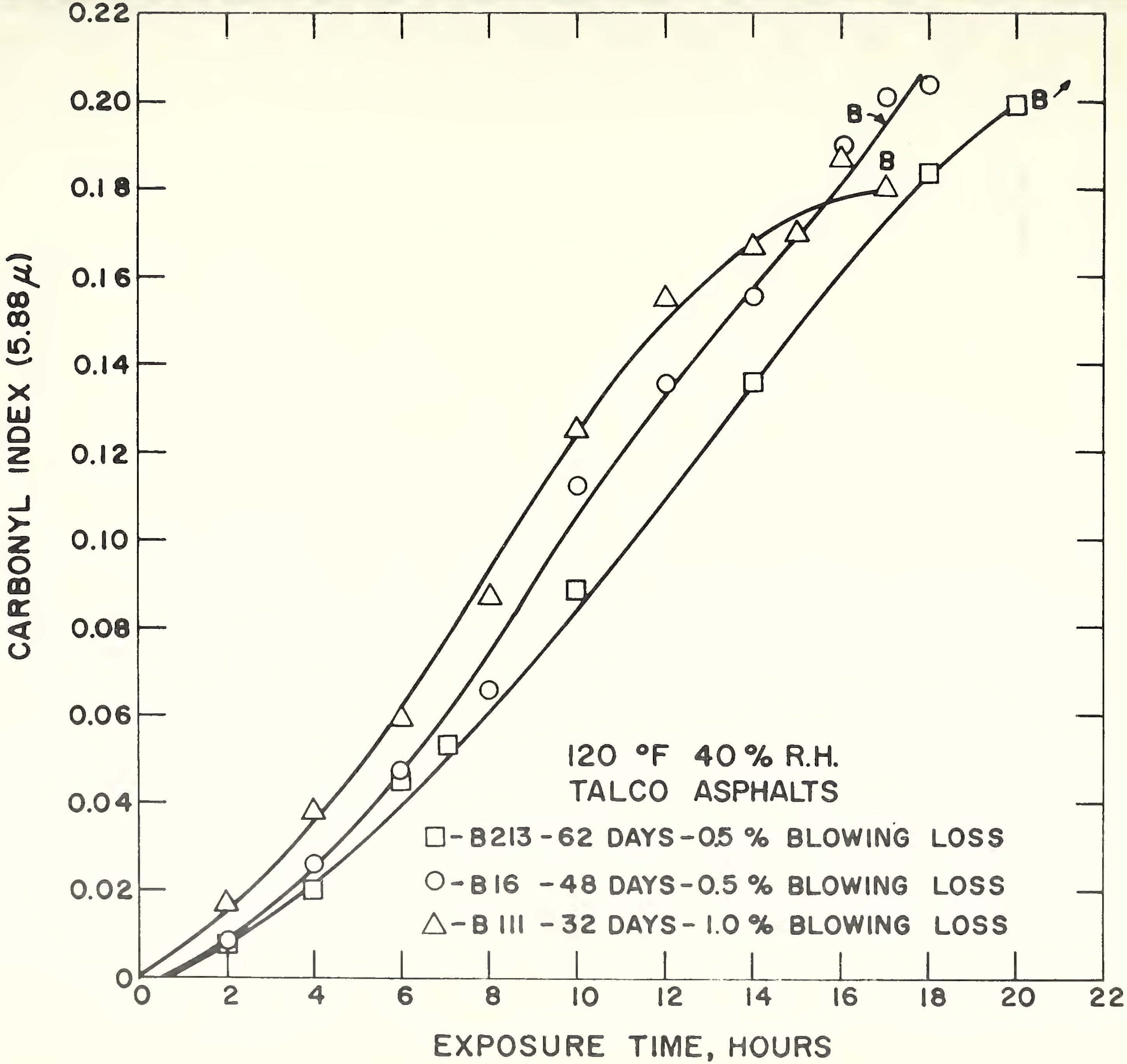

FIG. 4 - CARBONYL INDEX VS EXPOSURE TIME.

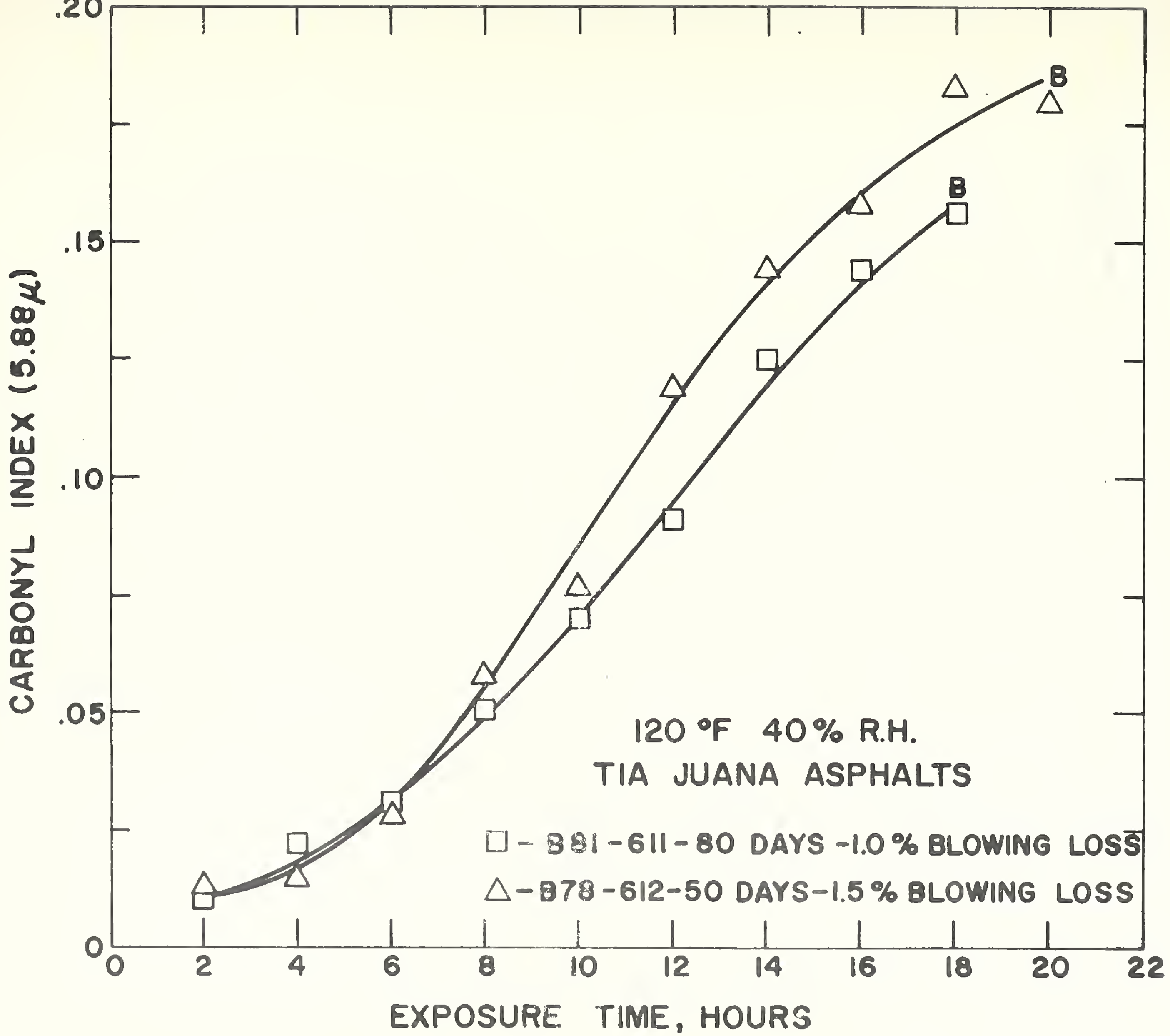

FIG. 5-CARBONYL INDEX VS EXPOSURE TIME.

TABLE 3.

Thin-Film Correlation Data
(120°F, 40% R.H.)

Run No.	Asphalt Source	Durability (51-9c), Days	Induction Period, Hr	Slope ΔA/hr, 1 Hr	ΔA=0.08, Hr	Second Inflection, Hr	Film Rupture, Hr
B38	California	68	1.4	0.0273	3.7	6.4	16
B39	California	50	0	0.0221	3.9	9.0	12-13
B52	California	41	0	0.0158	5.0	6.5	16
B85	Kansas L22	81	12.6	0.0159	11.9	16.3	>24*
B89	Kansas L22	65	12.5	0.0104	14.5	21.8	25
B217	Kansas L27	81	12.3	0.0136	12.3	16.7	>24*
B16	Talco 175/200	48	5.7	0.0134	8.4	None	17
B111	Talco 175/200	32	5.4	0.0154	7.2	11.0	16-17
B213	Talco 85/100	62	7.6	0.0122	9.6	17.2	20
B78	Tia Juana 612	50	6.6	0.0146	9.6	11.8	20
B81	Tia Juana 611	80	9.0	0.0139	10.8	14.9	18

* Had not ruptured when run was discontinued.

three asphalts, these data do fall on the correlation of durability vs. time to produce a carbonyl index of 0.080 (Figure 6).

There are several good reasons for their correlation in the one instance and lack of correlation in the other four. Looking at the lack of correlation first, the time to film rupture is the most readily explained, for a different type of specimen holder was used. The narrow, slit-type holder in this study supported the thin films of asphalt better than did the holder with a round opening used by Wright and Campbell and, thus, permitted the films to degrade more before film rupture occurred. However, the stress distribution was more uniform in the holder with the round opening and the repeatability was better.

Because the plots of carbonyl index vs. time generally produced S-shaped curves, the locating of the end of the induction period and the second inflection point (end of constant-rate period) were quite difficult and, consequently, not of very high precision. Similarly, there was sufficient scatter in the individual datum points to make the exact location of the straight line, constant rate, portion of the curve somewhat arbitrary. Thus, the lack of correlation in these latter three cases may be for purely mechanical reasons. Wright and Campbell, possibly for the same reasons, did not attempt to draw a quantitative correlation between durability and time to the end of the induction period or with the slope of the constant-rate portion of the curve.

Thus, only the time to a carbonyl index of 0.080 correlates well and agrees well with the correlation of Wright and Campbell (3). Their correlation with the addition of the data from this study are reproduced in Figure 6.

The California asphalt had essentially no induction period, as seen in Figure 2; the initial oxidation occurred at a constant rate. After about 6 to 8 hours, the rate of increase of carbonyl index began to slow and continued at a decreasing rate until film rupture. It is interesting to note that after three hours of oxidation the curves for the three California asphalts separated, with the most durable oxidizing at the most rapid rate and the least durable at the least rapid rate. This type of performance is contrary to what would be anticipated from earlier reported work. However, the California flux is relatively rich in low-molecular-weight, volatile oils. Apparently, these oils were the more readily oxidized components of the asphalt, for the weight losses during blowing were also inversely related to the oxidation rates. In service, however, these oils are distributed throughout the bulk of the asphalt and serve to plasticize it. Their diffusion from the deep interior to the surface apparently is slow enough to permit the plasticizing effect of the oils to contribute more to the durability than their ease of oxidation detracts from it, and the durability is effectively increased.

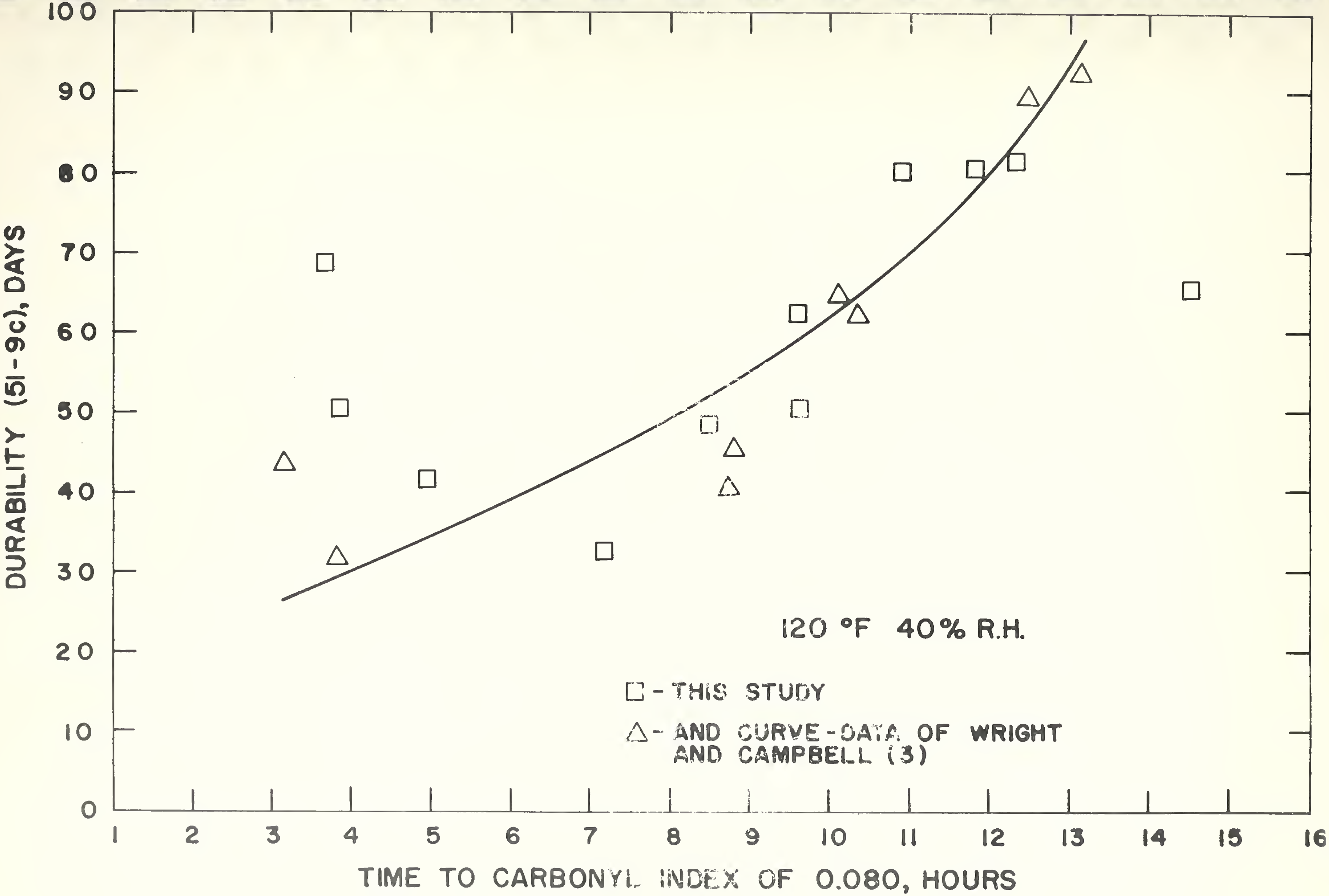

FIG. 6 - DURABILITY VS TIME TO CARBONYL INDEX OF 0.080.

Thus, the asphalt that shows the most rapid oxidation in the thin-film exposure is the most durable of the three and the one with the least readily oxidizable oils is also the least durable.

While the California asphalts oxidized most rapidly, the Kansas asphalts were most resistant to oxidation. All three of the Kansas asphalts in Figure 3 had induction periods of about 12 hours. However, the least durable of these asphalts had the lowest oxidation rate during the constant-rate period and the films of this asphalt remained intact the longest. All three Kansas asphalts had very low blowing losses and, again contrary to expectations, the one with the lowest losses had the lowest penetrations. While these low penetrations may tie in with the low oxidation rate and low durability, no basic reasons for this performance are apparent.

The three Talco asphalts in Figure 4 performed more in line with the previous work. The induction periods were directly proportional to the durability and the slope of the constant-rate period inversely proportional. The times to film rupture were also proportional to durability. All of the weight losses were low. These asphalts lined up well despite the fact that the most durable one was blown from the 85/100 penetration flux and the other two from the 175/200 flux. As in the case of the California asphalts, the lighter, more volatile oils were removed (this time by distillation) before exposure; these also could well have been the more easily oxidized oils.

The two Tia Juana asphalts in Figure 5 were blown from different grades of flux under the same conditions, B81, blown from the harder flux, was the more durable, and also oxidized least rapidly. Its blowing losses were about two-thirds of those of asphalt B78.

Thus, in all instances except for the Kansas asphalts the asphalts that had lost the most oils before exposure oxidized the least rapidly when exposed as thin films. However, the durability when exposed in the conventional manner was not related to this loss of oils. Only the time to produce a carbonyl index of 0.080 in the thin films correlated with conventional durability.

5. SUMMARY AND CONCLUSIONS

The thin-film oxidation characteristics of eleven laboratory-blown asphalts were investigated and compared with results on "similar" asphalts published by Wright and Campbell (3). Only the correlation of time to attain a carbonyl index of 0.080 with durability agreed with their correlation; length of induction period, slope of constant-rate period, end of constant-rate period, and film rupture did not correlate with durability.

The more volatile oils in the asphalts seemed to be the less resistant to oxidation, for the asphalts that had the highest blowing losses or were reduced the most before blowing were usually the ones that resisted oxidation the most (for each flux stock). However, these readily oxidized oils are necessary to plasticize the asphalt and, despite the fact that the asphalts with the higher percentages of these oils oxidized more rapidly than those from the same source with fewer oils, they tended to be more durable.

6. REFERENCES

(1) ASTM D 1669-59T; Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Coatings; ASTM D 529-59T, Accelerated Weathering Test of Bituminous Materials.

(2) Greenfeld, S. H. and J. R. Wright, "Four Methods for Predicting the Durability of Roofing Asphalts," Materials Research and Standards 2, 738-745, 1962.

(3) Wright, J. R. and P. G. Campbell, "Determination of Oxidation Rates of Air-Blown Asphalts by Infra-Red Spectroscopy," J. Appl. Chem. 12, 256-266, 1962.

(4) Greenfeld, S. H., "The Effect of Blowing Variables on the Durability of Coating Grade Asphalts," Ind. and Eng. Chem. Part 3, in press.

(5) Private communication. To be presented as "Oxidation of Asphalt in the Presence of Ozone" by J. R. Wright and P. G. Campbell at the April 1964 ACS Symposium on Asphalt.

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