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**NATIONAL BUREAU OF STANDARDS REPORT**

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THE DEGRADATION OF TWO COATING ASPHALTS

by

Sidney H. Greenfeld



**U. S. DEPARTMENT OF COMMERCE  
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## THE DEGRADATION OF TWO COATING ASPHALTS

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# THE DEGRADATION OF TWO COATING ASPHALTS

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Sidney H. Greenfeld

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## ABSTRACT

The changes that occurred when two coating asphalts, differing widely in durability, were exposed to heat; heat and light; heat, light and water and out of doors were followed by chromatographic and selective solvent analyses. In all four exposures the asphaltenes and degradation products increased at the expense of all of the n-pentane-soluble components. However, the magnitudes of the changes were different for the various exposures.

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## 1. INTRODUCTION

Numerous investigators have reported the results of accelerated (1)\* or outdoor (2) exposures of asphalts in which asphalt has been treated as a single material and its durability expressed in terms of physical changes, primarily cracking. In two instances the complex nature of asphalt was recognized and the changes in some of its components (3) reported at relatively short periods of exposure. However, no systematic study has been published of the changes that take place in the asphalt

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



constituents (4) as a function of time, when asphalts are exposed to different environments.

This paper describes the changes occurring in two asphalts of widely different origin and their components when they are exposed to heat; heat and light; heat, light and water and to the weather.

## 2. MATERIALS AND METHODS

### 2.1 Asphalts

The two asphalts used are described in Table I. They are typical shingle coating grade asphalts blown from residua from crudes produced in the United States.

### 2.2 Specimen Preparation

The exposure specimens were prepared by the hydraulic press method previously reported (5). Each coating was 25 or 26 mils thick with a tolerance of  $\pm 1$  mil. The coatings were nominally 2-1/4 by 5-1/4 inch in width and length, respectively, with permissible variations of 1/8 inch in each. This variation in area accounted for most of the variation of 0.57 grams in the weight of the coatings, which averaged 4.65 grams per specimen. All specimens of each asphalt were prepared at the same time and exposed within 24 hours of their preparation.





TABLE I.

CHARACTERISTICS OF ASPHALTS

CHARACTERISTIC	ASPHALT I	ASPHALT II
Softening Point <sup>a/</sup> , °F	223	224
Penetration <sup>b/</sup> at 32°F	10	11
Penetration at 77°F	17	17
Penetration at 115°F	30	26
Susceptibility <sup>c/</sup>	1.16	0.87
Loss on Heating, <sup>d/</sup> %	0.22	0.03
Pen. after Heating at 77°F	17	17
Specific Gravity at 77°F	1.0015	0.999
Durability, <sup>e/</sup> days	43	75
Component Analysis (4)		
Asphaltenes, %	39.0	38.4
Resins, %	10.3	9.9
Dark Oils, %	18.2	23.3
White Oils, %	27.4	24.4
Ethanol Extract, %	2.8	0.7
Recovery, %	97.7	96.7

<sup>a/</sup> ASTM D36-26.

<sup>b/</sup> ASTM D5-52.

<sup>c/</sup>  $S = \frac{P_{115} - P_{32}}{P_{77}}$

<sup>d/</sup> ASTM D6-39T

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



### 2.3 Specimen Exposure

Six specimens of each asphalt were exposed in an air oven at  $140^{\circ} \pm 5^{\circ}\text{F}$ .

Seven specimens of asphalt I were exposed in a single arc. accelerated durability machine, operated at 120-145 volts and 15-17 amperes, for 22 hours a day at  $140 \pm 5^{\circ}\text{F}$ .

Twenty-seven specimens of asphalt I and 26 specimens of asphalt II were exposed concurrently with those above to 22 hours per day in the accelerated durability machine followed by one hour of soaking in distilled water. This wash period was divided into 45 minutes in one pyrex container and 15 minutes in a second. The water was changed whenever specimens were removed for analysis.

This procedure is termed the 22-1 cycle. During the remainder of each day, the specimens were at ambient conditions.

Eighteen specimens of each asphalt were exposed on the roof of the Industrial Building of the National Bureau of Standards facing due South at an inclination of  $45^{\circ}$ . Thus, 58 specimens of asphalt I and 50 specimens of asphalt II were exposed in all.

In all of the accelerated durability machine exposures, the specimens were exposed two to an aluminum specimen holder, one above the other. On alternate days the specimens and the holders were inverted in order to approximate uniform exposure for all of the specimens.



## 2.4 Component Analysis

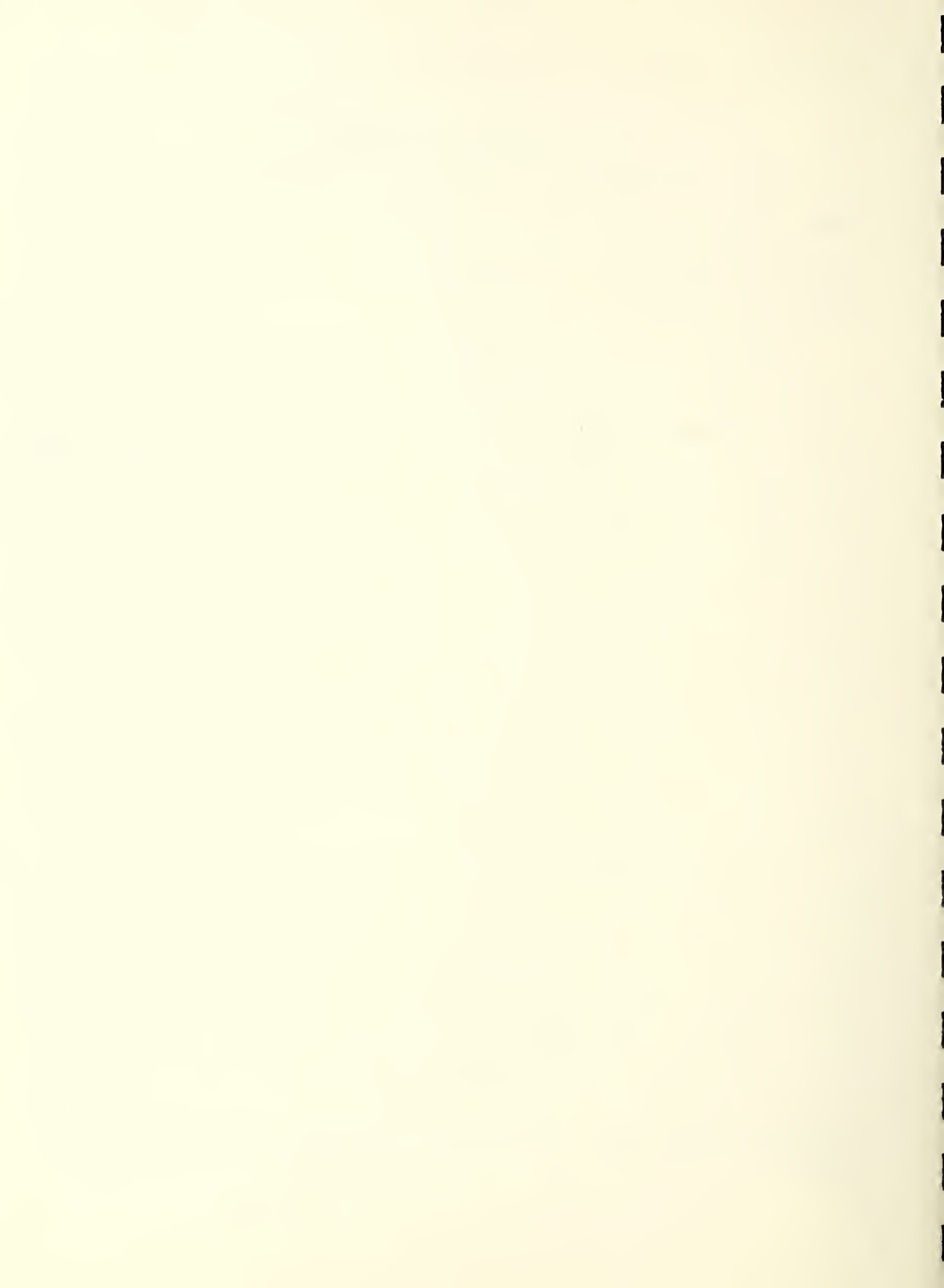
Before and periodically during exposure all of the specimens were weighed and from one to three were removed for analysis. These were separated into component groups: asphaltenes, resins, dark oils, white oils (4).

During exposure three types of products of degradation were formed. One was volatile, and escaped. Another was water-soluble and was removed readily. The third was soluble in ethanol, but insoluble in water and pentane. This material remained on the asphaltenes when they were extracted with n-pentane. However, extraction of the asphaltenes with ethanol removed the major portion of this product. In some asphalts a slight colored film still remained on the surface of the asphaltenes after extraction with ethanol, but any solvent that removed the entire film dissolved appreciable quantities of the asphaltenes as well. Hence, ethanol was used to extract the major portion of the degradation products that were not soluble in water.

One gram of asphaltenes was placed in a 150 ml beaker with 100 ml of ethanol and heated to about 70°C on a covered steam bath for three hours. The extracted asphaltenes were filtered from the solution in a weighed Gooch crucible, with an asbestos mat covered with a disc of filter paper, and dried and weighed. The quantity of ethanol extract was obtained by difference.\*

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\*Prolonged extraction in an soxhlet extractor produced the same results.



The components of the asphalt have been described by Kleinschmidt (4). Briefly, they are:

Asphaltenes - Black, brittle solids insoluble in n-pentane.

Water-white oils - Colorless, viscous oils not adsorbed from n-pentane solution by fuller's earth.

Dark oils - Highly viscous, reddish-brown oils eluted from the fuller's earth with methylene chloride.

Resins - Glossy, dark brown solids eluted from the fuller's earth with methyl ethyl ketone.

The changes that occur in each of these components as the asphalt is degraded are most easily followed if the component always is expressed as a percentage of the original weight of the asphalt. This common denominator permits direct subtraction at different periods of exposure. All component analyses in this paper are presented in this manner.

### 3. RESULTS

#### 3.1 Weight Changes - 22-1 Cycle

When asphalt is degraded by light, heat and water it undergoes a loss in weight that increases with exposure. Figure 1 illustrates the losses that occurred when the two asphalts were exposed simultaneously to the 22-1 cycle in an accelerated durability machine. The first two points for each asphalt are each averages of 26 specimens. Following points are of progressively fewer specimens, for specimens were periodically removed for analyses, until the





ASPHALT DEGRADATION  
22-1 CYCLE  
WEIGHT LOSS

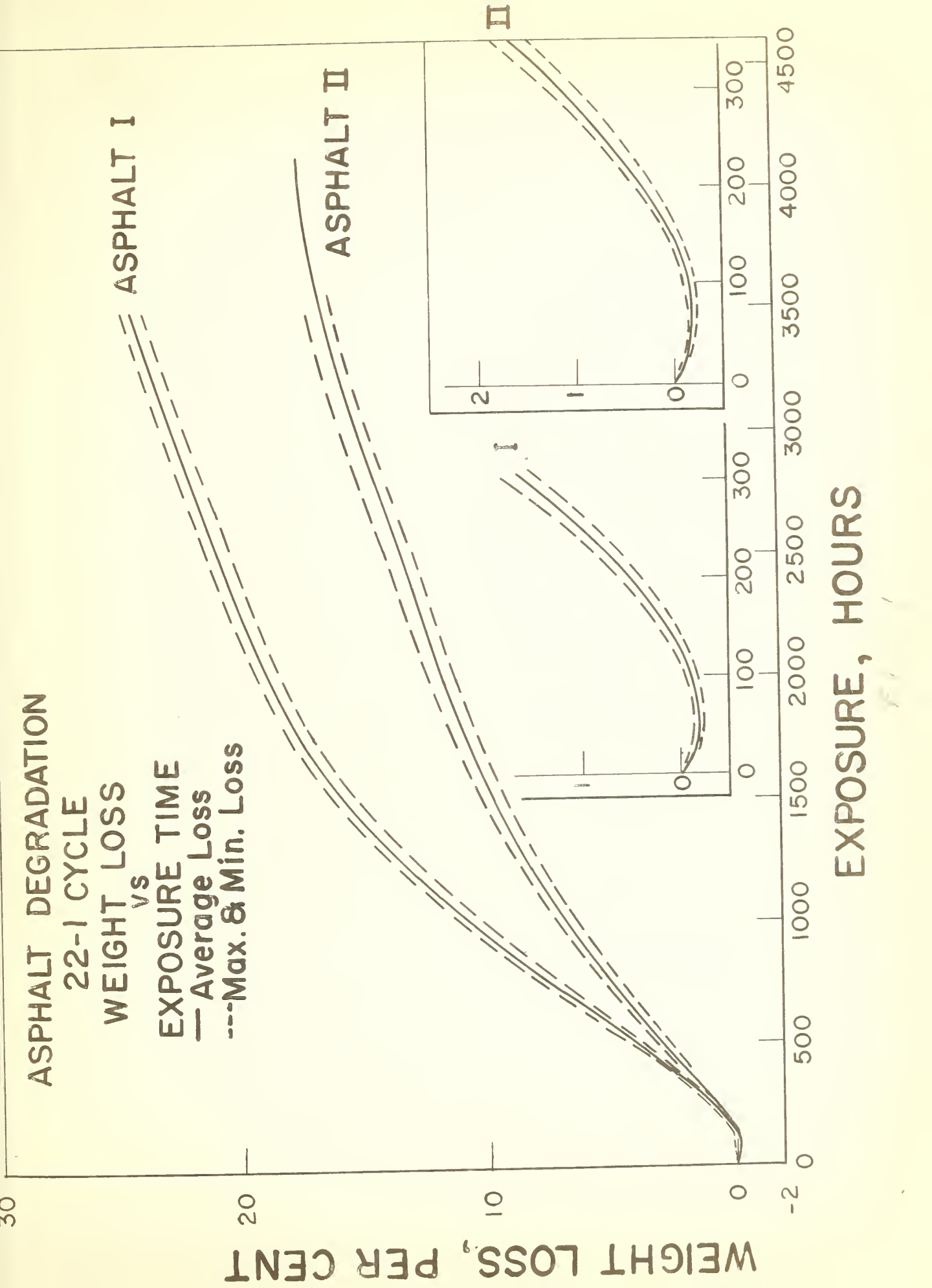
ASPHALT I

ASPHALT II

EXPOSURE TIME  
— Average Loss  
--- Max. & Min. Loss

WEIGHT LOSS, PER CENT

EXPOSURE, HOURS





last two panels. It was observed that even though the specimens were rearranged daily, there was a consistent variation in their weight changes. This variation, the extremes of which are represented by the dotted curves in Figure 1, were in no way related to the differences of  $\pm 1$  mil in coating thickness or  $\pm 1/8$ -inch in each of the other coating dimensions. The coatings that lost relatively more weight during the early periods of exposure continued to do so during the entire exposure and, conversely, those initially with low losses continued low. While the differences among replicate specimens were small in relation to the weight losses after a short period of exposure, they are significant and indicative of variations that should be considered normal in this type of exposure.

In the enlarged sections of Figure 1, it can be seen that during the early exposure both asphalts exhibited a net gain in weight, despite the daily soaking. However, by the end of six or seven days of exposure the specimens were all back to their initial weights, and they continued to lose weight thereafter. This loss amounted to 24% for asphalt I and 16.6% for asphalt II at 3500 hours of exposure. Asphalt I failed mechanically (6) at 1550 hours; asphalt II failed at 4150 hours.



### 3.2 Component Changes - 22-1 Cycle

Figures 2 and 3 are graphical presentations of the changes that took place in these two asphalts during exposure. Each point, except the last, is the average of analyses of three specimens. The weight loss curves on these two figures are of the particular specimens analyzed in each case, but they always agreed with the general averages in Figure 1 within 0.3%.

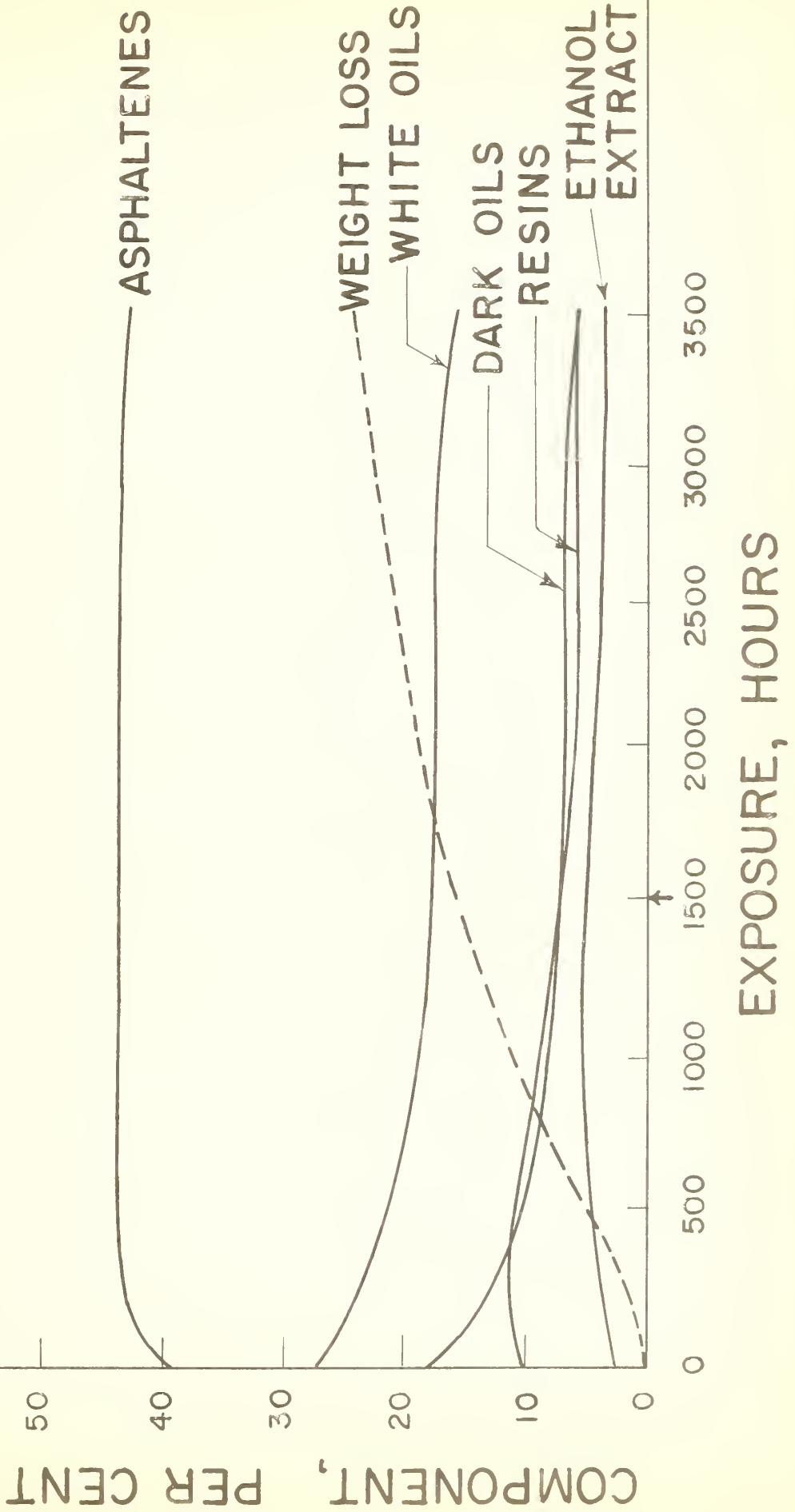
While the weight losses were measures of the water soluble and volatile, or gaseous, products of degradation formed, there was a third product of degradation that remained with the asphalt, the ethanol extract of the asphaltenes. There was some ethanol soluble in the asphaltenes before weathering, possibly formed during the "blowing" operation in the manufacture of the asphalt, but during exposure it increased, went through a broad maximum around 1000 hours and then slowly decreased. This material may well be an intermediate in the formation of the other degradation products.

During the early stages of exposure there was a rapid increase in the asphaltene content of both asphalts. This was followed by a slower increase in asphalt II, and in asphalt I, by a long period of constant value followed by a slow decrease.

The resins in both asphalts also increased for the first 400 hours, but then began to decrease at about the same rate as the dark oils, which had undergone a rapid decrease during the



CHANGE IN COMPONENTS  
22-1 CYCLE  
COMPOSITION  
vs  
EXPOSURE TIME  
ASPHALT I



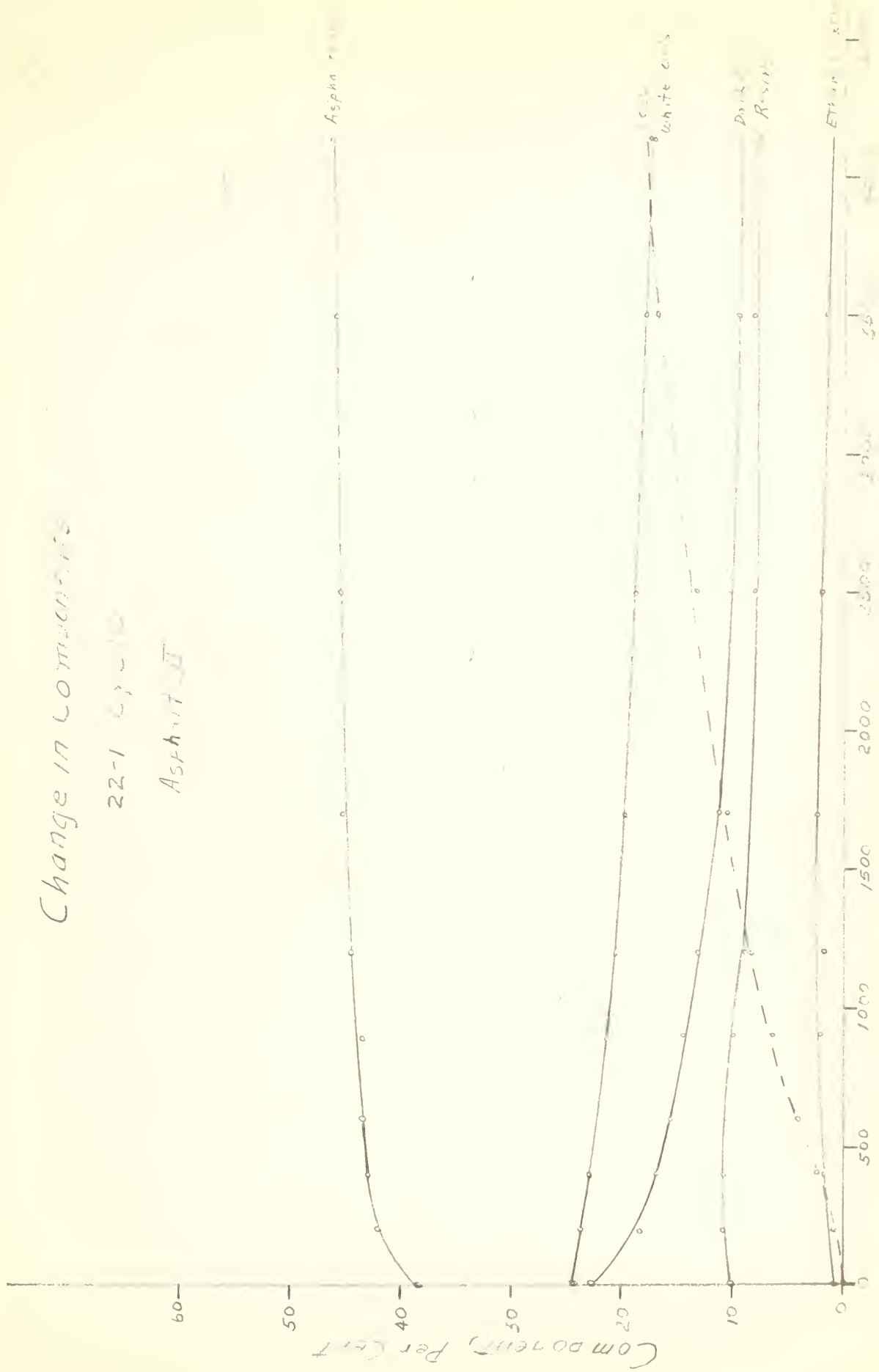




# Change in Components

22-1 63-10

Asphalt II



Exposure Hours  
Fig 3



early exposure. The white oils also decreased progressively during exposure. Thus, after some early changes, the degradation process seemed to be a gradual attrition of the entire n-pentane-soluble portion of the asphalt.

### 3.3 Component Changes - Dry Light

Exposed simultaneously with the above were a number of specimens of asphalt I which were not subjected to washing, termed dry light exposures. The results of these exposures are shown in Figure 4. A number of differences between these curves and those in Figure 2 are readily apparent. The most obvious is that the initial weight increase was greater and was continued for about 1200 hours (instead of 125 hours). At 3000 hours, when these exposures were discontinued, the loss amounted to only 0.5%, compared to 22.6% when the coatings were washed.

As might be expected, because no material was removed as water solubles, the ethanol extract continued to increase with time to over 6% at 3000 hours. Some of this material was undoubtedly water soluble also.

The rapid changes in the components that occurred during the first 200 hours of exposure also took place in these dry exposures, but for the next 1000 hours the composition remained static. After 1200 hours the normal changes were resumed and the asphaltenes increased to higher concentrations than when washing occurred.



# Change in Composition Dry Light Asphalt E



Experiment 10

Experiment 10



### 3.4 Heat Exposures

When light was omitted and specimens of the two asphalts were exposed to heat alone, in an air oven at 140°F, the changes that occurred were again very different; they are presented in Figures 5 and 6. There were, of course, no water-soluble products removed. There was no weight change in either asphalt for the first 200 hours. Asphalt I then lost weight progressively until its exposure was discontinued at 1320 hours; the total loss amounted to only 0.1%. Asphalt II, however, gained weight between 400 and 600 hours and then leveled off at a gain of 0.2%. The ethanol extract remained at a very low value. Instead of the rapid rise in asphaltene content previously observed, there was no change during the first 200 hours. Then the rapid change occurred and was followed by a period of decreasing value in asphalt I and constant value in asphalt II. The resins increased slightly and the dark oils decreased comparably. The white oils decreased slightly in asphalt I, but remained constant in asphalt II. Because each of the values in Figures 5 and 6 represents a single determination, there is slightly more scatter of these points than in the previously reported exposures.





Change in Comp. %  
 Heat Experiments  
 140°F  
 Acetone

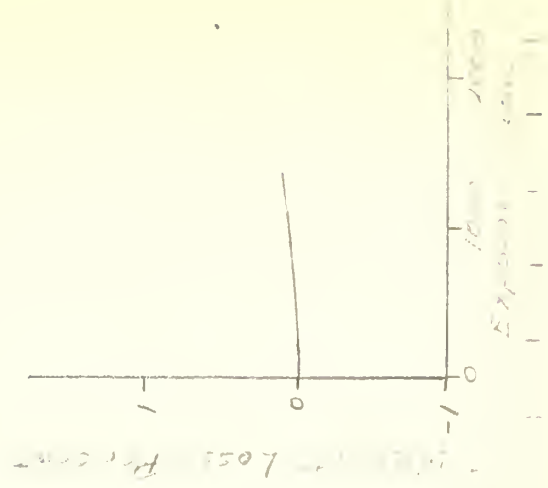
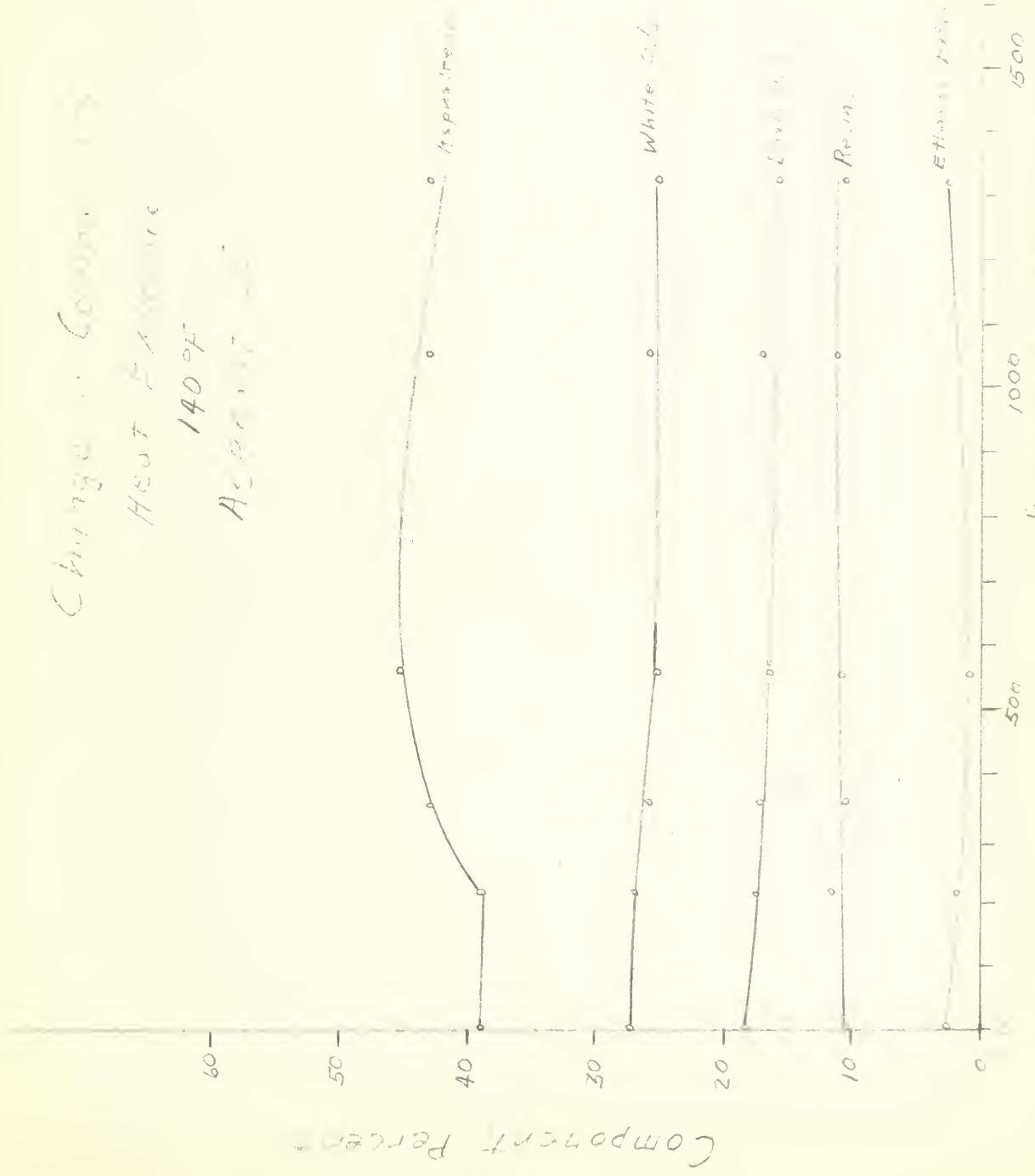


Fig 5



# Change of Resistance

At 100°C

At 100°C

60

50

Resistance

100°C

100°C

100°C

100°C

100°C

100°C

100°C

100°C

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W. E. - 22

Ex - 10

Ex - 10



### 3.5 Out-of-Door Exposures

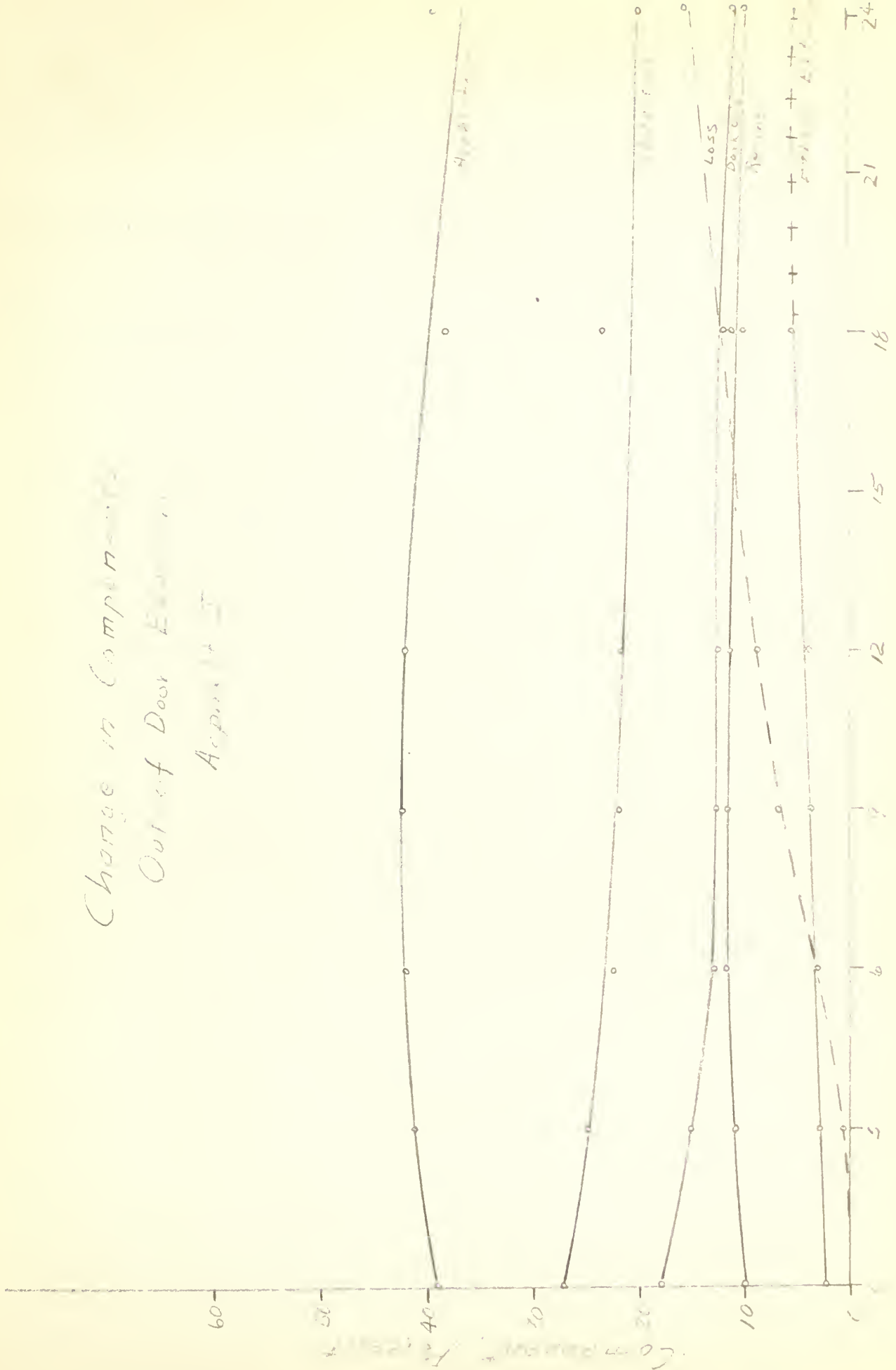
Figures 7 and 8 present the results of the out-of-door exposures on the roof of the Industrial Building at the National Bureau of Standards. During the first 24 months of exposure the changes that took place were similar to those that occurred in the 22-1 cycle in the accelerated durability machines. However, the timing ratio of all of the changes was not the same. At three months, the asphalts had already lost a little weight, the possible weight gained being overlooked because no weighings were made during the first three months. The ethanol extracts increased as weathering progressed and appear to be reaching maxima at about 18 to 24 months.

In asphalt I, the asphaltenes went through a maximum value of about 42.5% at 9 months, but in asphalt II, they were still increasing at 24 months (comparable trends existed in the 22-1 cycle). The resins in both asphalts went through the same maximum values as in the 22-1 cycle. In asphalt I, both the white and dark oils decreased rapidly for six months and then much more slowly, but in asphalt II, the white oils remained constant for six months, decreased rapidly for the next six months, then, with the dark oils, remained almost constant for the following year. All of these changes are similar to those that occurred in the 22-1 cycle, but because of the much slower rate of change of the asphalt, are somewhat subdued.



# Change in Compensability Out of Door Experiments

April 1955

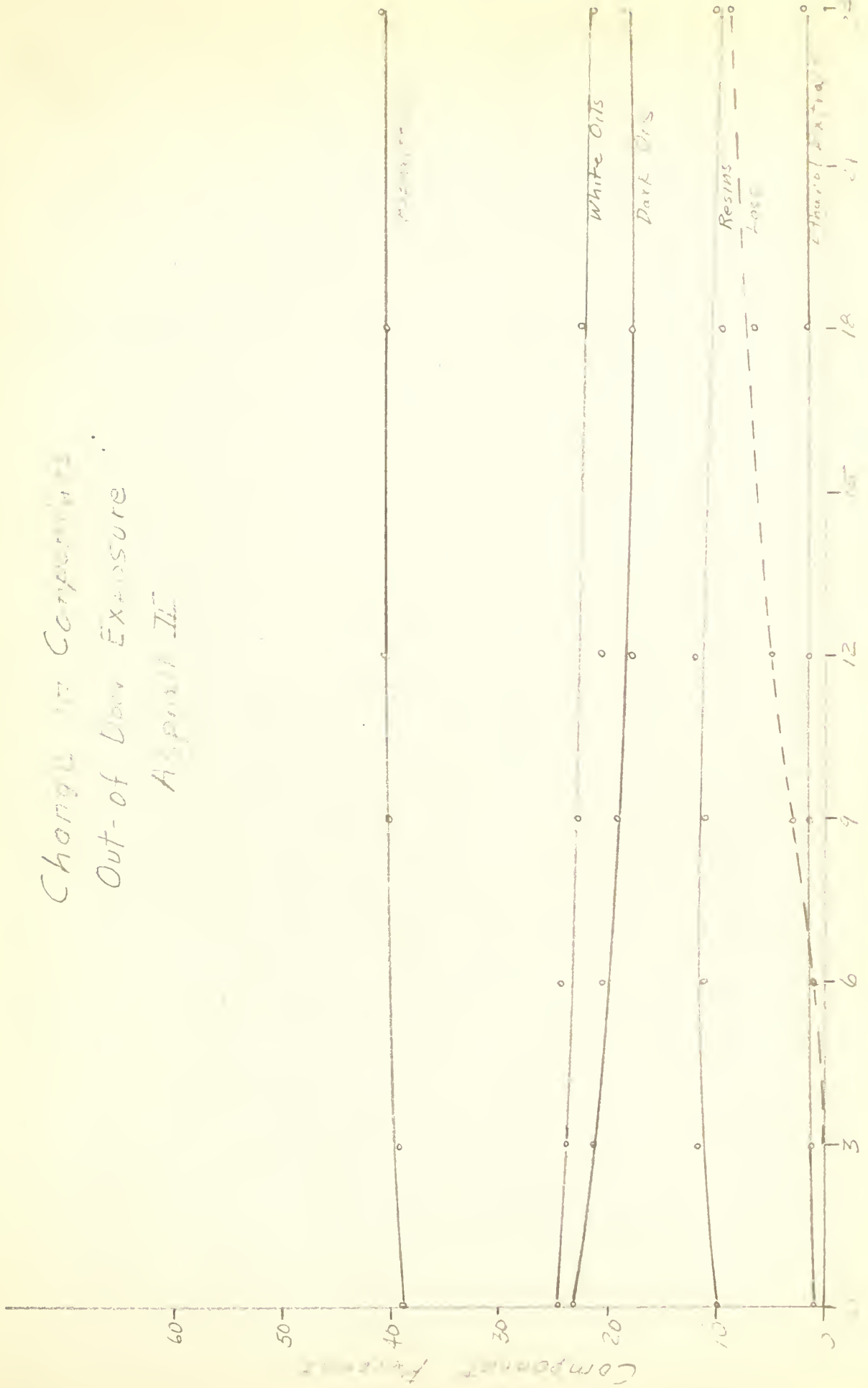


EXERCISE 7





Change in Components  
Out-of-Door Exposure  
Asphalt II



Exposure Months  
Fig. 5



#### 4. SUMMARY AND CONCLUSIONS

The degradation of asphalts varies with the source of the asphalt and in accordance with the exposure conditions. Different mechanisms of degradation seem to exist for thermal, dry light, and light and water exposures. Under normal exposure conditions, where light, heat and water enter into the degradation of asphalt, two types of products were isolated. These products were formed from, and the asphaltenes increased at the expense of, the three components of the pentane-soluble portion of the asphalt as degradation progressed.

Out-of-door exposures produced changes in components similar to those that occurred in the 22-1 cycle.



REFERENCES

- (1) Strieter, O. G. and Snoke, H. R., "A Modified Accelerated Weathering Test for Asphalts", J. Res. NBS 16, 481-5 (1936).  
Walther, H., "Influence of Weathering on Bitumen", Mitt. Dachpappen Ind., 135-52 (1938).  
Zapata, J., "Laboratory Accelerated Weathering", Proc. Assoc. Asph. Paving Tech. 16, 154-73 (1948).  
Fair, W. F., Jr., Beck, H. R., and McKee, B. K., "Accelerated Weathering of Pitches and Asphalts", ASTM Spec. Tech. Pub. No. 94, 109-21 (1949).
- (2) Oliensis, G. L., "Ten Years Outdoor Exposure of Filled Asphalt Coatings on Saturated Felts", ASTM Bulletin No. 144, 32-48, (Jan. 1947).  
Williams, D. M., "Correlating Laboratory and Outdoor Weathering Tests", *ibid.*, 49-56.  
Kirshbaum, L., Cubberly, R. H., and Yeager, F. W., "Mineral Stabilizers in Asphalt Roofing", ASTM Spec. Tech. Pub. No. 94, 122-136, (1949).
- (3) Thurston, R. R., "Constituents of Asphaltic Materials vs. Accelerated Weathering", Proc. ASTM 37, 569, (1937).  
Marcel, L., "Study of the Evaluation of Bitumens", Comptus Rendus, 233, 84-6, (1951).



REFERENCES (Continued)

- (4) Kleinschmidt, L. R., "Chromatographic Method for the Fractionation of Asphalt Into Distinctive Groups of Components", J. Res. NBS 54, No. 3, 163-166, 1955 (RP2577).
- (5) Greenfeld, S. H., "A Method for Preparing Uniform Films of Bituminous Materials", ASTM Bulletin No. 193, 50-53, Oct. 1953.
- (6) Greenfeld, S. H., "The Effects of Thermal Shock on the Durability of Asphalt Coatings Under Accelerated Test", ASTM Bulletin No. 193, 46-50, Oct. 1953. (Cracking to the metal in half the exposed area.)





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