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AN INVERSE GLC STUDY OF ASPHALTS USED IN THE ZACA-WIGMORE
EXPERIMENTAL ROAD TEST.

T. C. Davis and J. C. Petersen

# PROCEEDINGS

OF

# THE ASSOCIATION OF ASPHALT PAVING TECHNOLOGISTS

# AN INVERSE GLC STUDY OF ASPHALTS USED IN THE ZACA-WIGMORE EXPERIMENTAL ROAD TEST

T. C. DAVIS and J. C. PETERSEN[1]

## ABSTRACT

Inverse gas-liquid chromatography (GLC) was used to study asphalts evaluated in the Zaca-Wigmore Experimental Road Test. The retention behavior of a number of test compounds was determined on the asphalts both before and after oxidation within the GLC column. The retention behavior of the test compound phenol on the oxidized asphalts correlated with the performance of the asphalts in road service, and this was further supported by a similar correlation with accelerated weathering durabilities of coating-grade asphalts. The phenol test compound retention data on the oxidized road asphalts were also found to relate to changes in viscosity as measured by the microfilm durability test. Because test compound retention behavior is related to chemical composition and molecular association forces of the asphalt, the correlation with performance affirms the importance of chemical composition to asphalt performance on the road.

## INTRODUCTION

Inverse GLC, a technique for studying petroleum asphalts, was developed by Davis, Petersen, and Haines (3) and extended by Davis and Petersen (1,2). In the technique, asphalt is used as the liquid substrate in a GLC column and is characterized by measuring the retention behavior of selected test compounds possessing different functional groups. To study oxidation characteristics, the asphalt is oxidized within the GLC column, and retention behavior of the test compounds is determined on the oxidized asphalt. Retention behavior is a measure of functional group interactions between the test compound and the asphalt and is thus related to the chemical composition of the asphalt.

The Zaca-Wigmore Experimental Road Test, sponsored by the California State Department of Public Works, Division of Highways, has provided considerable test data on the behavior of a selected group of asphalts in highway pavements (6, 7, 8). With the exception of one asphalt produced from a Mid-Continent crude oil by a refinery in Arkansas, these asphalts represented different crude oil sources and methods of manufacture in California at the time. Although not fully accomplished, an effort was made in this road test to hold the design and construction variables constant in order that the performance of the various asphalt cements could be compared.

This report covers the Inverse GLC study of 15 of the 17 asphalts used in the Zaca-Wigmore test project (6). Relationships were found between Inverse GLC data on the oxidized Zaca-Wigmore asphalts and

their performance in road service. These results were supported by Inverse GLC—accelerated weathering studies of 20 coating-grade asphalts previously investigated by Greenfeld and Wright (4, 5). Relationships between the Inverse GLC data on the Zaca-Wigmore asphalts and viscosity changes during the microfilm durability test (7) were also found.

## EXPERIMENTAL

Inverse GLC data were obtained on a Beckman GC-2 gas chromatograph,[2] using a 1/4-inch by 13-foot GLC column packed with 1 part asphalt on 10 parts by weight of Fluoropak 80 (56 grams total). The column was then conditioned for a minimum of 6 hours, using a helium inlet gage pressure of 15 psi and an instrument operating temperature of 130 C (normal testing conditions). Following conditioning, the test compounds were introduced, and their retention behavior was determined, as previously described (3). The asphalt was then oxidized (1) within the column by replacing the helium carrier gas with filtered air at an inlet gage pressure of 15 psi; the flow rate was approximately 30 ml/min at the column exit. The column temperature was maintained at 130 C for an oxidation period of 24 hours. Following oxidation, normal testing conditions were reestablished, the column was reconditioned, and test compound retention data were again obtained.

The Interaction Coefficient (Ip) (3) was obtained by first determining on the asphalt the corrected retention volumes ($V_R^o$) for a series of n-paraffins covering the molecular weight range of the test compounds used. The logarithms of the $V_R^o$'s for the n-paraffins were then plotted as a function of their molecular weight. The Ip for a given test compound on the asphalt is defined as:

$$Ip = 100 \left[ \log V_{R_t}^o - \log V_{R_p}^o \right]$$

where

$V_{R_t}^o$ = corrected retention volume of test compound, and

$V_{R_p}^o$ = corrected retention volume of hypothetical n-paraffin.

The hypothetical n-paraffin is one having the same molecular weight as the test compound, and the logarithm of its $V_R^o$ is obtained from the plot described previously. The experimental value of Ip obtained has a reproducibility of ±1.

Retained samples of 15 Zaca-Wigmore asphalts were furnished by the Materials Division of the Bureau of Public Roads. The asphalts are

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[2] Reference to specific commercial materials or models of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

grouped in this paper according to construction periods in which they were used. Paving periods 1 and 1A were from October 14, 1954 to November 3, 1954 and December 16, 1954 to December 21, 1954, respectively; asphalts used during these periods were considered as one paving period for the purpose of data comparison in this and the initial report (6). Paving period 2 was from February 21, 1955 to March 21, 1955.

Samples of 20 coating-grade asphalts were supplied by Greenfeld and Wright of the National Bureau of Standards. These investigators obtained the carbon-arc accelerated weathering durability data (4, 5) cited in the present study.

The usual consistency tests, as well as a number of special characterization tests, on the asphalts used have previously been reported (4, 6).

## RESULTS AND DISCUSSION

### Inverse GLC-Asphalt Performance Studies

The Inverse GLC data for 15 of the Zaca-Wigmore asphalts are shown in Tables I and II. Service performance of the asphalts in the road was judged by a team of observers and reported in the original study (6) as the surface performance rating. Ratings after 51 months of service for paving periods 1 and 1A, and 47 months service for paving period 2 are reproduced in Table III. The ratings are based on visual observations and crack surveys and are reported as a numerical

Table 1. Inverse GLC Retention Data on Zaca-Wigmore Asphalts—
Paving Periods 1 and 1A

| Asphalt[3] / Test Compound | Before column oxidation | | | | | | | | After column oxidation[1] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | J | A | B-1[3] | H | D | G | F | E | J | A | B-1 | H | D | G | F | E |
| Butyl acetate | -5 | 0 | -1 | -1 | 0 | -1 | 0 | 0 | -5 | 0 | 0 | 1 | 2 | 0 | 1 | 1 |
| Triethylamine | -3 | 1 | 1 | 0 | -2 | 0 | 1 | 5 | 58 | * | * | * | * | * | * | * |
| Decene-1 | 2 | 3 | 2 | 2 | 3 | 2 | 3 | 3 | 3 | 2 | 3 | 2 | 2 | 2 | 4 | 3 |
| Acetaldehyde | 31 | 36 | 34 | 35 | 37 | 34 | 37 | 36 | 31 | 36 | 35 | 36 | 38 | 34 | 38 | 37 |
| 1-Methylpyrrolidine | 40 | 43 | 41 | 51 | 43 | 44 | 46 | 30 | 120 | * | * | * | * | * | * | * |
| Butanol | 45 | 49 | 47 | 49 | 52 | 50 | 54 | 51 | 47 | 54 | 55 | 58 | 58 | 54 | 61 | 59 |
| Toluene | 48 | 46 | 46 | 47 | 47 | 48 | 50 | 48 | 47 | 49 | 47 | 49 | 50 | 48 | 50 | 48 |
| Nitromethane | 53 | 52 | 53 | 55 | 57 | 56 | 60 | 59 | 54 | 59 | 58 | 63 | 62 | 58 | 61 | 66 |
| Piperidine | 60 | 67 | 73 | 74 | 66 | 72 | 76 | 84 | * | * | * | * | * | * | * | * |
| 2-Methylpyridine | 60 | 68 | 62 | 65 | 67 | 64 | 67 | 67 | 60 | 69 | 66 | 66 | 70 | 64 | 68 | 72 |
| Cyclohexylamine | 61 | 67 | 65 | 69 | 68 | 62 | 72 | 76 | * | * | * | * | * | * | * | * |
| Palmitic acid | 70 | 82 | 94 | 92 | 93 | 95 | 98 | 97 | 84 | 94 | 100 | 105 | 107 | 109 | 114 | 125 |
| Acetonitrile | 78 | 80 | 75 | 79 | 86 | 82 | 86 | 83 | 77 | 81 | 80 | 81 | 83 | 82 | 86 | 85 |
| Pyrrole | 90 | 89 | 87 | 91 | 95 | 93 | 98 | 96 | 97 | 102 | 103 | 108 | 99 | 104 | 111 | 109 |
| Dimethyl sulfoxide | 107 | 122 | 122 | 120 | 108 | 125 | 122 | 124 | 107 | 133 | 132 | 132 | 124 | 132 | 126 | 129 |
| Phenol | 118 | 123 | 118 | 124 | 127 | 127 | 133 | 134 | 141 | 145 | 148 | 150 | 154 | 160 | 165 | 170 |
| Formamide | 131 | 143 | 141 | 143 | 148 | 150 | 155 | 154 | 142 | 159 | 158 | 158 | 157 | 160 | 169 | 168 |

[1] 24 hours, 130°C, 15 psi air inlet pressure.
[2] State of California designations.
[3] Paving period 1A.
[4] Residence time in the GLC column greater than 150 minutes.

Table II. Inverse GLC Retention Data on Zaca-Wigmore Asphalts—Paving Period 2

| Asphalt[2] Test Compound | Interaction Coefficient (Ip) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before column oxidation | | | | | | | After column oxidation[1] | | | | | | |
| | C-2 | H-2 | A-2 | D-2 | G-2 | B-2 | E-2 | C-2 | H-2 | A-2 | D-2 | G-2 | B-2 | E-2 |
| Butyl acetate | 1 | 1 | -2 | 1 | 1 | 0 | 2 | 0 | 0 | 0 | 1 | 0 | 0 | 1 |
| Triethylamine | -1 | 3 | -1 | -2 | 5 | 1 | 6 | -3 | * | * | * | * | * | * |
| Decene-1 | 3 | 3 | 2 | 2 | 2 | 1 | 4 | 3 | 2 | 3 | 2 | 3 | 2 | 4 |
| Heptaldehyde | 37 | 37 | 35 | 37 | 35 | 35 | 39 | 36 | 37 | 36 | 37 | 37 | 37 | 38 |
| 1-Methylpyrrolidine | 45 | 39 | 41 | 41 | 50 | 44 | 51 | * | * | * | * | * | * | * |
| Butanol | 52 | 53 | 48 | 52 | 52 | 51 | 53 | 53 | 57 | 53 | 56 | 51 | 59 | 57 |
| Toluene | 49 | 50 | 46 | 47 | 49 | 49 | 49 | 48 | 50 | 47 | 50 | 50 | 50 | 49 |
| Nitromethane | 58 | 59 | 57 | 57 | 59 | 57 | 61 | 58 | 61 | 59 | 58 | 63 | 65 | 62 |
| Piperidine | 64 | 79 | 69 | 64 | 85 | 70 | 90 | * | * | * | * | * | * | * |
| 2-Methylpyridine | 67 | 67 | 67 | 66 | 67 | 65 | 68 | 68 | 71 | 68 | 69 | 70 | 72 | 69 |
| Cyclohexylamine | 66 | 74 | 67 | 66 | 76 | 70 | 86 | * | * | * | * | * | * | * |
| Propionic acid | 82 | 94 | 82 | 91 | 97 | 93 | 98 | 94 | 106 | 96 | 105 | 113 | 111 | 123 |
| Acetonitrile | 80 | 84 | 80 | 76 | 86 | 81 | 83 | 83 | 84 | 80 | 80 | 86 | 88 | 84 |
| Pyrrole | 93 | 96 | 90 | 94 | 96 | 94 | 95 | 100 | 109 | 99 | 97 | 102 | 112 | 109 |
| Dimethyl sulfoxide | 127 | 127 | 123 | 109 | 126 | 127 | 127 | 134 | 133 | 133 | 122 | 127 | 127 | 128 |
| Phenol | 124 | 120 | 124 | 125 | 128 | 127 | 137 | 150 | 150 | 147 | 151 | 164 | 162 | 170 |
| Formamide | 150 | 147 | 145 | 147 | 146 | 146 | 155 | 157 | 166 | 160 | 155 | 167 | 166 | 168 |

[1] 24 hours, 130° C, 15 psi air inlet pressure.
[2] State of California designations.
[3] Residence time in GLC column greater than 150 minutes.

scale with one (1) being the best. In Tables I and II the asphalts are arranged in the order of their decreasing performance in the road (increasing numerical ratings) from left to right. In Table I the test compounds are listed in the order of increasing Interaction Coefficient on asphalt J before column oxidation; the same order is used in Table II.

The ability of Inverse GLC to show differences among asphalts is demonstrated in Tables I and II. The large Ip's obtained with many of the test compounds indicate strong functional group interactions between the asphalt and the test compound. Oxidation of the asphalts increased the Interaction Coefficients for most test compounds; the increase was greater for the more polar test compounds. These

Table III. Surface Performance Ratings[1] on the Zaca-Wigmore Asphalts

| Paving periods 1 and 1A | | Paving period 2 | |
|---|---|---|---|
| Asphalt | Surface performance rating after 51 months | Asphalt | Surface performance rating after 47 months |
| J | 1 | C-2 | 1- |
| A | 2 | H-2 | 1- |
| B-1 | 3 | A-2 | 1- |
| C[2] | 3+ | D-2 | 1 |
| H | 4 | G-2 | 2- |
| D | 4 | 1-2[2] | 2- |
| G | 5 | B-2 | 2 |
| F | 7 | E-2 | 4 to 5 |
| E | Failed | | |

[1] Asphalts were rated numerically with 1 being the best (reference 6)
[2] This sample was not available for Inverse GLC study.

increases suggest that oxidation of the asphalt produces polar groups which interact more strongly with polar test compounds. The retention behavior of the basic test compounds on oxidized asphalts is highly dependent on the nature of the functional groups. For example, the Ip of 2-methylpyridine is only slightly affected by the oxidation of the asphalt, whereas the stronger base, piperidine, is held tightly by the oxidized column. These differences in the behavior of the organic bases may be indicative of the acidic character of the oxidation products formed. The acidic test compounds show a fairly regular increase in the Ip from left to right in Tables I and II, both before and after oxidation. This regularity suggests a relationship between the Ip of acidic test compounds and performance.

A good correlation was found between the road surface performance ratings and the Ip's after oxidation of the asphalts for the acidic test compound, phenol. Figure 1 shows the correlation for the asphalts used in paving periods 1 and 1A. The location of the points for asphalts J
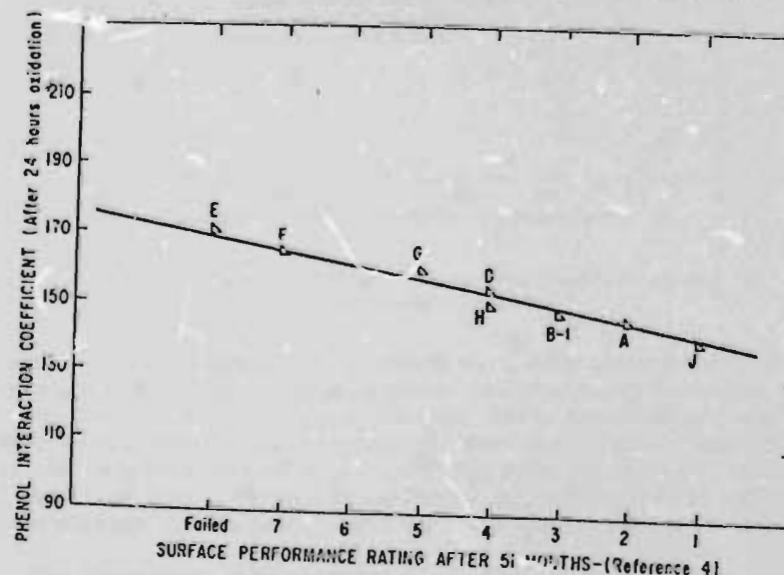


Fig. 1. Relationship between Interaction Coefficient and Pavement Surface Performance Rating—Paving Periods 1 and 1A.

and E with respect to performance is uncertain because the surface performance ratings of "1" and "failed" may not be linear with respect to the rest of the scale; however, the scale was assumed to be linear in plotting the data. As shown in Figure 1, those asphalts which perform better in service have lower phenol Ip's.

The performance data from paving period 2 are not comparable with those of paving periods 1 and 1A because of differences in the plant

mixes and in the properties of the completed roads. Hence, paving period 2 must be considered as a separate test. Although the performance data in this test (Table III) have insufficient spread to allow meaningful correlations, the data show the same trend as the paving period 1 and 1A asphalts. The complete Inverse GLC data on the paving period 2 asphalts are tabulated in this paper for use when final road performance data are available.

The correlation shown in Figure 1 is based on data on the oxidized asphalts, even though for this group of asphalts the as-received asphalts show a similar trend. The preference for the oxidized data is based on a previous study (2), which showed that the phenol Ip increases rapidly during the initial stages of oxidation, but levels off at a near maximum after 24 hours. Thus, comparison of the Ip's of as-received samples may not be reliable because the samples may be different distances up the steep part of the oxidation curve. Oxidation to the plateau portion of the curve provides an equitable state for comparison of properties. In a study of coating-grade asphalts in which the degree of oxidation of the as-received samples was highly diverse, durability as measured by carbon-arc accelerated weathering tests (Weather-Ometer) correlated with the Ip data from the column-oxidized samples; however, the relationship was poor on as-received asphalts. Although paving asphalts would, in general, receive less oxidation during manufacture than coating-grade asphalts, the differing degrees of prior oxidation play a sufficiently important role in affecting the Ip to dictate the use of data on uniformly laboratory-oxidized samples.

The correlation of phenol Ip's with surface performance of road asphalts is supported by the previously mentioned correlation of phenol Ip's with durability of coating-grade asphalts. Greenfeld and Wright (4, 5) conducted accelerated carbon-arc Weather-Ometer studies on thin films of the coating-grade asphalts and reported durability in terms of days-to-failure. Failure was defined by sufficient cracking to permit penetration of an electrical spark. Thus, this durability test depends upon the inability of the weathered asphalt to conform under stress, whether internal or external, to which it is subjected. Cracking of the asphalt pavement in service should also be a function of the inability of the asphalt serving as a binder to conform under imposed stress. Thus, if the phenol Ip data correlate with the tendency to form cracks in the road, they should also correlate with the tendency to form cracks in the Weather-Ometer. This is true, as shown in Figure 2 in which the durability data of Greenfeld and Wright are plotted against the Ip of phenol on oxidized samples.

The similar trends of the two tests strengthen the Zaca-Wigmore correlation in one of its weak points. The asphalts, with one exception, were from one geographical area. Results of several tests for predicting asphalt performance are highly dependent on the geographical area of the crude oil source (4, 9). Without further tests it might be suspected that it may not be possible to extrapolate the data from the Zaca-Wigmore asphalts to asphalts from other crude oil sources. The
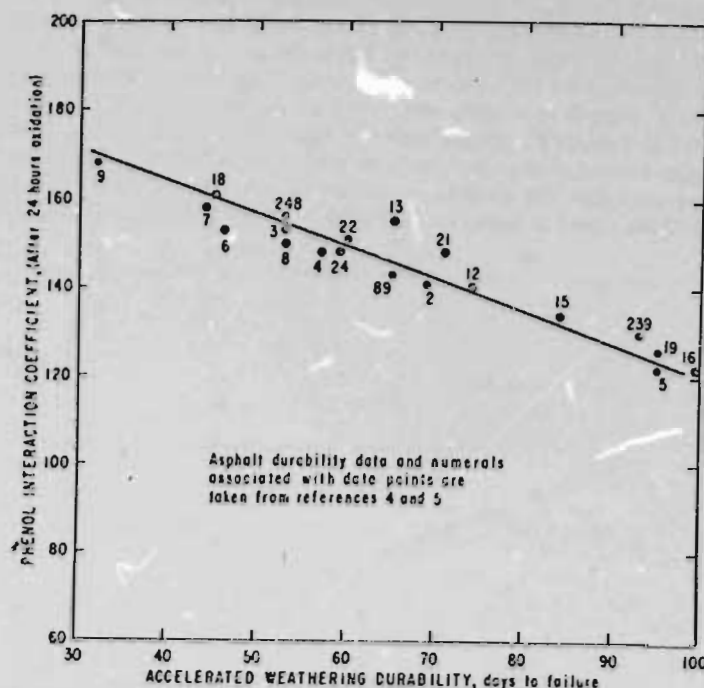
Fig. 2. Relationship between Interaction Coefficient and Durability of Twenty Asphalts.

asphalts studied by Greenfeld and Wright were manufactured from crude oils of four major producing areas—Mid-Continent, Venezuela, Southeastern United States, and California. Three experimental, laboratory-blown, Mid-Continent asphalts (5) were also included. Since the correlation between phenol Ip and durability holds for the wide variety of asphalts studied by Greenfeld and Wright, an extrapolation of the Zaca-Wigmore results to asphalts from other sources appears reasonable.

The correlations indicate that the cracking tendencies of asphalt—one of the prime causes of failure—can be measured by the phenol Ip. Also, because the value of the Ip obtained depends upon the chemistry of the asphalt, the importance of asphalt chemistry to performance is affirmed.

## Inverse GLC-Viscosity Studies

The viscosity of asphalts has long been considered important to their service performance. Changes in viscosity of the Zaca-Wigmore asphalts were studied by Simpson, et al. (7), using a microfilm

durability test. Simpson related the changes in viscosity (reported as the aging index, which is defined as the ratio of the viscosity after oxidation of a 5μ film of asphalt in air for 2 hours at 225 F to the initial viscosity) to the performance of the asphalt in service. In general, those asphalts showing the smaller aging indexes performed better in the road.

In Figure 3 the aging indexes obtained by Simpson are plotted as a function of the phenol Ip's on the Zaca-Wigmore asphalts after oxidation in the GLC column. A correlative trend is shown which is consistent with the correlation of pheoni Ip and service performance shown in Figure 1.

Simpson pointed out that the hardening of an asphalt during the microfilm durability test could result from either oxidation or loss of volatiles. To determine the effect of volatility, he ran the test in a nitrogen atmosphere as well as in air. Based on changes in viscosity in nitrogen, asphalts F, G, B-2, G-2, and particularly asphalts E and E-2 were found to be significantly more volatile than the other asphalts. Figure 3 shows that these more volatile asphalts have both higher aging indexes and higher Ip's.

The question arises as to the dependence of the phenol Ip's on the loss of volatiles during the inverse GLC-oxidation and testing procedure. The Ip's could be increased either by the concentration of phenol-active material through volatile or oxidative loss of phenol-inactive material, or by the oxidative formation of phenol-active sites. To determine the effect of volatile loss, asphalt E (one of the most volatile asphalts according to Simpson's test) was tested in the GLC column at 130 C under conditions described in the Experimental section, except that the helium carrier gas was allowed to flow through the column for an extended period of 96 hours prior to the 24-hour oxidation
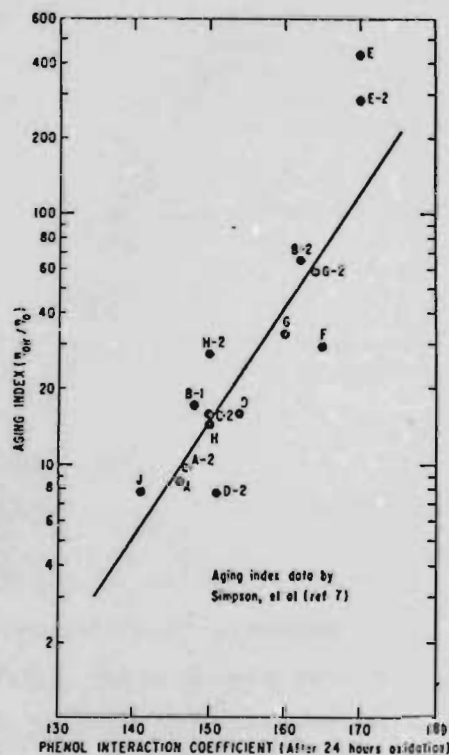
Fig. 3. Relationship between the Interaction Coefficient and the Aging Index.

period. The phenol Ip was measured after 6 hours and 96 hours of the helium treatment, and after the 24-hour air treatment. The nearly colorless volatile oils which were stripped from the column were collected and weighed at various time intervals. The weight-per cent of the oils collected is shown as a function of time in Figure 4. Phenol Ip's at selected time intervals are also shown. The rate of loss of volatile oils (exclusive of highly volatile hydrocarbons and oxidation products such as $CO_2$ and water) is apparently the same for both helium and air. The infrared spectra of the volatile oils collected under
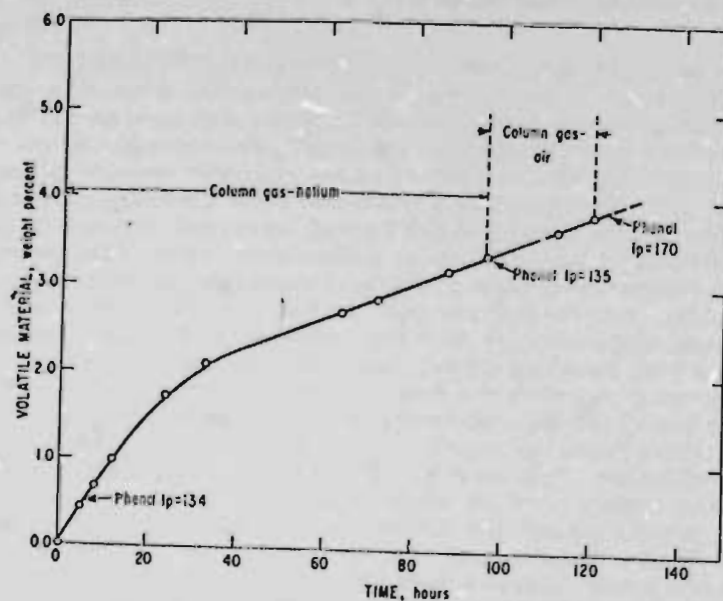
Fig. 4. Volatility Losses of Asphalt E in the GLC.

both conditions were similar, thus indicating that oxidation products are not being collected in the volatile oils. During the 96 hours under helium, the Ip only changed from 134 to 135; however, during the 24 hours under air the Ip increased from 135 to 170. Thus, the higher Ip's obtained on oxidation of asphalts are not a result of volatile losses during the determination, but must arise from an increase in polar groups in the asphalts.

To determine the effect on viscosity of the volatiles lost from asphalt E during the GLC determinations, the viscosity of a sample from a run similar to that reported in Figure 4 was measured after 96 hours of stripping with helium carrier gas. A viscosity ratio of 4.7 (final/initial) was obtained as compared with a viscosity ratio of 56.5 obtained by Simpson in the microfilm durability test under nitrogen. This

indicates that a large part of the volatiles lost in the determination of the aging index are retained and analyzed in the Inverse GLC-oxidation technique. The relationship between the amount of volatiles and the Ip is not understood at this time. It is probably indirect, although it is possible that the volatile materials are among those that produce high Ip's on oxidation. The fact remains that the phenol Ip is indicating a change in composition not resulting merely from volatile losses.

## SUMMARY AND CONCLUSIONS

Results of the Inverse GLC study of the Zaca-Wigmore asphalts show the potential usefulness of the technique in studying oxidative weathering characteristics of asphalts. The retention behavior of the test compound phenol on the oxidized asphalts correlates with the performance of the asphalts in road service, and this is supported by a similar correlation with accelerated weathering durabilities of coating-grade asphalts.

The phenol Ip's also correlate with the viscosity changes as measured by the microfilm durability test. Those asphalts that showed larger viscosity changes in the microfilm durability test showed larger phenol Ip's on oxidation. The higher phenol Ip's are not a direct result of volatile losses, but must result from an increase in polar groups on oxidation of the asphalts.

Because Inverse GLC measurements are directly related to chemical composition, future interpretations of test compound behavior should aid in understanding the chemistry of oxidative weathering.

## ACKNOWLEDGMENT

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## *Discussion*

CHAIRMAN W. J. HALSTEAD: We have no prepared discussions on this paper, so the paper will now be open for discussion from the floor.

MR. L. C. KRCHMA: You did mention that there were two test roads with very nearly the same asphalts in the Zaca-Wigmore experimental road test, one of them period No. 1 and the other period No. 2. You did show the asphalt property-performance relationship for period 1. Do your studies permit commenting on the same relationship for period 2?

DR. PETERSEN: I am not personally acquainted with these roads. They were put in service long before we began our work. However, they are reported on in the ASTM Special Technical Publication No. 277 by Hveem and coworkers. Paving period 2 asphalts were laid over existing concrete surfacing, and so, in this sense, they are different from paving period 1 which was laid over new alignment. They are also different in that paving period 2 was laid during the wet, winter season, and there was good weather for paving period 1. Steaming of the aggregate may have caused the reduction in the degradation of the asphalt in the mix plant. Anyhow, there was less oxidation during mixing, and these asphalts therefore went down in the road with less voids on the average. Also, because of the concrete pavement underneath the paving period 2 asphalts, there was much less deflection in service. So there are a number of things which are different with paving period 2 which make it really a separate test. There just aren't any failures in the performance data reported on paving period 2. Except for Asphalt E-2, the surface ratings have no spread, being either 1 or 2. As you well know, you can't make evaluations until you get failures.

I believe the final report on the Zaca-Wigmore test is due to come out shortly, if it's not already out. I haven't seen it. There may be more performance data yet to come. We hoped there would. That's why we included Inverse GLC data on paving period 2 asphalts. Our GLC analysis is as complete on the paving period 2 asphalts as on paving period 1, but we just don't have anything to run it against.

MR. KRCHMA: But they are about the same asphalts, are they not in spite of the fact the performance was materially different?

DR. PETERSEN: According to Hveem's paper, I think three or four of them were considered to be essentially the same. I understand that producers were just gearing up to comply with new specifications at the time, and some asphalts from the same producers for the two periods were different. However, as I recall, three or four of them were supposed to be nearly identical.

MR. KRCHMA: Your test, however, is independent of the different environment that existed in period two over period one.

DR. PETERSEN: Right.

MR. KRCHMA: Then the next question is: How well do the asphalts from Period 1 compare in your test with Period 2 in spite of the fact that the performance was different out in the field?

DR. PETERSEN: We have that information in the preprint. I think I will let Mr. Davis answer that question. Incidentally, he has done a good share of the work on the GLC technique.

MR. T. C. DAVIS: I believe there were four asphalts that were supposed to be the same, and we had three of them and the three looked very close on the inverse GLC.

MR. T. R. WELCH: Dr. Petersen, I am afraid I haven't had a chance to study your paper. But I am rather interested in your conclusion that the higher phenol interaction coefficients are not a direct result of volatile losses, but must result from an increase in polar groups on oxidation of asphalts. It is our experience that in an evaporation or distillation process there is a tendency for the chemical change to be mainly loss of saturates rather than that of aromatic compounds. Therefore, the asphalt during evaporation tends to become more aromatic and this is not through oxidation. I wondered, in fact, whether this could explain your higher interaction coefficients: namely, your loss of saturates making the asphalt more aromatic rather than the formation of other compounds.

DR. PETERSEN: I don't think so, based on the last slide. We ran 96 hours with a carrier gas of helium passing through the column, and it stripped the column at essentially the same rate as when we put air through. Now, 96 hours under helium did not significantly change the interaction coefficient. The change was almost within experimental error. However, with air going through the column for 24 hours, and with only a small per cent of the total volatile loss experienced in the first 96 hours, the interaction coefficient increased from 135 to 170.

So I don't see how you can explain this on the basis of volatile losses. There was just a fraction of one per cent volatile loss that took place along with this large increase in the interaction coefficient. Further, we don't lose much volatile material in the GLC determination.

DR. F. S. ROSTLER (written discussion): The paper by Davis and Petersen presents an original approach to the characterization of asphalts. It is an interesting contribution to our knowledge of asphalt chemistry in several respects. The paper is particularly valuable and informative because the asphalts investigated are well defined, well known, and have been studied by other investigators who use different techniques.

We believe it might be of interest to workers in the field to compare a set of data we collected on the same asphalts with those presented, since they are believed to support the findings of Petersen and coworkers. These data are for fractional composition of the Zaca-Wigmore asphalts and the calculated parameter, $(N + A_1)/(P + A_2)$, expressive of

Table A. Asphalts of Paving Period 1

| Asphalt Designation | J | A | B-1 | C | H | D | G | F | E |
|---|---|---|---|---|---|---|---|---|---|
| Surface Performance Rating* | 1 | 2 | 3 | 3+ | 4 | 4 | 5 | 7 | Failed |
| California Abrasion Test** | | | | | | | | | |
| Grams loss at 65 F. | 6.0 | 20.0 | 22.0 | 27.5 | 29.0 | 27.5 | 18.0 | 29.5 | 49.5 |
| Aging Index After Microfilm† | | | | | | | | | |
| Durability Test, $\eta_a/\eta_0$ | 7.8 | 8.5 | 17.1 | 17.8 | 14.3 | 15.8 | 33.2 | 29.6 | 428. |
| Phenol Interaction Coefficient, | | | | | | | | | |
| Original | 118 | 123 | 118 | -- | 124 | 177 | 137 | 133 | 134 |
| After 24 hours Oxidation | 141 | 146 | 148 | -- | 150 | 154 | 160 | 165 | 170 |
| Fractional Composition, % ‡ | | | | | | | | | |
| A | 16.0 | 10.5 | 21.7 | 11.6 | 14.9 | 9.5 | 26.6 | 25.6 | 27.3 |
| N | 15.7 | 37.2 | 26.8 | 39.8 | 36.5 | 34.3 | 21.8 | 26.7 | 28.3 |
| $A_1$ | 21.2 | 12.2 | 19.0 | 12.9 | 19.2 | 17.5 | 26.5 | 20.8 | 21.0 |
| $A_2$ | 34.3 | 24.6 | 18.2 | 20.6 | 17.0 | 24.0 | 14.9 | 15.3 | 14.7 |
| P | 12.8 | 15.5 | 14.3 | 15.1 | 12.4 | 14.7 | 16.2 | 11.6 | 8.6 |
| $(N + A_1)/(P + A_2)$ | 0.78 | 1.23 | 1.41 | 1.48 | 1.89 | 1.34 | 1.36 | 1.77 | 2.09 |

* After 51 months' service; data from Davis and Petersen reference 6.
** Aged 500 hr. at 140 F; data from Davis and Petersen reference 6.
† Data from Davis and Petersen reference 7.
‡ Unpublished data; test method described in Rostler and White, *Proceedings, Association of Asphalt Paving Technologists*, Vol. 31, January, 1962, pp. 35-89.

the ratio of more reactive to less reactive components. The two tables A and B show these data compared with some of the characteristic values determined by the authors and previous investigators.

Petersen and coworkers postulated in their previous publications (references 2 and 3) that Inverse GLC can be expected to be a measure of typical functional groups in asphalts and of the extent of oxidation and weathering. No correlation is shown in the present paper between functional groups of the retention compounds and functional groups in the asphalts. This correlation could, of course, not yet be found, since the functional groups present in the asphalts are not known, but further

Table B. Asphalts of Paving Period 2

| Asphalt Designation | C-2 | H-2 | A-2 | D-2 | G-2 | B-2 | E-2 |
|---|---|---|---|---|---|---|---|
| Surface Performance Rating* | 1- | 1- | 1- | 1 | 2- | 2 | 4-5 |
| California Abrasion Test** | | | | | | | |
| Grams loss at 65 F. | 24.0 | 33.0 | 16.0 | 27.0 | 30.0 | 26.0 | 62.0 |
| Aging Index after Microfilm† | | | | | | | |
| Durability Test, $\eta_a/\eta_0$ | 15.8 | 27.4 | 9.6 | 7.3 | 59.0 | 65.4 | 282. |
| Phenol Interaction Coefficient, | | | | | | | |
| Original | 124 | 120 | 124 | 125 | 128 | 127 | 137 |
| After 24 hours Oxidation | 150 | 150 | 147 | 151 | 164 | 162 | 170 |
| Fractional Composition, % ‡ | | | | | | | |
| A | 12.4 | 17.0 | 9.2 | 8.8 | 25.7 | 24.6 | 30.7 |
| N | 38.9 | 35.9 | 36.4 | 35.4 | 23.8 | 25.9 | 24.4 |
| $A_1$ | 14.7 | 15.3 | 13.4 | 13.7 | 19.7 | 19.1 | 21.3 |
| $A_2$ | 19.0 | 18.4 | 24.8 | 25.5 | 18.3 | 18.2 | 14.9 |
| P | 15.0 | 13.4 | 16.2 | 16.6 | 12.5 | 12.2 | 8.7 |
| $(N + A_1)/(P + A_2)$ | 1.58 | 1.61 | 1.21 | 1.17 | 1.41 | 1.48 | 1.94 |

* After 47 months' service; data from Davis and Petersen reference 6.
** Aged 500 hr. at 140 F; data from Davis and Petersen reference 6.
† Data from Davis and Petersen reference 7.
‡ Unpublished data; test method described in Rostler and White, *Proceedings, Association of Asphalt Paving Technologists*, Vol. 31, January, 1962, pp. 35-89.

work with well defined asphalt components might lead to some insight in this respect.

The mechanism of oxidation in the column and the effect of oxidation on retention, i.e., the difference between retention before and after oxidation, is difficult to understand. It might be valuable if the authors would elaborate on what they expect to determine and explain the underlying principles, and if they could give some examples. One would expect the degree of retention of specific test compounds to change because of oxidation and because of the corresponding change of specific functional groups in the asphalt. The data presented by Petersen and coworkers show increase of retention of all test compounds after oxidation. This is hard to understand.

It is demonstrated that the retention coefficient (especially of the test compound phenol) correlates well with performance of the Zaca-Wigmore asphalts. The authors point out that the measured retention behavior is related to chemical composition, as should be expected. The two sets of data indicative of chemical reactivity, Petersen's and ours, show the same trend, and both types of data correlate fairly well with performance rating and performance tests. This mutually supporting evidence affirms the fact, by now well established, that asphalt performance is governed by chemical composition and that durability is definitely linked to oxidation.

It would be valuable if others who have data on the same specimens would also make them generally available. The practice of various investigators using the same specimens and publishing their data is more apt to advance our knowledge of asphalt than papers contradicting other findings but showing data collected on specimens which are neither well defined nor available to others.

AUTHORS' CLOSURE: We wish to thank Dr. Rostler for making available his analytical data on the Zaca-Wigmore asphalts which support our Inverse GLC studies. We certainly concur that it is most helpful when different investigators can report data on the same samples.

Dr. Rostler has asked for some discussion of the mechanism of oxidation in the column and the effect of oxidation on retention behavior; what are the principles involved, and why does the Interaction Coefficient increase for all test compounds (or at least does not decrease) after oxidation?

Oxidation within the GLC column is simply a method of oxidizing the asphalt under controlled and reproducible conditions. The reactivity of the asphalt to oxygen is then reflected in the Interaction Coefficients obtained for the test compounds on the oxidized asphalts. As is well known, oxidation of an asphalt at 130 C causes the production in the asphalt of a number of different types of oxygen-containing functional groups; for example, carboxylic acid groups, carbonyl and hydroxyl groups, and groups containing the various oxidation states of sulfur.

With respect to the Inverse GLC interactions, we can consider the oxygen-containing functional groups as acids or bases, and often both.

We must not think in terms of the limited acid-base theory of aqueous systems, however, because we are dealing with a non-aqueous system. Thus, in the broad sense considered here, bases are those groups which are electronegative, or electron-rich, and acids are those groups which are electropositive, or electron-poor. For example, a carboxyl group has both acidic and basic character. The carbonyl and hydroxyl oxygen of the carboxyl group are electronegative and will interact with an acidic test compound (or one containing an electron-poor center). On the other hand, the hydroxyl hydrogen of the carboxyl group is electropositive or acidic in character and will interact with a basic test compound (or one containing an electron-rich center). The same arguments can be made for oxygen and hydrogen of the alcoholic or phenolic hydroxyl groups which may be formed on oxidation.

Because both acid and basic character are produced in the asphalt by incorporation of oxygen on oxidation, one might expect changes in the interactions of polar test compounds, whether these test compounds are acidic or basic in character, to be reflected as increased Interaction Coefficients. This is consistent with the data.

The important fact is that although the Interaction Coefficient increases on oxidation of the asphalt for polar test compound interactions, the nature or magnitude of these interactions is not the same for all test compounds. Certain interactions are stronger and more specific than others. It is for this reason that the Interaction Coefficient for phenol showed a correlation with performance, while the Interaction Coefficients for many other test compounds did not.

What we need now, as Dr. Rostler points out, is a knowledge of the nature of the interactions between specific functional groups in the asphalt and specific test compounds. Such information is fundamental and will make possible the interpretation of the Inverse GLC data in terms of the chemical composition of the asphalt. We hope information of this type will be forthcoming in the future, both from our own laboratory and the laboratories of others who are interested in the Inverse GLC technique.

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