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PAVING ASPHALTS: CHEMICAL COMPOSITION, OXIDATIVE WEATHERING, AND ASPHALT-AGGREGATE INTERACTIONS. Part II.

J.C. Petersen, S.M. Dorrence, and Others

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Interim Report

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16. Abstract

This report describes an interrelated study of the oxidation products formed in asphalt during the processing of road mixes and aging in the road and the interactions of asphalt and its oxidation products with aggregate to form the asphalt-aggregate adhesive bond.

A method for the qualitative and quantitave determination of ketones, carboxylic, acids, dicarboxylic anhydrides, and 2-quinolone types in asphalts was developed and applied to ten penetration-grade asphalts recovered from 11- to 13-year-old pavements. Carbonyl types strongly adsorbed on the aggregate surface were quantitatively determined. Independent studies identified ketones and dicarboxylic anhydrides as significant carbonyl-type oxidation products in asphalts. Evidence for the structural types of ketones and anhydrides in asphalts is given. Esters were not found in the asphalt oxidation products. Mineral surfaces and components naturally present in asphalt were both found to catalyze the oxidation of asphalt.

Asphalt-aggregate interactions were studied by microcalorimetry which gave evidence of multilayer adsorption of asphalt molecules in the asphalt-aggregate interphase region. Further evidence for the orientation of molecules in the interphase region was provided through photomicroscopic studies.

The significance of the work to asphalt paving technology is discussed.

17. Key Words
Asphalt, chemical composition, asphalt-aggregate interactions, molecular interactions, performance, properties, oxidation, adhesion, stripping infrared spectroscopy, microcalorimetry, photomicroscopy.

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UNITED STATES GOVERNMENT

Memorandum

DEPARTMENT OF TRANSPORTATION
FEDERAL HIGHWAY ADMINISTRATION

DATE: December 24, 1974

In reply refer to: HRS-23

SUBJECT: Transmittal of Research Report No. FHWA-RD-74-71 "Paving Asphalts: Chemical Composition, Oxidative Weathering, and Asphalt-Aggregate Interactions"

FROM : Project Manager, FCP Project 4A,
Minimize Early Deterioration of
Bituminous Concrete

TO : Individual Researchers

The subject report with this memorandum is intended primarily for asphalt researchers. The report will be of particular interest to asphalt technologists concerned with asphalt-aggregate interactions. This interim report describes a study of the oxidation products formed in asphalt during the processing of paving mixes and subsequent aging in the road, and the interactions of these oxidation products with aggregate to form asphalt-aggregate adhesive bonds.

The report is the second one resulting from research being conducted for the Federal Highway Administration at the Bureau of Mines' Laramie Energy Research Center in Laramie, Wyoming. A previous interim report for the period April 1969 - June 1972 has not been processed for distribution as the contents have been made available in reports in various technical journals.

Additional copies of this report are available from the National Technical Information Service (NTIS), Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22151. A small charge is imposed for copies provided by NTIS.

James M. Rice
James M. Rice

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INTRODUCTION

In 1969 the Bureau of Mines entered into a cooperative research program on asphalt composition and performance with the Federal Highway Administration (FHWA). Research conducted at the Laramie Energy Research Center (LERC) during the period FY 1969 through FY 1972 in this interagency effort to find solutions to problems related to the use of petroleum asphalt in the nation's roads is summarized in an interim report prepared for the FHWA (1)[1]. This interim report dealt with fundamental physiochemical studies of asphalt composition, oxidative weathering, and asphalt-aggregate interactions.

The present report summarizes results of additional studies in the same general area as the previous work. Although about 75 percent of the petroleum asphalt produced in the U.S. is used in road construction, little is known of the chemical composition factors in asphalt which are responsible for its road performance properties. A major objective of the present work was to identify and quantitatively measure the major chemical types present in asphalt or formed on oxidation which significantly change the physical properties of asphalt or influence the properties of the asphalt-aggregate bond. A second objective was to determine the nature of asphalt-aggregate interactions and how they influence the properties of the asphalt binder in the asphalt-aggregate interphase region.

The development of a method for the qualitative and quantitative determination of the carbonyl-type compounds in asphalts is described. This method, based on a combination of differential infrared spectroscopy and selective chemical reactivity, was used to determine carboxylic acids, dicarboxylic anhydrides, ketones, and 2-quinolone types. The method was also applied to ten asphalts recovered from road service to determine the compound types formed on aging and that are strongly adsorbed to the aggregate surface in the asphalt-aggregate bond. Work is also described

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[1] Underlined numbers in parentheses refer to the list of references at the end of this paper.

which led to the positive identification of ketones and dicarboxylic anhydrides as oxidation products in asphalts. The controversial question of the presence of esters in oxidized asphalts is considered. The catalytic effect of aggregate surfaces on the oxidation of asphalts and the presence of oxidation catalysts in the more polar asphalt fractions is also described.

Finally, the application of microcalorimetry to measure the heat of immersion of four FHWA study aggregates in four FHWA study asphalts is reported. Heats of immersion are believed related to the nature of the adhesive bond formed between asphalts and aggregates and to subsequent multilayer adsorption of highly oriented asphalt molecules in the asphalt-aggregate interface region. The highly oriented interfacial region was also studied using photomicroscopy.

In all of the work reported, sufficient experimental details are presented to enable the reader to understand the work; however, for the most part, the reader wishing detailed experimental procedures is referred to appropriate publications in the literature.

ANALYSIS OF CARBONYL-TYPE COMPOUNDS IN ASPHALTS

Preliminary Considerations

Although small amounts of compounds having functional groups that absorb in the carbonyl region of the infrared spectrum are naturally present in many asphalts, oxidative aging of asphalts produces significantly greater amounts of these functional groups (2-4). Oxygen-containing groups of this type are generally polar and capable of participating in strong functional group interactions (5-16). These interactions are believed to play a major role in the hardening and embrittlement of asphalt in use. Polar groups initially present, or formed on oxidation, may be strongly adsorbed on the aggregate surface in road mixes, thus affecting the adhesive bond between asphalt and aggregate and contributing to the water-stripping characteristics of the mix. Because of the complex nature of asphalt, satisfactory methods for the quantitative determination of the oxygen-containing functional types in asphalt have not been developed.

Knotnerus (17) proposed methods to identify and quantify several functional types formed in asphalt on oxidation which absorb in the carbonyl region. Acids and saponifiable material were estimated by neutralization and saponification with potassium hydroxide. He concluded that a large part of the oxygen in oxidized asphalts was present as esters and that a large part of the carbonyl absorption resulted from these esters. The conclusions of Knotnerus were disputed by Campbell and Wright (18) who, by adding model compounds to oxidized asphalts, concluded that esters were not present in oxidized asphalts in detectable amounts. They suggested several possible side reactions which might consume some of the alkali attributed by Knotnerus to ester hydrolysis. Based on their indirect evidence they concluded that the principal contributors to the carbonyl band of oxidized asphalts were aldehydes, ketones, and acids; however, no attempt was made to quantify the data or to directly confirm the presence of any one of these functional types in the asphalt samples.

Knotnerus (17) estimated the amounts of carbonyl compounds in oxidized asphalt by oxime formation. The method was based on titration of the HCl liberated from hydroxylamine hydrochloride used to derivatize the carbonyl compounds. The method was complicated by the possible decomposition of hydroxylamine by metallic oxides and salts present in asphalts and by possible reaction with unknown functional groups.

The present work describes a differential infrared technique that makes possible, without prior separations, the qualitative and quantitative determination in asphalts of the major compound types absorbing in the carbonyl region. These compound types include the ketones formed on oxidation, carboxylic acids, dicarboxylic anhydrides, and 2-quinolone types. The method is particularly applicable to the determination of carboxylic acids, dicarboxylic anhydrides and 2-quinolone types in oxidized asphalts in which the absorption bands of these functional types are masked by the intense band of the ketones formed on oxidation.

This new method for the analysis of compound types absorbing in the carbonyl region overcomes two major problems that have thwarted successful detailed analysis of the carbonyl region of asphalts. These problems result from intermolecular association of carbonyl types in asphalts and from severe overlap of the infrared absorption bands. In fact, intermolecular association severely complicates the band overlap problem, making resolution and identification of the individual bands of the compound types virtually impossible without special techniques.

Carboxylic acids and 2-quinolone types in asphalts have been shown to form cyclic dimers and mixed dimers in neat asphalt and in nonpolar solvents such as carbon tetrachloride (6, 7); the associated species are in equilibrium with their monomers, thus giving rise to a number of overlapping absorption bands. Success of the present method depends largely on the use of tetrahydrofuran(THF) as a spectral solvent. Because of its electron-donating properties, THF associates with the acidic hydrogen of the carboxylic acids and 2-quinolone types, thus freeing the carbonyl group and preventing dimer and mixed dimer formation (7). With intermolecular association eliminated, only the carbonyl absorption of the unassociated species need be considered.

Typically, oxidized asphalts have a broad absorption band centering at about 1700 cm^{-1} that is composed of the overlapping bands of ketones, dicarboxylic anhydrides, carboxylic acids, and 2-quinolone types. These compound types will be considered subsequently in detail, but suffice it to say that the anhydrides, acids and 2-quinolone types are usually unrecognizable shoulders on the much more intense ketone band centering at about 1695 cm^{-1}. Resolution problems resulting from band overlap in the carbonyl region are circumvented using selective chemical reactions with the asphalt components followed by analysis using differential infrared spectroscopy.

General Description of the Analytical Method

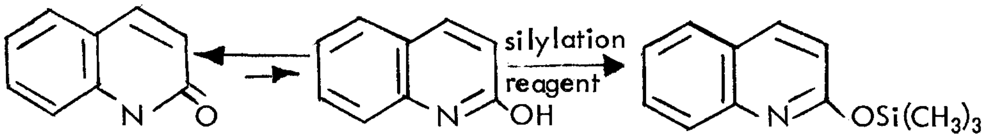
The method is not difficult nor does it require highly specialized equipment; however, careful attention must be given to experimental details to insure reliable results. Therefore those wishing to use the method are referred to the detailed published report (19).

The underlying principle of the present method is to react the anhydrides, acids, and 2-quinolone types with selective chemical reagents to alter or shift their absorption bands so that the bands may be identified and measured. The identification and measurement is facilitated by the use of differential spectra which null or cancel out the interfering bands produced by the unreactive components such as the ketones and thus show only net changes produced by the chemical treatment. Table 1 shows the approximate carbonyl absorption frequencies of the band maxima of the compound types determined in the analysis and the effect of the selective reagents on these frequencies. This table is useful in analyzing the differential spectra obtained in the analysis.

In the method, asphalt is reacted with sodium hydroxide to convert the carboxylic acids, dicarboxylic anhydrides, and other carboxylic acid derivatives to carboxylate ions, thus shifting their carbonyl absorption bands from the 1800 to

1700 cm^{-1} region to a broad band centering at about 1580 cm^{-1}. This shift is illustrated in Figure 1 by comparing spectra A and B. The shift is more vividly illustrated by spectrum C, which is the differential spectrum of B versus A. The area of the band above the null line (dashed baseline) in curve C from about 1850 to 1680 cm^{-1} represents the loss of the absorption of the carboxylic acids and their derivatives and is used in their quantitative determination. The band centering at about 1580 cm^{-1} (below the null line) represents the absorption of the corresponding carboxylate ions. Carboxylic acids (absorption band at about 1730 cm^{-1}) are differentiated from dicarboxylic anhydrides (doublet with bands at 1725 cm^{-1} and 1765 cm^{-1}) by their selective silylation and their selective reactivity with potassium bicarbonate. The silyl esters of carboxylic acids in asphalts absorb at about 1715 cm^{-1}.

2-Quinolone-type compounds are determined by silylation (7) which destroys their carbonyl group. The 1688 cm^{-1} band (Table 1) results from the silylation of the hydroxyl form as illustrated below for 2-quinolone. Under equilibrium conditions prior to silylation, however, 2-quinolone is virtually all in the carbonyl form.



Sample differential spectra showing the effects of silylation are shown elsewhere (19). The balance of the carbonyl absorption remaining in oxidized asphalts after the adsorption of the carboxylic acids, dicarboxylic anhydrides, 2-quinolone types, and the background have been accounted for results primarily from ketones. Although part of the background absorption in unoxidized asphalts may result from compounds containing the C=O group, the amount is small when compared with the ketone absorption in oxidized asphalts, as can be seen by comparing spectra H and A, Figure 1, of an unoxidized and an oxidized asphalt, respectively. The indications of bands at 1765 and

1700 cm^{-1} in the unoxidized asphalt result primarily from small amounts of oxidation which occurred in the asphalt during and/or after manufacture. A well-defined band attributable to ketones (1695 cm^{-1}) or anhydrides (1765 cm^{-1}) has not been found in fresh, unoxidized asphalts.

Actual concentrations of the different carbonyl types were estimated from the apparent integrated absorption intensities of the respective infrared absorption bands in the differential spectra and comparing these with the corresponding molar absorptivities of model compounds of the type believed present in asphalt. Spectra were obtained on 0.25 g samples dissolved in 5.00 ml THF using 1.00 mm sealed sample cells. The apparent integrated absorption intensity is defined as the area under the absorption band, $\int A_\nu d\nu$, where A is the absorbance and ν is the absorption frequency in cm^{-1}. The band area was estimated by counting squares on the recording chart paper on which the infrared spectra were obtained. The concentrations of functional types in the neat asphalt were then estimated using the equation:

$$C = \frac{\int \Delta A_\nu d\nu}{B \cdot l} \cdot \frac{5.25}{0.25}$$

The term 5.25/0.25 corrects for sample dilution by solvent and values of the molar integrated absorption intensities (B), as determined from model compounds, are listed in Table 2. The term, l, is the cell path length in centimeters.

Application of the Method to Asphalts Recovered From 11-13-Year-Old Pavement Cores.

In spite of the apparent importance of asphalt-aggregate interactions in the formation of a good adhesive bond and the prevention of water stripping of the asphalt from the aggregate surface, little fundamental knowledge of the nature of the interactions exists. Chemical reactions between asphalt components and the aggregate surface have not been conclusively shown even though certain asphalt components are apparently strongly adsorbed and not readily extracted from the aggregate in road cores by commonly used solvents such as benzene. Alcohol is often added to the solvent to effect more complete recovery; however, methods for establishing the functional types strongly adsorbed on the aggregate surfaces have not been available.

Following development of the analytical method for carbonyl types just described, the method was applied to a series of asphalts recovered from road cores by FHWA personnel. The concentrations of functional group types absorbing in the carbonyl region from 1850 to 1640 cm^{-1} were determined and are reported in Table 3. Asphalts 19 through 166 are representative of a collection of penetration grade highway asphalts previously studied by the Bureau of Public Roads (20, 21) (now Federal Highway Administration, FHWA) and others (22-24). Determinations were made on the original asphalts (columns Or), on corresponding asphalts recovered by FHWA from 11- to 13-year-old highway pavement cores with benzene (columns B) and 4:1 benzene-95 percent ethanol (columns BA), and on original asphalts oxidized in the laboratory at 130° C (columns CO).

Determination of Carbonyl Types. - Ketones were found to be the major product formed in asphalts on oxidation which absorb in the carbonyl region. Their concentration in laboratory-oxidized samples ranged from 0.41 mol $\cdot$ l^{-1} in asphalt 67 to 0.78 mol $\cdot$ l^{-1} in asphalt 72. Judging from the amount of ketone produced, the laboratory oxidation, except for asphalt 30, was slightly more extensive than the oxidation in the road. Because the roads were still in service when sampled, it is believed that the level of oxidation encountered in the laboratory oxidation would be quite representative of that produced in an asphalt road during its useful service life. The levels of oxidation found in the asphalts taken from road service cannot be compared to assess the relative susceptibility of the different asphalts toward oxidation because of the variations in environmental exposure in service; however, levels of oxidation in laboratory-oxidized asphalts can be compared.

Examination of the data in Table 3 indicates that dicarboxylic anhydrides are not naturally occuring in asphalts but are artifacts of oxidation. Dicarboxylic anhydrides and carboxylic acids were found in all oxidized asphalts although some unoxidized asphalts were void of detectable amounts of carboxylic acids. Only small amounts of free carboxylic acids were formed in any of the asphalts on oxidation. The dicarboxylic anhydrides accounted for a major part of the carboxylic functional group formed. This is unusual. Apparently, most oxidation not associated with anhydride formation, under the oxidation conditions imposed, terminates with the ketones. The unusually large amount of free acids found in the road-recovered asphalt 19 may have resulted from antistripping additives which might have been added to the asphalt prior to road construction but not present in the original asphalt. The large amount of free acids was not found in the laboratory-oxidized sample of the original asphalt. It is reported that the original asphalts were not all collected from the refineries at the actual time of road construction. Little or no 2-quinolone types were found in the asphalts. Unlike the other functional types determined, the 2-quinolone types are not formed on oxidation but are only naturally occurring.

To provide a physical concept of the amounts of polar functional groups absorbing in the carbonyl region which are introduced in asphalt molecules on oxidation, the following hypothetical calculation is made. If one assumes for asphalt a conservative average molecular weight of 700, a density of 1, and monofunctionality, then 49 percent of the molecules in asphalt 30 were altered on oxidation by the introduction of polar groups absorbing in the carbonyl region. Because of the ability of functional groups absorbing in the carbonyl region to form strong association complexes, this could have a significant effect on asphalt physical properties.

Component Types Strongly Adsorbed on Aggregates. - By comparing the analyses of the asphalts recovered independently from the aggregates with benzene and with benzene alcohol, the composition of the strongly adsorbed material (that fraction desorbed with benzene-alcohol but not with benzene only) was determined. The weight percent of the strongly adsorbed material is shown in Table 3. Calculated data on the strongly adsorbed materials are shown in Table 4. Details of the calculation procedures are presented elsewhere (26).

The composition of adsorbed material can be determined with reasonable accuracy unless concentrations become unduly small. However, individual estimates of the amounts of ketones in the strongly adsorbed material may be subject to considerable error becuase of the compounding of several factors: (1) the total ketones in the recovered samples are determined by difference after determination of acids and anhydrides, (2) the amounts of ketones strongly adsorbed are small relative to the total amount, and (3) the strongly adsorbed ketones are estimated by the difference between the asphalts recovered with benzene-alcohol and with benzene only. Although results for the individual road cores may vary, it is believed that the average value reported for the ten road core extracts is typically representative. Even though the estimates of the strongly adsorbed anhydrides and acids are determined by difference, individual estimates are inherently more reliable than those of the ketones because they are directly determined and the relative amounts of the total functional type which is strongly adsorbed is much greater. The accuracy of the determinations could have been improved by multiple determinations or by direct analyses of the strongly adsorbed materials had they been available. The number of significant figures shown in the table for the individual determinations does not necessarily represent accuracy but is carried for computation of averages.

The calculated data in Table 4 on the ketones, dicarboxylic anhydrides, and carboxylic acids strongly adsorbed from the asphalts by the aggregates are now considered. The concentration factor, which represents the concentration of the functional type present in the strongly adsorbed material relative to its concentration in the benzene-alcohol recovered asphalt, is a measure of the tendency of the functional type to be adsorbed by the aggregate. The average concentration factor for ketones was 1.9, these being the most weakly adsorbed materials. Dicarboxylic anhydrides were next in their affinity for the aggregate surface. On the average, these were concentrated in the strongly adsorbed material by a factor of 9.5. Finally, carboxylic acids were most strongly adsorbed, being concentrated by an average factor of 14.

Data in Table 4 show that although ketones were the most weakly adsorbed, because of their greater abundance, they represented an estimated 61 percent of the strongly adsorbed material. Anhydrides and acids accounted for a total of 13 and 10 percent of the strongly adsorbed materials, respectively. These estimates assume monofunctional compounds with an average molecular weight of 700 and are at best only approximate. Based on these assumptions, the last column in Table 4 shows that 84 percent of the strongly adsorbed material, on the average, was accounted for as ketones, anhydrides, and acids. The two individual estimates which are greater than 100 percent probably reflect inaccuracies in the assumptions--most likely the assumption that no more than one functional group is produced on an individual molecule on oxidation. Other work in our laboratory has shown 2-quinolones to be relatively strongly adsorbed; however, their low concentrations or virtual nonexistence in these samples made their quantitative determination unreliable, and no data on them are reported.

IDENTIFICATION STUDIES OF CARBONYL TYPES PRODUCED IN ASPHALTS ON OXIDATION

Identification of Dicarboxylic Anhydrides in Oxidized Asphalts

Although previous sections of this report deal with the quantitative determination of dicarboxylic anhydrides in asphalt, this section documents the proof of their identification in asphalts. Anhydrides were considered as possible contributors to the carbonyl region of asphalts by Knotnerus (17) and by Campbell and Wright (18); however, they concluded that if anhydrides existed at all they were present only in trace amounts. In our studies dicarboxylic anhydrides were identified by selective chemical reactivity and infrared spectroscopy. The carbonyl infrared bands of the anhydrides and their derivatives were made readily observable by using the differential spectral technique described in a previous section to eliminate the interference of the strong ketone band. Model anhydrides were also studied to determine the most probable structural type of anhydrides present. A more comprehensive account of the identification detailing the experimental procedures and materials used is published elsewhere (27).

Evidence for Dicarboxylic Anhydrides in Oxidized Asphalts. - The reactions that were used in this study to identify and characterize the dicarboxylic anhydrides in oxidized asphalts are illustrated in Figure 2, using 1,8-naphthalic anhydride as a model. These reactions and their significance when carried out on asphalt samples are discussed in detail in the sections that follow. The reactions were followed by observing changes in the infrared absorption spectra in the carbonyl region from 1500 to 1900 cm^{-1}.

An oxidized saturate fraction from a Wilmington (Calif.) asphalt was extensively used for illustrative purposes because it contained a relatively large amount of the proposed dicarboxylic anhydrides relative to other functional types absorbing in the carbonyl region and because of the virtual absence of any interfering bands prior to oxidation. The results obtained on this fraction, however, are qualitatively similar to those obtained on other fractions from the asphalt and on whole asphalts. That the absorption bands studied in the oxidized saturate fraction result from oxidation of the fraction is evidenced by comparing spectra A and B, Figure 3, obtained on the unoxidized and oxidized fractions, respectively.

The effects of the treatment of the oxidized saturate fraction with sodium hydroxide are shown by comparing infrared spectra B and C, Figure 3, which were obtained on samples before and after treatment, respectively. Treatment with sodium hydroxide caused a decrease in the absorption of the fraction in the 1700-to-1800-cm^{-1} region and a corresponding increase in absorption in the 1550-to-1650-cm^{-1} region. The decrease at 1700 to 1800 cm^{-1} and increase at 1550 to 1650 cm^{-1} are attributed to a shift in the C=O stretching frequency resulting from hydrolysis of the dicarboxylic anhydrides and neutralization of the carboxylic acids to form carboxylate ions as illustrated by the reaction equation in Figure 2. The changes in the spectra are best illustrated by spectrum D, Figure 3, which is the difference between spectra B and C; spectrum D was produced with a sodium hydroxide-treated sample in the sample beam and an untreated sample in the reference beam of the spectrophotometer. The infrared absorption band attributed to anhydrides in asphalts is the broad doublet band above the null line with a major peak at about 1725 cm^{-1} and a minor peak or shoulder at about 1765 cm^{-1}. Spectral data on model dicarboxylic anhydrides have been reported (27). The broad band below the null line in spectrum D and centering at 1580 cm^{-1} results from absorption of the C=O of the carboxylate ion, which was derived from the anhydrides and carboxylic acids.

Only a small component of the 1725 cm^{-1} peak in the anhydride doublet band shown in Figure 3 is believed to result from absorption by free carboxylic acids. The free acids are differentiated from the anhydrides by silylation with hexamethyldisilazane and trimethylchorosilane and by reaction with potassium bicarbonate; the acids react with these reagents and the anhydrides do not (cf. Figure 2). Thus the change from spectrum D to spectrum E in Figure 3 results from silylation of the small amount of acids in the fraction, shifting their carbonyl absorption from that of the free acids at about 1730 cm^{-1} to that of the corresponding silyl esters at about 1715 cm^{-1}. This results in an apparent shift of the 1725 cm^{-1} anhydride peak to a slightly lower frequency. The anhydride peak at 1765 cm^{-1} in spectrum E remains virtually unaffected. If however, the sodium hydroxide-treated sample was silylated, and a differential spectra obtained with the unsilylated sodium hydroxide-treated sample in the reference beam, a strong absorption band corresponding to silyl esters was observed at about 1715 cm^{-1} with the bands at 1725 cm^{-1} and 1765 cm^{-1} annihilated. This is evidence that the anhydrides, which were converted to the carboxylate of the corresponding carboxylic acids by sodium hydroxide, were converted to the silyl esters as indicated by the equation in Figure 2.

That both the 1725 cm^{-1} and 1765 cm^{-1} bands produced in asphalt on oxidation are associated with the same functional group was evidenced by changes in band areas of the differential spectra during stepwise partial hydrolysis of separate, but identical, asphalt samples. The ratios of the band areas of the two bands were essentially the same after each partial hydrolysis even though differing amounts of sodium hydroxide were used and differing amounts of hydrolysis occurred.

Another evidence for anhydrides in asphalt is the apparent complete reversibility of the sodium hydroxide reaction by acidification as indicated in Figure 2. When the hydrolyzed saturate fraction in benzene was acidified with stoichiometric amounts of hydrochloric acid followed by evaporation of the solvent, the infrared spectrum of the hydrolyzed-reacidified sample was identical with that of the untreated sample. Although free carboxylic acids would show a similar reversible reaction on acidification, their presence in significantly large amounts was ruled out by the silylation reaction. Hydrolysis of esters would have an effect similar to the hydrolysis of anhydrides on the infrared spectrum; however, esters would not be expected to re-form on acidification under the mild conditions used. Consideration will be given later to the possible presence of esters in oxidized asphalts.

To further substantiate that anhydrides were involved in the reversible reaction cited previously, we attempted to observe the spectra of the free acids during stepwise hydrolysis of a THF solution of the silyl esters of the anhydrides prior to ring closure to form the anhydrides. As the increments of water were added, the silyl ester band at 1715 cm^{-1} decreased and a new band appeared between 1725 and 1730 cm^{-1}, which could result from either anhydrides or acids. A small anhydride shoulder at 1765 cm^{-1} also began to appear. After complete hydrolysis of the silyl esters, however, the shoulder at 1765 cm^{-1} was smaller and the band at 1725 to 1730 cm^{-1} was larger than in the original sample. This indicated that the anhydrides had partially re-formed, leaving a mixture of anhydrides and free-acid precursors of the anhydrides. After the solvent was boiled from the sample, the anhydrides apparently completely re-formed, causing an increase in the 1765 cm^{-1} shoulder and a decrease in the 1725 to 1730 cm^{-1} band to produce a spectrum identical with the original sample. Although some free acid from the anhydride was observed, ring closure to form the anhydrides from the free acids was apparently highly favored. Except in this controlled experiment, the free acids corresponding to the anhydrides have not been observed in the asphalts studied to date.

The final evidence for the existence of anhydrides in oxidized asphalts is the formation of the phenylimide by reaction with aniline. The reaction is illustrated in Figure 2. Changes in the infrared spectra of the oxidized saturate fraction on imide formation are shown in Figure 4. Spectra A and B were obtained before and after imide formation, respectively, and spectrum C is the differential spectrum. Infrared absorption frequencies of the imides obtained for the saturate fraction and also for pure 1,8-naphthalic anhydride are reported in Table 5 together with the frequencies of the original anhydrides. Although the adsorption frequencies for 1,8-naphthalic anhydride and its derivative are higher than those for the anhydrides in the asphalt fraction, the spectra are similar in that both samples showed two major imide bands, the latter being a doublet. The anhydride and imide bands in the asphalt fraction are much broader than those of the pure compounds, as would be expected, because the asphalt anhydrides are undoubltedly a complex mixture of structural types. An additional band also appeared at 1597 cm^{-1} (spectrum C), which is attributed to absorption by the N-phenyl aromatic ring of the phenylimide.

Possible Types of Dicarboxylic Anhydrides in Asphalts. - Because dicarboxylic anhydrides are produced in greater amounts during the oxidation of asphalts than are free carboxylic acids, oxidation of ring-structure molecules to form the anhydrides is indicated. Random oxidation of noncyclic side chains to form carboxylic acids would produce free carboxylic acid groups having little tendency to form anhydrides. Carboxylic acid groups attached to non-ring systems, where molecular configuration is less restricted, would be expected to form anhydrides that are less stable than the asphalt anhydrides and that are not easily re-formed by neutralization of the acid salts.

Several structural variations of aromatic anhydrides will be considered on the assumption that aromatic dicarboxylic anhydrides are the most probable type formed in asphalts. Aromatic dicarboxylic anhydrides can be classified as those having five-, six-, and seven-membered anhydride rings as illustrated in Figure 5. The relative reactivity of two representative anhydrides of each ring size was examined using experimental procedures similar to those used in the study of the anhydrides in asphalt. Results of these studies are reported in Table 6.

As seen in the table, the chemical reactivity of the six-member-ring anhydrides most nearly matched that of the anhydrides produced in asphalt. Molecular models of the six-membered-ring anhydride showed almost no strain, indicating a stable ring structure. The six-member-ring anhydrides did not silylate under the usual silylation conditions, and their sodium salts readily reverted to the anhydride on neutralization with hydrochloric acid and the usual solvent evaporation.

The five- and seven-membered-ring anhydrides appear less favored than the six-membered ring anhydride as the anhydride type in asphalts. Unlike the anhydrides in asphalt, the five-membered-ring anhydrides were partially silylated as a result of ring opening. This is not surprising because of the apparent strain in the five-membered anhydride ring, as indicated by molecular models. The hydrolyzed five-membered-ring anhydrides studied did partially re-form, however, after acidification and solvent removal, as previously described to the asphalt fraction. One of the five-membered-ring anhydrides (benzo[ghi]perylene-1,2-dicarboxylic anhydride) was readily hydrolyzed to the free acid at room temperature in THF solvent containing trace amounts of water, in contrast to the anhydrides in asphalt which re-form from hydrolysis of their silyl esters under similar conditions. Although somewhat resistant to silylation, the seven-membered-ring anhydrides, after hydrolysis with sodium hydroxide, did not easily revert to the anhydride on acidification. This property, characteristic of the anhydrides in asphalts, sets the seven-membered-ring anhydrides apart from the anhydrides in asphalts.

The Ester Controversy and Its Relationship to Anhydrides. - As previously indicated, the existence of esters in oxidized asphalts has been disputed (17, 18, 28). When our investigations of oxidized asphalts showed that most of the sodium hydroxide-reactive material absorbing in the carbonyl region was not free carboxylic acids, the possibility that esters might account for this material was considered (27). The arguments against the presence of significant amounts of esters in oxidized asphalts are summarized as follows: 1) the sodium hydroxide-sensitive band at 1765 cm^{-1} is too high for esters, 2) esters would not be expected to re-form after simple acidification of the sodium-hydroxide-treated sample as observed for the 1725 cm^{-1} and 1765 cm^{-1} bands in asphalts, 3) essentially all of the sodium-hydroxide-sensitive bands can be quantitatively accounted for by free carboxylic acids, dicarboxylic anhydrides, and 2-quinolones, and 4) the 1725 cm^{-1} and 1765 cm^{-1} bands were shown to be interdependent doublet bands (esters do not have doublet bands).

Consideration should be given to reports by Knotnerus (17, 28) that esters were the major sodium-hydroxide-reactive components absorbing in the carbonyl region. He ruled out anhydrides because he did not observe a significant infrared band. Because the anhydride bands in asphalt are broad and are superimposed on the intense ketone band they are usually impossible to observe unless differential spectroscopy and selective chemical reactions are used. Although Knotnerus states that the strong carbonyl absorption at 5.8 μ (about 1720 cm^{-1} and presumed by him to be mainly esters) largely disappears on reaction with sodium hydroxide and a new band representative of the C=O vibration of carboxylic acid salts is formed, examination of his spectra shows that after sodium hydroxide treatment most of the 5.8-μ band still remains.

This is consistent with our work, which indicates that the major oxidation products abosrbing in the carbonyl region are ketones. We believe that the new carboxylate band at 6.3 μ (about 1580 cm^{-1}) in Knotnerus' spectrum can be accounted for largely by the shift or loss in the high-frequency wing of the carbonyl band resulting from anhydride hydrolysis. We believe that what was interpreted as a loss of the 5.8 μ carbonyl band was primarily a loss of the low-frequency wing of the band resulting from a broad baseline depression (19) in the 6.3 μ region caused by treatment with sodium hydroxide.

Campbell and Wright (18) disagreed with the conclusion of Knotnerus that esters were major contributors to the carbonyl region of oxidized asphalts, largely on the basis of spectral data obtained by the addition of model esters to oxidized asphalts. Their work showed no apparent reinforcement of observable bands in the asphalts. They eliminated the possibility of the presence of significant amounts of anhydrides by similar experiments with model anhydride additions. We believe that Campbell and Wright were also unable to observe existing anhydride bands in oxidized asphalts because the broad overlapping bands were not distinguishable on the wing of the intense carbonyl band. These bands are less distinct in neat films as used by Campbell and Wright than in THF solutions used in our work.

Direct Evidence for Ketones in Oxidized Asphalt

This section of the report provides direct evidence that ketones are the major carbonyl oxidation product in asphalt. Data were obtained using the much studied Wilmington (Calif.) asphalt (5, 29-32) and the asphalts used in the Zaca-Wigmore Experimental Road Test (33). A recent publication (34) provides greater detail of the experimental work than is reported here.

In the current study, infrared spectra were obtained on asphalt samples that had been air oxidized in an IGLC column using established procedures (25). These spectra were compared with spectra obtained after selective reactions that were chosen for specificity toward carbonyl group types (aldehydes and ketones) absorbing in the 1695 cm^{-1} region of the infrared. Sodium borohydride was used for reduction experiments because it selectively reduces ketones or aldehydes. Hydroxylamine hydrochloride was used with the thought of preparing oximes of ketones or aldehydes suspected of being present. In order to simplify the discussion, results obtained using these two reagents will be discussed separately.

Sodium Borohydride Reduction. - Three oxidized asphalt samples were reduced using sodium borohydride. The only component of the complex carbonyl band affected by the reduction procedure was the band centering at about 1695 cm^{-1}. The area of this band was decreased by 64 to 83 percent as a result of this treatment. Infrared spectra of reduced asphalts showed a new band at about 3640 cm^{-1}. This band corresponds to the published range for free OH stretching of alcohols that are expected products of reduction of ketones or aldehydes. Data in Table 7 show that decreases in the 1695 cm^{-1} band are roughly proportional to increases in the band at 3640 cm^{-1}. This supports the hypothesis that ketones or aldehydes were reduced to the corresponding alcohols in the manner usually observed for borohydride reduction. The fact that the alcohols appear in roughly the same ratio as the carbonyls disappear suggests that most (if not all) of the alcohol produced is derived from the carbonyl reacted.

Oxime Formation. - Reaction of hydroxylamine hydrochloride with oxidized asphalt is not new. Knotnerus (17) previously used it to estimate carbonyl groups by titrating the hydrochloric acid generated during the reaction. Our work depends on direct infrared spectral evidence of oxime formation in the derivatized asphalt samples. This, it is believed, is an improvement over the titration procedure that might have interference. Spectra were obtained on four oxidized asphalt samples from which oximes had been prepared. Decreases between 60 and 80 percent were observed for the area of the carbonyl band at about 1695 cm^{-1} after oxime preparation. Concurrently, a band at about 3590 cm^{-1} appeared in the infrared spectra of all four samples.

This band is in the published range of values of 3500 to 3650 cm^{-1} for OH stretching frequencies of oximes. This is strong evidence that the majority of functional groups that absorb in the 1695 cm^{-1} region react to form oximes. Additional evidence is provided by data in Table 8. In this table the decrease in area of the 1695 cm^{-1} band is compared with the increase in absorbance for the OH stretching band of oximes formed. That data show an excellent correspondence. Decreases in carbonyl content are accompanied by nearly equivalent increases in oxime content.

Although the C=N group in oximes has an infrared absorption band at about 1650 cm^{-1} to 1685 cm^{-1}, which could interfere with the determination of the loss of the ketone band at 1695 cm^{-1} on oxime formation, the absorption intensity is only about 5 percent of the absorption intensity of ketones; therefore, the effect of the C=N band on the ketone band can be ignored.

Although the afore mentioned studiesdo not differentiate between ketones and aldehydes, the virtual absence of aldehydes as a significant oxidation product in asphalt was concluded based on the absence of a characteristic aldehyde absorption band at about 2820 cm^{-1}. No infrared band in this region in asphalts appears related to the presence of the carbonyl band (a requirement for aldehydes).

Possible Type of Ketones in Oxidized Asphalts. - Literature provides evidence relative to the type of ketones which might be expected to form upon oxidation of asphalts. Information about the ease of oxidation of various hydrocarbon substrates using air (or oxygen) (35) shows that benzylic positions are most readily oxidized, tertiary and secondary alkyl positions are next, and primary alkyl positions are the least susceptible to oxidation. Oxidation of the most reactive sites (benzylic positions) would produce alkyl aryl ketones.

Data (shown in Table 9) support the contention that ketones in oxidized asphalts are of the alkyl aryl type. Ketone carbonyl absorption bands for oxidized asphalts occur at about 1695 cm^{-1}. Model alkyl aryl ketones (acetophenone, 3,4-dihydro-1 (2H)-naphthalenone, valerophenone, and laurophenone) have absorption bands between

1685 and 1692 cm^{-1}. Dialkyl or cycloalkyl ketones absorb at about 1715 cm^{-1}, with the exception of cycloalkyl ketones with rings of five carbons or less which absorb at 1740 to 1775 cm^{-1}. Diaryl ketones and α, β unsaturated ketones absorb at between 1660 and 1670 cm^{-1}.

For comparison purposes, acetophenone oxime was prepared by the method (34) used to prepare oximes of asphalts. The model compound had an OH absorbance at 3593 cm^{-1}, while the asphalt derivatives abosrbed at about 3590 cm^{-1}. Published values for oximes show that the free OH stretching bands for diaryl ketoximes are at about 3580 cm^{-1}; cyclohexanone oxime absorbs at 3570 cm^{-1}, and dialkyl ketoximes absorb at about 3650 cm^{-1}. The alkyl aryl ketones and their oxime derivatives fit the data more closely than any other type of ketone considered.

CATALYSIS OF OXIDATION BY MINERAL AGGREGATE SURFACES AND ASPHALT COMPONENTS

Oxidation of asphalt is generally accepted as a major factor contributing to the hardening and embrittlement of asphalt roads (5, 36-40). This oxidation occurs both in the preparation and laydown of hot-mix pavements (37, 40, 41-44) and from environmental aging while in service (36, 37, 40).

Knotnerus (45) studied the uptake of oxygen by toluene solutions of asphalts and asphalt fractions and found that certain metal salts increased the rate of oxygen uptake. Traxler and Scrivner (46) have suggested a relationship between vanadium content and the hardening rate of asphalt. Research in our Bureau of Mines laboratory on asphalt composition and oxidation has indicated that components are present in asphalt that catalyze its oxidation. Recent studies of asphalt-aggregate interactions using a modification (47) of the inverse gas-liquid chromatography (IGLC) technique (25, 31, 39) suggested that aggregate surfaces also catalyzed the air oxidation of certain asphalt fractions. In the present work, asphalt samples recovered from previous IGLC studies of asphalt-aggregate interactions (26, 47) were analyzed for possible catalytic effects during their oxidation. Briefly, the asphalts and asphalt fractions were coated on particles of aggregates and on inert fluorocarbon and oxidized in an IGLC column. Oxidized samples were recovered from the aggregates. The oxidation products absorbing in the carbonyl region of the infrared spectra (ketones, dicarboxylic anhydrides, 2-quinolone types, and carboxylic acids) were determined using the previously described differential infrared spectrometric technique. The results are discussed as they relate to the catalysis of asphalt oxidation by mineral surfaces and by catalysts inherently present in the asphalts. Additional description of the experimental details can be found elsewhere (48).

The results of two studies are reported. In the first, a Wilmington (Calif.) asphalt (5, 29, 30, 32, 47) was separated by chromatography on alumina (8, 47) into fractions of increasing polarity prior to air oxidation. One major advantage of using fractions was that some fractions were nearly void of the chemical types produced on oxidation, thus making the determination of oxidation products in these fractions more definitive. Another advantage was that the nonpolar fractions were free of compounds containing metals and other possible oxidation catalysts, thus facilitating the investigation of the catalysis of asphalt oxidation.

The second study was a four-by-four matrix in which four FHWA study asphalts (26, 49-51) were oxidized on four different aggregates (26); this study was designed to determine relative amounts of oxidation on inert surfaces.

Oxidation of Wilmington Asphalt and Fractions

Results of the analysis of carbonyl compounds in the Wilmington asphalt and Wilmington fractions are shown in Table 10. Carbonyl functional groups have been recognized as a major oxidation product in asphalts (2-4, 27, 34) and probably contribute significantly to asphalt hardening upon aging. Table 10 shows the concentration of ketones, dicarboxylic anhydridrides, carboxylic acids, and 2-quinolone types in unoxidized samples, in samples oxidized while coated on an inert fluorocarbon (Fluoropak), and in samples oxidized on quartzite. For comparative purposes the weight-percent of the fractions containing the particular functional group was calculated after estimating molecular weights and assuming that no more than one functional group was formed on any molecule during oxidation. Results of these calculations are also reported in Table 10. Although these estimates are approximate, they show that major changes in molecular composition occur in asphalt on oxidation. The level of oxidation shown for the oxidized Wilmington asphalt approximates that which normally occurs during the preparation of a typical hot-plant mix followed by 5 to 10 years of service in a road. The last column in Table 10 shows the ratios of the concentrations of ketones to anhydrides produced upon oxidation.

The results shown in Table 11 were calculated from data in Table 10 to assist in comparing the total carbonyl types formed after oxidation on quartzite with the carbonyls formed after oxidation on Fluoropak. Data in the two tables will be considered together.

The catalytic effect of quartzite on the oxidation of the saturates fraction was pronounced. As shown in Table 11, the amount of carbonyl types formed in the saturates during oxidation on quartzite was 10 times the amount formed on Fluoropak. The saturates, which were 23 percent of the whole asphalt, were almost completely resistant to oxidation on the inert Fluoropak surface (Table 10).

The ratio of ketones to anhydrides produced on oxidation was lower for the saturates than for any other fraction, indicating differences in the ratios of their precursors in this fraction.

The level of oxidation of the aromatic fraction was intermediate between that of the saturates and the polar aromatics and asphaltenes. Significantly greater amounts of oxidation products were formed in the aromatics on Fluoropak than were formed in the saturates on the same surface (Table 10). However, the aromatics, which were 31 percent of the whole asphalt, oxidized 3.6 times as much on quartzite as on Fluoropak (Table 11).

The two polar fractions--polar aromatic and asphaltene--behaved in a somewhat similar manner on oxidation and will be discussed together. As indicated in Table 10 the amounts of oxidation on either quartzite or Fluoropak were similar for the two fractions. The similarity in the amounts of oxidation products formed on either the potentially active or the inert surface indicates that the catalytic activity of the quartzite surface had been greatly reduced. The polar aromatic and asphaltene fractions contain nearly all of the highly polar functional compounds that were initially present in the asphalt. Many of these compounds have been shown to be strongly adsorbed on the quartzite surface (47) and may thus inactivate, either physically or chemically, the catalytic sites on the quartzite thus reducing their ability to promote oxidation. The high level of oxidation in both the polar aromatics and asphaltenes, when compared with the saturates and aromatics, probably results largely because of internal oxidation catalysts present, although the polar aromatics and asphaltenes may inherently be more easily oxidized. The subject of internal oxidation catalysts in asphalt will be discussed later in detail.

The smaller amount of oxidation in the asphaltenes oxidized on quartzite than in the asphaltenes oxidized on Fluoropak probably results from a combination of several factors. The oxidation catalysts present in the asphaltenes may be adsorbed on, and inactivated by, the quartzite surface. Also, small amounts of polar oxidation products may have been irreversibly adsorbed on the quartzite surface and not recoverable for subsequent determination, although this is probably a minor factor. Finally, asphaltene molecules are probably strongly adsorbed on the polar sites of the quartzite surface; in this immobilized state, their ability to undergo oxidation reactions would be reduced.

The catalytic effect on asphalt oxidation of materials naturally present in asphalt is demonstrated by data in Table 11. If the amount of total carbonyl groups formed in each fraction is prorated according to its weight fraction of the whole asphalt, and the pro rata amounts summed for all the fractions, the sum of the fractions on Fluropak was less than for the whole asphalt on Fluoropak; conversely, on quartzite, more carbonyl was formed in the fractions than in whole asphalt. The decrease in total carbonyl compounds formed when the fractions were oxidized separately on the inert Fluoropak surface resulted primarily because of the small amounts of oxidation in the saturate and aromatic fractions. The absence of significant amounts of oxidation products in the saturate fraction when oxidized on Fluoropak indicates that this fraction is relatively stable in the absence of oxidation catalysts. These results strongly suggest that oxidation catalysts are present in the more polar fractions such as the polar aromatics and asphaltenes. This presumption is further supported by data on the polar aromatics (Tables 10 and 11), which show similar amounts of oxidation on both quartzite and Fluoropak. If the quartzite surface had retained significant catalytic activity when coated with polar aromatics, one would expect significantly more oxidation on quartzite than Fluoropak. However, if catalytic sites on the quartzite were inactivated by polar groups from the fraction, then the similar amounts of oxidation products can be explained primarily as the effect of catalytic components present in the polar aromatic fraction. A similar argument holds for the asphaltenes.

Although the saturate fraction was resistant to oxidation when oxidized separately on an inert Fluoropak surface, its susceptibility to catalytic oxidation in the presence of the more polar asphalt fractions was demonstrated by two additional experiments. When whole Wilmington asphalt was oxidized on Fluoropak, nearly half of the saturates were oxidized to polar, oxygen-containing compounds. This behavior is readily explained by the presence of oxidation catalysts in the polar, nonsaturates fraction. Finally, we were able to demonstrate the catalytic effect of the asphaltenes on the oxidation of saturates by oxidizing the saturate fraction containing 1 percent asphaltenes on Fluoropak. The amounts of oxidation products formed in the saturates were much greater than could be accounted for by oxidation of the added asphaltenes.

Oxidation of FHWA Study Asphalts

The Wilmington asphalt fraction study indicated that even though a quartzite aggregate surface may effectively catalyze the oxidation of certain asphalt components, this surface might also be nearly inactivated by components from the more polar asphalt fractions. It was therefore desirable to study the catalytic effect of aggregate surfaces using a series of several different asphalts and aggregates. It was desirable to use the asphalts and aggregates supplied by the FHWA and which we had used in a previous study (26) of asphalt-aggregate interactions by the IGLC technique. Individual asphalt samples that had been oxidized on four different aggregates and on Fluoropak were recovered, and their carbonyl compounds were determined. The concentrations of individual carbonyl compounds were determined on the asphalts from each asphalt-aggregate system and are reported elsewhere (48). In every case more carbonyl compounds were found in the oxidized asphalts recovered from aggregates than in the corresponding oxidized asphalts recovered from the inert Fluoropak. This strongly supports the case for catalytic oxidation of whole asphalts by aggregate surfaces.

To assist in determining the effects of the aggregates on the oxidation of the asphalts, the sum of the ketones and anhydrides formed on oxidation were averaged and compared; results are presented in Tables 12 and 13. In Table 12, the data for all aggregates with each asphalt with each asphalt were averaged and compared with Fluoropak data. This comparison showed that the susceptibility of the asphalts to catalysis of oxidation by the aggregates increases in the order B-2959 < B-3036 < B-3051 < B-3602. This also is evidenced by the ratios showing the average oxidation on aggregates over the oxidation on Fluoropak. The ratios show that from 21 to 39 percent more oxidation occurred in asphalts oxidized on aggregates that on those oxidized on the inert Fluoropak surface.

In Table 13 the averaged data for all asphalts oxidized on each aggregate are presented and compared with the average data for the asphalts oxidized on Fluoropak.

Although the differences among aggregates are small, less oxidation occurred on Riverton limestone and granite P-6 than on quartzite 15 and Hol limestone. In an IGLC study (26) of asphalt-aggregate interactions, using the same aggregates and asphalts, Riverton limestone and granite P-6 interacted more strongly with polar compounds in the asphalts than quartzite 15 and Hol limestone. These results suggest that strong interactions of asphalt components with the aggregate surface reduce the surface catalytic activity in asphalt oxidation.

MOLECULAR ORIENTATION IN THE ASPHALT-AGGREGATE INTERPHASE REGION

Many properties of asphalt roads and the practices of road builders attest to the importance of the interactions between asphalt and mineral aggregate. The mineralogical composition of aggregates appears to be of primary importance to asphalt-aggregate adhesion and to the resistance of the adhesive bond to the stripping action of water. The chemical nature of the surface of the aggregate is sometimes intentionally altered by treatment with lime, metal salts, or other materials. Adhesion promotors, which are believed to affect the asphalt-aggregate interface, are sometimes added to the asphalt to improve the adhesive characteristics of the road mix. The voluminous literature in this area is summarized in a state-of-the-art report by Majidzadeh and Brovold (52).

In addition to the interactions between asphalt and aggregate at the aggregate surface, there is evidence to suggest that the chemical nature of the aggregate has long-range influences that extend deep into the asphalt interface region. Mack (53) suggested that asphalt molecules are aligned on the aggregate surface, causing a similar alignment of molecules within the liquid, which extends for a distance of thousands of molecules. Asphalt technologists know that mineral fillers have profound effects on the properties and performance of asphalt mixes which are not precisely predicted from well recognized properties of the fillers themselves such as density, particle size, etc.

Watanabe and Abe (54) rationalized this unpredictability by assuming that a "solid asphalt" layer exists around the filler particle. Asphalt technologists talk of "slow-setting" or "tender" mixes and the effects of asphalt components such as asphaltenes and of additives on the "setting rate" of road mixes. These phenomena may well have their bases in long-range molecular interactions in the asphalt which are promoted by the aggregate surface (55).

Asphalt-Aggregate Interactions Studied by Microcalorimetry

Description of Method and Materials. - This study examines the phenomena associated with the formation of interfacial bonds rather than the usual approach of examining the fracturing of bonds. Formation of the asphalt-aggregate bond is observed by measuring the energy liberated when aggregate is immersed in asphalt. The heat-of-immersion data suggest that the asphalt-aggregate interactions lead to a multilayer adsorption of asphalt molecules. Because of the small amount of energy released in the adsorption process a sensitive microcalorimeter was constructed for detecting the energy released when aggregate was immersed into asphalt. Construction of the calorimeter and experimental procedures are discussed in detail elsewhere (55, 56).

The asphalts and aggregates studied were those supplied by FHWA and were identical with those used by others (1, 26). The ultimate analyses of the asphalts and the properties of the aggregates are shown in Tables 14 and 15, respectively.

When aggregate is immersed into asphalt a slow exothermic reaction occurs. Immersion curves representative of the exothermic interaction have been reported (55). The flow of energy as measured by the microcalorimeter reaches a maximum in 5 to 15 minutes and then decreases, leveling off to produce a steady energy flow in about three hours. Typically, the immersion data are reported in tabular form as peak height (maximum energy) and tail height (steady-flow energy). In the present work, immersion data were obtained at both 130° and 150° C in a 4 x 4 study of the FHWA asphalts and aggregates. These data are reported in Table 16.

Immersion curves with a high initial peak usually have a high tail height, and curves with low peak heights usually have low tail heights, but exceptions exist. An example where high peak heights are followed by low tail heights is seen in Table 16 for B-3036-granite at 130° C and B-3036-quartzite at 150° C. In contrast, a low initial peak may be followed by a relatively high curve tail height; i.e., the B-2959-quartzite system at 130° C.

Large initial peak heights reflect both the "initial" surface area (Table 15) of the aggregate and strong interactions between the first adsorbed asphalt molecules and the aggregate surface. The surface areas of the aggregates were determined by the BET method using krypton as the adsorbate. Large asphalt molecules probably would not "see" the same surface area that the smaller krypton atoms would "see", particularly if the aggregate surface has appreciable minute pore structure. Even relatively large pore structure would probably be masked by adsorption of several layers of asphalt molecules. Therefore, the surface areas listed in Table 15 are not used in the calculations, but they are useful in comparing the surfaces of aggregates used in the immersion work.

If the peak heights represent the energy released in a monolayer adsorption process, then the tail heights probably represent a multilayer adsorption process. This concept and the possibility of a surface-catalyzed reaction are compared in a later section.

Comparison of Immersion Data with Results of Water-Stripping Tests. - If the immersion energy results from multilayer absorption of asphalt molecules on aggregate surfaces as proposed, then one might expect a relationship between immersion energy and water-stripping resistance of asphalt-aggregate mixes. To look for this relationship a comparison was made of the heats of immersion of the FHWA asphalts and aggregates (Table 16) with water-stripping data (ASTM D-1664, modified by changing temperature to 100° F) on these asphalts and aggregates supplied by FHWA (1).

The stripping resistances for each asphalt on all aggregates were averaged to give an average "asphalt stripping resistance;" likewise stripping resistances for each aggregate using all asphalts were averaged to give an average "aggregate stripping resistance." The stripping resistance is defined as the percent of the aggregate remaining coated after the water-stripping test. Average stripping resistances for the aggregates, listed in increasing order, were 38 (quartzite), 55 (Hol limestone), 90 (Riverton limestone), and 96 (granite). Similarly, average stripping resistances for the asphalts were 53 (B-3602), 67 (B-3036), 77 (B-2959), and 82 (B-3051).

The best correlation between stripping resistance and heat-of-immersion data was found by averaging the tail heights at 130° C for each aggregate with all asphalts and for each asphalt with all aggregates in a similar manner as with the water-stripping data. The average tail heights on aggregates were 0.57 (Hol limestone), 0.58 (quartzite), 0.86 (granite), and 0.89 (Riverton limestone); average tail heights for the asphalts were 0.50 (B-3602), 0.67 (B-3051), 0.79 (B-3036), and 0.92 (B-2959). Upon comparing the stripping resistance and tail height data on the different aggregates it is apparent that asphalts on Riverton limestone and granite showed both greater tail heights and greater stripping resistance; the opposite was true for both Hol limestone and quartzite. The correlation of the averaged data on asphalts was not as good as for the aggregates. If one ignores asphalt B-3051, then tail heights and stripping resistances both increased in the order B-3602, B-3036, and B-2959. Asphalt B-3051, however, had the greatest stripping resistance of all the asphalts although its tail height was next to the lowest.

Work is currently in progress in our laboratory to identify the chemical types strongly adsorbed at the asphalt-aggregate interface. When these data are available an attempt will be made to relate the data to heats of immersion. It is also planned to measure physical property data on asphalt-aggregate mistures for comparison with heats of immersion. Results of this work will appear in the final report.

Mechanisms for Asphalt-Aggregate Interactions. - The heat of immersion of asphalt-aggregate systems might result from either a multilayer adsorption process or from chemical reactions which are promoted by the aggregate surface. Arguments supporting the multilayer adsorption process have been presented (1, 55). The asphalt-aggregate systems in the present work were studied at two temperatures, 130° and 150° C, to investigate the mechanism manifested in the immersion curves. The results of the two-temperature study lend more credence to the multilayer concept than the chemical reaction concept. This is apparent from Table 16 which shows that several of the asphalt-aggregate interactions release more energy at the lower temperature, 130° C, than at 150° C. However, both chemical reactions and adsorption via multilayer adsorption will be considered and compared.

For chemical reactions, two possible rate-controlling steps must be considered: (a) rate of chemical reaction and (b) rate of diffusion to the surface. For chemical reaction at the surface, the rates are a function of the energy of activation; a "rule of thumb" states that a 10 degree increase doubles the rate of reaction. Although only an approximation, this "rule" has been universally applied to rates of catalysis at surfaces. Therefore, for a 20° C increase, a fourfold increase in reaction rate would be reasonable. No such increase was ever observed. Diffusion-controlled chemical reactions at the surface should also show an increase in rate of reaction as temperatures are increased. Diffusion rates are proportional to the diffusion coefficient, which is inversely proportional to viscosity. The viscosities of the four FHWA asphalts decreased by a factor of 4 for a 20° C temperature increase. Thus, although the tail heights of the immersion curves must reflect an interaction between asphalt and aggregate, that interaction is probably not a chemical reaction process that is either diffusion- or reaction-rate controlled. Any interaction between the asphalt and aggregate that proceeds faster at a lower temperature is unlikely to be chemical. Even those systems releasing energy at a faster rate at the higher temperature do not show enough of an increase to lend much support to chemical reaction.

The multilayer adsorption process is therefore a more plausible explanation for the immersion curve tail heights. Asphalt films with molecular orientation beyond a monolayer were first proposed by Mack (53) in his study of ruptures of asphalt films. He proposed that film thicknesses between 0.02 and 0.007 cm were a result of the orientation of surface molecules "in the direction of their polarization and that this causes a similar alignment of the molecules within the liquid which often extends to a distance of thousands of molecules from the surface." A similar mechanism was discussed previously (55).

A Study of the Asphalt-Aggregate Interphase Region by Photomicroscopy

If asphalt and aggregate surfaces interact to produce multilayer adsorption then the multilayer region should be observable. Photomicrographs do indeed indicate a region in the asphalt near the asphalt-aggregate interface that differs from the bulk of the asphalt. The multilayer region will hence be referred to as the interphase region.

Asphaltic materials used in the microscopic study included asphalt B-3036, doped to contain 1 percent Redicote[2] 80-S; a roofing asphalt, supplied by the Asphalt Institute; and an asphalt derived from gilsonite. Substrates used included specimen-grade calcite crystals, the bottom of a disposable aluminum evaporating dish, and a mica disk glued to the bottom of an evaporating dish. Asphalt was poured into a dish to obtain thicknesses of 3 to 5 mm on the substrate. The pans were kept at 130° C or 150° C under nitrogen for 2 weeks after which they were removed from the oven and cooled with Dry Ice. Some samples fractured as a result of the fast cooling. Others were fractured by pressing a sharp pointed nail into the Dry Ice-cooled samples. Cooling with Dry Ice assisted both in fracturing the asphalt specimens to expose the asphalt-substrate interfacial region and in separating the asphalt from the substrate. In the case of the asphalt-calcite specimen the calcite was dissolved in an acid and the separated asphalt was fractured as above.

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

Photomicrographs of the interphase region of the asphalt, i.e. the region adjacent to the substrate, are seen in Figures 6-A, 6-B, 6-C, and 6-D. Figure 6-A shows the interphase region in doped B-3036 asphalt that had been in contact with a calcite surface at 130° C for 12 days; the interphase thickness was about 0.12 mm. A similar interphase region was noted (Figure 6-B) for the roofing asphalt that had been in contact with mica at 150° C for two weeks; the interphase thickness was about 0.18 mm. Although some striations perpendicular to the interphase are shown in the photographs 6-A and 6-B, they are more defined in 6-C and 6-D. The latter two photographs are for the systems B-3036 doped asphalt-mica and gilsonite asphalt-aluminum with both systems having contact times of 14 days at 130° C. Boundary thickness based on the average ends of striations were respectively 0.05 and 0.07 mm.

The striation perpendicular to the interface infer that the proposed large sheet-like conjugated asphalt molecules are adsorbed perpendicular to the substrate.

SUMMARY AND CONCLUSIONS

A method for the qualitative and quantitative determination of ketones, dicarboxylic anhydrides, carboxylic acids, and 2-quinolone types in asphalts was developed. The technique is based on differential infrared spectroscopy combined with base hydrolysis and silylation reactions.

The method was applied to a collection of FHWA penetration-grade asphalts recovered after 11 to 13 years of road service to determine the nature of the oxidation products formed during service and the adsorption of carbonyl types at the asphalt-aggregate interface. Ketones were found to be the major oxidation product in asphalts absorbing in the carbonyl region. Dicarboxylic anhydrides were formed on oxidation in considerably greater amounts than carboxylic acids. 2-Quinolone types were not formed on oxidation. Significant amounts of ketones and detectable amounts of dicarboxylic anhydrides were not found in fresh, unoxidized asphalts. Ketones, dicarboxylic anhydrides, and carboxylic acids were found to be the major components in asphalts that were strongly adsorbed to the surface of road aggregates; they were concentrated in the strongly adsorbed fraction by factors of 1.9, 9.5, and 14, respectively.

Dicarboxylic anhydrides and ketones were independently identified and chemically characterized as significant oxidation products in asphalts. Previously, only indirect evidence had existed for the presence of ketones in asphalts. The presence of significant amounts of anhydrides had been discounted by earlier workers. The chemical reactivity of the anhydrides in asphalts most nearly matched that of six-membered-ring aromatic anhydrides; the chemical reactivity and spectral data on the ketones strongly suggest that they are of the alkyl aromatic type. Clarification was given to the controversy over the presence of esters in oxidized asphalts. It was concluded that significant amounts of esters were not produced on oxidation.

The oxidation of asphalt fractions showed that the saturates and aromatic fractions (about 50 percent of the asphalt), although resistant to oxidation when isolated, were readily air-oxidized when in contact with a quartzite surface or in the presence of the polar aromatic or asphaltene fractions. The polar aromatic and asphaltene fractions were shown to contain components that catalyzed the oxidation of the saturates and aromatics and probably the other fractions of asphalt. Components in asphalt, probably the polar nitrogen- and oxygen-containing compounds, inhibited the catalytic effect of the quartzite surface on asphalt oxidation. Using four different asphalts and aggregates in a four-by-four study, the catalytic effect of aggregate surfaces on the oxidation of whole asphalts was demonstrated. The aggregate that had shown the least interaction with components in the asphalts appeared to exhibit the greatest catalytic effect on asphalt oxidation (i.e., quartzite). The converse was also true (i.e., granite). This may result from inactivation of the catalytic sites on the aggregate surface by adsorption of components from the asphalts. Although aggregate surfaces appear to be potent catalysts for asphalt oxidation, the catalytic effect appears to be greatly reduced by components in the asphalt; as a consequence, it is believed that a large portion of the oxidation in asphalt-aggregate mixes results from catalysis by components naturally present in asphalt.

Heat-of-immersion data indicate that asphalt molecules are adsorbed on aggregate surfaces at hot-mix processing temperatures via a multilayer adsorption mechanism. The adsorption process is slow, continuing for hours or even days at 150° C. The slow rate undoubtedly results from the extreme molecular complexity and high viscosity asphalt. Heats of immersion vary from one asphalt-aggregate system to another. Based on the limited data from the systems studied, a correlation was apparent between heats of immersion and water stripping resistance of asphalt-aggregate mixes as measured in the laboratory. This might be expected if heats of immersion reflect a multilayer adsorption process.

Molecular orientation in the bulk of the asphalt that was promoted by and eminated from a mineral surface was observed using photomicroscopic technique. The molecular orientation was observed as striations on the fracture surfaces of asphalts which were aged while in contact with the mineral.

POSSIBLE SIGNIFICANCE TO ASPHALT PAVING TECHNOLOGY

One might speculate on the significance of the reported work to asphalt paving technology. The chemical identification work showed that products of oxidation in asphalt interact with the aggregate surfaces. Microcalorimetry and previous IGLC studies (26) showed that different aggregate types have quite different responses to these oxidation products. Because considerable oxidation of asphalt occurs in a hot-mix plant and during laying of a road, the amounts and nature of the oxidation products adsorbed on the aggregate surfaces must be important to adhesion and water-stripping resistance. Because these oxidation products and other interacting species must migrate to the aggregate surface, the viscosity of the asphalt at elevated temperatures may be quite important. Significant molecular migration is unlikely after the asphalt has cooled to ambient temperatures, except over long periods of time.

Furthermore, multilayer adsorption to produce immobilized layers in the asphalt-aggregate interphase region appears to take place very slowly--even at 130° to 150°C (near plant-mix temperatures). A "solid" layer of asphalt on the aggregate surface might be of considerable benefit in preventing deterioration of the mix by water. Thus, the potential improvement of stripping resistance by hot storage prior to lay-down should be investigated.

Any immobilization of asphalt in the asphalt-aggregate interphase region after the road has been compacted should increase the bonding strength or friction at the points of contact between aggregate particles; this would be reflected in the physical properties of the asphalt concrete. This reasoning suggests that the cooling rate of a freshly laid road mix may be important. The buildup of an immobilized asphalt layer may thus be related to such phenomena as "setting rate" and "tender mixes."

The oxidation products, because of their polar nature and tendency to associate, should also play a significant role in the determination of final bulk properties (viscosity, temperature susceptibility, brittleness, etc.) of the asphalt in the road mix. It is believed that hardening of the asphalt in service, both permanent hardening and so-called reversible "steric" hardening, result primarily from the oxygen-containing oxidation products produced during processing and oxidative aging in the road.

Finally, the apparent catalytic affect of both components in asphalt and mineral surfaces on the oxidation of asphalt should have great practical significance. Although the surface area of large aggregate particles may not be large enough to make a major contribution to asphalt hardening, the large surface area of small aggregate, fillers, and dust may significantly affect the age hardening rate. This should be studied, particularly with the advent of the drum dryer which might cause more retention of fines and dust in the mix. The future identification of the internal catalysts in asphalt could eventually lead to their inactivation. Should this be possible, it is conceivable that the hardening rates of asphalts in service could be greatly reduced. Many asphalts which now have marginal performance might be upgraded to highly durable asphalts, thus not only producing considerable savings in construction and maintenance costs, but also conserving asphalt whichin the current energy situation may eventually be in short supply.

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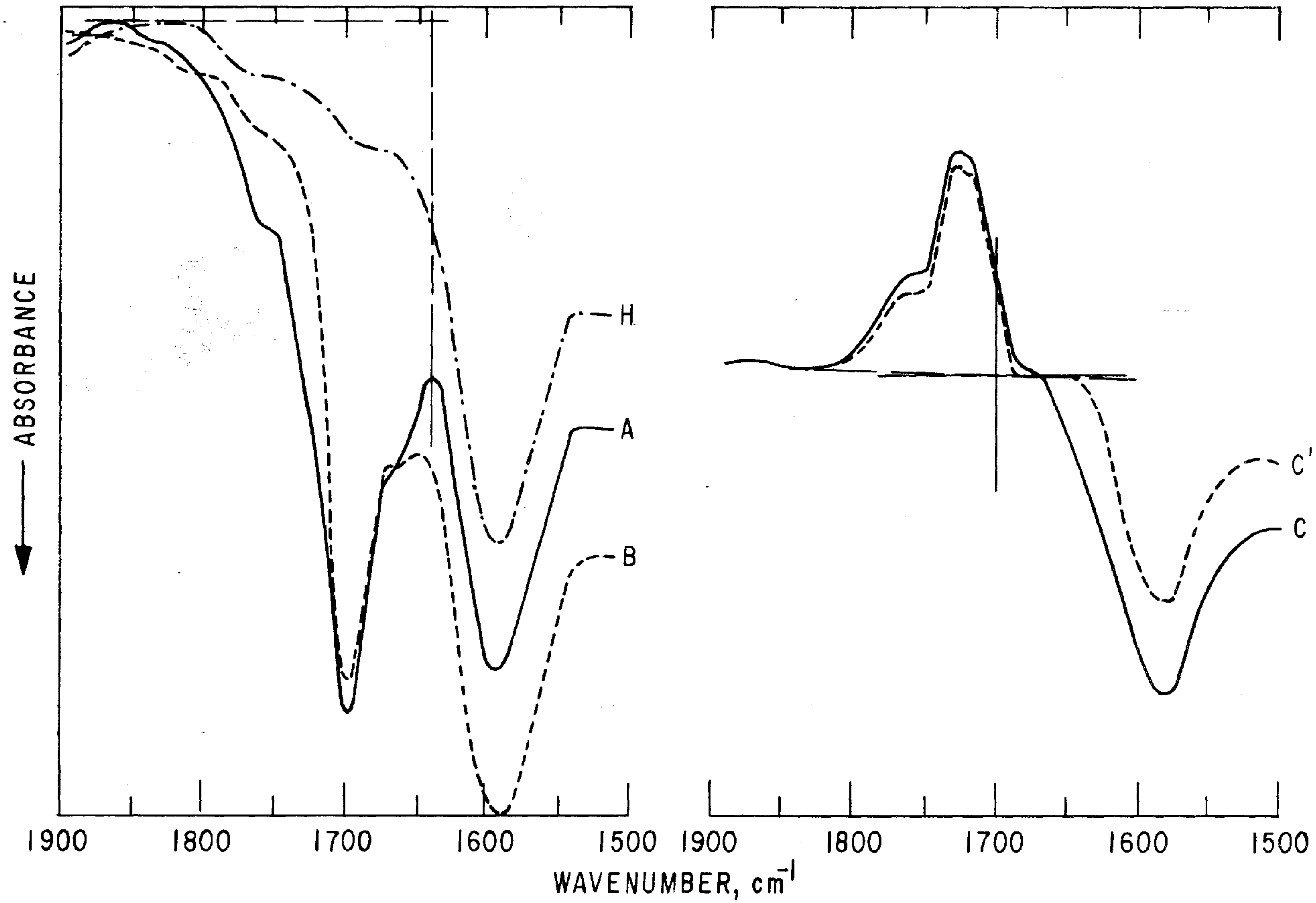


FIGURE 1. - Examples of Infrared Spectra Used in Analysis of Carbonyl Region

(H - unoxidized-untreated; A - untreated; B - NaOH-treated; c' - differential spectra of NaOH-treated vs untreated using a deficiency of NaOH; C - differential spectra of B vs A. All spectra obtained using road-oxidized asphalt 30, except spectra H was obtained using unoxidized asphalt 30.

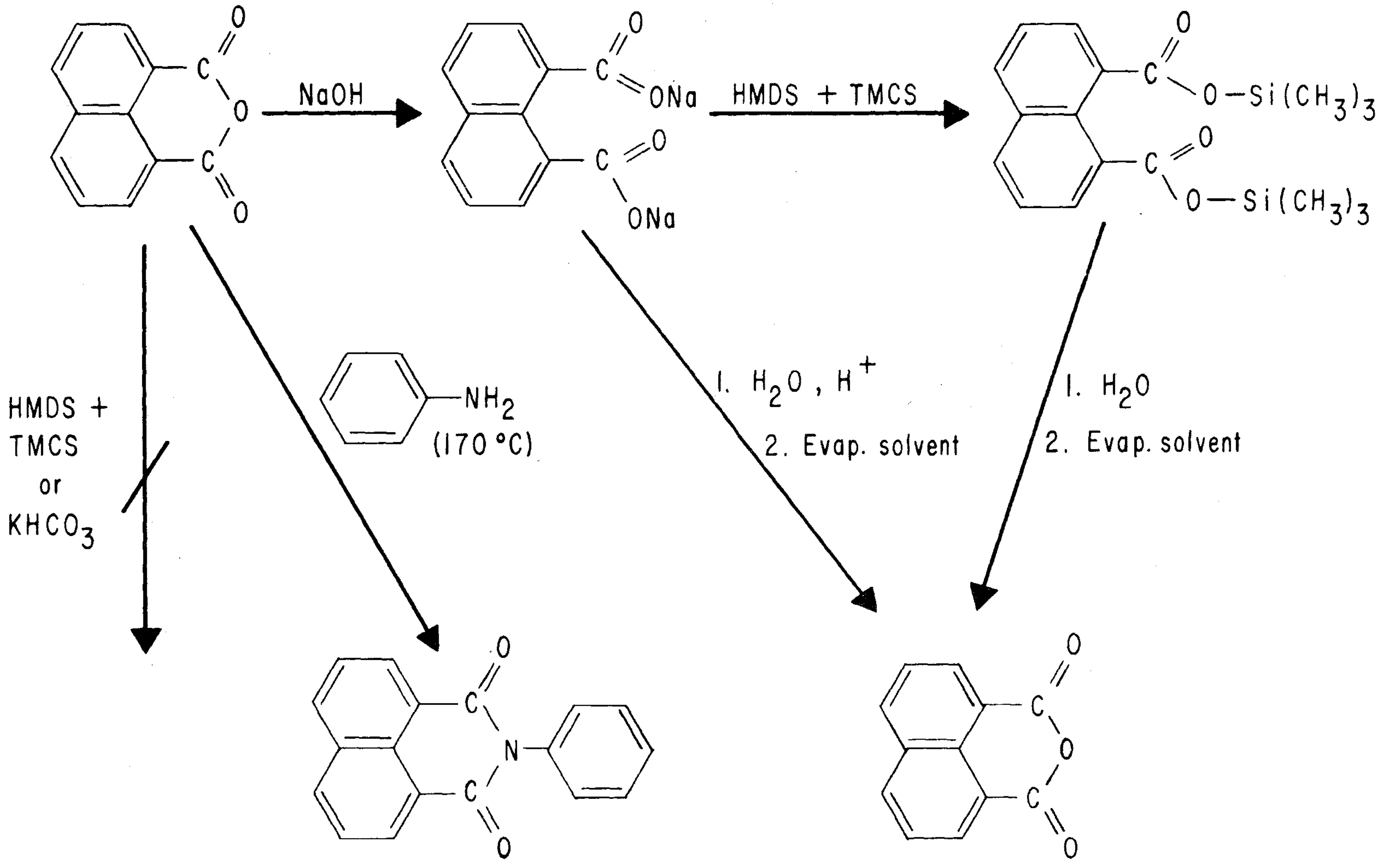


FIGURE 2. - Typical Reactivity of Dicarboxylic Anhydrides
(1,8-naphthalic anhydride used for illustration only)

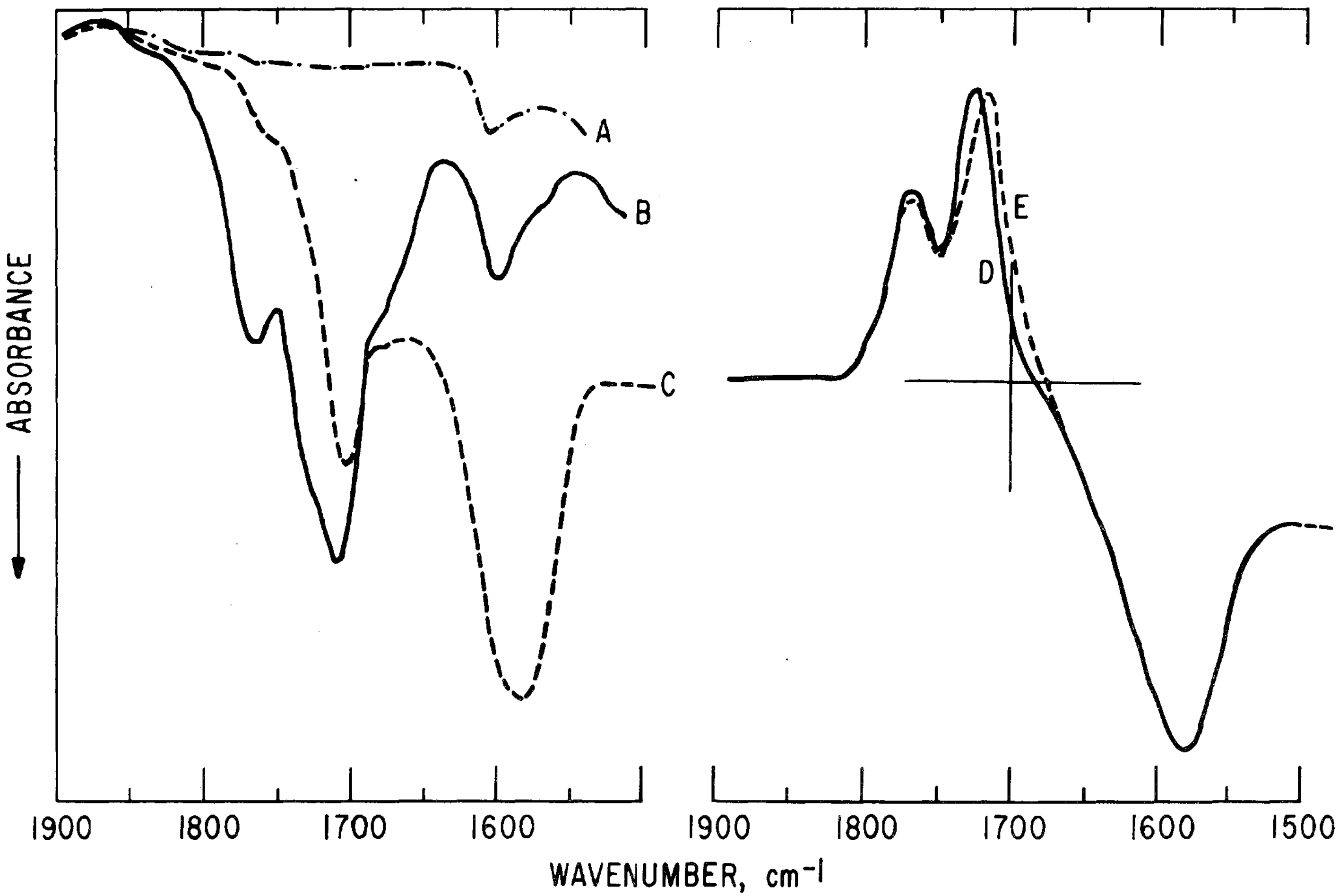


FIGURE 3. - Infrared Spectra Showing Effects of Sodium Hydroxide Treatment and Silylation of Oxidized Wilmington Saturates Fraction

(A - unoxidized; B - oxidized; C - NaOH-treated, oxidized; D - differential spectrum of C vs B; E - differential spectrum of NaOH-treated, oxidized vs silylated, oxidized).

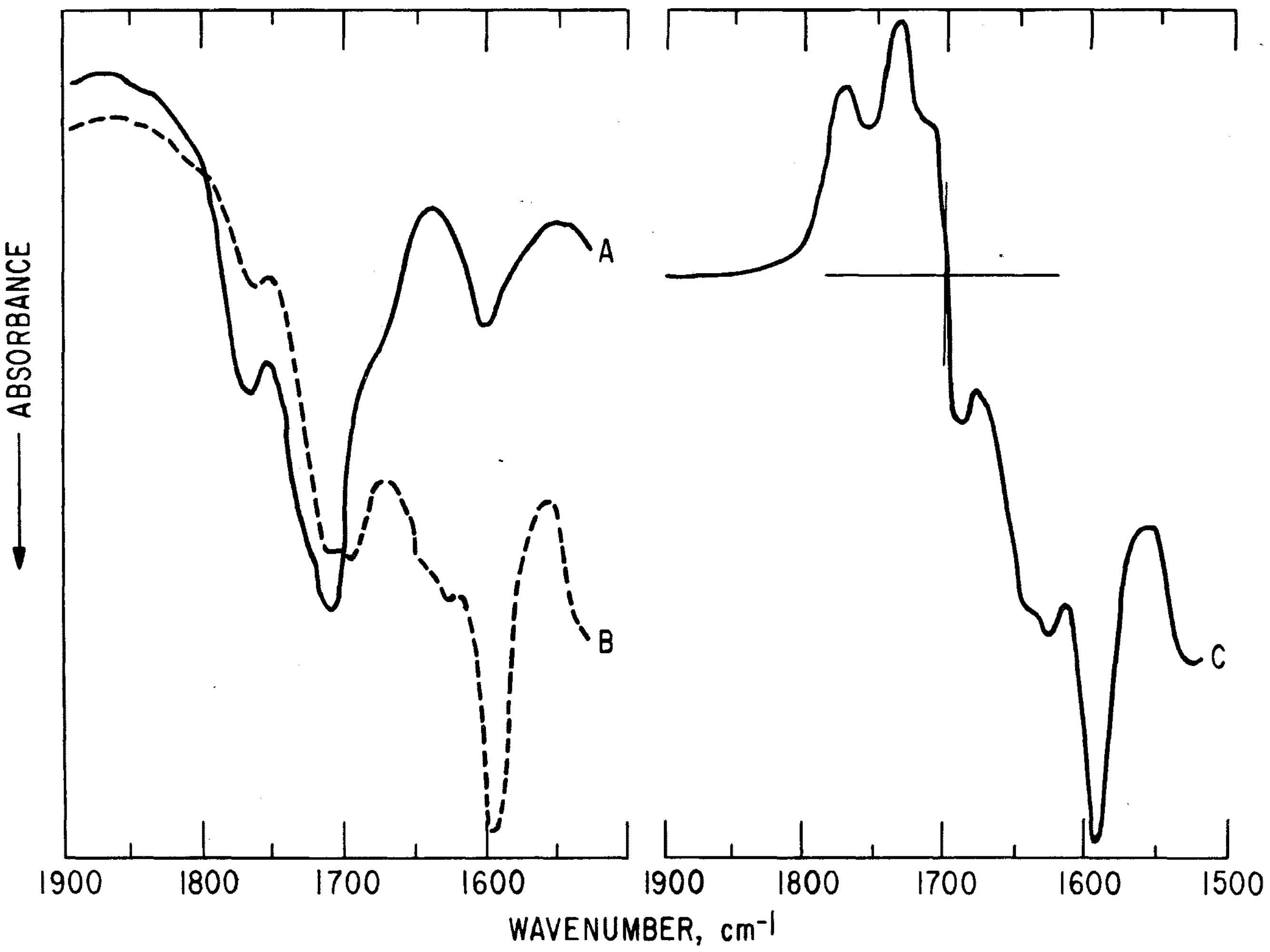
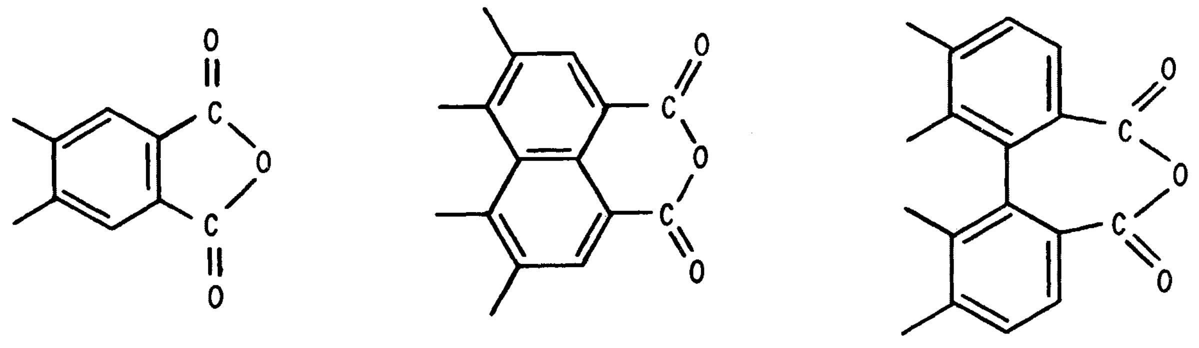


FIGURE 4. - Infrared Spectra Showing Phenylimide Formation in Oxidized Wilmington Saturates Fraction (A - untreated; B - after reaction with aniline; C - differential spectrum of B vs A).



5-membered ring

6-membered ring

7-membered ring

FIGURE 5. - Anhydride Types Considered as Possible Types Formed in Asphalt on Oxidation

49

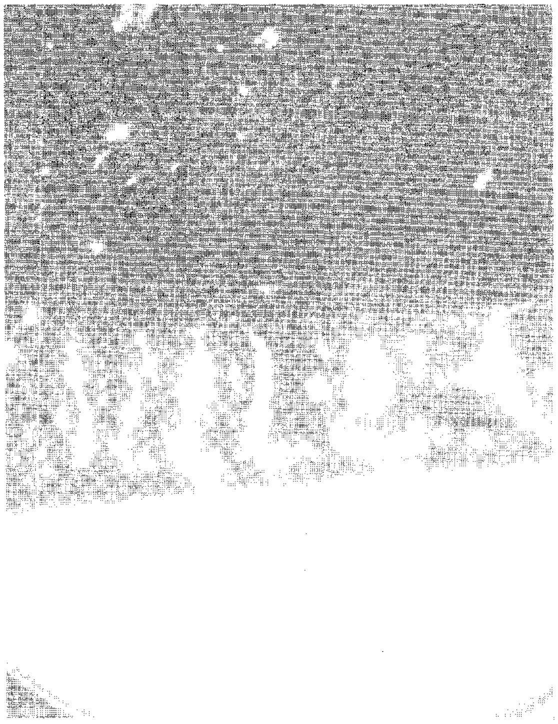


FIGURE 6A. - Interphase region of the system $CaCO_3$-B-3036 doped with an antistripping agent

FIGURE 6B. - Interphase region of the system mica-roofing asphalt

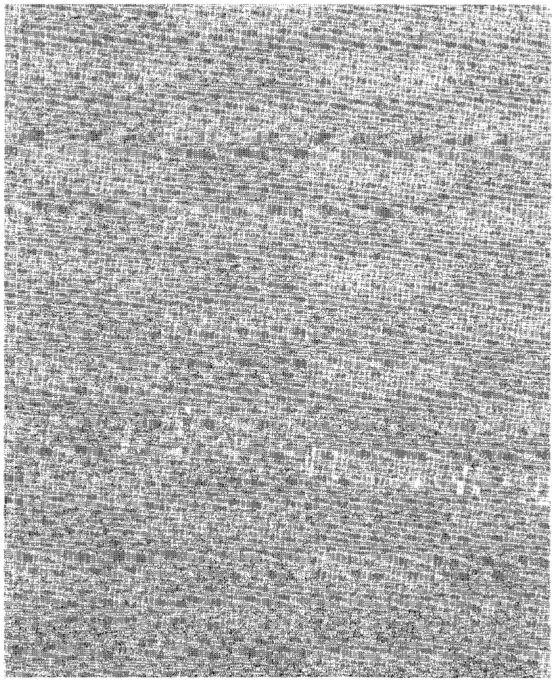


FIGURE 6C. - Interphase region of the system mica-B-3036 dopes with an antistripping agent

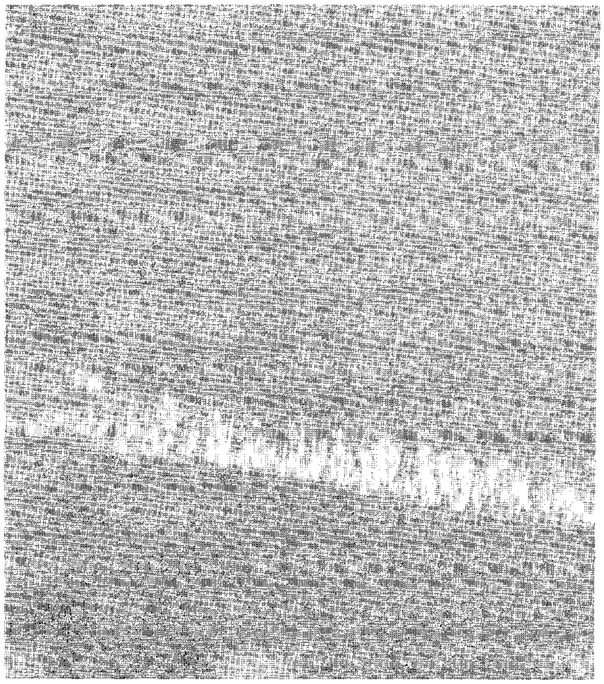


FIGURE 6D. - Interphase region of the system aluminum pan-gilsonite asphalt.

TABLE 1. - Effects of various treatments on carbonyl absorption frequencies in asphalts

	Approximate frequencies of band maxima, cm^{-1}			
Reagent treatment	Carboxylic acids	Dicarboxylic Anhydrides	2-Quinolone types	Ketones
Untreated	1730	1725, 1765	1668	1695
NaOH	1580[a]	1580[a]	1668[b]	1695
Silylation	1715[c]	1725, 1765	band annihilated	1695
NaOH + silylation	1715[c]	1715[c]	band annihilated	1695
$KHCO_3$	1580[a]	1725, 1765	1668	1695

[a] Carboxylate ion

[b] Sometimes 2-quinolone types react causing partial loss of band

[c] Silyl ester

TABLE 2.- Values of apparent integrated absorption intensity (B) used to estimate compound-type concentrations in asphalts

Functional type	B, $l \cdot mol^{-1} \cdot cm^{-2} \times 10^{-4}$
Carboxylic acids	1.2
Dicarboxylic anhydrides	3.1
Ketones	0.7
2-Quinolones	3.2

TABLE 3. - Concentrations of ketones, dicarboxylic anhydrides, and carboxylic acids in asphalts recovered from 11-13-year-old FHWA study road cores and amounts of strongly adsorbed asphalt

	Concentration, mol · l^{-1} x 10^2													
	Non-acid carbonyls[b] as ketones				Carboxlic acid types								Strongly adsorbed asphalt, wt. percent of total[g]
					Dicarboxylic Anhydrides				Carboxylic Acids				
Asphalt[a]	Or[c]	B[d]	BA[e]	CO[f]	Or	B	BA	CO	Or	B	BA	CO	
19	0	51.9	52.5	73.5	0	1.6	1.8	2.5	1.0	2.1	2.5	1.6	2.0
25	0	50.8	52.5	70.8	0	1.8	2.2	2.6	1.6	0.9	1.6	1.9	3.9
30	0	63.3	64.2	60.0	0	2.9	3.8	2.8	0	0.9	1.6	0.7	3.5
61	0	45.3	44.1	65.4	0	0.8	2.0	2.8	0	0.4	0.7	0.4	1.4
67	0	30.9	31.5	41.4	0	0.6	1.0	1.4	0.4	0.4	0.5	0.5	2.3
71	0	49.8	51.0	73.0	0	1.8	2.2	2.7	0	0.2	0.4	0.5	3.7
72	0	64.5	67.5	78.3	0	2.5	2.9	3.5	0	0.4	0.7	0.7	3.4
73	0	33.3	35.3	47.4	0	0.7	1.1	1.5	0.4	0.2	0.4	0.7	3.0
74	0	40.5	42.6	68.7	0	1.2	1.7	2.9	0.5	0.2	0.7	1.2	4.3
166	0	21.3	22.5	----	0	0.8	0.9	---	0.7	0.5	1.0	---	1.2
Average	0	46.16	46.37	64.3	0	1.47	1.96	2.5	0.8	0.62	1.01	0.9	2.87

(a) Sample numbers correspond to FHWA numbers in references 20 and 21.

(b) Background absorption of about 6.4 $\int A_\nu d\nu$ units in unoxidized asphalts not attributable to carboxylic acids and 2-quinolones was not included in analyses.

(c) Original asphalt.

(d) Asphalt recovered from road cores by extraction with benzene.

(e) Asphalt recovered from road cores by extraction with benzene-95 percent ethanol (4:1, v/v).

(f) Asphalt oxidized in IGLC column for 24 hr at 130° C (method, ref. 25).

(g) Calculated from differences between total amounts desorbed with benzene and with benzene-alcohol.

TABLE 4. - Calculated data on the ketones, dicarboxylic anhydrides, and the carboxylic acids strongly adsorbed from asphalts by the aggregates in 11-13-year-old FHWA study road cores

Asphalt no.	Strongly adsorbed[a] functional type, percent of total			Estimated concentration factor[b] of strongly adsorbed material			Strongly adsorbed, percent[b] of total adsorbed			Sum of strongly adsorbed ketones, anhydrides, and acids; percent[c] of total strongly adsorbed asphalt
	Ketones	Anhydrides	Acids	Ketones	Anhydrides	Acids	Ketones	Anhydrides	Acids	
19	3.12	12.9	17.7	1.56	6.45	8.85	57.5	8.1	6.5	72
25	7.0	21.3	46.0	1.79	5.47	11.8	66.2	8.4	13.2	88
30	4.86	26.3	45.7	1.39	7.52	13.1	62.3	20.0	14.6	97
61	-1.28	60.5	43.7	-0.92	43.1	31.2	-28.6	60.5	15.3	47
67	4.17	41.4	21.8	1.81	18.0	9.5	40.0	12.6	33.3	86
71	5.96	21.2	51.9	1.61	5.73	14.0	57.3	8.8	3.9	70
72	7.7	16.7	44.8	2.26	4.91	13.2	107.0	10.0	6.5	123
73	8.5	38.5	51.5	2.83	12.8	17.2	70.0	9.8	4.8	85
74	9.03	32.4	72.6	2.10	7.55	16.9	62.5	9.0	8.3	80
166	6.47	12.2	50.6	5.38	10.1	42.2	85.0	6.4	29.5	121
Average[d]	5.40	27.1	40.5	1.88	9.46	14.1	61.0	13.0	9.9	84

[a] Not desorbed with benzene but desorbed with a 4:1 mixture of benzene:95 percent ethanol.

[b] Percent of functional type in strongly adsorbed asphalt divided by percent of total strongly adsorbed asphalt (cf. Table 3).

[c] Calculated assuming monofunctional molecules and a molecular weight of 700.

[d] Calculations based on averages of concentrations (cf. Table 3).

TABLE 5. - Carbonyl absorption frequencies of selected dicarboxylic anhydrides and their phenylimide derivatives

Anhydride type	Frequency, cm^{-1}	
	Anhydride	Phenylimide
1,8-Naphthalic anhydride	1782, 1747 (sharp)	1712, 1670-1680 (latter a doublet)
Wilmington saturates fraction oxidized on quartzite	1765, 1725 (broad)	1690, 1630-1650 (latter a doublet)

TABLE 6. - Relative reactivity of anhydride ring in oxidized asphalts and model compounds

Anhydride	Ring size	Silylates	Re-forms [(a)] on acidification
3,3',4,4'-Benzophenonetetracarboxylic anhydride	5	partial	partial (20%)
Benzo[ghi]perylene-1,2-dicarboxylic anhydride	5	partial (hydrolyzed easily in THF)	most
1,8-Naphthalic anhydride	6	no	yes
3,4,9,10-Perylenetetracarboxylic anhydride	6	no	yes
Benzo[ghi]perylene-7,8-dicarboxylic anhydride	7	almost none	no
Diphenic anhydride	7	small amount	no
Asphalt anhydrides	?	no	yes

(a) Neutralization of sodium salts with slight excess of dilute HCl followed by removal of water by azeotroping with benzene.

TABLE 7. - Relationship between decrease in the ketone band and increase in the alcohol band upon sodium borohydride reduction of oxidized asphalts

Asphalt sample	A Decrease in the 1695 cm^{-1} (ketone) band, area units[a]	B Increase in the 3640 cm^{-1} (alcohol) band, absorbance x 10^3[a]	Ratio of A to B
F	192	24	8.0
Wilmington	219	30	7.3
E	254	35	7.3

---

[a] Decrease in area of the ketone band is compared with increase in absorbance of the alcohol band because the latter band is narrow, thus causing difficulty in measuring the area reproducibly.

TABLE 8. - Relationship between decrease in the ketone band and increase in the OH band upon oxime formation of oxidized asphalts

Asphalt sample	A Decrease in the 1695 cm^{-1} (ketone) band, area units[a]	B Increase in the 3590 cm^{-1} (OH) band absorbance x 10^3[a]	Ratio of A to B
J	69	26	2.7
D	74	30	2.5
A	178	70	2.5
Wilmington	273	100	2.7

---

[a] Decrease in area of the ketone band is compared with increase in absorbance of the alcohol band because the latter band is narrow, thus causing difficulty in measuring the area reproducibly.

TABLE 9. - Infrared spectral data in the carbonyl region for selected ketones

Sample	Solvent	Frequency cm^{-1}
Ketones in oxidized asphalts	THF	1695-1700
	CCl_4	1695-1700
Acetophenone	THF	1690
	CCl_4	1692
3,4-Dihydro-1(2H)-naphthalenone	THF	1688
	CCl_4	1689
Laurophenone	THF	1686
	CCl_4	1688
Valerophenone	THF	1690
	CCl_4	1692
Cyclohexanone	THF	1710
	CCl_4	1708
Benzophenone	THF	1662

TABLE 10. - Analysis of carbonyl compounds in Wilmington asphalt and asphalt fractions

Sample	Percent of total asphalt	Treatment	Concentration, mol · l^{-1}				Calculated Wt. percent of fraction[(a)]				Ratio: ketones/ anhydrides
			Ketones	Dicarboxylic anhydrides	Carboxylic acids	2-Quinolone types	Ketones	Dicarboxylic anhydrides	Carboxylic acids	2-Quinolone types	
Saturates	23	Unoxidized	0	0	0	0	0	0	0	0	---
		Ox. on Fluoropak	0.045	0.0095	trace	0	2.1	0.4	trace	0	4.7
		Ox. on quartzite	0.46	0.062	0	0	21.4	2.9	0	0	7.4
Aromatics	31	Unoxidized	trace	0	0	0	trace	0	0	0	
		Ox. on Fluoropak	0.32	0.017	---	0	16.0	0.8	---	0	19.7
		Ox. on quartzite	1.09	0.072	trace	0	54.5	3.6	trace	0	15.1
Polar aromatics	33[(c)]	Unoxidized	---	0	0[(b)]	---	---	0	0	---	---
		Ox. on Fluoropak	1.48	0.088	---	0.058	85.0	5.1	---	3.3	16.6
		Ox. on quartzite	1.55	0.092	0	0.066	89.2	5.3	0	3.8	16.8
Asphaltenes	13	Unoxidized	---	0	0.061	0.039	---	0	6.1	3.9	---
		Ox. on Fluoropak	1.82	0.080	0.026[(d)]	0.053[(e)]	182	8.0	2.6	5.3	22.8
		Ox. on quartzite	1.63	0.064	0.023[(d)]	0.048[(e)]	163	6.4	2.3	4.8	25.4
Whole Wilmington asphalt	100	Unoxidized	---	---	0.026	0.017	---	---	1.6	1.0	---
		Ox. on Fluoropak	1.02	0.0515	0.033	0.018	61.3	3.0	2.0	1.1	20.4
		Ox. on quartzite	1.11	0.0563	0.038	0.018	66.7	3.3	2.3	1.1	20.2

(a) Calculated assuming a density of 1, one functional group per molecule, a molecular weight for saturates = 475, aromatics = 500, polar aromatics = 575, asphaltenes = 1000, whole Wilmington asphalt = 600.

(b) Some naturally occurring acids lost to column during separation on alumina.

(c) Increased by 8 percent to account for 8 percent loss during chromatographic separation on alumina.

(d) Difference in this value and value for unoxidized sample probably due to association in oxidized sample.

(e) These values probably high because band is increased by association of 2-quinolone types with carboxylic acids (cf. note d).

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TABLE 11. - Comparison of carbonyl compounds formed in Wilmington asphalt and Wilmington fractions after oxidation on quartzite and Fluoropak 80

	Wt. Fraction of Total Asphalt	Prorato amount[(a)] of carbonyls formed on oxidation, mol · l^{-1}		Ratio of Total Carbonyls: Quartzite/ Fluoropak 80
		On Fluoropak 80	On Quartzite	
Saturates	0.23	0.012	0.12	10
Aromatics	.31	.10	.36	3.6
Polar aromatics	.33(b)	.52	.54	1.04
Asphaltenes	.13	.25	.22	.88
Sum of fractions	1.00	.88	1.24	1.41
Whole asphalt	1.00	1.07	1.16	1.08

(a) Sum of ketones, acids, and anhydrides in fraction, times weight fraction of total asphalt

(b) Corrected by addition of a factor of 0.08 to adjust for material lost to chromatographic column during preparation of fractions.

TABLE 12. - Ketones and Anhydrides formed in oxidized asphalts--averaged data for all aggregates with each asphalt

Asphalt No.	Sum of ketones and anhydrides		Ratio of average on aggregates to Fluoropak 80
	On Fluoropak 80, mol · l^{-1} x 10^3	Average for all aggregates mol · l^{-1} x 10^3	
B-2959	718	868	1.21
B-3036	667	832	1.25
B-3051	801	1043	1.30
B-3602	940	1306	1.39

TABLE 13. - Ketones and anhydrides formed in oxidized asphalts--averaged data for all asphalts with each aggregate

Aggregate	Sum of ketones and anhydrides	
	Average on all asphalts mol · $l^{-1} \times 10^3$	Ratio of average on aggregates to average on Fluoropak 80
Fluoropak 80	781	1.00
Riverton limestone	971	1.24
Granite P-6	984	1.26
Hol limestone	1038	1.33
Quartzite 15	1057	1.35

TABLE 14. - Analyses of FHWA study asphalts

Asphalt	Composition, wt. percent				
	C	H	N	S	Ash
B-3602	86.60	10.44	1.015	1.052	.707
B-3051	82.64	10.13	0.740	5.675	.249
B-2959	83.40	9.95	0.321	5.728	.036
B-3036	85.23	10.06	0.253	3.521	.021

TABLE 15. - Surface areas and mineralogical characteristics of FHWA study aggregates

Aggregate	Surface area m^2/g	Characteristics
Granite	0.561	Mixture biotite, hornblende, albite, quartz
Quartzite	0.515	Tan colored, principally SiO_2
"Hol" limestone	0.104	Coarse white material, principally $CaCO_3$
Riverton limestone	1.09	Grey mixture of $CaCO_3$ and $CaCO_3 \cdot MgCO_3$
Fluoropak 80	1.70	Inert fluorocarbon

TABLE 16. - Heat-of-immersion data on FHWA study asphalts and aggregates

Asphalt	Aggregate	Temp °C	Peak height μ-cal/g-min x 10^{-3}	Tail height (at 3 hrs) μ-cal/g-min x 10^{-3}
B-3602	Quartzite	130	5.10 ± .38	.80 ± .13
		150	8.82 ± .38	1.89 ± .26
	Riverton limestone	130	7.62 ± .66	.54 ± .24
		150	13.74 ± .78	1.98 ± .28
	"Hol" limestone	130	4.38 ± .24	0.00
		150	7.98 ± .84	.60 ± .22
	Granite	130	7.5 ± 1.6	.64 ± .11
		150	9.66 ± .88	1.36 ± .12
B-3051	Quartzite	130	3.36 ± .30	.42 ± .10
		150	2.58 ± .30	.18 ± .12
	Riverton limestone	130	6.84 ± .42	1.02 ± .12
		150	8.16 ± .12	.37 ± .03
	"Hol" limestone	130	2.04 ± .18	.48 ± 0.0
		150	2.40 ± .18	.24 ± .16
	Granite	130	6.57 ± 1.11	.87 ± .19
		150	8.58 ± 1.32	.52 ± .15
B-2959	Quartzite	130	2.34 ± .42	.93 ± .27
		150	4.02 ± .42	.66 ± .12
	Riverton limestone	130	7.32 ± 1.32	.86 ± .20
		150	9.90 ± .90	.24 ± .12
	"Hol" limestone	130	1.87 ± .11	1.11 ± .15
		150	4.08 ± .24	1.26 ± .29
	Granite	130	4.42 ± .44	.78 ± .18
		150	5.91 ± .21	1.34 ± .06
B-3036	Quartzite	130	3.24 ± .78	.16 ± .07
		150	3.90 ± 0.0	1.29 ± .15
	Riverton limestone	130	10.20 ± .60	1.14 ± .06
		150	10.20 ± .72	.63 ± .12
	"Hol" limestone	130	2.59 ± .15	.70 ± .19
		150	2.72 ± .19	.80 ± .11
	Granite	130	8.44 ± .25	1.15 ± .12
		150	8.40 ± .96	.66 ± .06

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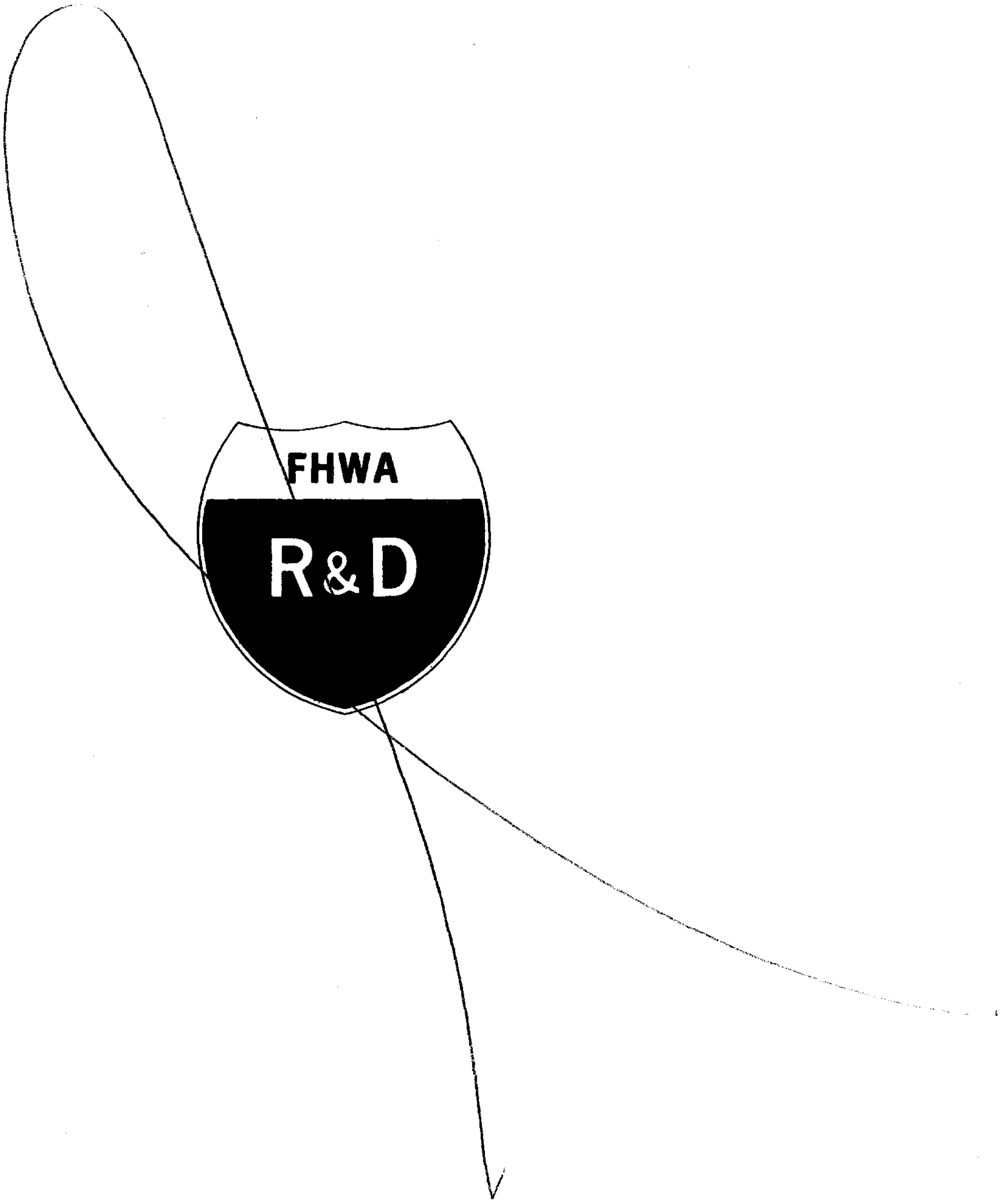
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