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IDENTIFICATION OF CHEMICAL TYPES IN ASPHALTS STRONGLY ADSORBED AT THE ASPHALT-AGGREGATE INTERFACE AND THEIR RELATIVE DISPLACEMENT BY WATER

By

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ABSTRACT

The asphaltic components strongly adsorbed on a number of asphalt-aggregate interfaces were isolated and characterized both quantitatively and qualitatively, and their relative displacement from an aggregate surface by a moisture-damage test was determined. Oxygen- and nitrogen-containing compounds were concentrated on the aggregate surfaces. Of the five different oxygen-containing functional types examined, carboxylic acids were the compound type most strongly adsorbed by the aggregates and were also the compound type most readily displaced from the aggregates by water. Dicarboxylic anhydrides were also selectively displaced by water; sulfoxides showed either selective retention or displacement with different asphalt-aggregate systems. Nitrogen compounds and ketones were the compound types least affected by the moisture-damage test. Model compound studies were used to support the relationships determined between asphalt functional groups and their affinity for various aggregate surfaces.

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INTRODUCTION

Moisture damage to bituminous-aggregate paving mixtures is well known. These adverse effects cause premature road failure and waste of valuable resources. Moisture damage of asphalt pavements, generally believed to involve the rupturing of the adhesive bond at the asphalt-aggregate interface, has been the subject of numerous investigations (1-7).

Petersen and co-workers in an earlier study (8, 9) characterized several asphaltic components strongly adsorbed on aggregate surfaces by comparing asphalts from ten benzene-extracted road cores with the corresponding asphalts from benzene-alcohol-extracted road cores. Differences in composition between the two extracts were attributed to the strongly adsorbed materials that were extracted by benzene-alcohol but not by benzene. This indirect analysis of the strongly adsorbed materials was not sufficiently precise to show the differences between individual asphalt-aggregate systems. Furthermore, subsequent work in our laboratory showed that benzene-alcohol was not as efficient as pyridine in removing the strongly adsorbed materials from the aggregate surfaces and that extractions involving alcohol may form artifacts. In the present study, analytical measurements were made directly on the strongly adsorbed fractions after they were desorbed with pyridine.

The purpose of this investigation was to (1) isolate the components strongly adsorbed at the asphalt-aggregate interface, (2) characterize both quantitatively and qualitatively the chemical functional types strongly adsorbed by aggregates, (3) support this study by determining the relative affinity of model compounds for aggregate surfaces, and (4) determine those strongly adsorbed components easily displaced from aggregate surfaces by water during a moisture-damage test. This investigation thus provides both a better understanding of the molecular bonding interactions involved at the asphalt-aggregate interface and the susceptibility of these bonded components to displacement from the interface by water.

EXPERIMENTAL

Materials

Asphalts. - Four viscosity-graded AC-10 asphalts, identified by code numbers B-2959, B-3036, B-3051, and B-3602, were supplied by the Materials Division, Office of Research and Development, Federal Highway

Administration (FHWA). These asphalts, which varied widely in chemical composition, have been used in other studies (9-16).

Aggregates. - Four of the five aggregates, used in this study have also been used in previous studies (9-12). The aggregates, supplied by the FHWA's Material Division, were quartzite 15, Hol limestone, Riverton limestone, granite, and granite P-6. Granite P-6, because of a limited supply of material, was used in only part of the present study. The aggregates were crushed, wet-screened to 20-42 mesh size, rinsed with distilled water, and dried at 150 C for 24 hours prior to use. Surface areas were determined by the BET (Brunauer, Emmett, and Teller) method using krypton as the adsorbate. Surface area measurements are derived from measuring the amount of krypton necessary to cover the aggregate surface with a monomolecular layer of the adsorbed gas.

Solvents. - Reagent-grade solvents were used. Benzene and pyridine were dried by refluxing for 8 hours over calcium hydride before final distillation through a Vigreaux column. Peroxide-free tetrahydrofuran (THF) (17-18) was kept dry by storing it over 4-A molecular sieves.

Procedures

Asphalt-Coated Aggregates. - The asphalts and aggregates were preheated at 150 C for 1 and 3 hours, respectively. Each aggregate (1197 g) was then mixed with each asphalt (63 g). The coated aggregates remained at 150 C for a total of 4.5 hours before the oven was shut off and the mixtures slowly cooled to ambient temperature. Coated aggregates were stored in the dark at ambient temperature for an additional 62 hours before further treatment.

Isolation of the Strongly Adsorbed Asphalt Fraction. - The asphalt-coated aggregate was transferred as a benzene slurry into a separatory funnel that contained a glass wool plug between the main body of the funnel and the stopcock. The asphalt-coated aggregate was washed by slowly percolating cold benzene through the aggregate bed without agitation. This process was continued until the benzene extract became colorless. The strongly adsorbed material remaining on the aggregate was then desorbed by an 8-hour pyridine extraction in an all-glass modified Soxhlet extractor (10). The pyridine extract, concentrated by solvent removal in a rotary film evaporator, was filtered through a 0.9- to 1.4-micron fritted glass funnel before final solvent removal at 92°C in a rotary film evaporator at 2 mm Hg pressure. Trace amounts of pyridine sometimes remained in the extract and were readily detected by its intense odor. These traces of solvent were removed by adding benzene to the pyridine-extracted fraction and repeating the solvent-removal procedure until the pyridine odor was undetectable. The absence of benzene and pyridine in the recovered asphalts was established by the absence of intense infrared absorption bands at 670 and 698 cm^{-1}, respectively, in a carbon disulfide solution. The aggregates after desorption with pyridine were discarded.

Trace mineral and solvent residues were removed and verified in a similar manner from the benzene-desorbed asphalt fraction not strongly adsorbed on the mineral aggregate surfaces of the asphalt-coated aggre-

gates as described above for the strongly adsorbed pyridine-displaced fraction.

Water Displacement of Strongly Adsorbed Materials from the Aggregate Surface. - A second set of new aggregate samples containing only the strongly adsorbed asphalt components was generated by the benzene-wash procedure described above. The benzene-washed aggregate particles were dried overnight at 30 C and 60 to 100 mm Hg pressure. The dried aggregate containing the strongly adsorbed asphalt components was transferred into a glass vessel containing distilled water. Pressure within the vessel was slowly reduced to 0.5-1 mm Hg, and this pressure was maintained until gas bubbles ceased to appear in the 2-in. water layer above the aggregate surface (about 1 hour). The reduced pressure was maintained for an additional half-hour before returning the vessel and its contents to atmospheric pressure. This vacuum-water-saturation procedure was followed sequentially by a 21-hour freeze cycle at -5 C and a 24-hour heat cycle at 60 C. This procedure was similar to that used by R. P. Lottman in his current National Cooperative Highway Research Program moisture-damage studies (19).

After the moisture-damage test was completed, the contents in the glass vessel were transferred to a separatory funnel and the water was drained from the aggregate. Several bed volumes of benzene were slowly percolated through the wet aggregate and combined with the water initially drained from the aggregate. Water was then distilled from the combined water-benzene mixture using the benzene-water azeotrope. The resulting fraction represents the strongly adsorbed material displaced with water. Other strongly adsorbed materials that remained on the aggregate surface were removed by several pyridine washes followed by an 8-hour pyridine extraction in the modified Soxhlet extractor (10) to obtain the strongly adsorbed fraction not displaced by water. Identical sample filtration and solvent removal techniques described in the section on the isolation of strongly adsorbed asphalt fractions were used to recover both the water-displaced and the pyridine-desorbed fractions.

Analytical Methods. - Ketones, carboxylic acids, dicarboxylic anhydrides, and 2-quinolone types were quantitatively determined by a differential infrared spectrometric technique previously described (18). Sulfoxide concentrations were determined from the area of the 1030 cm^{-1} infrared absorption band also previously described (10). Concentrations of functional groups were obtained (18) by using apparent integrated absorption intensities (B) determined from the areas under the absorption bands of selected model compound types containing the corresponding functional group being determined in asphalt. For each functional group averaged data and a series of model compounds with molecular structural variations were used to estimate the corresponding (B) values used in calculating the functional group concentration in asphalt. Carbon and hydrogen contents were determined on a Carlo ERBA* analyzer, and vanadium

*Mention of specific brand names or models of equipment is for information only and does not imply endorsement by the Energy Research and Development Administration.

and nickel contents were determined by a colorimetric technique (20). Nitrogen and sulfur contents were determined with an Antek chemiluminescence digital nitrogen analyzer and a Dohrmann sulfur microcoulometer.

Adsorption of Model Compounds on Aggregate Surfaces. - Nine model compounds, each containing one of the following functional groups: carboxylic acid (benzoic acid), ketone (valerophenone), phenol (phenol), ester (benzyl benzoate), basic nitrogen (quinoline), sulfoxide (phenyl sulfoxide), sulfone (phenyl sulfone), and two different aromatic hydrocarbons (naphthalene and 1,2,3,4-dibenzanthracene), were used to prepare standard solutions. Concentrations of the standard solutions were adjusted to give an ultraviolet absorbance intensity between 0.7 and 0.85 (between 10^{-4} and 10^{-6} molar) in cyclohexane.

To determine the extent of adsorption of each model compound from solution, nine aggregate samples (100-150 mesh, water washed, and dried at 150 C) ranging from 0.1 to 2.0 g were weighed into 2-dram vials and stoppered. Five-ml aliquots of each model compound standard solution were added to the aggregate samples, and the mixtures were shaken intermittently for 5 minutes. After a few minutes, the clear solutions were decanted from the aggregates into UV cells and the absorbances were measured. Absorbance values of each solution were plotted against the amount of aggregate used. The differences between absorbances of the initial standard solutions and the corresponding solutions after shaking with 2 g of aggregate were used to rank the relative affinities of the various model compounds for the aggregate surfaces. These values were normalized for differences in model compound concentrations and sample surface areas.

RESULTS AND DISCUSSION

The objectives of this study were to isolate the strongly adsorbed chemical components in asphalts that comprise the bond at asphalt-aggregate interfaces, to quantitatively and qualitatively identify these components, and to determine the effect of water on their displacement from aggregate surfaces. Adsorption of various model compounds on aggregate surfaces was also determined to compare these results with the data obtained on the strongly adsorbed asphalt fractions. Five aggregates and four asphalts of varying composition were used in this study. Various relationships between asphalt and aggregate composition and adsorption and water displacement of the strongly adsorbed components of the asphalt-aggregate interface were also determined. Since only a limited quantity of granite P-6 was available, the results and discussions pertain to this aggregate are limited and properly identified when used. Properties of the original aggregates and asphalts are shown in Tables 1 and 2, respectively.

Isolation of Asphalt Components Strongly Adsorbed on Aggregate Surfaces

The strongly adsorbed fraction was isolated by first dissolving the asphalt fraction not strongly adsorbed on the aggregate surface with benzene followed by desorption of the strongly adsorbed fraction from the aggregate surface with pyridine. Recovery data on the two fractions are shown in Tables 3 and 4. In all cases the strongly adsorbed frac-

tion was less than 1 percent of the total asphalt sample; the average amount for all asphalt-aggregate systems was about 0.4 percent. This amount is in contrast with earlier work (8, 9) which showed an average of 2.9 percent of strongly adsorbed material on the road core aggregates even though the asphalt content of asphalt-aggregate mixtures in both studies was about 5 percent. These quantitative differences between the two sets of strongly adsorbed materials were attributed primarily to differences in aggregate surface areas and possibly contact times of the asphalts with the aggregate surfaces. Mineral fines possess high surface-to-volume ratios and thus are capable of adsorbing relatively large amounts of asphalt components. These mineral fines were present in the road cores used in the original study; however, only 20-42 mesh size aggregate particles with no fines were used in the present study.

A good correlation is shown in Figure 1 between the aggregate surface areas (Table 1) and the amount of strongly adsorbed material (Table 3); the latter values are the averaged percents of the original asphalt samples strongly adsorbed on each aggregate system. Data on an additional aggregate that was in short supply (granite P-6) are included in Figure 1. If one assumes that a monomolecular layer of asphalt was adsorbed on aggregate surfaces, the area occupied by one molecule of adsorbed material can be calculated by selecting an arbitrary point from the plot in Figure 1. For example, the point representing 0.5 m^2/g and 0.6 percent of the original asphalt corresponds to 0.378 g of strongly adsorbed material removed from the 63 g of asphalt used to prepare the asphalt-aggregate mixtures. If a density of 1 and molecular weight of 700 are assumed, then the calculated area occupied by one molecule (using the number of molecules per mole as 6.02×10^{23}) would be 184 square angstroms (A^2).

The area calculated above compares favorably with an independent estimate of the size of a planar asphalt molecule of 700 molecular weight based upon the size of a benzene molecule as a model. Benzene (molecular weight of 78 and a surface area of about 20 A^2) occupies about one-ninth of the area of a planar aromatic molecule having a molecular weight of 700; thus, the latter molecule should occupy about 180 A^2 of surface area. This number agrees well with the previous calculation of 184 A^2, which assumed a monomolecular layer of asphalt. Ring systems in asphalt molecules contain some nonaromatic rings and heteroatoms and therefore may not be perfectly planar or symmetrical. Steric hindrance from attached side chains may also inhibit planar absorption on the aggregate surfaces. Thus the close agreement between the two surface-area calculations may be fortuitous. However, the calculations indicate that a monolayer of asphalt molecules could be accommodated on the aggregate surface even if they were adsorbed with their aromatic ring systems planar to the surface. The results from these calculations, therefore, strongly suggest that the aggregate surfaces in all systems studied were covered with a monomolecular layer of strongly adsorbed asphalt molecules. The consistency of the data also indicates that the aggregate surface area measurements by the BET method are meaningful when applied to the strongly adsorbed asphalt components found at the asphalt-aggregate interface.

Characterization of Chemical Components Strongly Adsorbed on Aggregate Surfaces

Several of the functional group types strongly adsorbed on aggregate surfaces have been previously identified (8, 9). However, accurate concentration data on individual asphalt-aggregate systems were not obtained because the measurements were not made directly on the strongly adsorbed material. In the current study, quantitative analyses of five oxygen-containing functional group types (ketones, carboxylic acids, dicarboxylic anhydrides, 2-quinolone types, and sulfoxides) were determined on each asphalt-aggregate system. The anhydrides analysis may also include small amounts of other hydrolyzable carboxylic acid derivatives. Tables 3 through 6 summarize the chemical characterization of the strongly adsorbed fractions.

The amounts and concentrations of the chemical components in asphalt fractions strongly adsorbed on the mineral aggregate surfaces are shown in Table 3. These data were obtained by cumulative summing of the data from the water-displaced (Table 8) and not-water-displaced (Table 9) fractions of the strongly adsorbed material. Amounts and concentrations of those components not strongly adsorbed (removed by the benzene wash) are presented in Table 4.

Comparison of the data in Tables 3 and 4 shows that all five oxygen-containing functional group types were concentrated in the strongly adsorbed fraction. Nitrogen was also concentrated in the strongly adsorbed fraction, and the adsorption of nitrogen components was particularly noticeable with those asphalts initially low in nitrogen content. Sulfur, however, was not always found in higher concentrations in the strongly adsorbed fraction.

Ketones, some carboxylic acids, dicarboxylic anhydrides, and sulfoxides are formed during oxidative aging of the asphalts (18); however, most of the carboxylic acids and all of the 2-quinolone types are naturally occurring in asphalts. The oxidation products are produced in sufficient excess during the preparation of a hot mix to make significant amounts available for adsorption at the asphalt-aggregate interfaces. The relative amounts of oxidation products formed during laboratory preparation of asphalt-aggregate mixtures can be assessed by comparing the data in Tables 3 and 4 on the fractions recovered from the aggregates with comparable data on the original asphalts in Table 2.

Analysis of the data in Tables 3 and 4 shows that about 1 percent of the ketones, 2 to 30 percent of the carboxylic acids and anhydrides, 2 to 20 percent of the 2-quinolone types, and 1 to 3 percent of the sulfoxides present in the recovered asphalt samples are found in the strongly adsorbed fractions. Even though only a small amount of the total ketones and sulfoxides in the asphalts were found in the strongly adsorbed fraction, their potential importance to the asphalt-aggregate bond should not be overlooked because these two functional groups comprise over 65 percent of the oxygen-containing functional group types found at the asphalt-aggregate interface. For example, calculations based on the concentration data in Table 3 for asphalt B-2959 on quartzite show that ketones and sulfoxides account for 42.5 and 50.8 percent,

respectively, of the strongly adsorbed chemical components. With asphalts initially containing more acids such as B-3602, the concentration of acids in the strongly adsorbed fraction becomes significant.

Although data in Table 3 were useful for detailed comparisons of the strongly adsorbed fractions, the averaged data in Table 5 (derived from Table 3) are more convenient for discussing the general trends observed. Data averaged for each asphalt on all aggregates show differences among the asphalts, and data averaged for each aggregate with all asphalts show differences among aggregates. Data for nitrogen in Table 5 were converted to concentration units for direct comparison with data from the other functional groups. Sulfur analyses are not included in this table because, as discussed later, only the sulfoxide sulfur is believed to interact strongly with aggregate surfaces.

The sum of the chemical functional type concentrations shown in Table 5 is surprisingly constant for all asphalts and aggregates. This constancy suggests that each aggregate has adsorption sites available for a given number of asphalt molecules and that the functional types are adsorbed in some relationship to their relative concentration in the asphalt and their affinity for the aggregate surface. Putting it another way, adsorption sites or spaces are available for a given number of asphalt molecules, and the functional types compete with each other for the adsorption sites either randomly or selectively. For example, the increased adsorption of acids from asphalt B-3602 (the asphalt that originally contained the most acids, including acid salts) appears to be largely offset by a decreased adsorption of sulfoxides. The adsorption of the other chemical types appears to be fairly constant regardless of asphalt type even though concentrations in the nonadsorbed fractions vary widely (Table 4). This indicates that certain sites on various aggregate surfaces may have selectivity for specific functional types in the asphalts.

Summarized data in the lower half of Table 5, averaged for each aggregate on all asphalts, show differences in the reactivity of the four aggregates toward the asphalts. The greater reactivity of Hol limestone for carboxylic acids is apparent; on the average this aggregate had about twice the concentration of acids in the strongly adsorbed fractions as did the other aggregates. This affinity is even more apparent with asphalt B-3602 (Table 3), in which carboxylic acids account for about 30 percent of the strongly adsorbed fraction. In this case, the high acid concentrations were partly offset by a corresponding decrease in both ketone and sulfoxide content.

Table 6 was developed to assess the relative affinity of each functional type for aggregate surfaces. This tendency to be adsorbed is measured as a concentration ratio (CR); the CR is the ratio of the concentration of the functional type in the strongly adsorbed fraction (Table 3) divided by its concentration in the nonadsorbed fraction (Table 4). Care must be exercised in comparing CR's between different systems, particularly when comparing different asphalts, because the concentration of functional groups available in the asphalt and the limited number of adsorption sites on the aggregate surface affect the CR values. For example, CR's for carboxylic acids were lower for asphalt

B-3602 than for asphalts B-2959 and B-3036, primarily because there were larger amounts of acids initially present in asphalt B-3602. In spite of its limitations, the CR provides a semi-quantitative measure of the asphalt-aggregate interactions, particularly for a given asphalt with different aggregates.

Data in Table 6 rank the relative affinity of the functional types for the aggregate surfaces as follows: carboxylic acids >dicarboxylic anhydrides >2-quinolone types >sulfoxides >nitrogen >ketones. For asphalts initially low in acid content (e.g., B-2959 and B-3036), acids have concentrations 15 to 60 times greater on aggregate surfaces (strongly adsorbed fraction) than in the bulk (nonadsorbed) asphalt fraction. Correspondingly, anhydrides showed concentrations 7 to 36 times greater in the strongly adsorbed fractions than in the nonadsorbed fraction. 2-Quinolones have been shown to have hydrogen-bonding properties similar to carboxylic acids and to form mixed dimers with carboxylic acids (17, 21); thus, similarities between the complexing of carboxylic acids and 2-quinolones with aggregate surfaces are not surprising. However, similarities between the affinities of the carboxylic acids and the anhydrides may be fortuitous because, even though anhydrides are derivatives of carboxylic acids, they cannot supply hydrogen to participate in the hydrogen bond as do acids. They may, however, convert to carboxylic acid salts of cations from the aggregate surface during adsorptions.

Ketones, sulfoxides, and nitrogen types (except 2-quinolones) were the least strongly adsorbed, as indicated by their relatively lower CR values. Because of the relatively high abundance of these functional types in the asphalts (Table 4), small CR's might be expected for reasons described earlier. However, should any of these functional types be more readily adsorbed than the acidic types, the acidic types would be displaced, resulting in lower CR's for the acidic types than for the ketones, sulfoxides, and nitrogen types. This, however, was not observed, thus substantiating the assumption that they are more weakly adsorbed.

Both limestones showed a greater affinity for the acidic functional types present in all asphalts than did either quartzite or granite. Hol limestone showed the greatest affinity for acidic types.

It is instructive to compare the results of this study with the earlier study (9), in which asphalts were recovered from cores taken from ten 10- to 13-year-old pavements. CR values from the road cores obtained for ketones, acids, and anhydrides were 1.9, 14.1, and 9.5, respectively (average of ten different asphalt-aggregate systems); these data agree reasonably well with the data in Table 6. Methods for analysis of the remaining functional groups cited in the present study were not available when the earlier study was conducted.

Adsorption of Model Compounds on Aggregate Surfaces

The relative affinity values for a selected group of model compounds for aggregate surfaces are given in Table 7. These compounds contained functional group types present or potentially present in asphalts. The relative affinities were determined by equilibrating the

standard solutions with the aggregates. The decrease in concentration of each model compound from the solution was attributed to adsorption of that compound on the aggregate surface. Because the standard solutions contained a large excess of model compound relative to the amount needed to saturate the aggregate surface, we assumed that the surface would be saturated at equilibrium. This assumption was supported by the relatively straight-line plots obtained for the changes in UV absorbance intensity vs weight of aggregate sample used. Before the relative affinities were calculated, the UV absorbance changes were normalized by adjusting for differences in solution concentrations and aggregate surface areas.

Benzoic acid showed the greatest affinity for aggregate surfaces--especially for Hol limestone. Thus, the affinity of Hol limestone for benzoic acid was arbitrarily assigned a value of 100. All other values were normalized relative to this interaction. The interactions of benzoic acid with the aggregates are consistent with the asphalt data in Tables 3, 5, and 6, that show carboxylic acids to be the most strongly adsorbed functional group type.

Quinoline, a pyridine-type nitrogen compound, had a significantly greater affinity for quartzite and granite than for Riverton or Hol limestones. This was expected because quartzite and granite contain more acidic sites than the limestones. However, data on the strongly adsorbed fractions (Table 3) generally show a smaller adsorption of nitrogen compounds on Hol limestone than on Riverton limestone. The reason for this difference between the model compound and the strongly adsorbed fraction data is not known. However, both the model compound data and the strongly adsorbed fraction data showed that nitrogen compounds have a significant affinity for aggregate surfaces.

Phenyl sulfoxide showed an affinity for aggregate surfaces comparable to quinoline, except for the limestones for which the sulfoxide affinity was almost two times greater. The similarity in the relative affinities of model compound sulfoxides and pyridine-type nitrogen with these functional types in asphalt is also apparent from comparison of the data in Table 7 with that in Table 6.

Valerophenone, an alkyl aromatic ketone, generally showed an affinity for the aggregates similar to phenyl sulfoxide. The affinity of this ketone is greater than would be expected from the data on asphalts (Table 6) that showed that sulfoxides generally have greater affinities for the aggregates than ketones. However, differences in molecular geometry and variations in the polarity between the functional groups in the model compounds and those in the asphalts could account for this apparent discrepancy.

Sulfones, although not determined in asphalt, showed considerably less affinity for the aggregates than did sulfoxides. Sulfones could be produced in asphalt from subsequent oxidation of sulfoxides. Phenol, having counterparts in asphalts in small concentrations, showed a moderate interaction with the aggregates. The ester, benzyl benzoate, showed interactions lower than those of phenol. Anhydrides of the type believed present in asphalts were not studied because of the low solubility of the model compounds in cyclohexane.

To summarize, where comparisons could be made, the model compound data ranked the relative affinities of the functional types for the aggregate surfaces in the same order as those determined for the strongly adsorbed asphalt fractions.

Large aromatic ring systems in asphalt might be expected to contribute significantly to asphalt-aggregate interactions (22). The surfaces of minerals are known to contain OH groups and other electron deficient (acidic) centers that could coordinate with the polarizable pi electrons in aromatic ring systems (23, 24). The effect of ring size on adsorption is evidenced by comparing the relative affinities of naphthalene (a 2-ring compound) and 1,2,3,4-dibenzanthracene (a 5-ring compound). Naphthalene showed no measurable affinity; however, the dibenzanthracene showed measurable adsorption, particularly on granite. The greater adsorption with higher molecular weight probably reflects the increased ability of the pi electrons to become delocalized and participate in association reactions with polar sites on the aggregate surfaces. Although the affinity of the dibenzanthracene for aggregates is small compared with the other polar compounds, it should be remembered that the polar functional groups (e.g., acids, pyridine-type nitrogen, and sulfoxides) in asphalt may be found in the same molecule with large aromatic ring systems. The combined effect of the polar group and ring system is probably synergistic with respect to adsorption on the aggregate surface (25). Therefore, aromatic ring systems must play an important role in promoting adsorption of asphalt molecules.

Displacement of Strongly Adsorbed Material From Aggregate Surfaces by Water Treatment

Having isolated and characterized both quantitatively and qualitatively the various asphaltic components strongly adsorbed on the aggregate surfaces and having provided confirmatory evidence for the relative affinities of certain functional groups for aggregates by model compound interactions, a study was begun to determine the tendency of these strongly adsorbed components to be displaced by water. Aggregates containing only the strongly adsorbed components were subjected to a moisture-damage test, and the displaced components were recovered by a benzene wash.

Table 8 shows the amounts and concentrations of functional types present in the strongly adsorbed fractions that were displaced from the aggregate surfaces by water; Table 9 shows the amounts and concentrations of the functional types that remained on the aggregate surfaces after the moisture-damage test. The amount of strongly adsorbed material displaced by water varied considerably, depending on the asphalt-aggregate system (Table 8). For example, the strongly adsorbed components on Riverton limestone were more resistant to displacement by water (between 2 and 9 percent) than those adsorbed on Hol limestone (between 10 and 22 percent). The small amount of displaced material on Riverton limestone undoubtedly has a strong influence on the low susceptibility of Riverton limestone mixtures to water stripping, as indicated by ASTM water-stripping data on standard mixes shown in Table 11.

The strongly adsorbed components from asphalt B-3602 generally showed a greater sensitivity towards water displacement as shown by the larger amounts displaced (Table 8) than for the other asphalts. These water-displacement results are also consistent with the ASTM water-stripping data reported in Table 11, which show asphalt B-3602 to be the most sensitive asphalt to water stripping. Unfortunately, the supply of granite P-6 was exhausted before water-displacement data could be obtained on this aggregate; however, its sensitivity to water stripping (Table 11) was extremely low.

The possible relationship between functional group types displaced by water and the sensitivity of the asphalt-aggregate mixtures to water stripping will next be considered. The carboxylic acid concentration data in Table 8 includes both the acids displaced as free carboxylic acid and as carboxylate salts because in several instances a significant amount of the acidic material strongly adsorbed on the aggregate surfaces was displaced by water as the carboxylate salts. The only asphalt in which the acids were initially present almost entirely as carboxylate salts was asphalt B-3602, and a large part of these salts was converted to free acids (9) during the preparation of the asphalt-aggregate mixtures. No measurable carboxylate salts were found in the remaining three asphalts prior to contact with the aggregates. It is possible that some acids in these asphalts were converted to the salts by cation exchange at the aggregate surface. The relative amounts of carboxylate salts displaced from the aggregate surfaces appear to be somewhat dependent on the nature of the surface. For example, compare the concentrations of water-displaced free acids and acid salts for asphalt B-3602 in Table 8. The ratio of free acids to acid salts displaced from quartzite and granite is about 0.5 compared with a ratio of about 2 for the limestones. Whether the cation of the acid salt comes from the asphalt or from exchange with a cation on the mineral surface is not known.

The ratios between the corresponding concentrations of the functional types in the water-displaced fraction to the non-water-displaced fraction were calculated from the data in Tables 8 and 9. These displacement ratios (DR), shown in Table 10, were derived to assess the relative tendency toward water displacement of the various chemical functional types from the aggregate surfaces. A number greater than 1 indicates selective displacement and a number less than 1, selective retention. Care must be exercised in comparing the DR's between different asphalt systems.

The susceptibility of the various functional groups to water displacement is ranked by Table 10 as follows: carboxylic acids > dicarboxylic anhydrides > sulfoxides >nitrogen >2-quinolone types >ketones. It is significant that carboxylic acids are the compound type most readily adsorbed on aggregate surfaces and are also the type most readily displaced by water. With the high acid-containing asphalt, B-3602, carboxylic acids (including their salts) were the major component displaced by water from all the aggregates. This acid displacement probably results from the great affinity of the carboxyl group for the water molecules through the hydrogen bond. In addition, the affinity of water for the aggregate adsorption sites that hold the carboxylic acids may also contribute to the displacement. The relative ease of water dis-

placement of carboxylic acids from the aggregate surface may play a significant role in contributing to the water-stripping problem (cf., B-3602, Table 11).

Powdered hydrated lime has been added to asphalts as an anti-strip agent to reduce the effects of water damage and to reduce age hardening (26). In a recent study we showed that polar asphalt molecules which interacted strongly with hydrated lime were predominantly carboxylic acids and 2-quinolone types (10). These acids not only interact strongly with hydrated lime but also interact strongly with aggregate surfaces and were readily displaced from the aggregate surfaces by water, as shown in the present study. Thus it becomes apparent that the beneficial effects of hydrated lime when added to an asphalt as an anti-strip agent may be caused in part by hydrated lime's ability to strongly interact with carboxylic acids so that less acids are adsorbed by the aggregate surfaces, thus making the asphalt-aggregate bond more resistant to moisture damage.

Dicarboxylic anhydrides were also selectively displaced with water, although not in concentrations as large as for carboxylic acids. Anhydrides might be expected to be less sensitive to water displacement because they do not possess an acidic hydrogen to contribute to a hydrogen bond with water.

Sulfoxides showed either selective displacement or retention on water-treated aggregates. This behavior suggests that both an asphalt and an aggregate factor contribute to this effect. Sulfoxides were concentrated by a factor of about 2 to 3 in the water-displaced fraction on all aggregates contacted with asphalts B-2959 and B-3051; however, sulfoxides from asphalt B-3036 were selectively retained on all aggregates. With asphalt B-3602, sulfoxides were selectively displaced from quartzite and granite but were strongly retained on the two limestones. These data indicate that the molecules containing the sulfoxide group may differ structurally from one asphalt to another. Polyfunctionality on the same molecule may also be indicated.

It should be noted that even though sulfoxides were not as readily displaced from the aggregates by water as were the more acidic materials, they were, with the exception of asphalt B-3602 (the highest acid-containing asphalt), present in high concentrations in the strongly adsorbed fractions. Thus, in many instances over 50 percent of the functional types displaced by water were sulfoxides. A correlation between sulfoxides displacement and water stripping was not apparent.

A comparison of the concentrations of water-displaced sulfoxides with the concentrations of the other water-displaced functional types for asphalts B-2959 and B-3036 shows disproportionately smaller concentrations of displaced sulfoxides for asphalt B-3036 than for B-2959. These data suggest that the sulfoxides in asphalt B-2959 are polyfunctional. Other possibilities are that a functional type is present in asphalt B-3036 that is not being accounted for or that the molecules of this asphalt have higher molecular weights than B-2959. Another unusual feature of the sulfoxides is that even though the amounts displaced by water vary considerably from one system to another, the corresponding amounts retained on the aggregate (Table 8) remain relatively constant.

Both ketones and most nitrogen compounds were selectively retained on aggregate surfaces during water treatment (DR's less than one, Table 10). As with sulfoxides, significant amounts of nitrogen compounds were found in the water-displaced fractions even though they are selectively retained on aggregate surfaces. The high concentrations of nitrogen compounds in the water-displaced fractions were attributed to their initially high concentrations in the strongly adsorbed fractions. Retention of nitrogen compounds on granite (Table 10) may relate to the observed resistance of granite P-6 (not the same granite samples) to water stripping (Table 11) although we had insufficient granite P-6 to measure its nitrogen retention on the aggregates. The greater affinity of aromatic types for granite (Table 7) may also relate to the low sensitivity of granite P-6 to water stripping (c.f., Table 11). When comparing the acids adsorbed on the different aggregates (Table 3), a much lower acid concentration was noted for granite P-6 than for the other aggregates. Acids were previously implicated as contributing to water stripping. Unfortunately, moisture-damage test data are not available for granite P-6. These results again imply that acids may contribute to water stripping and that, in the case of granite P-6, other functional types resistant to water displacement occupy sites that might otherwise be occupied by carboxylic acids or its derivatives. The composition of both the aggregate surface and the asphalt appear to be important variables affecting moisture damage of asphalt pavements.

Displacement ratios of 0.1 to 0.2 for ketones show that water has little effect on their displacement from the aggregate. It is possible that they are associated with other functional types or aromatic ring systems as suggested by earlier work in this laboratory (27). These factors could contribute to their retention; however, the low DR's for ketones do show that most of the adsorbed ketones are not associated with the more readily displaced acids, anhydrides, and sulfoxides.

With two exceptions, DR's for nitrogen compounds were less than unity and nitrogen compounds from asphalt B-3051 showed the least sensitivity to water displacement. Generally, 2-quinolone types, also containing nitrogen, showed selective retention on aggregate surfaces. Thus, nitrogen compounds (evidenced by infrared and pyridine-aggregate adsorption data to be largely of the basic pyridine type) are selectively retained on the aggregate surfaces in the presence of water. These data contrast with data showing selective water displacement of the acidic compound types.

Although not considered in this study, the physical characteristics of the aggregate surface (roughness, etc.) undoubtedly contribute to sensitivity to moisture damage. This may account for some of the differences between the two limestones used.

A logical extension of this work is to study the effects of adding anti-stripping agents to asphalts to determine their interaction with aggregate surfaces and to determine if anti-stripping agents displace those functional types shown to be sensitive to water displacement. Work is planned in this area to elucidate more clearly the chemistry of asphalt-aggregate bonds and the mechanism of water damage in asphalt-aggregate mixtures.

SUMMARY AND CONCLUSIONS

This study showed that the strongly adsorbed asphaltic components found at asphalt-aggregate interfaces (less than 1 percent of the original asphalt sample in our nearly uniform samples containing no fines) formed a monomolecular layer that consisted primarily of five oxygen-containing functional group types and nitrogen compounds believed to contain basic pyridine-type nitrogen. The five oxygenated functional types were: ketones, carboxylic acids, dicarboxylic anhydrides, 2-quinolone types, and sulfoxides. Carboxylic acids were the compound type most selectively adsorbed from the asphalts on all aggregate surfaces. Adsorption studies involving model compounds gave results supporting those observed in the asphalt-aggregate adsorption study.

The moisture-damage test showed that carboxylic acids, the compound type most selectively adsorbed by all aggregate surfaces, was also the compound type most readily displaced by water. Anhydrides were displaced, but to a lesser extent than acids. Sulfoxides showed either selective retainment or displacement behavior, depending on the aggregate and asphalt system involved. Ketones and nitrogen compounds were selectively retained by aggregates during moisture-damage tests. Although sulfoxides and nitrogen compounds comprise a significant amount of the material displaced from the aggregate surface by water, their role in water stripping is not clear. It appears that both the relative amount and chemical type of the strongly adsorbed material displaced by water and the nature of the aggregate surface play an important role in moisture damage of asphalt pavements.

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TABLE 1 - PROPERTIES OF AGGREGATES

Aggregates	Surface Area, m^2/g	Composition, Wt. Percent
Quartzite 15	0.145	Quartz, 94
Hol limestone	.104	Calcite, 93
Riverton limestone	.655	Dolomite, 18 Calcite, 78
Granite	.141	Quartz, 78 Albite, Biotite, Hornblende] 18
Granite P-6	.552	Quartz, 64 Albite, Biotite, Hornblende] 23

TABLE 2 - COMPOSITIONAL DATA ON ORIGINAL ASPHALTS

Asphalts	Weight Percent				PPM		Concentration, Moles/Liter				
	C	H	N	S	V	Ni	Ketones	Carboxylic Acids	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides
B-2959	83.77	9.91	0.34	6.06	160	22	0.015	trace	0.0014	0.003	0.015
B-3036	85.78	10.19	.26	3.72	8	0.4	.021	trace	.0014	.001	.022
B-3051	82.90	10.45	.73	6.59	1300	109	.017	0.014	.003	.009	.010
B-3602	86.77	10.94	1.03	1.01	36	5.6	.045	.06*	**	.011	.015

*Present as carboxylate salts
**Below level of detection

TABLE 3 - AMOUNTS AND CONCENTRATION OF CHEMICAL COMPONENTS IN ASPHALT FRACTIONS STRONGLY ADSORBED ON MINERAL AGGREGATE SURFACES

Aggregates	Asphalts	Percent of Original Asphalt	Concentration, Moles/Liter*					Percent	
			Ketones	Carboxylic Acids**	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides	Sulfur	Nitrogen
Quartzite 15	B-2959	0.29	0.76	0.04	0.06	0.02	0.91	7.13	1.04
	B-3036	.26	.83	.06	.06	.01	.85	4.74	.81
	B-3051	.41	.88	.11	.08	.04	.73	6.79	1.38
	B-3602	.26	1.00	.49	.15	.03	.28	1.29	1.24
Hol limestone	B-2959	.18	0.79	.12	.11	.04	.92	7.08	.90
	B-3036	.14	.89	.11	.12	.02	.80	4.00	.76
	B-3051	.19	.79	.22	.11	.05	.79	6.27	1.19
	B-3602	.13	.77	.76	.19	.02	.14	1.04	1.02
Riverton limestone	B-2959	.80	.62	.05	.08	.03	.82	7.21	.81
	B-3036	.71	.74	.05	.08	.02	.86	4.59	.97
	B-3051	.94	.66	.17	.10	.03	.84	6.21	1.38
	B-3602	.72	.84	.39	.12	.03	.25	1.39	1.50
Granite	B-2959	.33	.75	.07	.10	.03	.85	6.99	.74
	B-3036	.27	.88	.06	.09	.01	.74	4.06	.85
	B-3051	.40	.77	.09	.09	.03	.69	5.72	1.28
	B-3602	.24	1.01	.27	.12	.03	.30	1.30	1.02
Granite P-6	B-2959	.76	.50	trace	.06	.03	.92	--	--
	B-3036	.61	.66	.01	.07	.01	.84	--	--
	B-3051	.92	.42	.02	.05	.02	.82	--	--
	B-3602	.55	.88	.22	.12	.04	.36	--	--

*Derived from Tables 8 and 9 except for Granite P-6

**Includes carboxylate salts

TABLE 4 - AMOUNTS AND CONCENTRATION OF CHEMICAL COMPONENTS IN ASPHALT FRACTIONS NOT STRONGLY ADSORBED ON MINERAL AGGREGATE SURFACES

Aggregates	Asphalts	Percent of Original Asphalt	Concentration, Moles/Liter					Wt. Percent	
			Ketones	Carboxylic Acids	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides	Sulfur	Nitrogen
Quartzite 15	B-2959	99.7	0.33	0.002	0.006	0.002	0.20	6.06	.33
	B-3036	99.7	.33	.004	.008	trace	.20	3.72	.26
	B-3051	99.6	.37	.014	.010	.008	.25	6.59	.73
	B-3602	99.7	.54	.074*	.028	.010	.13	1.01	1.03
Hol limestone	B-2959	99.8	.38	trace	trace	.002	.27	6.06	.33
	B-3036	99.9	.38	.002	.004	.001	.27	3.72	.26
	B-3051	99.8	.41	.012	.013	.005	.27	6.59	.73
	B-3602	99.9	.73	.067*	.037	.007	.16	1.01	1.03
Riverton limestone	B-2959	99.2	.26	.002	.003	.001	.20	6.05	.33
	B-3036	99.3	.25	trace	trace	trace	.19	3.71	.25
	B-3051	99.1	.29	.012	.006	.004	.22	6.59	.73
	B-3602	99.3	.46	.065*	.025	.009	.13	1.01	1.03
Granite	B-2959	99.7	.41	.004	.015	.005	.26	6.60	.33
	B-3036	99.7	.48	.002	.010	trace	.24	3.72	.25
	B-3051	99.6	.44	.021	.016	.008	.25	6.59	.73
	B-3602	99.8	.65	.056*	.029	.010	.14	1.01	1.03

*Includes carboxylate salts

TABLE 5 - AVERAGED CONCENTRATIONS OF CHEMICAL COMPONENTS IN ASPHALT FRACTIONS STRONGLY ADSORBED ON MINERAL AGGREGATE SURFACES

Asphalts	Concentration, Moles/Liter						
	Ketones	Carboxylic Acids	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides	Nitrogen	Sum, All Types
	Averaged for each asphalt on all aggregates						
B-2959	0.73	0.07	0.09	0.03	0.88	0.62	2.42
B-3036	.84	.07	.09	.02	.81	.61	2.44
B-3051	.78	.15	.10	.04	.76	.94	2.77
B-3602	.91	.48	.15	.03	.24	.86	2.67
Aggregates	Averaged for each aggregate on all asphalts						
Quartzite 15	0.87	0.18	0.09	0.03	0.69	0.80	2.66
Hol limestone	.81	.30	.13	.03	.66	.69	2.62
Riverton limestone	.72	.17	.10	.03	.69	.83	2.54
Granite	.85	.12	.10	.03	.65	.70	2.45

TABLE 6 - RELATIVE AFFINITY OF STRONGLY ADSORBED ASPHALT COMPONENTS FOR AGGREGATE SURFACES

Asphalts	Aggregates	Concentration Ratio*						
		Ketones	Carboxylic Acids	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides	Sulfur	Nitrogen
B-2959	Quartzite 15	2.3	20	10	10	4.6	1.18	3.15
	Hol limestone	2.1	>60	>36	20	3.4	1.17	2.73
	Riverton limestone	2.4	25	27	30	4.1	1.19	2.45
	Granite	1.8	18	6.7	6	3.3	1.06	2.24
B-3036	Quartzite 15	2.5	15	7.5	>10	4.3	1.27	3.12
	Hol limestone	2.3	55	30	20	3.0	1.08	2.92
	Riverton limestone	3.0	>30	>27	>20	4.5	1.24	3.88
	Granite	1.8	30	9	>10	3.1	1.09	3.40
B-3051	Quartzite 15	2.4	7.9	8	5	2.9	1.03	1.89
	Hol limestone	1.9	18	8.5	10	2.9	.95	1.63
	Riverton limestone	2.3	14	17	7.5	3.8	.94	1.89
	Granite	1.8	4.3	5.6	3.8	2.8	.87	1.75
3-3602	Quartzite 15	1.9	6.6	5.4	3.0	2.2	1.28	1.20
	Hol limestone	1.1	11	5.1	2.9	0.9	1.03	.99
	Riverton limestone	1.8	6	4.8	3.3	1.9	1.38	1.46
	Granite	1.6	4.8	4.1	3.0	2.1	1.29	.99

*Concentration in fraction strongly adsorbed/concentration in fraction not strongly adsorbed

TABLE 7 - RELATIVE AFFINITY OF MODEL COMPOUNDS FOR AGGREGATE SURFACES

Model Compound	Relative Affinity for Aggregate Surface*			
	Quartzite 15	Hol Limestone	Riverton Limestone	Granite
Benzoic acid	46.8	100	38.3	45.6
Quinoline	11.5	2.7	3.8	11.8
Phenyl sulfoxide	8.6	6.9	6.0	12.7
Phenyl sulfone	4.3	3.3	3.0	7.2
Valerophenone	8.5	9.2	5.0	8.8
Phenol	5.8	7.0	4.5	6.7
Benzyl benzoate	<0.1	5.3	3.0	3.1
1,2,3,4-Dibenzanthracene	<0.1	<0.1	<0.1	0.2
Naphthalene	0	0	0	0

*Excess model compound used--aggregate surface assumed to be saturated. Benzoic acid with Hol limestone arbitrarily set at 100. Values are adjusted for differences in both aggregate surface area and model compound concentration so that data are comparable from one system to another.

TABLE 8 - AMOUNTS AND CONCENTRATION OF CHEMICAL COMPONENTS IN ASPHALT FRACTIONS DISPLACED FROM MINERAL AGGREGATE SURFACES BY WATER TREATMENT

Aggregates	Asphalts	Percent of Strongly Adsorbed Fraction	Concentration, Moles/Liter									Wt. Percent	
			Ketones	Carboxylic Acids			Di-carboxylic Anhydrides	2-Quino-lone Types	Sulf-oxides	Nitrogen	Total	Sulfur	Nitrogen
				Free	Salts	Total							
Quartzite 15	B-2959	8.40	0.14	0.16	0.06	0.22	0.19	0.02	1.92	0.63	3.12	6.70	0.88
	B-3036	7.44	.14	.13	.12	.25	.17	<.01	.68	.47	1.72	3.05	.64
	B-3051	9.01	.10	.32	.06	.38	.18	.02	1.87	.76	3.31	7.55	1.06
	B-3602	14.14	.14	.51	1.10	1.61	.17	<.01	.49	.56	2.98	1.12	0.79
Hol limestone	B-2959	12.61	.14	.27	.18	.45	.25	.04	1.38	.73	2.99	6.56	1.02
	B-3036	9.75	.14	.27	.33	.60	.17	<.01	.63	.56	2.11	3.10	.79
	B-3051	11.19	.10	.32	.26	.58	.23	.06	1.54	.83	3.34	6.29	1.16
	B-3602	21.50	.05	1.34	.40	1.74	.21	<.01	.03	.46	2.50	1.00	.64
Riverton limestone	B-2959	4.40	.14	.24	.14	.38	.25	.03	2.15	.44	3.39	8.57	.61
	B-3036	2.49	.14	.24	.24	.48	.32	<.01	.76	.41	2.12	3.05	.57
	B-3051	6.80	.14	.40	.11	.51	.25	.02	1.99	.49	3.40	7.54	.68
	B-3602	8.57	.10	1.15	.54	1.69	.18	.02	.14	.46	2.59	.88	.64
Granite	B-2959	10.93	.14	.27	.15	.42	.23	.02	1.64	.49	2.94	7.03	.68
	B-3036	12.42	.14	.15	.08	.23	.16	<.01	.59	.34	1.47	2.33	.48
	B-3051	9.33	.14	.25	.49	.74	.24	.01	1.71	.63	3.47	6.23	.88
	B-3602	11.12	.15	.38	.78	1.16	.31	.01	.35	.64	2.62	1.30	.90

TABLE 9 - AMOUNTS AND CONCENTRATION OF CHEMICAL COMPONENTS IN ASPHALT FRACTIONS REMAINING STRONGLY ADSORBED ON MINERAL AGGREGATE SURFACES AFTER WATER TREATMENT

Aggregates	Asphalts	Percent of Original Asphalt	Concentration, Moles/Liter					Wt. Percent	
			Ketones	Carboxylic Acids*	Dicarboxylic Anhydrides	2-Quinolone Types	Sulfoxides	Sulfur	Nitrogen
Quartzite 15	B-2959	0.267	0.82	0.02	0.05	0.02	0.82	7.17	1.05
	B-3036	.241	.89	.04	.02	.01	.86	4.88	0.82
	B-3051	.369	.96	.08	.07	.04	.62	6.72	1.41
	B-3602	.221	1.14	.30	.15	.03	.25	1.32	1.31
Hol limestone	B-2959	.153	.88	.07	.09	.04	.85	7.15	0.88
	B-3036	.128	.97	.06	.11	.02	.82	4.10	0.76
	B-3051	.170	.88	.18	.10	.05	.69	6.27	1.19
	B-3602	.103	.97	.49	.19	.02	.17	1.05	1.12
Riverton limestone	B-2959	.762	.64	.04	.07	.03	.76	7.15	0.82
	B-3036	.696	.76	.04	.07	.02	.86	4.63	0.99
	B-3051	.877	.70	.15	.09	.03	.76	6.11	1.43
	B-3602	.654	.91	.27	.11	.03	.26	1.44	1.58
Granite	B-2959	.290	.83	.03	.08	.03	.75	6.98	0.75
	B-3036	.232	.98	.03	.08	.01	.76	4.31	0.90
	B-3051	.358	.83	.06	.08	.03	.59	5.67	1.32
	B-3602	.213	1.12	.24	.10	.03	.29	1.30	1.04

*Includes carboxylate salts

TABLE 10 - DISPLACEMENT OF STRONGLY ADSORBED ASPHALT COMPONENTS BY WATER TREATMENT

Asphalts	Aggregates	Displacement Ratio*						
		Ketones	Carboxylic Acids	Dicarboxylic Anhydrides	2-Quinolcne Types	Sulfoxides	Sulfur	Nitrogen
B-2959	Quartzite 15	0.2	11.0	3.8	1.0	2.3	0.93	.84
	Hol limestone	.2	6.4	2.8	1.0	1.6	.92	1.16
	Riverton limestone	.2	9.5	3.6	1.0	2.8	1.20	.74
	Granite	.2	14.0	2.9	.7	2.2	1.01	.91
B-3036	Quartzite 15	.2	6.3	8.5	<1.0	.8	.63	.78
	Hol limestone	.1	10.0	1.5	< .5	.8	.76	1.04
	Riverton limestone	.2	12.0	4.6	< .5	.9	.66	.58
	Granite	.1	7.7	2.0	<1.0	.8	.54	.53
B-3051	Quartzite 15	.1	4.8	2.6	.5	3.0	1.12	.75
	Hol limestone	.1	3.2	2.3	1.2	2.2	1.00	.97
	Riverton limestone	.2	3.4	2.8	.7	2.6	1.23	.48
	Granite	.2	12.3	3.0	.3	2.9	1.10	.67
B-3602	Quartzite 15	.1	5.4	1.1	<0.3	2.0	.85	.60
	Hol limestone	.1	3.6	1.1	< .5	.2	.95	.57
	Riverton limestone	.1	6.3	1.6	.7	.5	.61	.41
	Granite	.1	4.8	3.1	.3	1.2	1.00	.87

*Concentration in fraction displaced by water/concentration in fraction not displaced by water

TABLE 11 - WATER-STRIPPING DATA ON ASPHALT-AGGREGATE MIXTURES USING A MODIFIED ASTM DI664 IMMERSION TEST*

Aggregates	Asphalts	Percent Stripped
Quartzite 15	B-2959	40
	B-3036	80
	B-3051	40
	B-3602	90
Hol limestone	B-2959	45
	B-3036	40
	B-3051	20
	B-3602	75
Riverton limestone	B-2959	5
	B-3036	5
	B-3051	10
	B-3602	20
Granite	B-2959	not obtained
	B-3036	"
	B-3051	"
	B-3602	"
Granite P-6	B-2959	1
	B-3036	8
	B-3051	0
	B-3602	5

*Water-stripping data obtained by FHWA. Immersion temperature changed to 37.8 C (100 F).

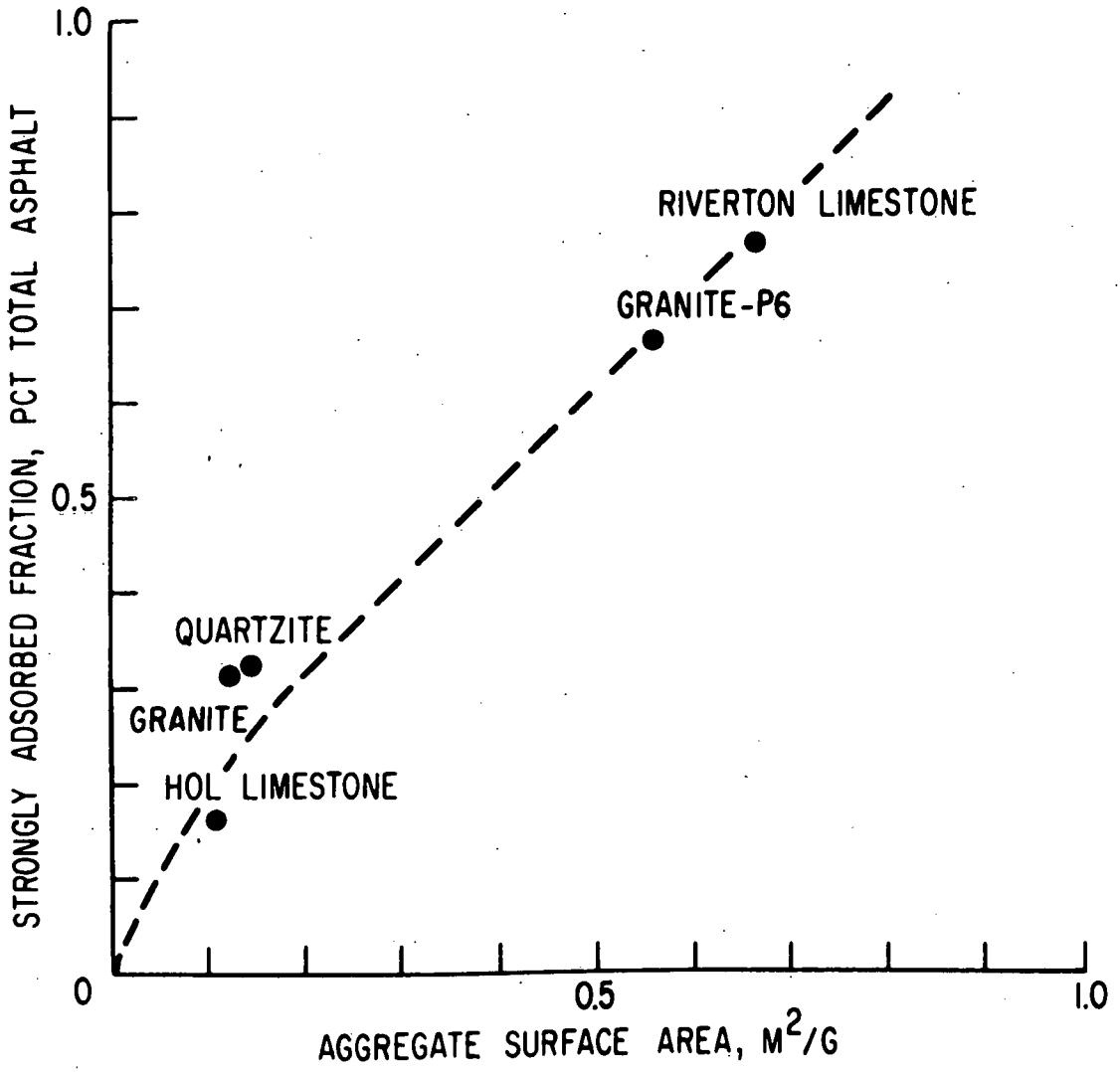

FIGURE 1. - COMPARISON OF AGGREGATE SURFACE AREA AND AMOUNT OF STRONGLY ADSORBED ASPHALT FRACTION