MOLECULAR INTERACTIONS OF ASPHALT IN THE ASPHALT-AGGREGATE INTERFACE REGION

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Evidence for molecular interactions in the asphalt-aggregate interface region was demonstrated by using 3 different approaches: a study of asphalt-aggregate interactions by inverse gas-liquid chromatography (IGLC), chemical analysis of strongly adsorbed species, and physical measurements of molecular adsorption. IGLC studies showed that polar asphalt molecules, initially present or formed on oxidation, interact strongly with aggregate surfaces. Asphalt fractions showed more interaction with limestone than with quartzite. The catalytic effect of a mineral surface on the oxidation of asphalt fractions was shown. Limited IGLC studies also showed a correlation between asphalt-aggregate interactions and water-stripping resistance. Ketones, dicarboxylic anhydrides, and carboxylic acids were found to be the major asphalt components strongly adsorbed to road aggregates; they were concentrated in the strongly adsorbed fraction by factors of 1.9, 9.5, and 14 respectively. Evidence for multilayer adsorption of asphalt molecules on mineral surfaces was obtained by heats of immersion, flow through porous media, and photomicroscopy studies. The results indicated that adsorption, or molecular orientation, of asphalt molecules in the asphalt-aggregate interface region is a slow process and often continues for many hours and even days at 150 C (423 K). The adsorbed layer appears immobile at 150 C (423 K), and its buildup rate, typically of the order of 20 Å/min with normal aggregates, is affected by both the nature of the mineral surface and the composition of the asphalt. Speculation about the possible significance of the reported studies to asphalt paving technology is presented.

●MINERALOGICAL composition of aggregates appears to be of primary importance to asphalt-aggregate adhesion and resistance of the adhesive bond to the stripping action of water. The chemical nature of the aggregate surface sometimes is altered intentionally by treatment with lime, metal salts, or other materials. Adhesion promotors, which are believed to affect the asphalt-aggregate interface, sometimes are added to the asphalt to improve the adhesive characteristics of the road mix. The voluminous literature in this area is summarized by Majidzadeh and Brovold (1).

In addition to the influence of the interactions between asphalt and aggregate at the aggregate surface, the chemical nature of the aggregate has long-range influences that extend deep into the asphalt-aggregate interface region. Mack (2) 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 that cannot be precisely predicted from the well-recognized properties of the fillers such as density and particle size. Watanabe and Abe (3) 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 additives and asphalt components such as asphaltenes on the "setting rate" of road mixes. These phenomena may well have their bases in long-range molecular interactions in the asphalt that are promoted by the aggregate surface. Recent work by Ensley (4) supports this.

In spite of the apparent importance of asphalt-aggregate interactions, little fundamental knowledge of the nature of the interactions exists. Chemical reactions between asphalt components and the aggregate surface have not been shown conclusively even though certain asphalt components apparently are strongly adsorbed and not readily extracted from the aggregate in road cores by commonly used solvents such as benzene. Alcohol often is 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 readily available. Reversible changes in the bulk properties of the asphalt sometimes referred to as "steric hardening," which may be promoted by the aggregate surface, have eluded direct study in the past because this hardening is destroyed during solvent recovery of the asphalt from road mixes.

Several years ago the Bureau of Mines's Laramie Energy Research Center began to study both the chemical and physical nature of asphalt-aggregate interactions. Several new experimental techniques have been developed and applied, and considerable progress has been made toward a more fundamental understanding of the asphalt-aggregate interaction. The purpose of this Bureau of Mines paper is to highlight the current findings of these studies and to suggest their implications for asphalt technology.

For convenience, the studies have been divided into 3 areas on the basis of the experimental approach.

First, the interactions between chemical functional groups in asphalt and the functional groups on the aggregate surface were studied by IGLC. The IGLC technique (5) was developed in our laboratory and applied originally to the study of asphalt composition (5, 6, 7, 8, 9). In the present work, asphalt was coated on sized aggregate particles that served as the gas chromatographic column packing (10), thus allowing study of the chemical interactions between asphalt and aggregate while they are in intimate contact.

Second, the chemical functional types strongly adsorbed on the aggregate surface were studied both qualitatively and quantitatively by an analytical technique using both selective chemical reactivity and differential infrared spectroscopy (11).

Finally, the interactions at the asphalt-aggregate interface and their long-range effects on reversible changes in the properties of the asphalt binder while in contact with the aggregate surface were studied by several physical methods. These included heats of immersion of aggregate in asphalt (4, 12), flow through a porous medium of aggregate particles (13), and photomicroscopy of the asphalt interface region previously in contact with a mineral surface (13).

<div align="center">EXPERIMENTAL WORK</div>

Materials

Four study asphalts (B-2959, B-3036, B-3051, and B-3602) and 4 study aggregates (quartzite "15," "Hol" limestone, Riverton limestone, and granite "P-6") were supplied by the Federal Highway Administration (FHWA) (14, 15, 16). The FHWA also supplied 2 sets of 10 asphalts each that were recovered from duplicate 11- to 13-year-old pavement cores. One set of asphalts was extracted from the pavement cores by FHWA personnel with benzene only; the other set was extracted with a 4:1 mixture of benzene and 95 percent ethanol. Extractions in each case were continued until the extracting solvent issuing from the aggregate was colorless. The sample numbers of these asphalts correspond to those used in previous publications (17, 18, 19, 20). The Wilmington, California, asphalt and the preparation of the Wilmington asphalt fractions by pentane precipitation of the asphaltenes and by chromatography of the maltenes on basic alumina have been described previously (5, 10, 21, 22, 23, 24, 25).

The quartzite and limestone used in the IGLC study were obtained from the Laramie, Wyoming, area. Fluoropak 80 was the nonpolar fluorocarbon gas chromatograph solid support. Bauxite used in heat-of-immersion studies was regular grade Porocel.

Aggregate surface area measurements were made on -35+48-mesh particles by using the BET method with krypton as the adsorbate. The antistripping agent was Redicote 80S.

Procedures

Inverse Gas-Liquid Chromatography—IGLC characterization of the interactions between aggregates and asphalts or asphalt fractions was carried out by using a modification (10) of the original IGLC procedure (5) in which the inert solid column packing on which the asphalt was coated was replaced by -20+40-mesh aggregate. Oxidation of the asphalts in the laboratory was accomplished by replacing the inert column carrier gas with air (6). Both the oxidation and the test compound determinations were carried out at 130 C (403 K).

Analysis of Chemical Types—Ketones, carboxylic acids, and dicarboxylic anhydrides in oxidized asphalts generally have overlapping and indistinguishable absorption bands in the carbonyl region of the infrared spectrum. The amounts of these functional types were therefore determined by using a recently developed method that combines chemical reaction and differential infrared spectroscopy (11). In brief, the acids and anhydrides were reacted with sodium hydroxide and the acids were independently silylated and reacted with potassium bicarbonate; the resulting changes in the infrared absorption bands of the functional types were measured quantitatively by using selected sets of differential spectra from which concentration data were calculated (11). Ketone concentrations were obtained by difference.

Physical Measurements of Multilayer Adsorption—Heat-of-immersion studies of the asphalt-aggregate interaction energy were performed at 130 C (403 K) by using an extremely sensitive differential microcalorimeter designed and built by Ensley (4). This calorimeter is capable of measuring temperature changes of less than 5×10^{-6} K. The rate of association of asphalt molecules was also measured in the microcalorimeter (12). Flow-through-porous-media (FTPM) experiments were performed by flowing melted asphalt through a porous bed of aggregate under a nitrogen atmosphere and noting changes in the flow rate of the asphalt through the aggregate (13). Photomicroscopy using both optical and scanning electron microscopy were used in a conventional manner to examine striated fracture surfaces in asphalt samples (13).

Calculations

Calculation methods used to determine the interaction coefficient (I_g) from IGLC data, to determine the concentrations of functional compound types in asphalts, and to determine heats of immersion in the microcalorimetry have been reported previously (4, 5, 9, 11).

The asphalt fraction strongly adsorbed to the aggregate surface in the FHWA road cores was not isolated. It was therefore necessary to calculate the concentrations of functional types in this fraction from the differences in composition between the asphalts extracted from the road cores with benzene only and the corresponding asphalts extracted from the road cores with benzene-alcohol. By assuming that the asphalts have a specific gravity of unity, one can compare the concentration in moles per litre and the weight of asphalt. If one assumes 1 litre of the benzene-alcohol-recovered asphalt, then

$$X = BA - B(1 - W) \qquad (1)$$

where

    X = moles of functional type that was strongly adsorbed contained in 1 litre of benzene-alcohol-recovered asphalt;

  BA = concentration of functional type as measured in benzene-alcohol-recovered asphalt, mol/l;

    B = concentration of functional type as measured in benzene-only-recovered asphalt, mol/l; and

    W = weight fraction strongly adsorbed.

BA and B were calculated from the infrared analysis (11), and W was obtained from the mass balance data obtained during the recovery of the asphalts from road cores. The term 1 - W corrects the term B for material lost on the aggregate in the benzene extraction.

Knowing X, then

$$\frac{X}{BA} \cdot 100 = \text{percent of functional type strongly adsorbed} \tag{2}$$

and

$$CF = \frac{X/BA}{W} \tag{3}$$

where CF = concentration factor representing the increase in concentration of the functional type in the strongly adsorbed layer over that in the whole asphalt recovered with benzene-alcohol. If one assumes that the molecules are monofunctional and have a molecular weight of 700, then

$$\frac{X \cdot 700}{10} = \text{strongly adsorbed functional type as percent by weight} \atop \text{of total strongly adsorbed material} \tag{4}$$

RESULTS AND DISCUSSION

IGLC Studies of Chemical Interactions

Initial investigations in our laboratory of asphalt-aggregate interactions were carried out by using a modified IGLC technique. In brief, the technique involved preparing a gas chromatographic column consisting of a thin coating of asphalt or asphalt fraction on 20- to 40-mesh particles of aggregate. This asphalt-aggregate column was analyzed by passing known chemical compounds with carefully selected functional groups (test compounds) through the column and measuring the time required for them to emerge. Interactions between the functional group of the test compound and functionality on the column increased the emergence time. From the emergence times, the specific interaction coefficients, I_g, were calculated (9). The I_g is referenced to the behavior of a hypothetical nonpolar hydrocarbon of the same molecular weight as the test compound; therefore, the I_g is a measure of the interaction of the chemical functional group of the test compound with functionality on the column.

Interpreting the data was difficult because of the complexity of the interactions. Emergence times, and thus I_g values, can be increased by interactions of functional groups in asphalt with the test compound or by interactions between the test compound and chemical functionality on the aggregate surface. Of particular interest in the present study were the interactions between the asphalt and the aggregate; these interactions reduce the number of reactive asphalt and aggregate sites that are available for interaction with the test compound and thus reduce the I_g. Thus, IGLC data on an asphalt-aggregate column must be interpreted as the net result of all these interactions. In spite of the complexity of the system, qualitative meaning can be given to the results of the asphalt-aggregate data by comparing them with data obtained on the asphalt alone by using an inert solid support instead of aggregate and data obtained on columns of aggregate only.

Interaction data for 3 test compounds (propionic acid, phenol, and 2-methylpyridine) on 4 fractions from a Wilmington, California, asphalt coated on inert Fluoropak 80, quartzite, and limestone are given in Table 1. Data on 7 additional test compounds are reported elsewhere (10). The test compounds were selected to represent functional types known to be present in asphalt and capable of forming strong molecular complexes. Specific interaction coefficients on uncoated quartzite and limestone could not be calculated because emergence times for hydrocarbon references were too short for accurate measurement and test compounds did not emerge from uncoated limestone

after 150 min (5, 9). Interactions with bare quartzite were much less intense than with bare limestone, and all test compounds emerged from the quartzite column.

Data on the saturates fraction in Table 1 show that interactions on both quartzite and limestone were greater than on the inert Fluoropak. Test compounds permeated the nonpolar saturates fraction and interacted with sites on the aggregate surfaces. In fact, the data on unoxidized saturate-coated limestone were similar to data on bare limestone in that none of the test compounds emerged from the columns. The data show that the unoxidized saturates fraction does not contain significant amounts of strongly interacting functional groups that are capable of interacting with reactive sites on the aggregate surface. These sites are thus blocked from interaction with the test compounds.

After oxidation of the saturates on quartzite, the interaction of the test compounds with polar groups produced by oxidation is apparent from the increase in the I_g values in the oxidized column. On limestone, however, interaction of the oxidation products with the limestone surface, which blocks reactive sites on the aggregate, is evidenced by a decrease in the I_g for phenol and 2-methylpyridine. Of additional interest is the apparent absence of significant amounts of oxidation products in the saturates fraction oxidized on Fluoropak as indicated by the absence of significant changes in the I_g values on oxidation. The data on quartzite, when compared with the Fluoropak data, indicate that the quartzite surface catalyzed the oxidation of the saturates fraction. Examination of the infrared spectra of the recovered fractions showed the virtual absence of oxidation products in the saturates oxidized on Fluoropak, the presence of significant amounts of oxidation products in the saturates oxidized on limestone, and the presence of even greater amounts in saturates oxidized on quartzite.

The unoxidized aromatics fraction on Fluoropak showed greater interactions with the test compounds than did the saturates, suggesting more polar groups are in this fraction. The unoxidized aromatics apparently have sufficient polar groups to inactivate enough sites on the limestone surface to allow phenol and 2-methylpyridine to emerge from the column. Data for the oxidized aromatics on limestone show that the net effect of the interactions of the oxidation products with the limestone surface is greater than that of the interactions of the oxidation products with the test compounds. On the other hand, data for oxidized aromatics on quartzite show that the net effect of interactions of the oxidation products with test compounds is greater.

The polar aromatics and asphaltenes contain most of the highly polar functional groups initially present in the asphalt as evidenced by their large I_g values on Fluoropak and by their infrared spectra. The unoxidized polar aromatics and asphaltenes have sufficient polar groups to interact with and block many sites on the aggregate surfaces. This is shown by increases rather than decreases in the I_gs (except propionic acid) after oxidation of the fractions on limestone; increase results from interaction of the test compounds with oxidation products in excess of those interacting with the aggregate.

Evidence for the association of asphaltenes into molecular aggregates, or micelles, is found by comparing the I_gs for the polar aromatics and asphaltenes on both Fluoropak and limestone. Data on the inert Fluoropak show that interactions between the test compounds and the 2 fractions are very similar. Note, however, that I_gs on limestone are significantly greater for asphaltenes than for polar aromatics. This is interpreted as an increase in interaction between the test compounds and the limestone surface in the asphaltene-coated sample. Aggregation of the asphaltene molecules would reduce the number of functional groups in the asphaltenes that are physically able to interact with the aggregate surface. More sites on the aggregate surface would, therefore, be exposed to the test compounds.

IGLC data for 4 asphalts and 4 aggregates from the FHWA cooperative study are shown in Table 2. Also included in the table are surface areas of the aggregates and water-stripping data obtained by FHWA by using the ASTM D 1664 procedure modified by changing the immersion temperature to 100 F (311 K). In spite of the complexity of the IGLC data, some general differences between asphalts and aggregates are apparent.

Upon oxidation of the asphalts, interactions of oxidation products with the aggregates become apparent when data on Fluoropak are compared with data on aggregates; this is

Table 1. Specific interaction coefficients for unoxidized and oxidized Wilmington asphalt fractions on Fluoropak 80, quartzite, and limestone.

| Asphalt Fraction | Percent of Total[a] | Specific Interaction Coefficient | | | | | |
| | | Propionic Acid | | Phenol | | 2-Methylpyridine | |
		Unoxidized	Oxidized	Unoxidized	Oxidized	Unoxidized	Oxidized
Saturates	23.3						
On Fluoropak 80		16	15	65	67	44	43
On quartzite		45	68	80	118	61	89
On limestone		—[b]	—[b]	—[b]	93	—[b]	62
Aromatics	31.0						
On Fluoropak 80		59	78	118	143	64	67
On quartzite		90	105	141	171	87	103
On limestone		—[b]	—[b]	183	147	79	77
Polar aromatics	25.0						
On Fluoropak 80		133	133	164	183	84	88
On quartzite		156	163	199	228	103	114
On limestone		—[b]	153	189	207	100	109
Asphaltenes	13.3						
On Fluoropak 80		138	146	166	197	90	95
On quartzite		173	190	193	230	109	123
On limestone		—[b]	—[b]	206	264	120	145

[a]7.4 percent loss during chromatographic separation.   [b]Retention time greater than 150 min or emergence undetectable.

Table 2. Specific interaction coefficients and water-stripping data for FHWA study asphalts on mineral aggregates.

| Aggregate-Asphalt System | Specific Interaction Coefficient | | | | | | Stripping Test (percent stripped) | Surface Area (m²/g) |
| | Propionic Acid | | Phenol | | 2-Methylpyridine | | | |
	Unoxidized	Oxidized	Unoxidized	Oxidized	Unoxidized	Oxidized		
Fluoropak 80								—
Asphalt B-2959	61	95	107	158	63	91	—	
Asphalt B-3036	57	90	104	152	63	76	—	
Asphalt B-3051	85	108	129	170	68	90	—	
Asphalt B-3602	—[a]	148	137	146	69	72	—	
Quartzite "15"								0.515
Asphalt B-2959	92	104	144	171	82	97	40	
Asphalt B-3036	84	94	137	168	80	95	80	
Asphalt B-3051	108	113	147	185	88	102	40	
Asphalt B-3602	93	148	158	179	93	97	90	
"Hol" limestone								0.104
Asphalt B-2959	112	113	152	183	82	101	45	
Asphalt B-3036	101	105	143	172	79	84	40	
Asphalt B-3051	—[a]	128	155	192	86	101	20	
Asphalt B-3602	—[a]	164	169	175	87	92	75	
Riverton limestone								1.09
Asphalt B-2959	—[a]	—[a]	—[a]	178	77	85	5	
Asphalt B-3036	—[a]	139	—[a]	191	78	103	5	
Asphalt B-3051	—[a]	152	163	206	99	111	10	
Asphalt B-3602	—[a]	160	157	173	86	90	20	
Granite "P-6"								0.561
Asphalt B-2959	—[a]	113	140	178	90	120	1	
Asphalt B-3036	—[a]	106	134	176	88	99	8	
Asphalt B-3051	—[a]	110	144	187	86	106	0	
Asphalt B-3602	—[a]	123	151	172	89	94	5	

[a]Retention time greater than 150 min or emergence undetectable.

indicated by generally greater increases in I_gs for asphalts oxidized on Fluoropak than for asphalts oxidized on aggregates. In some cases, such as propionic acid on limestone columns, I_gs were actually lower on oxidized columns than on unoxidized columns, which indicates considerable interaction of the oxidation products with the aggregate surface thus reducing the interaction of the asphalt and aggregate functions with the test compounds.

A significant observation relating water-stripping resistance to asphalt-aggregate interactions can be made by comparing the changes in the I_gs for propionic acid to the stripping resistance of road mixes made from the corresponding materials. For example, the I_gs on all asphalts increase with oxidation on quartzite "15," indicating a minimum interaction of the oxidation products with the aggregate surface; the asphalts when coated on quartzite "15" are also readily stripped in the stripping test. On the other hand, propionic acid did not emerge from any unoxidized asphalt columns on granite "P-6" although after oxidation the propionic acid I_gs were as low as, or lower than, the corresponding I_gs on any other aggregate except for 2 asphalts on quartzite "15." This indicates considerable interaction of the oxidation products with the granite "P-6"; the asphalt-granite "P-6" mixes were also those most resistant to water stripping. Mixes made with "Hol" and Riverton limestones showed interactions of oxidation products with the aggregates and stripping resistances in between those for quartzite "15" and granite "P-6" mixes; the Riverton limestone was more resistant to stripping and showed greater interactions with the asphalts than did the "Hol" limestone.

Unlike the rest of the asphalts, asphalt B-3602 showed a decrease in the propionic acid I_g on oxidation on Fluoropak. Independent studies showed that this asphalt contained an excess of strong base (possibly alkali) and the carboxylic acids present were carboxylate ions. Oxidation either destroyed much of the base or produced functional types that consumed it, thus reducing interaction with the acidic test compound and restoring free acid in the asphalt. Whether the basic nature of the asphalt is related to its comparatively lower resistance to stripping is unknown.

Analyses of Chemical Types Strongly Adsorbed on Aggregate Surfaces

Chemical groups involved in the asphalt-aggregate interactions were identified and quantitatively determined in a study of 10 asphalts recovered from 11- to 13-year-old road pavements. Ketones, carboxylic acids, and dicarboxylic anhydrides were identified and quantitatively determined in material that was strongly adsorbed by the aggregates. The strongly adsorbed material (although not isolated) is defined as that not desorbed from the aggregate with benzene but desorbed with a 4:1 benzene-ethanol mixture. (All of the benzene-alcohol-recovered asphalts were soluble in benzene when separated from the aggregate.) Quantitative results were calculated by using data on independent sets of samples recovered with benzene and with benzene-alcohol; thus the data on the strongly adsorbed material were calculated from the differences in the 2 sets of samples.

The concentrations of the ketones, dicarboxylic anhydrides, and carboxylic acids in the recovered asphalts and estimates of the amounts of these chemical types in the strongly adsorbed material are given in Table 3. The amounts of these functional types present in the recovered samples vary from one asphalt to another. Except for small amounts of carboxylic acid initially present, this variation is primarily a result of the oxidation that took place in the asphalt during construction and service in the roads.

The amounts of functional types are 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 because of the compounding of several factors such as

1. Total ketones in the recovered samples are determined by difference after determination of acids and anhydrides;
2. Amounts of ketones strongly adsorbed are small relative to the total amount; and

3. Strongly adsorbed ketones are estimated by the difference between the asphalts recovered with benzene-alcohol and benzene only.

Although results for the individual road cores may vary, it is believed that the average value reported for the 10 road core extracts is typical. Even though the estimates of the strongly adsorbed anhydrides and acids are determined by difference, individual estimates are inherently more reliable because they are determined directly, and the relative amounts of the total functional type that is strongly adsorbed are 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 given in the table for the individual determinations does not necessarily represent accuracy but is carried for computation of averages.

Calculated data on the ketones, dicarboxylic anhydrides, and carboxylic acids strongly adsorbed from the asphalts by the aggregates are given in Table 4. 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, the most weakly adsorbed materials, was 1.9. Dicarboxylic anhydrides were next in their affinity for the aggregate surface. The average concentration factor in strongly adsorbed material was 9.5. Carboxylic acids, the most strongly adsorbed, had an average concentration factor of 14.

Data in Table 4 show that although ketones were the most weakly adsorbed, they represented an estimated 61 percent of the strongly adsorbed material because of their great abundance. Anhydrides and acids accounted for a total of 13 and 10 percent respectively of the strongly adsorbed materials. 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 ketones, anhydrides, and acids. The 2 individual estimates that are greater than 100 percent probably reflect inaccuracies in the assumptions—most likely, that no more than 1 functional group is produced on an individual molecule on oxidation.

Physical Measurements of Multilayer Adsorption of Asphalt Molecules

Considerable evidence has been collected in our laboratory supporting the thesis that many thousands of molecular layers of asphalt molecules are adsorbed on mineral surfaces (4, 12, 13). Only a summary of the findings dealing with this phenomenon, known as multilayer adsorption, will be presented here.

We first studied multilayer adsorption of asphalt by immersing -35+48-mesh aggregate particles in melted asphalt in a specially built differential microcalorimeter (4) to measure the energy released from interactions between the asphalt and aggregate as a function of time. The data are collected as a curve on a strip-chart recorder. Immersion curves (4) characteristically have an initial peak believed to be largely representative of the initial interactions of asphalt with the aggregate surface, followed by a long tail that remains nearly constant for hours or days. This tail on the curve is believed to represent energy released from multilayer adsorption or molecular orientation of asphalt molecules in the asphalt-aggregate interface region. The amounts of energy released in the heat-of-immersion studies are orders of magnitude greater than normal heats of wetting and can only be explained by a chemical reaction or by a continuous adsorption process. Arguments leading to the conclusion that heats of immersion are primarily a manifestation of multilayer adsorption rather than chemical reaction have been considered previously (4, 11, 12).

Heats of immersion have been determined on a number of different asphalt-aggregate systems at 130 and 150 C (403 and 432 K). Peak heights of the immersion curves were typically in the range of 2 to 15 mcal/g·min. Tail heights after 3 hours were 0.2 to 1.5 mcal/g·min. Values obtained on differing asphalt-aggregate systems were quite different from each other. Immersion energy at 150 C (423 K) may be either higher or lower than that at 130 C (403 K), depending on the particular asphalt-aggregate

Table 3. Concentrations of ketones, dicarboxylic anhydrides, and carboxylic acids in asphalts recovered from 11- to 13-year-old FHWA study road cores.

| Asphalt Number | Strongly Adsorbed Asphalt (weight percent of total)[a] | Concentration (mol · 1^{-1} × 10^{-2}) | | | | | | Strongly Adsorbed Functional Type (percent of total)[d] | | |
| | | Nonacid Carbonyls as Ketones | | Dicarboxylic Anhydrides | | Carboxylic Acids | | | | |
		B[b]	BA[c]	B	BA	B	BA	Ketones	Anhydrides	Acids
19	2.0	51.9	52.5	1.6	1.8	2.1	2.5	3.12	12.9	17.7
25	3.9	50.8	52.5	1.8	2.2	0.9	1.6	7.0	21.3	46.0
30	3.5	63.3	64.2	2.9	3.8	0.9	1.6	4.86	26.3	45.7
61	1.4	45.3	44.1	0.8	2.0	0.4	0.7	-1.28	60.5	43.7
67	2.3	30.9	31.5	0.6	1.0	0.4	0.5	4.17	41.4	21.8
71	3.7	49.8	51.0	1.8	2.2	0.2	0.4	5.96	21.2	51.9
72	3.4	64.5	67.5	2.5	2.9	0.4	0.7	7.7	16.7	44.8
73	3.0	33.3	35.3	0.7	1.1	0.2	0.4	8.5	38.5	51.5
74	4.3	40.5	42.6	1.2	1.7	0.2	0.7	9.03	32.4	72.6
166	1.2	21.3	22.5	0.8	0.9	0.5	1.0	6.47	12.2	50.6
Average	2.87	45.16	46.37	1.47	1.96	0.62	1.01	5.40	27.1	40.5

[a]Calculated from differences between total amounts desorbed with benzene and with benzene-alcohol.
[b]Concentration (mol/litre) of functional type in benzene extract.
[c]Concentration (mol/litre) of functional type in benzene-alcohol extract.
[d]Not desorbed with benzene but with a 4:1 mixture of benzene, 95 percent ethanol.

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

| Asphalt Number | Estimated Concentration Factor of Strongly Adsorbed Material[a] | | | Strongly Adsorbed Material (percent of total adsorbed)[b] | | | Sum of Strongly Adsorbed Materials[bc] |
	Ketones	Anhydrides	Acids	Ketones	Anhydrides	Acids	
19	1.56	6.45	8.85	57.5	8.1	6.5	72
25	1.79	5.47	11.8	66.2	8.4	13.2	88
30	1.39	7.52	13.1	62.3	20.0	14.6	97
61	-0.92	43.1	31.2	-28.6	60.5	15.3	47
67	1.81	18.0	9.5	40.0	12.6	33.3	86
71	1.61	5.73	14.0	57.3	8.8	3.9	70
72	2.26	4.91	13.2	107	10.0	6.5	123
73	2.83	12.8	17.2	70.0	9.8	4.8	85
74	2.10	7.55	16.9	62.5	9.0	8.3	80
166	5.38	10.1	42.2	85.0	6.4	29.5	121
Average[d]	1.88	9.46	14.1	61.0	13.0	9.9	84

[a]Percent of functional type in strongly adsorbed material divided by percent of total asphalt in same fraction (compare Table 3).
[b]Calculated by assuming monofunctional molecules and a molecular weight of 700.
[c]Values are presented as percent of total strongly adsorbed asphalt.
[d]Calculations based on averages of concentrations (compare Table 3).

system. This apparent contradiction can be explained by considering the processes involved in multilayer adsorption. The rate of migration of molecules to adsorption sites is diffusion- (viscosity-) controlled and increases with temperature; but, in a reversible adsorption process, the tendency of the molecules to be adsorbed after collision with the adsorption sites is reduced with increasing temperature. The temperature dependence of the total adsorption process is therefore a net result of these 2 opposing effects.

Adding 1 percent Redicote 80S (an antistripping agent) to the asphalt before determining the heat of immersion greatly increased the immersion energy of some asphalt-aggregate systems, particularly that represented by the tail of the immersion curve. Treatment of the aggregate surface with silylating reagents or with diazomethane apparently inhibited multilayer adsorption because it caused a complete loss of the tail of the immersion curve.

Of particular significance is the apparent slow rate of the proposed multilayer adsorption process. Heat-of-immersion data suggest that this goes on for several days at the test temperatures. The slow rate of the asphalt molecular association reactions also has been demonstrated in independent microcalorimetric studies without aggregate. Reversible interactions of the order of 1 to 2 cal/g have been shown to take place in asphalt (12); these interactions take hours to reach equilibrium at 150 C (423 K). The slow nature of the interactions is undoubtedly influenced by viscosity and the complexity of the system. Asphalt is a complex mixture of many structurally different molecules, and the concentration of any one is extremely low. Association reactions are specific for molecular type and orientation; therefore the probability of a molecular collision in asphalt resulting in an association reaction is low.

Additional evidence for multilayer adsorption was obtained from FTPM experiments (13). For example, when filtered asphalt B-3036 containing 1 percent of the antistripping agent Redicote 80S was flowed at constant static pressure through a bed of -100+150-mesh phosphate slag at 130 C (403 K) in a nitrogen atmosphere, the flow rate decreased in a regular fashion. After 9 days the flow rate decreased from 6.1×10^{-3} g/min to 0.33×10^{-3} g/min, indicating that the "free" volume through which the asphalt could flow was reduced from its initial 45 percent to 5 percent. Thus it appears that asphalt molecules gradually build up on the surface of the aggregate in an immobilized layer to restrict the normal flow through the plug. The calculated buildup rate was 17.5 ± 1.5 Å/min. Assuming molecular interactions in the adsorption process on the order of a fraction of a calorie per mole, the buildup rate is consistent with the energy released in heat-of-immersion studies.

The immobilized asphalt material in the plug from the FTPM experiment was dissolved from the aggregate with carbon tetrachloride. The recovered material was analyzed by infrared spectroscopy and found to be essentially identical to the original asphalt. No significant concentration of antistripping agent was found in the material from the plug. Molecular weight determinations by vapor pressure osmometry in benzene of the material from the plug and the original asphalt were 910 and 876 respectively. Thus it appears that although the asphalt was immobilized in the plug it was not significantly fractionated or altered chemically.

A general correlation exists between the data from the heat-of-immersion and FTPM studies. For example, in a number of different systems the heat-of-immersion energy and the decrease in flow rate in FTPM experiments were both greater when the antistripping agent was added to the asphalt. Also, in a model FTPM study, the flow of asphalt B-3036 through a laboratory adsorbent of bauxite ($Al_2O_3 \cdot 2H_2O$) nearly ceased in an unusually short time—5 hours at 130 C (403 K)—indicating that 95 percent of the void space had closed off; the calculated buildup rate of the immobilized layer was about 3000 Å/min. Heat-of-immersion experiments on this system showed peak and tail heights of 264 and 3.6 mcal/g· min respectively, much greater than for normal aggregates.

Recently, both optical and scanning-electron photomicroscopy provided evidence of molecular orientation of asphalt on mineral surfaces (13). Oriented layers were prepared by heating $\frac{1}{8}$ to $\frac{1}{4}$ in. of asphalt in an aluminum dish under nitrogen atmosphere for 10 to 14 days at 130 or 150 C (403 or 423 K). The aluminum surface may be replaced

by mica, calcite, or some other mineral by placing a smooth wafer of the mineral in the bottom of the dish before adding asphalt. After heating for the extended period, the samples were rapidly cooled and fractured perpendicular to the surface that was previously in contact with the bottom of the pan. Microscopy showed a striated region with sharply defined boundaries emanating from and perpendicular to the surface initially in contact with the mineral. A general correlation was found between the thickness of the striated regions and the buildup rate of the immobilized layers calculated from FTPM experiments. For example, when Asphalt B-3036 containing 1 percent Redicote 80S was heated on a mica surface for 2 weeks at 130 C (403 K), cooled, and fractured, a striated region 0.04 mm thick was observed. The calculated buildup rate was 24 Å/min, which is of the same order of magnitude as the buildup rate calculated from FTPM.

POSSIBLE SIGNIFICANCE TO ASPHALT PAVING TECHNOLOGY

One might speculate on the significance of the work reported in this paper to asphalt paving technology. The IGLC and chemical identification work showed that products of oxidation in asphalt interact with aggregate surfaces and that different aggregates have quite different responses. Because considerable oxidation of asphalt occurs in a hot-mix plant and while a road is being laid, 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 interface region appears to take place very slowly—even near plant-mix temperatures, 130 to 150 C (403 to 423 K). 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 before asphalt lay-down should be investigated.

Any immobilization of asphalt in the asphalt-aggregate interface region after the road has been compacted should increase the bonding strength or friction at the points of contact between aggregate particles, which 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 possible relationship between the data presented in this paper, which suggest that certain antistripping agents affect the rate of multilayer adsorption of asphalt molecules, and data reported from field observations, which suggest that antistripping agents often alter mix characteristics, might well be studied.

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