

Effect of Aggregate Chemistry and Modification on Moisture Sensitivity

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The effects of aggregate chemistry and modification of that chemistry by organosilane coupling agents were examined by using a variety of adsorption and desorption methods. The combination of adsorption and desorption as in the net adsorption test offers a means of predicting adhesion propensity and water resistance of aggregates. Changing the aggregate surface by bonding a chemical species to it, such as a hydrocarbon or amino group, can radically change the adsorptive behavior of aggregates. The aggregate surfaces of two asphalt model compounds, benzoic acid and phenanthridine, and an asphalt were modified with organosilane coupling agents, and the effect on their adsorption and desorption behavior was investigated. Organosilane coupling agents—hydrocarbon silane of C₈ chain length, thiol silane, and amino silane—were used to modify the surface of aggregates composed of limestone and gravel. The adsorption and desorption behavior of selected asphalt model compounds and AAD-1 asphalt was determined on the modified aggregates and compared with that obtained on natural aggregates. This comparison has been reported as the percent change in the water sensitivity between asphalt and aggregate. Each asphalt model compound or asphalt-aggregate combination was observed to present highly specific behavior that was dependent on the chemistry of the compound or asphalt as well as on the chemistry of the silane coupling agent.

Asphalt-aggregate interactions are important for the adhesion of asphalt to aggregate because the initial layers of asphalt must adhere sufficiently to the aggregate surface for the binding of asphalt to occur. An asphalt-aggregate mix is composed of 94 to 95 weight percent aggregate and 5 to 6 weight percent asphalt. The aggregate is present in a multiplicity of sizes ranging from a fraction larger than $\frac{3}{4}$ in. to fines that are -200 mesh. Aggregates used for road pavements typically come from local sources and vary widely in terms of composition, surface chemistry, and morphology. When asphalt contacts aggregate, the asphalt molecules interact with a variety of active and inactive sites on the aggregate surface for binding. The asphalt directly in contact with the aggregate is important because asphalt must adhere and remain adherent under different stresses. However, the asphalt that lies between the aggregate particles serves a major cohesive role for the asphalt-aggregate mix by binding the particles together and maintaining the integrity of the mix. Many different stresses bombard an asphalt pavement daily. These stresses include shear and tensile forces, the vibration and wear of traffic, changes in daily and seasonal temperatures, the radiation of

actinic light, and the attritional force of water. Water is an insidious force that penetrates the asphalt medium and competes for the aggregate surface. Water can then change the environment of the mix from an organic medium absorbed onto a solid to a system that resembles an emulsion in which asphalt and water are mixed and compete for the aggregate surface. Water can also have a deleterious effect on the aggregate, causing it to slough off outer layers of water-soluble minerals. This cohesive failure within the aggregate leaves the aggregate surface bare and nonadherent. Once the integrity of the asphalt-aggregate bond is broken, restoration of that bond is difficult if not impossible.

EVALUATION OF ASPHALT-AGGREGATE INTERACTIONS

The objective of the research presented in this paper was to evaluate the effect of asphalt-aggregate interactions on adhesion. Central to this objective was to examine the effect of water on adhesion. The strong influence that aggregate chemistry and morphology have on establishing and maintaining the adhesive bond between asphalt and aggregate became apparent in this investigation. The different research aspects that elucidate the key role of aggregate chemistry in adhesion and how modification of that aggregate chemistry can either enhance or deter the resistance of the asphalt-aggregate bond to water are described. Once the role that aggregates play in adhesion in the presence of water is thoroughly understood, modification of the aggregate can be tailored to address the specific chemical requirements for maintenance of that adhesion.

A methodology for adsorption of asphalt or asphalt components on aggregate followed by desorption with water was previously developed to characterize the interaction of the aggregate surface with asphalt in the presence and absence of water (1). This methodology allowed investigation of a number of parameters that directly influenced asphalt-aggregate interactions: the interaction of compounds containing specific functional groups with aggregates (2); the competition of different chemical functional groups, such as carboxylic acids, nitrogen bases, or phenols, for active sites (3); the effect of changing the aggregate's surface chemistry by coating the surface with different chemical species (4); the adsorption and desorption behavior of three asphalts with a series of 11 aggregates of vastly different bulk composition (5); and modification of the aggregate surface with organo-

silane coupling agents and their subsequent effect on the adsorption and desorption behavior of the aggregate. Organosilane coupling agents were chosen for study because of their reported ability to increase the adhesion between asphalt and aggregate (6,7).

A question always arises about the correct methodology for evaluating asphalt-aggregate interactions. Laboratory methods should be chosen to simulate as closely as possible the actual phenomenon under typical field conditions. Most laboratory methods cannot fully represent field conditions, so it is necessary to focus on testing the particular phenomenon essential to the process. In adhesion, the primary requirement is that asphalt adsorb onto aggregate for adhesion to occur. For maintenance of adhesion, the asphalt must be retained on the aggregate surface under conditions of stress, in this case under wet or moist conditions. Adsorbing from solution allows asphalt molecules to be free moving, disassociated, and able to contact the aggregate; this state is similar to the freedom of movement afforded to asphalt molecules at high temperature. Desorption by water places the adsorbed asphalt in a similar condition as when water percolates through the pavement mix and penetrates to the asphalt-aggregate interface, affecting the interaction between asphalt and aggregate.

METHODOLOGY OF ADSORPTION AND DESORPTION

Two primary methods were employed to measure the adsorption of asphalt and desorption of adsorbed components by water: a batch equilibrium method (2) and a continuous recirculating method (8). In both methods, the amounts of adsorbed and desorbed material were determined.

The batch equilibrium method in which asphalt or asphalt components were adsorbed onto the surface of aggregate was performed by introducing the asphaltic material at a given concentration in either a cyclohexane or toluene solution (2). The adsorption amounts on different aggregates obtained under equivalent conditions were then compared. Desorption with water was performed using aggregate that contained substantial amounts of asphaltic material adsorbed on its surface. Water was introduced in the desorption step in an amount equivalent to the organic solvent used in the adsorption. The amount of asphalt or asphalt components desorbed was measured in both the organic and aqueous phases.

The continuous recirculating method allowed a toluene solution of asphalt to flow over a bed of aggregate (8). Asphalt solutions of different concentration levels were allowed to circulate until the adsorption of asphalt onto the aggregate surface reached an equilibrium value. The amount of asphalt adsorbed was measured. Then a small amount of water, ~280 mmolar, was added to the solution. The solution was circulated over the aggregate bed until desorption equilibrium was achieved; at that time the amount of asphalt desorbed from the aggregate was determined. The difference between the amount initially adsorbed and that desorbed was the amount remaining on the aggregate surface, which was termed the net adsorption. This latter method was subsequently developed into the net adsorption test (5).

Adsorptive Behavior of Aggregate

The adsorption and desorption methodology provides a means to measure and characterize the adsorptive capacity and water resistance of different aggregates. Model compounds, containing functional groups of differing polarity but representative of those in asphalt (9,10), were used to evaluate the behavior of the different constituents (1). These model compounds were adsorbed onto the surface of the aggregate, and the adsorbed material that was susceptible to water was desorbed. Adsorption tests involving model compounds gave the following adsorption ranking averaged over a series of aggregates, including granites, limestones, gravels, and a greywacke: phenylsulfoxide > benzoic acid > phenanthridine > 1-naphthol > fluorenone > indole > pyrene > naphthalene. Although the amount of adsorption varied according to the type and characteristics of the specific aggregate, the adsorption of polar model compounds was much greater than the less polar and nonpolar compounds on each aggregate. The more polar model compounds such as those containing carboxylic acid or sulfoxide functional groups were also the most susceptible to water and desorbed readily. By contrast, the compounds containing functional groups of phenols or nitrogen bases were more able to withstand the presence of water and remain on the surface of the aggregate.

The aggregate surface contains a multiplicity of sites, some of which are more active and polar than others. Competition among the different compound types occurs for these active sites, but the driving force and chemical attraction of the widely varying molecules to the active sites are different. The chemical components with the strongest affinity for a particular site compete most effectively and win a position on the site. Adsorption of model species indicates for a grouping of compounds with the functional groups of carboxylic acids, phenolics, nitrogen bases, and sulfoxides that the following ranking occurs: phenylsulfoxide > phenanthridine \equiv benzoic acid > naphthol (3).

Modification of the aggregate surface changes the surface chemistry and hence the adsorption and desorption behavior of the aggregate. An illustrative set of experiments was performed using silicas and coated silica that demonstrated the sensitivity of adsorption to surface chemistry of the aggregate (1,4). Model compounds containing a variety of functional groups were adsorbed onto silica and silica coated with C₈ and C₁₈ hydrocarbons or with polyethyleneimine, which contains primary, secondary, and tertiary amine groups. The adsorption and desorption behavior of the model compounds varied considerably depending on the surface coating. For example, all of the model compounds adsorbed strongly on the uncoated silica, whereas the C₈ and C₁₈ hydrocarbons completely masked the surface, not allowing any adsorption of any model compound; the basic surface of the amine-coated aggregate only adsorbed the more acidic compounds and completely repelled the nonacidic model compounds.

Net Adsorption Test

The net adsorption test provides a quantitative measure of the affinity and water sensitivity of asphalt-aggregate pairs. This test measures the amount of asphalt remaining on the

aggregate surface after asphalt has first been adsorbed and then desorbed by water (5). Testing 11 different aggregates from the Strategic Highway Research Program (SHRP) with three different asphalts clearly showed that the net adsorption was strongly dependent on the aggregate surface composition. For example, when SHRP asphalt AAD-1 was adsorbed on the SHRP aggregates, the amount of asphalt adsorbed varied over an order of magnitude, as shown in Figure 1. These same adsorption ranges were observed for AAK-1 and AAM-1 asphalts. For some asphalt-aggregate pairs, half or more of the initial amount of adsorbed asphalt could be desorbed into toluene solution containing only a very small amount of water, whereas some asphalt-aggregate pairs showed little water sensitivity. The aggregates, which showed substantial water sensitivity, also were more sensitive to the asphalt chemistry in both the adsorption and desorption process.

Aggregate Modification: Organosilanes as Bonding Promoters

The research described in detail here is an evaluation of the effect of aggregate modification by organosilane coupling agents. The overall objective of this research was to evaluate the potential of selected organosilanes for inhibiting and preventing removal of asphalt from aggregates in asphalt pavements by changing the aggregate chemistry. In order to examine the effect of silane treatments on asphalt-aggregate pairs, the adsorption and desorption behavior of two selected asphalt models in combination with selected natural aggregates was evaluated. AAD-1 asphalt was also adsorbed and desorbed from natural aggregate. Three organosilane coupling agents were used to treat the natural aggregates. The asphalt model compounds and the asphalt were tested for their adsorption and desorption in order to evaluate the effect

of these silane treatments in inhibiting the deleterious effects of water on the adhesive bond in asphalt pavements.

EXPERIMENTAL

Materials

Benzoic acid and phenanthridine were purchased from Aldrich with purities of 99+ percent and used as received. AAD-1 asphalt was obtained from the SHRP Materials Reference Library (MRL) at the University of Texas, Austin, and used as received. Chemical and physical characteristics of the asphalt are presented in Table 1. Aggregates—RC-limestone, RJ-gravel, and RL-gravel—were also obtained from MRL. The chemical and physical properties of the aggregates are given in Table 2. Spectroanalyzed solvents, cyclohexane and toluene, were obtained from Fisher Scientific and used for dissolution of asphalt model compounds and asphalt, respectively. Each solvent was dried before use with activated 4A molecular sieves. Three organosilanes—3-mercaptopropyltrimethoxysilane (thiol), *n*-octyltrichlorosilane (C_8), and a proprietary water-stable amino silane (amino), purchased from Petrarch Systems, Bristol, Pennsylvania, were used as received.

Preparation of Organosilane Aggregate

RC-limestone, RJ-gravel, and RL-gravel were used in all investigations. Aggregates were sized to -40+80 mesh; washed thoroughly with distilled, deionized water to remove fines; dried in an oven at 110°C for 7 days; and stored in dark glass containers. Aggregates were dried for an additional 24 hr just before adsorption and desorption testing or organosilane pre-

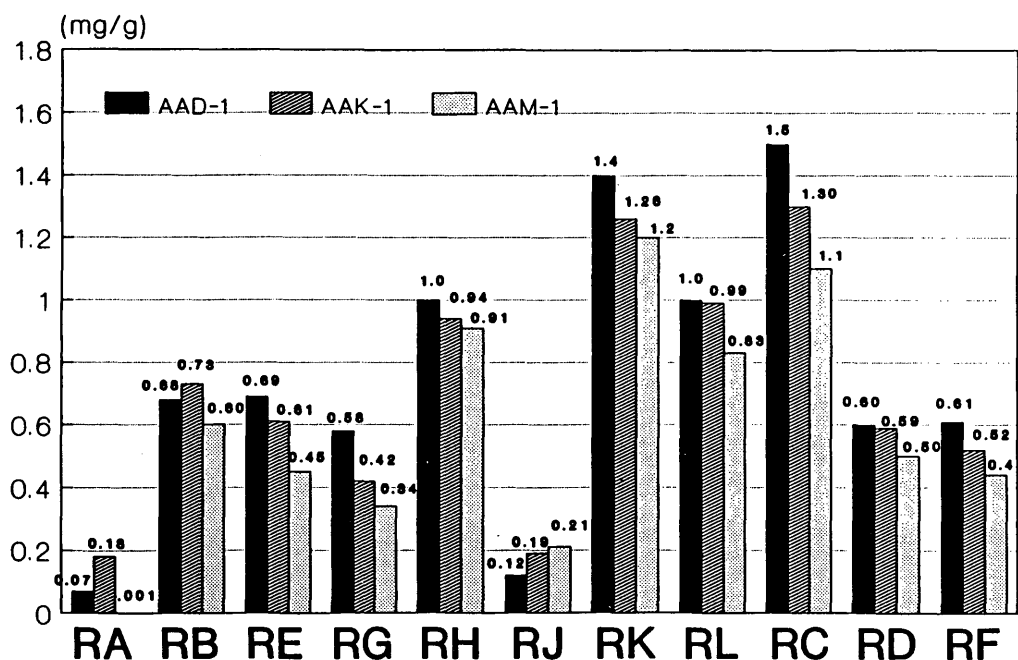


FIGURE 1 Net adsorption of asphalts on MRL aggregates.

TABLE 1 Physical and Chemical Properties of AAD-1 Asphalt

140°F, Viscosity Poise		1055	
275°, cst		309	
Elemental Analysis		Functional Group Analysis by IR	
Carbon, %	81.6	Carboxylic Acids	0.011
Hydrogen, %	10.8	Acid Salts	0.000
Oxygen, %	0.9	Acid Anhydrides	0.000
Nitrogen, %	0.9	Quinolones	0.024
Sulfur, %	8.6	Ketones	trace
Vanadium, ppm	293	Phenols	0.124
Nickel, ppm	145	Sulfoxides	trace
C _{aromatic} , %	23.7	Pyrroles	0.168
H _{aromatic} , %	6.8		

Data supplied by SHRP A-001, University of Texas, are internal SHRP analyses for MRL asphalts. They are intended for comparison only.

TABLE 2 Physical and Chemical Properties of Aggregates

Property	Aggregates		
	RC	RJ	RL
POROSITY ^a			
Avg. Pore Diam. (μm)	0.0611	0.0151	0.0138
Total Pore Area (m ² /g)	2.546	1.888	3.027
WATER ABSORPTION ^a			
% Absorption	0.37	0.7	0.9
BULK SPECIFIC GRAVITY ^a	2.536	2.625	2.568
ACID INSOLUBLES ^a			
Insoluble Residue %	4.8	99.2	88.2
WATER INSOLUBLES ^a			
Water solubles %	2.4	4.1	1.8
pH	9.47	9.12	9.18
SURFACE AREA (m ² /g) ^{b,c}	1.79	0.37	0.93
MAJOR OXIDES ^b			63.1
SiO ₂ , %	6.49	76.5	4.66
Al ₂ O ₃ , %	1.23	12.2	1.67
Fe ₂ O ₃ , %	0.78	1.09	0.32
MgO, %	2.52	0.27	14.5
CaO, %	48.9	1.45	0.92
Na ₂ O, %	0.24	2.91	1.72
K ₂ O, %	0.22	4.31	<0.2
Other, %	<0.2	<0.2	11.2
Loss of Volatiles, %	40.3	0.59	
Lithology ^b	100% limestone	59.1% Chert 18.2% Limestone 11% Granite 5.8% Basalt	98.6% Granite 1.4% Basalt

^a Porosity, water absorption, bulk specific gravity, acid insolubles and water insoluble data were obtained from SHRP A-001.

^b Surface areas and major oxides were obtained from Western Research Institute in SHRP A-003B.

^c Surface area measurements were obtained by N₂ BET by WRI.

treatment. Organosilane treatment consisted of contacting the aggregate with 100 ml of 1 percent by volume silane solution for 3 min, followed by gravity filtration, and subsequently curing in a vacuum oven at 70°C for 48 hr. The solvent used for the hydrocarbon silane solution was 95:5 ethanol/water by volume, and the thiol silane was prepared using water adjusted to pH 4.5 with acetic acid. The amino silane was prepared as a water-stable solution by the manufacturer and required dilution with distilled, deionized water before use.

Adsorption and Desorption Experiments

The experimental setup for adsorption and desorption experiments for the different asphalt model and aggregate combinations was identical. Four samples of each asphalt model and aggregate combination were prepared for analysis, two for adsorption and two for desorption testing. For each sample, 3.0000 ± 0.0005 g of aggregate was weighed, recorded, and placed into a 60-ml serum bottle. Exactly 20 ml of cyclohexane solution containing 100 mg/L of asphalt model was added to each serum bottle before sealing with Teflon-lined aluminum caps. The samples were agitated for 1 hr in an orbital shaker (Labline, Fisher Scientific) with temperature controlled at 25°C and then allowed to settle overnight. Agitation was repeated for 1 hr the next day, followed by 1 hr of settling. Two samples were filtered through a 0.22- μ m filter and analyzed by ultraviolet-visible spectroscopy at the wavelength of maximum absorbance. The concentration of adsorbate remaining in solution after the experiment was determined and the amount of adsorbate adsorbed onto the aggregate was calculated as reported previously (2,8). Benzoic acid and phenanthridine were analyzed at 274 and 270 nm, respectively. The adsorption of asphalt was performed in the same manner except that asphalt solutions, 100 ppm, were prepared in toluene and analyzed at 283 and 450 nm.

The desorption experiments for both the asphalt models and the asphalt were conducted similarly; the procedure has been reported previously (2). Upon completion of the adsorption test, 20 ml of water was introduced at an equivalent volume to the organic solution in each of the two remaining adsorption samples. Both the organic and aqueous phases were monitored for the desorbed material after 48 hr. Increases in the amount of model component or asphalt present in the aqueous and organic solvents after desorption equilibrium had been established were summed and reported as the amount of material desorbed. All data reported here used the experimental average of two experiments. The amount of adsorbed material was calculated for each system after adsorption and desorption testing. The difference in the amount of material obtained from the adsorption test and after the desorption experiment was reported as the amount of material desorbed. Comparison of the amount of material desorbed to the amount of material adsorbed initially in the adsorption experiment was reported as the percent change in desorption. Comparison of the percent change in desorption mass of asphalt model compounds and asphalt observed for natural aggregates to the percent change determined on the same aggregate treated with organosilane was reported as percent change in water sensitivity caused by silane treatment.

Standard deviations for replicate samples were determined and reported for all adsorption and desorption data. The relative error was reported for all percent desorptions, and the propagated error was reported for the percent change in water sensitivity for the various asphalt model compound and asphalt-aggregate combinations.

RESULTS AND DISCUSSION

Two asphalt model compounds, benzoic acid and phenanthridine, were adsorbed from cyclohexane onto three natural aggregates. Each model compound was chosen to represent chemical functional groups that have previously been reported to be present at the asphalt-aggregate interface (9,10). Acidic and basic functional groups were represented by benzoic acid and phenanthridine, respectively. Each model exhibited absorbance characteristics in the same region as asphalt and was tested for adsorption and desorption on each of the selected aggregates.

Three aggregates were chosen from the MRL for all investigations. RC-limestone, RJ-gravel, and RL-gravel were selected because of their different chemical compositions and lithologies (Table 2). RL-gravel is a granite and highly siliceous, RC-limestone is 100 percent limestone, and RJ-gravel contained granite, limestone, chert, and basalt but was primarily siliceous. The differences in aggregate chemical and physical properties directly influenced the adsorption and desorption behavior of each adsorbent.

The physical and chemical properties of AAD-1 asphalt, which was chosen for these investigations, are presented in Table 1. AAD-1 had a viscosity corresponding to an AR4000 and an average molecular weight of 700. Infrared functional group analysis of AAD-1 indicated the presence of carboxylic acids, quinolones, phenols, and pyrroles. Additional chemical information on AAD-1 asphalt was provided by SHRP A-001, University of Texas, with ion exchange and component analyses. Component analysis of AAD-1 indicated the following percentage contents: asphaltene, 23; polar aromatics, 41.3; naphthene aromatics, 25.1; and saturates, 8.6. Ion exchange chromatographic analysis of AAD-1 indicated that this asphalt consisted of 26.1 percent strong acids, 7.8 percent strong bases, 7.8 percent weak acids, 5.5 percent weak bases, and 51.7 percent neutrals.

The results of the investigation into the adsorption and desorption of the two asphalt model compounds and the AAD-1 asphalt on natural aggregates and on organosilane-treated aggregates are discussed in the following sections.

Asphalt Model Compounds

On Natural Aggregates

Asphalt model compounds of benzoic acid and phenanthridine were adsorbed from cyclohexane solution onto 3-g samples of natural aggregates and then desorbed by water. The mass of asphalt model compound adsorbed onto and desorbed from all aggregates was determined by ultraviolet-visible spectroscopy at a wavelength of maximum absorbance for the

adsorbing compound. The percent desorption was calculated by determining the difference in adsorbed material obtained from the adsorption and desorption experiments. The adsorption and desorption behavior obtained for each asphalt model in combination with the three selected aggregates is shown in Table 3.

The largest mass of benzoic acid or phenanthridine adsorbed per gram of aggregate occurred on RJ-gravel and the smallest on RC-limestone. Ranking for adsorption mass of these models was RJ-gravel \geq RL-gravel $>$ RC-limestone. Benzoic acid yielded 11 to 16 percent larger adsorption masses, in milligrams of model compound per gram of aggregate, than phenanthridine for all three aggregates. The relative standard

deviation (RSD) for the adsorption experiments on natural aggregates was less than ± 3 percent for all asphalt model and natural aggregate combinations except phenanthridine and RC-limestone, which had an RSD of ± 5 percent (Table 3). RC-limestone produced the largest percent errors in the adsorption measurements.

The effect of water on the asphalt model compounds adsorbed on the natural aggregate is reflected in the percent desorptions recorded in Table 3. Water produced substantial debonding of benzoic acid (54 to 63 percent) and phenanthridine (29 to 54 percent) from each of the natural aggregates tested. Propagated errors for the percent desorption of asphalt models from natural aggregates were usually ± 6 percent.

TABLE 3 Adsorption and Desorption Data for Asphalt Models

Aggregate	Silane Treatment	Initial Amount Adsorbed (mg/g)	Final Amount Adsorbed (mg/g)	Amount Desorbed (mg/g)	Percent Desorbed (%)
Benzoic Acid					
RC-limestone	Natural	0.480 ± 0.006^a	0.221 ± 0.001	0.259 ± 0.001^b	54.0 ± 0.7^c
	Hydrocarbon	0.535 ± 0.001	0.370 ± 0.067	0.165 ± 0.067	30.8 ± 13
	Thiol	0.599 ± 0.000	0.343 ± 0.016	0.256 ± 0.016	42.7 ± 2.7
	Amino	0.496 ± 0.004	0.433 ± 0.006	0.063 ± 0.007	12.7 ± 1.4
RJ-gravel	Natural	0.654 ± 0.001	0.243 ± 0.002	0.411 ± 0.002	62.8 ± 0.3
	Hydrocarbon	0.145 ± 0.002	0.334 ± 0.003	0	+130.3 \pm 3
	Thiol	0.302 ± 0.007	0.356 ± 0.004	0	+17.9 \pm 2.7
	Amino	0.247 ± 0.008	0.386 ± 0.007	0	+56.3 \pm 4.7
RL-gravel	Natural	0.637 ± 0.003	0.297 ± 0.007	0.340 ± 0.007	53.4 ± 1.8
	Hydrocarbon	0.635 ± 0.012	0.362 ± 0.038	0.273 ± 0.040	43.0 ± 6.4
	Thiol	0.616 ± 0.063	0.359 ± 0.054	0.257 ± 0.083	41.7 ± 14.1
	Amino	0.563 ± 0.004	0.397 ± 0.006	0.166 ± 0.007	29.5 ± 1.3
Phenanthridine					
RC-limestone	Natural	0.405 ± 0.020	0.186 ± 0.000	0.219 ± 0.020	54.1 ± 5.6
	Hydrocarbon	0.254 ± 0.001	0.243 ± 0.049	0.011 ± 0.049	$4.3 \pm 19.3^*$
	Thiol	0.408 ± 0.012	0.296 ± 0.006	0.112 ± 0.013	27.5 ± 3.3
	Amino	0.046 ± 0.001	0.059 ± 0.007	0	+28.3 \pm 15.2
RJ-gravel	Natural	0.578 ± 0.003	0.408 ± 0.020	0.170 ± 0.020	29.4 ± 3.5
	Hydrocarbon	0.249 ± 0.001	0.197 ± 0.001	0.052 ± 0.001	20.9 ± 0.4
	Thiol	0.082 ± 0.000	0.082 ± 0.002	0	0
	Amino	0.071 ± 0.007	0.096 ± 0.002	0	+35.2 \pm 10.9
RL-gravel	Natural	0.567 ± 0.007	0.364 ± 0.008	0.203 ± 0.008	35.8 ± 2.0
	Hydrocarbon	0.613 ± 0.017	0.517 ± 0.043	0.096 ± 0.046	15.7 ± 7.5
	Thiol	0.640 ± 0.005	0.370 ± 0.075	0.270 ± 0.075	42.2 ± 11.7
	Amino	0.324 ± 0.004	0.245 ± 0.005	0.079 ± 0.006	24.4 ± 1.9

$$^a \text{ Standard deviation of replicates, } S = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

$$^b \text{ Absolute error, } e_1 = \sqrt{S_1^2 + S_2^2}$$

$$^c \text{ Propagated error in percent, } e_2 = [(\text{Amount Desorbed})/(\text{Amount Adsorbed})] \times 100.$$

* Values were considered insignificant due to large propagated error.

+ Adsorption increased in presence of water. No desorption occurred.

On Organosilane-Treated Aggregates

RC-limestone, RJ-gravel, and RL-gravel, pretreated with organosilanes, were used to study the effect of silane treatment on adsorption of asphalt model compounds and their retention in the presence of water. Three organosilane coupling agents containing different chemical functional groups were investigated: hydrocarbon silane of C_8 chain length, thiol silane, and amino silane. The asphalt model compounds, benzoic acid and phenanthridine, were tested for adsorption and desorption behavior on organosilane-treated aggregates and compared with the behavior obtained on natural aggregates (Table 3).

For all silane treatments of RC-limestone, increased adsorption masses (3 to 25 percent) of benzoic acid were observed. In addition, the percent desorptions ranged from 13 percent \pm 1 percent to 43 percent \pm 3 percent for benzoic acid in combination with all silane treatments of RC-limestone as compared with 54 percent \pm 1 percent desorption of benzoic acid from natural RC-limestone. Silane-treated RL-gravel yielded small decreases (12 percent or less) in adsorbed masses of benzoic acid. Desorption testing of thiol- and hydrocarbon-treated RL-gravel showed approximately 10 percent more retention of benzoic acid than observed for the natural aggregate. Likewise, amino-treated RL-gravel also retained more benzoic acid (23 percent) after desorption testing in comparison with natural aggregate. All silane treatments of RJ-gravel produced substantially decreased adsorption amounts of benzoic acid (54 to 78 percent) relative to the adsorption amount obtained on the natural aggregate. Conversely, the addition of water resulted in increased adsorption (18 percent \pm 3 percent to 130 percent \pm 3 percent), rather than desorption, of benzoic acid onto all silane-treated RJ-gravel in contrast to 63 percent \pm 0 percent desorption observed for natural RJ-gravel aggregate. The observed increased adsorption amounts of benzoic acid in the presence of water may have been caused by one of two factors. First, water may have solubilized aggregate components to leave new bonding sites for benzoic acid. Alternatively, since water is attracted to the aggregate surface rather than the organic solvent medium, water may have hydrogen-bonded to both the aggregate surface and benzoic acid, thus acting as a bridge. Neither situation would suggest durable bonding or an actual decrease in water sensitivity for road pavements.

All silane treatments of RC-limestone aggregate resulted in increased adsorption masses of benzoic acid and decreased sensitivity to water. By contrast, silane treatment of RJ-gravel yielded less adsorption mass of benzoic acid and no desorption in the presence of water. In fact, additional adsorption of benzoic acid occurred in the presence of water. Silane treatments of RL-gravel produced similar adsorption masses to those obtained on natural aggregate and 11 to 23 percent less desorption than natural aggregate.

The adsorption of phenanthridine on organosilane-treated aggregates was affected by the type of silane agent used to pretreat the aggregate, but the effect of the individual agent was different than that for benzoic acid. Hydrocarbon treatment of RC-limestone and RJ-gravel resulted in less phenanthridine adsorption (37 and 57 percent, respectively) than the natural aggregates, whereas for RL-gravel slightly increased adsorption of 8 percent occurred. Hydrocarbon treat-

ment of RJ-gravel resulted in 21 percent desorption of phenanthridine compared with 29 percent \pm 3 percent on the natural aggregate, whereas hydrocarbon-treated RL-gravel showed desorption of 16 percent \pm 8 percent compared with 36 percent \pm 2 percent on natural RL-gravel. Thiol treatment of RC-limestone produced an adsorption mass of phenanthridine similar to that of the natural aggregate. An increase in adsorption mass of phenanthridine (13 percent) was observed for thiol-treated RL-gravel and a substantial decrease (86 percent) for thiol-treated RJ-gravel. Thiol treatment of RJ-gravel prevented desorption of phenanthridine by water in contrast to 29 percent \pm 3 percent desorption observed for natural RJ-gravel. Also, thiol-treated RC-limestone showed 28 percent \pm 3 percent desorption of phenanthridine compared with 54 percent \pm 6 percent desorption for the natural aggregate. Thiol treatment of RL-gravel resulted in greater desorption (42 percent \pm 12 percent) of phenanthridine than was observed for the natural aggregate (36 percent \pm 2 percent). Amino treatment of all aggregates resulted in decreased adsorption amounts (43 to 89 percent) of phenanthridine and increased retention (at least 25 percent) in the presence of water compared with the natural aggregates.

Nearly all the percent error (RSD) for adsorption masses of benzoic acid and phenanthridine in combination with the silane-treated aggregates was less than \pm 5 percent. Propagated error was calculated for desorption measurements and was usually less than \pm 10 percent. A few silane-treated aggregate and asphalt model compound combinations produced propagated error of \pm 11 percent to \pm 19 percent. The largest propagated errors consistently occurred for phenanthridine desorptions.

Asphalt

On Natural Aggregates

MRL Asphalt AAD-1 was adsorbed from toluene solution onto 3 g of silane-treated or natural aggregates, RC-limestone, RJ-gravel, and RL-gravel. The amount of asphalt adsorbed on the treated aggregates was monitored at 283 and 450 nm and compared with asphalt adsorbed onto natural aggregates (Table 4). Asphalt components containing chemical functional groups similar to benzoic acid and phenanthridine absorbed around 283 nm. The 450-nm absorbance region was chosen to monitor those asphalt components, such as the larger organometallic complexes and polynuclear aromatics, that absorbed in the visible region. At adsorption equilibrium, water was added to determine the sensitivity of the adhesive bond to water. The amount of adsorbed asphalt removed from the aggregate surface was reported as the percent desorbed. Most of the asphalt components desorbed in the presence of water, although a few systems showed increased adsorption. Positive signs in Table 4 indicate that asphalt adsorption was increased by water and that no desorption occurred. For most of the adsorption experiments, the RSD for adsorption mass on natural aggregates was less than \pm 5 percent for all combinations, except for the AAD-1 asphalt components adsorbing onto RC-limestone at 450 nm, which had a relative error of \pm 20 percent. Propagated error for desorption measurements for AAD-1 usually was

TABLE 4 Percent AAD-1 Asphalt Desorbed from Natural and Silane-Modified Aggregate

Aggregate	Amount Adsorbed (mg/g)	Amount Adsorbed after Desorption (mg/g)	Amount Desorbed (mg/g)	Percent Desorbed (%)
Natural				
283 nm				
RC-limestone	0.445 ± 0.007 ^a	0.428 ± 0.010	0.017 ± 0.012 ^b	3.8 ± 2.7 ^c
RJ-gravel	0.272 ± 0.006	0.271 ± 0.004	0.001 ± 0.007	0.4 ± 2.7*
RL-gravel	0.428 ± 0.010	0.283 ± 0.005	0.145 ± 0.011	33.9 ± 2.7
450 nm				
RC-limestone	0.554 ± 0.110	0.624 ± 0.016	0	+12.6 ± 20.2*
RJ-gravel	0.443 ± 0.016	0.428 ± 0.022	0.015 ± 0.027	3.4 ± 6.2*
RL-gravel	0.595 ± 0.011	0.492 ± 0.045	0.103 ± 0.046	17.3 ± 7.8
Hydrocarbon				
283 nm				
RC-limestone	0.357 ± 0.007	0.358 ± 0.008	0	+0.3 ± 3.0*
RJ-gravel	0.231 ± 0.002	0.250 ± 0.001	0	+8.2 ± 1.0
RL-gravel	0.303 ± 0.004	0.329 ± 0.004	0	+8.6 ± 1.3
450 nm				
RC-limestone	0.627 ± 0.011	0.584 ± 0.004	0.043 ± 0.012	6.9 ± 1.9
RJ-gravel	0.451 ± 0.009	0.411 ± 0.003	0.040 ± 0.010	8.9 ± 2.1
RL-gravel	0.522 ± 0.020	0.483 ± 0.005	0.039 ± 0.021	7.5 ± 4.0
Thiol				
283 nm				
RC-limestone	0.425 ± 0.006	0.379 ± 0.018	0.046 ± 0.019	10.8 ± 4.5
RJ-gravel	0.238 ± 0.007	0.369 ± 0.003	0	+55.0 ± 3.6
RL-gravel	0.411 ± 0.002	0.223 ± 0.003	0.188 ± 0.004	45.7 ± 0.9
450 nm				
RC-limestone	0.627 ± 0.011	0.616 ± 0.014	0.011 ± 0.018	1.8 ± 2.8*
RJ-gravel	0.394 ± 0.022	0.529 ± 0.009	0	+34.3 ± 6.3
RL-gravel	0.578 ± 0.018	0.392 ± 0.009	0.186 ± 0.020	32.2 ± 3.6
Amino				
283 nm				
RC-limestone	0.341 ± 0.001	0.297 ± 0.010	0.044 ± 0.010	12.9 ± 2.9
RJ-gravel	0.228 ± 0.006	0.215 ± 0.017	0.013 ± 0.018	5.7 ± 7.9*
RL-gravel	0.329 ± 0.001	0.271 ± 0.000	0.058 ± 0.001	17.6 ± 0.3
450 nm				
RC-limestone	0.557 ± 0.016	0.532 ± 0.007	0.025 ± 0.018	4.5 ± 3.1
RJ-gravel	0.424 ± 0.011	0.432 ± 0.018	0	+1.9 ± 5.2*
RL-gravel	0.498 ± 0.005	0.483 ± 0.000	0.015 ± 0.005	3.0 ± 1.0

^{a, b, c} See Footnotes Table 3.

±6 percent or less for components absorbing at 283 nm and ±8 percent or less for 450 nm. In the few cases where the propagated error for desorption was greater than the percent desorbed, desorption was considered not to have occurred.

The adsorption data for asphalt and natural aggregate combinations are shown in Table 4. Both the 283- and 450-nm absorbing components of AAD-1 asphalt indicated adsorption affinities for the aggregates as follows: RC-limestone > RL-gravel > RJ-gravel. For the aggregates tested, the adsorption masses of the 450-nm absorbing asphalt components were consistently larger than those observed for those compounds adsorbing at 283 nm on the same aggregates.

The 283- and 450-nm absorbing components of AAD-1 asphalt in combination with natural RC-limestone showed

high resistance to removal by water. Natural RJ-gravel gave no desorption at 283 or 450 nm for AAD-1 asphalt. Natural RL-gravel yielded significant desorptions for both the 283- and 450-nm absorbing components of AAD-1: 34 percent ± 3 percent for the 283-nm absorbing components and 17 percent ± 8 percent for the 450-nm absorbing components.

On Organosilane-Treated Aggregates

Three silane treatments—hydrocarbon, thiol, and amino—were used to pretreat RC-limestone, RJ-gravel, and RL-gravel. The effects of organosilane treatment were determined for the adsorption and desorption of AAD-1 asphalt (Table 4).

The RSD and propagated error of the adsorption and desorption measurements were ± 6 percent or less, with a few exceptions.

Hydrocarbon-treated aggregates resulted in less adsorption (15 to 29 percent) of the 283-nm absorbing AAD-1 components than the natural aggregates. No desorption of the 283-nm AAD-1 asphalt components was observed for any of the hydrocarbon-treated aggregates; increased adsorption of about 8 percent ± 1 percent was observed for hydrocarbon-treated RJ-gravel and RL-gravel. For the 450-nm absorbing components, hydrocarbon-treated RL-gravel showed a 12 percent decreased adsorption mass compared with that observed on natural aggregate. In contrast, hydrocarbon treatment of RC-limestone produced an increased adsorption mass (13 percent), whereas a slight change (a 2 percent increase) was noted for RJ-gravel. Each of the hydrocarbon-treated aggregates in combination with AAD-1 showed a small amount of desorption of the 450-nm absorbing AAD-1 components: RC-limestone yielded 7 percent ± 2 percent desorption; RJ-gravel, 9 percent ± 2 percent; and RL-gravel, 8 percent ± 4 percent.

Thiol treatment of all aggregates promoted decreased adsorption amounts (4 to 13 percent) of 283-nm absorbing components of AAD-1 in comparison with natural aggregates. Desorption of 11 percent ± 5 percent was observed at 283 nm on thiol-treated RC-limestone, whereas substantial desorption (46 percent ± 1 percent) of these components occurred on thiol-treated RL-gravel. In contrast, increased adsorption (55 percent ± 4 percent) rather than desorption was observed for thiol-treated RJ-gravel. At 450 nm, thiol-treated RC-limestone yielded an increased adsorption amount of 13 percent compared with natural aggregate. A decrease of 11 percent in adsorbed mass of 450-nm components was observed for thiol-treated RJ-gravel, and a small decrease (3 percent) was obtained on thiol-treated RL-gravel. Thiol treatment of the selected aggregates produced variety in the results obtained in desorption testing. Substantial desorption (32 percent ± 4 percent) was observed for the 450-nm absorbing components on thiol-treated RL-gravel in contrast with no desorption of these components from thiol-treated RC-limestone. Increased adsorption rather than desorption of the 450-nm absorbing components (34 percent ± 6 percent) was observed for thiol-treated RJ-gravel.

Amino treatment for all three aggregates resulted in decreased adsorption amounts (16 to 23 percent) of AAD-1 asphalt components absorbing at 283 nm compared with natural aggregates. Amino-treated RC-limestone and RL-gravel yielded 13 percent ± 3 percent and 18 percent ± 0 percent desorption of the 283-nm absorbing components, respectively, whereas amino-treated RJ-gravel showed no desorption by water. At 450 nm, AAD-1 gave decreased adsorption amounts (4 percent and 16 percent, respectively) for amino-treated RJ-gravel and RL-gravel when compared with natural aggregate. Virtually no change in adsorption amount at 450 nm was observed for amino-treated RC-limestone. Desorption was not observed for the 450-nm absorbing asphalt components on amino-treated RJ-gravel, whereas only slight desorptions were observed for amino-treated RC-limestone and amino-treated RL-gravel.

The specificity of the chemical interactions between asphalt chemical functional groups and treated aggregate constituents defined the water sensitivity for each asphalt-aggregate com-

bination. The effect of organosilane treatment of aggregate on change in water resistance has been summarized in Table 5 and is reported as percent change in water sensitivity of the asphalt components as a consequence of organosilane treatment of aggregates. The percent change in water sensitivity defined the effect of organosilane treatment on the removal of asphalt or asphalt model compounds relative to that obtained on natural aggregates.

SUMMARY OF FINDINGS

A study was made of the effectiveness of organosilane treatments for aggregates in increasing the affinity of the asphalt model compounds and asphalt for the aggregate surface and, subsequently, increasing the resistance to water of the adsorbed asphalt components. The different combinations of asphalt or asphalt model compounds and aggregate, silane-treated or natural, showed unique adsorption and desorption behavior. Thus, overall generalizations were difficult to make, although differences were observed in adsorption and resistance to water that could be attributed to silane treatment of aggregate. Even though increased adsorption mass of the asphalt models and several asphalt components was observed by treating aggregates with organosilanes, increased adsorption mass did not directly translate into increased resistance to water. The effect of organosilane treatment of aggregate for change in water resistance has been summarized (Table 5). The percent change in water sensitivity of asphalt components was calculated as the difference between the percent desorption obtained on natural aggregate and on silane-treated aggregate.

For many model-aggregate combinations, silane treatment of the selected aggregates resulted in increased resistance to water. Thiol-treated RL-gravel in combination with phenanthridine showed no change in resistance to water. The most outstanding enhancement in water resistance effected by organosilane treatment of aggregates was observed with RJ-gravel aggregate. RJ-gravel treated with any of the three selected organosilanes in combination with benzoic acid produced increased resistance to water of more than 80 percent when compared with that of the natural aggregate. Although all silane treatments of RC-limestone combined with either model compound resulted in increased resistance of both asphalt model compounds to removal by water, the increases were less than those observed for RJ-gravel. The increased resistance to water produced by silane treatments of RC-limestone ranged from 11 percent ± 3 percent for thiol treatment to 41 percent ± 2 percent for amino treatment. Increased resistance to water was also observed for hydrocarbon-treated RL-gravel at 23 percent ± 2 percent. The best silane treatment for retaining benzoic acid on RC-limestone and RL-gravel was amino silane, whereas hydrocarbon treatment of RJ-gravel proved best for that aggregate.

Treatment of RJ-gravel with thiol or amino silane yielded 29 percent ± 4 percent and 65 percent ± 11 percent, respectively, increased water resistance for phenanthridine, whereas hydrocarbon-treated RJ-gravel produced a small increase of 9 percent ± 4 percent. Hydrocarbon-treated RC-limestone in combination with phenanthridine produced 50 percent ± 20 percent increased resistance to water. Hydro-

TABLE 5 Percent Change in Water Sensitivity of Asphalt Components to Organosilane-Treated Aggregate

Model/Asphalt Aggregate	Percent Change in Water Sensitivity ^a		
	Organosilane Treatments		
	Hydrocarbon	Thiol	Amino
Benzoic Acid			
RC-limestone	+23.2±13 ^b	+11.3±2.8	+41.3±1.6
RJ-gravel	+193.1±3.0	+80.7±2.7	+119.1±4.7
RL-gravel	+10.4±6.6	+11.7±14.2*	+23.9±2.2
Phenanthridine			
RC-limestone	+49.8±20.1	+26.6±6.5	+82.4±16.2
RJ-gravel	+8.5±3.5	+29.4±3.5	+64.6±11.4
RL-gravel	+20.1±7.8	-6.4±11.9*	+11.4±2.8
AAD-1 (283)			
RC-limestone	+4.1±4.0	-7.0±5.2	-9.1±4.0
RJ-gravel	+8.6±2.9	+55.4±4.5	-5.3±8.3*
RL-gravel	+42.5±3.0	-11.8±2.8	+16.3±2.7
AAD-1 (450)			
RC-limestone	-19.5±20*	-14.4±20*	-17.1±20*
RJ-gravel	-5.5±6.5*	+37.7±8.8	+5.3±8.1*
RL-gravel	+9.8±8.8	-14.9±8.6	+14.3±7.9

^a Percent Change in Water Sensitivity defines the effect of organosilane treatment on stripping relative to stripping obtained on natural aggregate.

^b Propagated Error, Percent.

+ Organosilane treatment favorable for retaining asphalt model compounds or asphalt on the aggregate surface.

- Organosilane treatment unfavorable for retaining asphalt model compounds or asphalt on the aggregate surface.

* Values were considered insignificant due to large propagated error.

carbon was the best silane treatment observed for increasing water resistance of phenanthridine on RL-gravel by 20 percent \pm 8 percent. Thus, the best enhancer for increased water resistance for phenanthridine on RC-limestone or RL-gravel was hydrocarbon treatment, whereas amino treatment was best for RJ-gravel.

For ease of discussion, each asphalt component measured at a specified wavelength, 283 or 450 nm, has been treated as an individual entity, that is, as a single system. As is apparent in Table 5, the AAD-1 asphalt components absorbing at 283 and 450 nm responded dissimilarly to each particular organosilane treatment. Hydrocarbon treatment of the aggregates combined with the 283-nm absorbing components yielded increased resistance to removal by water. The most favorable increase in resistance to water was observed for hydrocarbon-treated RL-gravel at 43 percent \pm 3 percent. Amino treatment of RL-gravel yielded 16 percent \pm 3 percent increase in resistance to water, whereas thiol treatment produced a loss (12 percent \pm 3 percent) in resistance to water of the 283 absorbing components relative to the natural aggregate. Thiol treatment of RJ-gravel produced 55 percent \pm 5 percent increased resistance to water at 283 nm, whereas amino treatment yielded no change in resistance to water. All silane treatments of RC-limestone yielded either decreased or no enhancement for water resistance of the 283-nm absorbing components.

All silane treatments of RC-limestone aggregate in combination with the AAD-1 components absorbing at 450 nm produced no change in water resistance relative to the natural

aggregate. Of the three organosilane treatments used for RJ-gravel, thiol treatment yielded increased resistance (38 percent \pm 9 percent) to removal by water of the 450-nm absorbing components relative to natural aggregate, whereas no change was observed for hydrocarbon and amino treatment. RL-gravel, in contrast, showed some increased resistance to water (14 percent \pm 10 percent) at 450 nm with amino treatment and decreased resistance (15 percent \pm 9 percent) with thiol treatment.

CONCLUSIONS

- The adsorption and desorption methods presented here offer a means for predicting adhesion propensity and water resistance of aggregates.

- Polar species are more competitive for the aggregate surface and tend to adsorb more. They are also more sensitive to water than less polar species.

- Masking the aggregate surface with a hydrocarbon or modifying the surface with an amino group radically changes the adsorptive behavior of aggregates.

- The different combinations of asphalt model compounds and silane-treated aggregates showed unique adsorption and desorption behavior.

- Organosilane treatment, in many cases, increased the resistance of the asphalt-aggregate bond to water.

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