An Investigation of Asphalt-Aggregate Adhesion by Measurements of Heats of Immersion

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This paper discusses the problems in studying asphalt-aggregate adhesion and the relation between adhesion and heats of immersion. The construction of a microcalorimeter and its application in measuring the energy of interaction between road asphalts and aggregates are described. Experimental heat of immersion curves are presented on quartz, calcite, a phosphate slag, and 4 Montana aggregates used with a commercial asphalt. The effect of an antistripping agent on heats of immersion was evaluated.

•THEORETICAL calculations of the microscopic properties at the asphalt-aggregate interface will probably remain impossible to perform for asphalt-aggregate interactions. Such a statement is secured by the variances and complexities of asphalts and surfaces of aggregates. Asphalt researchers have, therefore, had to rely on empirical and semi-empirical approaches to their problems. Examples of purely empirical approaches to asphalt-aggregate adhesion are peeling, scraping, and stripping techniques (1, 2, 3). Although such disciplines may not excite the pure scientist, they nevertheless have been useful in evaluating asphalt-aggregate interactions. The methods are not free of problems. Often the percentage of asphalt adhering to the aggregate surface is determined by unreliable visual observation. Another problem is surface roughness that leads to spurious results.

Semi-empirical approaches to asphalt-aggregate adhesion include contact angle (1) and sessile drop (2) studies. Again surface variations impair reproducibility. Also, the contact angle studies do not allow accurate measurements, because the angle is too small and they are further plagued with a hysteresis effect.

These approaches have been mentioned to point out the need for a reliable method for studying asphalt-aggregate interactions. With such a purpose as a goal, a thermodynamic approach through the study of heat of immersion was pursued.

The heat of immersion is the energy released when an insoluble solid is dropped into a liquid. The energy is proportional to the adhesion or interfacial bond between the liquid and the solid surface. It is highly probable that for a given adsorbent and adsorbate the bond strength will vary over the surfaces. For example, molecules adsorbed in a crevice will be bonded stronger than those on the edge or on flat surfaces. Also, heterogeneity is certain to be present because of Schottky and Frenkel defects or dislocations. Naturally occurring aggregates or minerals would add another variable, heterogeneous chemical composition.

Zettlemoyer (6) sums up the various contributions to immersional energy by stating that the heat liberated will be determined by "...the average polarity of solid surfaces, site energy distribution or heterogeneity of solid surfaces, solution adsorption,...and heat of formation of double layers."

Because of the complex nature of the aggregate surfaces, as well as the complexities of the asphalt, we cannot attribute immersional energy to any one type of bond. Rather we can expect several types of bonds to be present because of forces such as ionic, permanent dipole, induced dipole, and dispersion. Regardless of which forces

are present, it should be reasonable to assume that the greater the energy that is released in the immersional process, the stronger will be the asphalt-aggregate bond. We can extend this postulate by stating that the stronger the bond the better will be the performance of the asphalt in the road.

EXPERIMENTAL SECTION

The energy released in the heat of immersion is always small and requires a very sensitive calorimeter for detection. To measure the energy released in the asphalt-aggregate interaction, a differential microcalorimeter (7) of the Tian-Calvet type was constructed.

Construction of the Microcalorimeter

The thermopile assembly consists of 1,200 electroplated copper-constantan thermocouples. Earlier works discuss electroplated thermocouples (8, 9) and the application to microcalorimetery (10). The assembly contains 40 mica disks or wafers ($\frac{3}{8}$-in. inner diameter and $2\frac{1}{4}$-in. outer diameter), each wrapped 30 times with constantan wire. One side of each disk was electroplated with copper while the opposite side was masked. (The electroplated junctions are 50 percent as efficient was welded junctions.) The wafers are stacked around the cell holder (Fig. 1, E) and sandwiched between small anodized aluminum rings (Fig. 1, C), large anodized aluminum rings (Fig. 1, B), and additional mica wafers to eliminate shorting between wire-wrapped wafers. Two similar thermopile assemblies were constructed and connected in opposition as in differential thermal analysis. The signal from the differential thermopile is fed into a Keithley 149 millimicro-voltmeter and into a recorder.

The reaction cell holder (4 in long and $\frac{5}{8}$ in. inner diameter) was anodized on the outside to eliminate shorting the junctions that were in thermal contact with the holder. The inner wall is in good thermal contact with the reaction cell containing the asphalt. A Teflon aggregate holder is clamped to the top of the reaction cell. The aggregate is held in the container by a trapdoor that is sprung by a trip wire extending to the outside of the oven. A 10.0-ohm manganin wire-wound calibrating resistor is connected to the Teflon holder and is immersed into the asphalt as the holder is connected to the reaction cell. (After each run a calibration was performed by passing a known quantity of electricity through the coil.) Small mica shelves were placed on the coil for dispersing the aggregate.
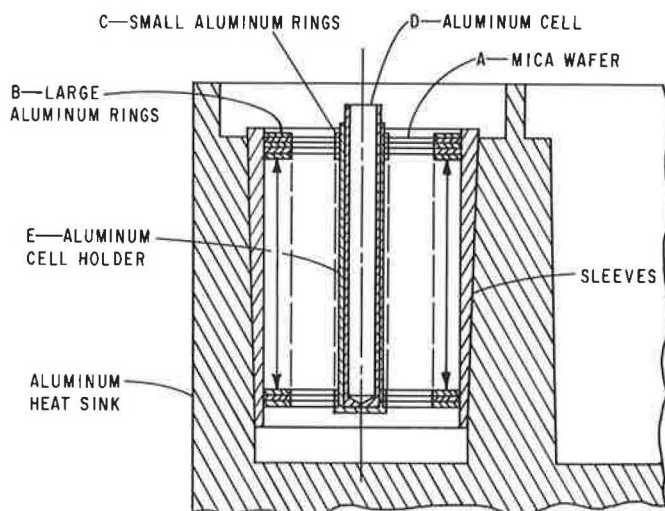

Figure 1. Cross section of the reaction cell and thermopile assembly.

The cylindrical heat sink (Fig. 1) and tapered sleeves constitute the heat sink. The sleeves are split to aid in removal of the thermopile. Thermal fluctuations within the heat sink are reduced to a minimum by a 20-lb aluminum heat-sink lid, a $\frac{1}{2}$-in. thick aluminum can surrounding the microcalorimeter, and a $\frac{3}{8}$-in. thick steel can surrounding the aluminum can.

The total assembly is enclosed in a constant temperature oven at 150 C. Three parallel heating coils are on continuously; a fourth coil is controlled by a thermistor.

Materials

Specimen-grade quartz and calcite were tested as aggregate standards. Also tested were 2 aggregates from Glacier County (differentiated by No. 2 and No. 3), one from Teton County and one from Lewis and Clark County, and a phosphate slag from Silver Bow County.

The aggregate samples were prepared by crushing, screening to obtain -35 +48 M size, and washing with distilled water. They were dried overnight at 150 C. (No difference could be detected in the heat of immersion between these samples and samples that had been dried at 400 C for 12 hours under a vacuum of 10^{-6} torr.) The surface area of the aggregates was assumed to be 149 cm^2/g, a value given by Bikerman (11) for quartz.

Only one asphalt was tested. It was an Arkansas penetration grade 36 asphalt (Bureau of Public Roads No. B-3036). The asphalt was tested both untreated and treated with 1 percent Armour Diamine-Redicote 80-S, which is a fatty acid salt of a long-chain fatty diamine.

Procedure

In a typical run, 5 g of asphalt was poured into the reaction cell. A $\frac{1}{2}$-g sample of aggregate was accurately weighed in the Teflon sample holder and the calibration coil attached to the holder. Inasmuch as the holder was connected to the reaction cell, the coil was immersed into the asphalt. The reaction cell was placed in the cell holder in the reaction side of the microcalorimeter. A blank cell containing asphalt but not aggregate was placed in the other side of the microcalorimeter. After a period of 48 hours the trapdoor was sprung allowing the aggregate to drop into the asphalt.

The immersional energy produced was recorded for 3 hours or more. The curves were calibrated and replotted in ergs/cm^2-min versus time in minutes.

RESULTS AND DISCUSSION

The nature of the reaction between asphalt and aggregates prohibits the usual method of reporting immersional data. No finite value is obtained but rather energy is released for a long period of time. A typical example is quartz into asphalt.

The bottom curve shown in Figure 2 represents the immersion of quartz into B-3036 test asphalt at 150 C. The shape of the curve is similar to shapes of curves obtained for all aggregates, an initial peak followed by a long tail. A second curve, shown in Figure 2, represents the immersion of quartz into B-3036 asphalt containing 1 percent of the Armour amine salt. The initial peak height is doubled and the tail height is 10 times higher with the amine present. Weber (12) noted by strip tests that the amine additive does improve certain asphalt-aggregate adhesion. Based on the analysis of the strip test data, the tail height may be more representative of resistance to stripping than the initial peak height.

Calcite was selected to represent the alkaline class of rocks. The surface area was assumed to be the same as that for the quartz; however, this is recognized as only an approximation. The immersion curve for the calcite-asphalt reaction is shown in Figure 3. The initial peak is about equal to the peak height for quartz, but the tail is 6 times higher for calcite. This would indicate that, if the strip test correlation cited earlier holds, then calcite bonds better than quartz to the test asphalt. The type of material that gives the best bond is a controversial topic (13).
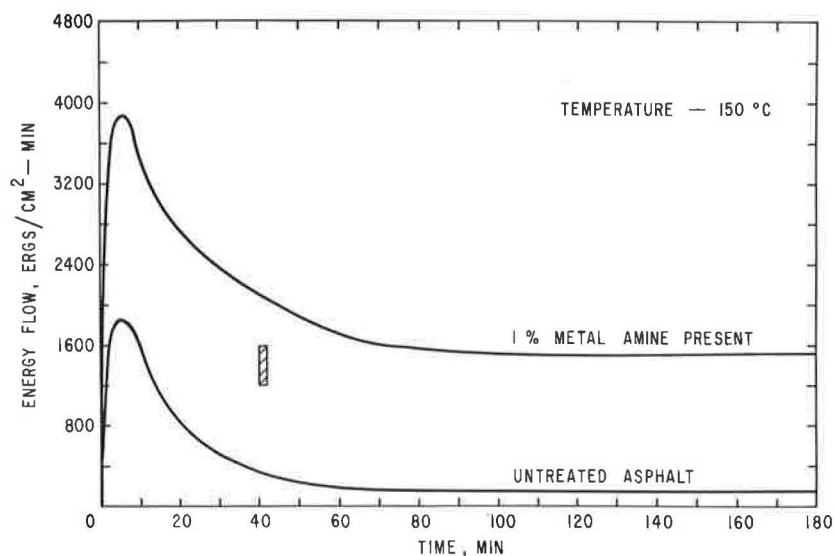
Figure 2. Heat of immersion of quartz into treated and untreated asphalt. (The shaded rectangle in this and following figures represents 800 ergs/cm² and is given for comparative analysis.)
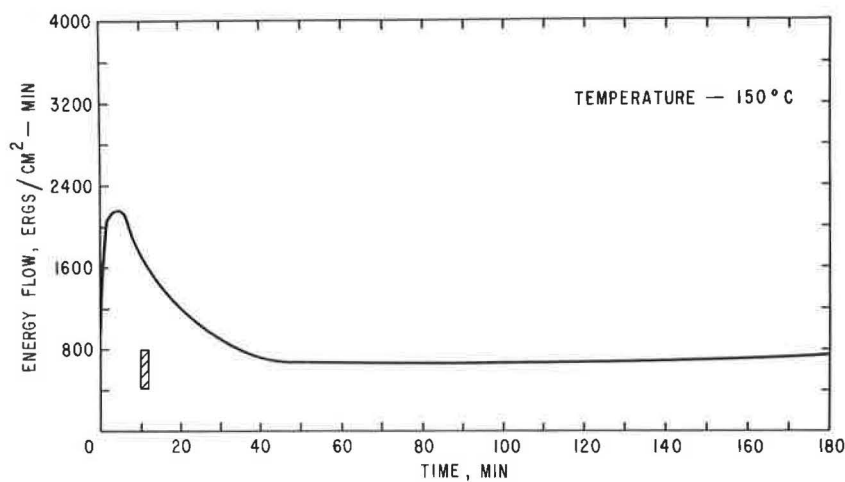

Figure 3. Heat of immersion of calcite into untreated asphalt.

A phosphate slag, which was used in highway construction near Butte, was investigated by immersion studies. Figure 4 shows 2 curves resulting from the immersion of the slag into asphalt. The bottom curve was obtained for untreated asphalt and the upper curve for the amine salt-treated asphalt. Doping produced a large increase in area under the curve. This increase is probably due to the acidic surface of the slag forming an excellent bond with the amine salt.
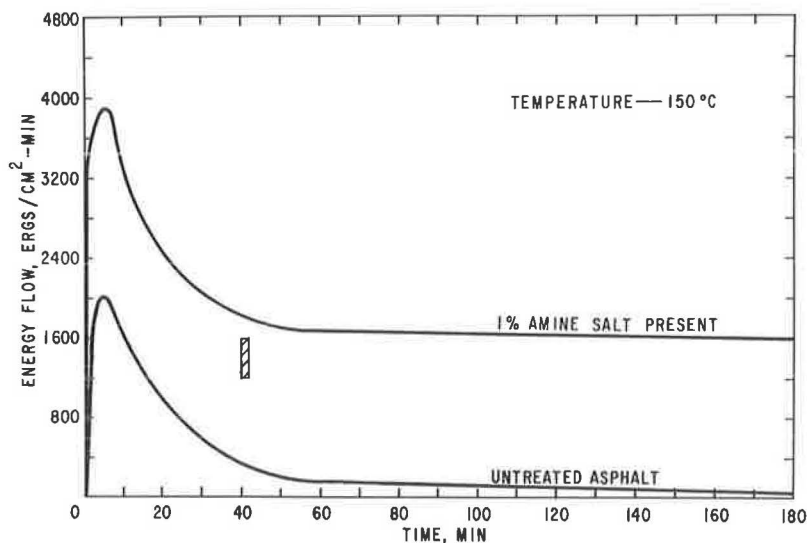
Figure 4. Heat of immersion of a phosphate slag into treated and untreated asphalt.

The aggregates from Glacier County and Lewis and Clark County were principally silicate rocks. The Teton County aggregate was limestone. The immersion curves for Teton County and Glacier County No. 3 aggregates are shown in Figure 5. They had higher curve tails but lower initial peaks than the other 2 Montana aggregates (Fig. 6). All the aggregates had higher curves than pure quartz.

The adhesion of asphalt to these 4 aggregates has been examined by Weber (12). He has shown by a strip test that Teton County and Glacier County No. 3 aggregates gave the best adhesion with asphalt and that the former being was the best of the two. His
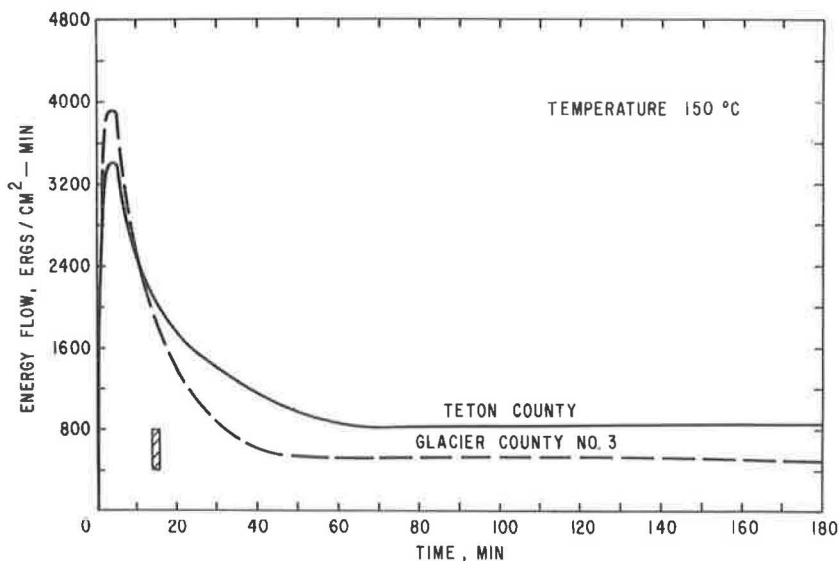

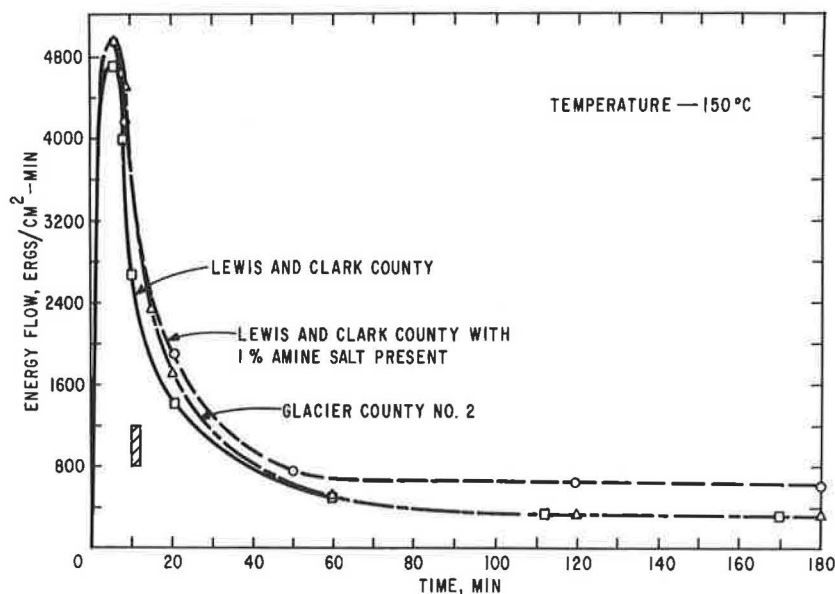Figure 5. Heat of immersion of two Montana aggregates into asphalt.

Figure 6. Heat of immersion of Glacier County No. 2 aggregate into untreated asphalt and Lewis and Clark County aggregate into both treated and untreated asphalt.

observations agree with the immersion data, assuming that greater tail heights indicate better resistance to stripping. Weber also observed that the addition of the amine salt to the asphalt improved the adhesion to Glacier County No. 2 and Lewis and Clark County aggregates. Adhesion that was poor with untreated asphalt became comparable to that observed for the Teton County and Glacier County No. 3 aggregates with the untreated asphalts. We did not detect a large difference in treated and untreated asphalts with Glacier County No. 2 aggregate, but the tail height was doubled for Lewis and Clark County aggregates (Fig. 6).

The immersional energy from asphalt-aggregate interactions differs in 2 respects from typical immersional data: (a) the energy released is much greater, and (b) the energy is released over a long period of time. In fact, little change is noted in tail height after 3 hours even when the reaction has been followed for 24 hours. Both observations deserve comment.

For comparative analysis, the following immersional energies are cited (14): liquid, energy in ergs/cm^2 for water, 261; benzene, 218; n-octane, 185; cyclohexane, 68; and methanol, 185. Comparing these values with the immersional curves, we observe that within a few minutes the energy released is much greater than any of those values presented for simple liquids. Because asphalt contains a greater variety of polar groups than are represented by this short list, other functional groups present in asphalt could be principal contributors to the immersional energy. But even with this consideration, the large amount of energy released cannot be explained by monolayer wetting. What is the source of this large immersional energy? It is either (a) a chemical reaction catalyzed by the surface, or (b) physical adsorption not just of a monolayer but of a multilayer buildup.

The amount of energy released in the asphalt-aggregate interaction is proportional to the surface area; therefore, if a chemical reaction is occurring, it is surface catalyzed and the flat tail of the curve indicates the reaction is diffusion controlled.

A second possible explanation of the shape of the curves is that a monolayer produces the peak and a multilayer buildup produces the tail. This postulation would lead one to

expect greater peak heights to be accompanied by greater tail heights. Examination of the curves shows this is not so. With the limited asphalt-aggregate immersion data, an explanation of this anomaly is difficult.

Comparative analysis of the curves and strip tests shows the tail height correlates better with resistance to stripping than does the peak height. This statement is supported by the Montana aggregate immersion curves for both untreated and amine salt-treated asphalts.

Henniker (15) has presented a comprehensive list of examples where multilayer formation has been observed. He states, "The concept is therefore that, although the powerful forces are of very short range, they are transmitted by successive polarization of neighboring molecules to an impressive depth. ... The effective depth of the surface zone is tens or hundreds in low molecular weight liquids, thousands of angstroms in long-chain molecules."

The molecular "melting-pot" mixture of asphalt includes not only long-chained molecules but also polar ring compounds of various types. The combination of high molecular weight compounds and an abundance of polar groups would enhance multilayer formation.

Whether the long tail on the curves represent multilayer buildup or not, the area under the curve definitely appears to be related to adhesion. More microcalorimetric work is needed to probe farther into the phenomena of asphalt-aggregate interactions.

ACKNOWLEDGMENTS

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