

Utility of Low Value Liquefaction Products
as a High Value Additive

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Characteristic to many coal liquefaction processes is that certain streams have objectionable properties in terms of ease of upgrading, and as a result, these streams not only complicate downstream processing but have a very low value. A specific objective of this research was to identify a high value application for these streams. This can impact the entire coal liquefaction processing train and its economics. By finding a high value application for these streams, it becomes economical to remove them early in the processing train for separate processing. This simplifies downstream processing of other streams, reducing overall processing costs, with there being an actual higher value for the entire product slate.

Typical objectionable properties of certain coal liquefaction streams are: 1) high molecular weight distribution, 2) high heteroatomic content, and 3) high metals content. (1) It was thought that these objectionable properties could actually prove to be advantageous for utilizing these fractions as a high value antistripping additive for asphaltic pavement cement.

Stripping of asphaltic cement from pavement aggregates has long been recognized as a major cause of failure in asphaltic concrete pavements. The cause of stripping is attributed to water or moisture penetrating the asphalt-aggregate matrix. Stripping, which is the loss of adhesive bond between the asphalt and aggregate surface, results in a loss in integrity of the asphaltic concrete and subsequent failure, requiring early and costly maintenance.

A number of methods have been developed for reducing stripping damage in asphaltic concrete pavements. Of these methods, the addition of a chemical antistripping (AS) additive has become the most widely practiced method for maintaining pavement durability, because of its relatively low cost and ease of implementation. A large number of AS additives, which are normally surfactants, are commercially available today. According to the 1984 survey of state highway agencies by Tunncliffe and Root (2), more than 100 chemical AS additives are used in the United States.

AS additives are substances added to asphalt cement to promote adhesion of the asphalt cement to the aggregate surface and thus to improve the resistance of the asphalt pavement to stripping damage. Most AS additives are mixtures of proprietary chemical compounds, and detailed characterizations of these compound mixtures are usually not available; however, most of the active compounds are probably amines or chemical compounds derived from ammonia. Usually these compounds act as cationic surfactants to reduce surface tension at the aggregate surface (3). However, it has been shown that many AS additives are susceptible to heat and thus, with storage in hot asphalt cement, the effectiveness of these additives could be severely reduced. Figure 1 shows the loss in effectiveness for different typical commercial AS additives with storage of the additives at 325°F in an asphalt cement. Four

different commercial AS additives from different manufacturers were used in this study. The additives were labeled Additive Nos. 1, 2, 3, and 4. The stripping propensity of an asphalt-aggregate mixture was measured in terms of the percentage coverage of aggregate after the boiling water test. If the asphalt separated from the aggregate surface after boiling the asphalt-aggregate mixture in water for 10 minutes, it was said to have stripped, and the asphalt - aggregate bond was concluded to have been weak and to have a high stripping propensity.

In addition to evaluating the heat sensitivity characteristics of AS additives, it was shown that only a small fraction of the AS additive migrates to the aggregate surface and acts to improve the asphalt cement/aggregate bonding: most of the additive remains in the bulk of the asphalt and never comes in contact with the aggregate surface. For this reason, such chemical AS additives not only change the asphalt cement/aggregate bonding, but can also change the properties of the bulk asphaltic cement significantly.

In order to minimize AS additive dosage requirements, direct application of AS additive to the aggregate surface was investigated. Table 1 shows the result of direct application of an AS additive (Additive No. 1) to the aggregate surface. The additive, which is water soluble, was dissolved in water to form treatment solutions having concentrations ranging from 0.05 to 0.5 wt%. Then the aggregate (granite 3/8 in. - No. 4 mesh size) was immersed in the respective solution for 10 minutes. After towel drying and preheating the aggregate at 275°F, the boiling water test was performed. Based on the results given in Table 1, it was calculated that direct application of AS additive to the aggregate surface requires only about 5% of the amount of additive which would be required to provide an equivalent effective amount of additive at the aggregate surface when the additive is added in the asphalt.

With direct application, the commercial AS additive, a polyamine-type additive, appeared to degrade at relatively high temperatures (250°C) and become ineffective, as shown in Figure 2. The preheating temperature was varied from 135°C to 350°C to simulate the temperature range in which aggregates may be heated in a commercial aggregate dryer. The temperature of combustion gases and air used to dry aggregate in a commercial dryer ranges from about 250 to 315°C.

In an earlier work (4), it was found that stripping of asphalt cement from pavement aggregates was very much an aggregate problem. That is, physico-chemical properties of the aggregate surface have a very significant effect on the stripping propensity of an asphalt-aggregate mixture. Figure 3 shows how the surface charge density (Zeta Potential) varied among some different types of common aggregates. Interestingly, the aggregates which had a relatively high surface charge were found to be more susceptible to stripping as measured by the boiling water test.

It was thought that by impregnating the aggregate surface with an easily polymerized compound prior to its being dried, it would become coated with molecular layers of polymerized (coked) material. This could serve to reduce the surface charge of the aggregate surface and make it easier for the asphalt to adsorb (or bond) to the aggregate.

Aggregate surfaces were assumed to interact strongly with high molecular weight, aromatic compounds in a manner similar to how coke forms on catalyst surfaces. High molecular weight aromatic compounds have high coking propensities. For this reason, a granite aggregate was precoated with a phenanthrene solution (10 wt% in toluene) and then preheated at 135, 250, and 350°C. Figure 4 shows that the effectiveness of the phenanthrene pretreatment increased as the preheating temperature was increased. A similar result was obtained for an actual coal liquid (10 wt% toluene), as is shown in Figure 4. The coal liquid was obtained from the Wilsonville coal liquefaction plant. It was therefore thought that the formation of coke-like compounds on the aggregate surface during the aggregate preheating (drying) period could be the primary cause of the observed pretreatment effect of phenanthrene and/or heavy coal liquid on the asphalt-aggregate bond, as was measured here using the boiling water test.

While performing the above aggregate surface conditioning studies, it was observed that reheating an asphalt-aggregate mixture usually resulted in an increase in its stripping resistance. Asphalt-aggregate mixtures were cured (reheated) by holding the mixtures at a fixed temperature for a set period of time. It was observed that the performance of an asphalt-aggregate mixture was improved with curing at about 300°F for several hours. This apparent improvement in adhesion between the asphalt and the aggregate surface with curing was again thought to be, in part, due to coke-like compounds being formed on the aggregate surface. For this reason, pretreatment of a granite aggregate with phenanthrene, which has high coking propensity, was evaluated for accelerating the curing effect on stripping propensity. Indeed, this was found to accelerate curing, as shown in Figure 5.

It appears then that compounds having a high coking propensity, like phenanthrene and heavy coal liquid, have potential usage as an AS additive.

References

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3. Mathews, D.H., "Surface-Active Agents in Bituminous Road Materials." J. Appl. Chem. 12, February, 1962.
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Table 1. Effect of Aggregate Pretreatment with a Commercial AS Additive (Additive No. 1) on the Boiling Water Test Results.

Additive Content in Water	Water Content of Aggregate after Soaking	Amount of Additive on Aggregate	Percent Coating Retained after Boiling
%	g water/g agg.	g add./g agg.	%
0.5	0.0232	1.60×10^{-4}	100
0.1	0.0281	0.28×10^{-4}	100
0.05	0.0430	0.21×10^{-4}	95
0.05	0.0221	0.11×10^{-4}	65
0.05	0.0201	0.10×10^{-4}	60

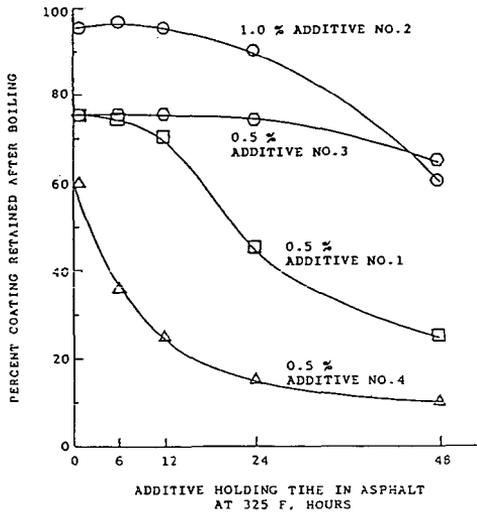


Figure 1. Heat Stability of Antistripping Additives in Asphalt as Determined by the Boiling Water Test.

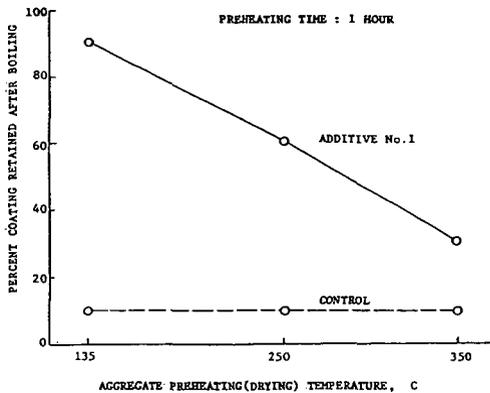


Figure 2. Response in Effectiveness of a Typical Commercial AS Additive to Changes in Aggregate Preheating (Drying) Temperature with Direct Application of the Additive to Granite Aggregate.

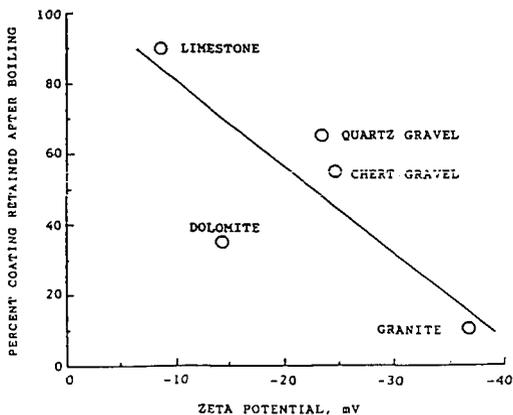


Figure 3. Comparison of Aggregate Surface Potential and Stripping Propensity as Determined by the Boiling Water Test.

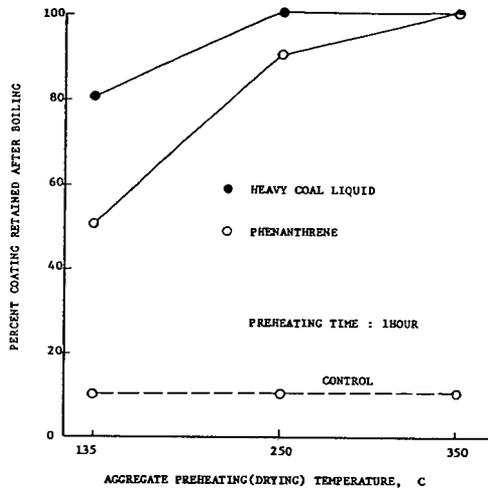


Figure 4. Response in Effectiveness of Phenanthrene and of Coal Liquid as AS Additives to Changes in Aggregate Preheating (Drying) Temperature with Their Direct Application to Granite Aggregate.

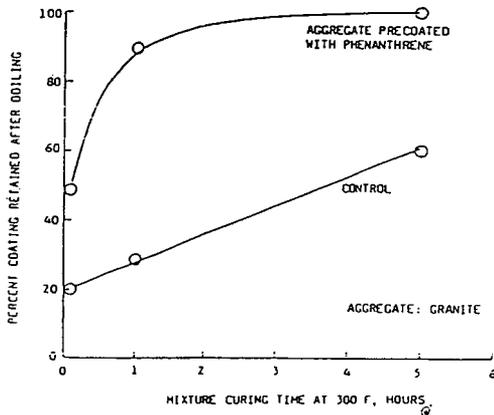


Figure 5. Acceleration of Curing Effect on Stripping Resistance by a High Coking Propensity Additive, Phenanthrene.