NATIONAL BUREAU OF STANDARDS REPORT

5436

SEPARATION OF THE WATER-SOLUBLE DEGRADATION PRODUCTS OF ASPHALT

by

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NBS

U. S. DEPARTMENT OF COMMERCE
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Building Technology Division

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SUMMARY

Several methods for separating the water-soluble degradation products of asphalt, including paper and column chromatography, ion exchange, sublimation, derivative formation and liquid-liquid, pH and liquid-solid extraction, were evaluated. Only the liquid-solid extraction gave reasonably quantitative and reproducible results. However, during a secondary breakdown by this procedure some of the materials apparently polymerized and lost oxygen. It was decided that none of the techniques investigated was adequate to separate the water-soluble degradation products quantitatively and reproducibly without changing some of them.

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1. INTRODUCTION

During the course of studying the mechanism of degradation of asphalt, it became apparent that the asphalt itself was too complex to yield the solution to the problem if studied only in its entirety. Observation of changes taking place in certain components of asphalts[1] during exposure indicated that even the components were too complex for satisfactory evaluation and that further separations would be necessary if this approach were to be continued.

The components that were separated were subjected to ultimate chemical analysis[2] and though considerable light was thrown on the process of degradation, the mechanism of was still obscure.

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[1] Greenfeld, S. H., "The Degradation of Two Coating Asphalts", NBS Report No. 4621, April 16, 1956.

[2] Greenfeld, S.H., "The Chemical Changes Occurring During the Degradation of Two Coating Asphalts", NBS Report No. 4861, October 1, 1956.

remove any contaminating cations[5/]. The solutions became appreciably lighter during this treatment. The solutions were then evaporated to dryness under reduced pressure at about 50-60°C. The solid water-soluble degradation products were stored for future work. The following quantities of materials were collected at various periods of exposure in the accelerated durability machines:

TABLE 1. DEGRADATION PRODUCTS OF ASPHALT C190

Period of Exposure	Weight of Degradation Products Machine #1	Machine #2
Hr.	g.	g.
0 - 250	---	7.7
250 - 500	---	15.4
0 - 550	Not determined	----
500 - 750	---	11.6
550 - 850	9.4	----
750 - 1000	---	11.2
850 - 1350	16.0	----
1000 - 1500	---	14.0
1350 - 1800	Not determined	----
1500 - 2000	---	7.8

The weights of the other samples of degradation products were not determined.

3. FRACTIONATION OF WATER-SOLUBLE DEGRADATION PRODUCTS

3.1 Liquid-Liquid Extraction

Because the degradation products were always collected in large volumes of water and eliminating the water was a laborious, time-consuming job, methods were sought that might fractionate the degradation products while they were present in their original solution form. Continuous extraction with such water-insoluble solvents as ether, benzene or

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[5/] Preliminary work indicated that the acidic, water-soluble degradation products reacted with the specimen supports and materials in the containers in which the specimens were soaked. A. Schriesheim and S. H. Greenfeld, "Water-Soluble Degradation Products of Asphalt", A.S.T.M. Bulletin No. 220, February 1957.

pentane yielded only traces of extractable materials. It was realized that these products were soluble only in appreciably oxygenated solvents, the best of which (acetone and ethanol) were also very soluble in water. Methyl ethyl ketone extracted portions of the products, but it was impossible to determine whether the products were dissolved in the methyl ethyl ketone or in the water that dissolved in the methyl ethyl ketone. Higher molecular weight ketones, such as methyl isobutyl ketone, cyclohexanone and acetophenone, all were tried and found to be partially sucessful. However, their boiling points are all in the neighborhood of that of water and involve the same problems of solvent elimination that water does. Furthermore, a large fraction of the degradation products was not extracted.

3.2 pH Extraction

When simple solvent extraction proved unsuccessful, modifications of the method were attempted. The acids in the degradation products were completely neutralized and an attempt made to extract any non-acidic material with benzene and ether. Again only slight traces of material were extracted after prolonged contact between the two phases in a continuous extractor.

The pH was lowered two units at a time (with HCl) and further extraction was attempted with both of these solvents and methyl ethyl ketone and cyclohexanone. Very little material was extracted evan at a pH of 2. The ketones affected the pH of the aqueous phase considerably as it became saturated with them and made the pH readings almost meaningless. For example the cyclohexanone dropped the pH reading of the neutralized aqueous solution from 10.5 to 5.8 during the course of the first extraction.

3.3 Column Chromatography

There are several ways of utilizing columns of adsorbents for separating mixtures of acids in solution. These range from partition chromatography, in which the solid adsorbent functions primarily as a support for an immobile liquid phase, to adsorption chromatography, in which the solids actually adsorb the acids and the separation is accomplished by the use of several desorbing solvents. Many practical separations are accomplished through combinations of the several phenomena involved. A large number of

combinations of supports, solvent systems and conditions were evaluated. Such materials as silicic acid, celite, silica, carborundum, crushed glass and cellulose were used as supports. These were used "as received", washed, acid washed, buffered (glycine plus NaOH or HCl), and activated to various degrees. They were used as adsorbents and with varying ratios of immobile phases. Many different solvent systems, including numerous combinations of the following solvents: water, acetone, ethanol, methyl ethyl ketone, butanol, iso-butanol, ter-butanol, amylol, iso-amylol, ter-amylol, chloroform, benzene, ether, cyclohexanol, cyclohexanone, methyl cyclohexanone, dimethyl formamide, 2-ethyl-1-hexanol and 4-methyl-2-pentanol, were used.

The degradation products were always more or less separated into from 3 to 10 or 12 fractions, but the separations were not very reproducible and the recoveries were rarely quantitative. Very frequently, even though recoveries of over 100% were measured, the columns of adsorbent were still colored, indicating the presence of degradation products. Functional group analyses of some of the separated materials were often negative and inconclusive.

3.4 Paper Chromatography

Both ascending and circular paper chromatography were used to try to separate the water-soluble degradation products. The former was the more successful, resulting in one instance in five spots. However, despite the fact that ionization was suppressed with formic acid, "tailing" was usually prevalent and reproducibility was not good. No quantitative evaluation was attempted.

3.5 Ion Exchange

Ion-exchange resins have been used successfully to separate both cations and ions. The Project has used a Dowex-50X8 resin to remove all cations from the degradation products. In doing so, certain organic cationic materials, which comprised a small percentage of the degradation products, were also removed. These materials were regenerated with a 5% sodium hydroxide solution and were found to contain amines or amino acids.

In order to remove the anions from solution, a different type of resin, an anion-exchange resin, was used. This polyamine-type resin, marketed under such names as Amberlite IRA400 or 4B, De Acidite, Permutite S-2 or Dowex 3, removed all of the acids from solution until it approached saturation. However, only about 60% of the anions could be recovered even with regenerants strong enough to attack the resins. This phenomenon has been observed by other investigators with some high molecular weight acids.

3.6 Sublimation

The volatility of the water-soluble degradation products is very low and the use of distillation as a method of separation was beyond consideration. However, preliminary work indicated that a component of these materials might possibly be separated from the bulk of them by sublimation at low pressure. A white, powdery material sublimed from a sample of degradation products that was obtained from a roof. When an attempt was made to check these results on degradation products collected in the laboratory, however, only a slight, oily product was obtained at a relatively high temperature. There was evidence that decomposition had occurred. The original sublimation product had probably been some impurity.

3.7 Derivative Formation

In many instances when satisfactory separations of organic materials cannot be accomplished by conventional techniques, derivatives can be made that are more readily separable. Two such attempts were made on the water-soluble degradation products.

Hydrogen bonding of many organic acids results in their having volatilities considerably lower than other closely related derivatives and makes separation of the acids by distillation unfeasible. Conversion to the methyl esters often reduces the boiling points of acids as much as 100°C, bringing them into a range where they can be distilled without decomposition.

Two samples of water-soluble degradation products were esterified with methyl alcohol (sulfuric acid as catalyst) and attempts made to distill out the ester after the catalyst had been neutralized and removed. The principal ingredient that distilled over was water. Apparently the esters were not volatile. No further work was done because insufficient material was available.

In several instances it has been reported that derivatives or organic acids were separated by paper chromatography more readily than the acids themselves, because the derivatives did not exhibit as much hydrogen bonding or ionization. Attempts to make the anilides of the water-soluble degradation products were unsuccessful because of very poor conversions and the formation of insoluble compounds.

3.8 Decarboxylation

Another procedure for increasing the volatility of organic acids is to remove their carboxyl groups. Since the degradation products averaged 2.4 carboxyl groups per molecule, in addition to reducing hydrogen bonding, removal of the carboxyl groups would lower the average molecular weight by 110.

An attempt was made to decarboxylate about 3-1/2 grams of degradation products in quinoline, with copper sulfate as the catalyst. Collection of the carbon dioxide liberated indicated that the reaction had gone to completion, but recovery of the liquid and solid products was not quantitative. The copper sulfate had decomposed, introducing sulfur into other molecules. This type of reaction should be repeated, using copper oxide as a catalyst, in order to yield materials which might be separated by distillation, or fed into the mass spectrometer for analysis.

3.9 Extraction from Solid Phase

Among the more promising techniques evaluated was extraction of components of the water-soluble degradation products by various solvents while the products were present in a finely divided solid state. Considerable effort was expended in exploring various techniques involving this principle.

Extraction from the solid state proved very slow when first tried, because the material tended to cake in the extraction apparatus. Both Soxhlet and batch extraction were interminable and not reproducible. In order to overcome these problems of caking and incomplete extraction, the material was dispersed on numerous, more or less inert, finely divided carriers. The same difficulties were encountered in the extraction operation as were in the column chromatography work. No satisfactory quantitative and reproducible system was found. Usually recoveries were too high.

In the course of the extractions it was found that the process was considerably accelerated if the carrier material was kept in suspension by stirring with a magnetic stirrer. Pursuit of this approach indicated that the extraction of the finely divided degradation products themselves could be greatly improved by this technique. The carrier was then eliminated. Primary extractions were made with ether, methyl ethyl ketone, acetone and water. The materials from each exposure interval were separated into two parts in order to check the precision of the method. The average results are reported in Table 2.

TABLE 2. EXTRACTION OF WATER-SOLUBLE DEGRADATION PRODUCTS

Exposure Period	0-250	500-750*	750-1000	1000-1500
Hr.	%	%	%	%
Ether Soluble	24.7	25.5	30.9	25.3
MEK Soluble	58.7	60.2	57.7	68.5
Acetone Soluble	3.8	6.2	2.5	7.9
Water Soluble	**	2.4	5.4	0.0
Water + Acetone Soluble	12.2	5.7	0.4	0.0
Recovery	99.4	100.0	96.9	101.7

*Single Determination.
**Not Determined.

Just as in the infrared analyses, these extractions indicate that there are differences in the materials collected during the several exposure periods, but the degrees and types of differences are not clear. Since most of the degradation products were soluble in methyl ethyl ketone, it was decided to fractionate that portion further first.

When the MEK fraction was extracted with water, the recovery was very poor and the material had apparently undergone some changes. The work was repeated, with the same results, as shown in Table 3.

TABLE 3.

	Secondary Extraction				
Sample	% of Fraction	Mol. Wt.	Neutral Equiv.	COOH/Mol.	% Oxygen
MEK	100	760	184	4.12	33.5
Water Sol. of MEK	55.9	560	162	3.46	36.9
Water Insol. of MEK	31.1	2000	297	6.73	29.9
Recovery	87.0				

These data indicate that polymerization has taken place either during the extraction or during the vacuum drying operation following it. The molecular weight has increased and the oxygen content decreased. It is apparent that much more highly refined techniques will have to be developed if these degradation products are to be separated without being changed.

Based on a discussion of these data, it has been decided to divert the efforts of the project to approaches to the problem of degradation that may be expected to yield more immediate results.

4. REFERENCES

The following list of references will prove helpful to those interested in general treatments of the various techniques employed. No effort has been made to include all of the references consulted because in many instances only minor contributions were obtained from them.

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