

PREPARATION OF BIODEGRADABLE SYNTHETIC
DETERGENTS FROM LOW-TEMPERATURE LIGNITE TAR

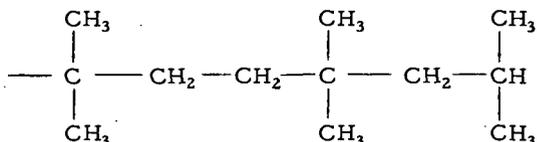
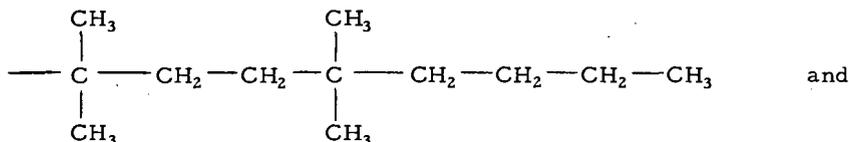
John S. Berber, Robert V. Rahfuse, and Howard W. Wainwright

U. S. Department of the Interior, Bureau of Mines
Morgantown Coal Research Center, Morgantown, W. Va.

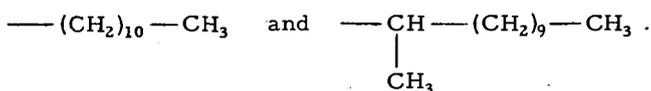
INTRODUCTION

Search for biodegradable synthetic detergents from low-temperature tar is part of a broad research program on low-temperature coal tar by the Bureau of Mines, U. S. Department of the Interior. Fundamental objectives of this research on tars resulting from the low-temperature carbonization of coal are to (1) characterize these tars in some detail; (2) investigate means of upgrading them economically into marketable products; and (3) obtain information that can increase production of coal for use in carbonization through establishment of a coal-chemicals industry based on the utilization of low-temperature tars.

Synthetic detergents in waste water is a controversial topic. Branched-chain alkylbenzene sulfonate (ABS), the principal surfactant used in detergents, is difficult to remove from waste water because of its resistance to biological degradation. Conventional ABS is also being blamed for many sewage plant foaming problems (12). As a result, extensive research is being conducted in this country and abroad on producing a "soft" type of ABS (3), one that is more easily degraded by the bacteria present in sewage plants than is the conventional ABS. Conventional ABS consists of a mixture of mono-substituted benzenes, the alkyl substituent being highly branched, e. g. :



No evidence has been found of the presence of methylene chains exceeding three carbons. "Soft" ABS, on the other hand, has less branched alkyl chains than the old "hard" ABS and contains methylene chains exceeding three carbons, e. g. :



Low-temperature lignite neutral oil fractions contain as much as 17 to 20 percent alpha olefins in addition to trans-internal and tertiary ones (9). These olefins are valuable as charge stock for the synthesis of alcohols, acids, and surfactants for detergents. Other Bureau scientists have demonstrated the feasibility of producing alcohols (1). This report covers laboratory-scale research on the preparation of biodegradable alkylbenzene sulfonates (ABS) using straight-chain olefins extracted from a low-temperature Texas lignite tar.

EXPERIMENTAL

Preparation of Feed Stock. - The tar used in this study was produced from a Texas lignite carbonized at about 950°F by the Parry carbonization process (10). The crude tar was vacuum distilled (25" Hg) to an atmospheric pressure end boiling point of 350°C. Distillation cutoff temperature of 350°C was chosen because the pitch residue has a softening point of 110°C, the generally accepted softening point for use of pitch as electrode binder. Under these distillation conditions, yields were as follows:

	<u>wt pct</u>
Distillate	51.2
Pitch	43.7
Water	2.1
Distillation losses	3.0

The distillate consisted of:

	<u>wt pct</u>
Tar acids	31.0
Tar bases	3.9
Neutral oils	65.1

The tar acids and bases were removed from the distillate by conventional caustic-acid extraction. A fluorescent indicator adsorption analysis of the neutral oil fraction showed 51.9 pct aromatics, 37.0 pct olefins, and 11.1 pct paraffins.

Urea Adduction. - Straight-chain olefins and paraffins were removed from the neutral oil by the urea adduction method (5, 7).

The general technique involved thorough mixing of neutral oil, urea, and a solvent for one hour at room temperature. Methanol was chosen as the solvent. The crystalline adduct and excess urea were recovered by vacuum filtration and washed with 2, 2, 4-trimethylpentane to remove unadducted neutral oil components. A sufficient amount of water was added to the crystals to decompose the adduct. The ether solution was placed in a flask, and the solvent was removed at room temperature by a stream of nitrogen. As shown in Table 1, yields of pure product ranged from 12.0 to 15.0 pct. The extracted material was distilled to an end temperature of 300°C. The fraction 170° to 300°C containing the C₁₀ to C₁₆ normal olefins was considered suitable for detergents. Infrared analysis of the product showed a strong concentration of alpha olefins with a trace of branched chains.

The 170° to 300°C fraction subsequently was analyzed by gas-liquid chromatography by an established procedure (2). Table 2 gives the retention times of some paraffins and olefins, and their relative retentions referred to n-dodecane. Figure 1 is the chromatogram. Volume percentages of the different compounds were calculated by measuring the peak heights and multiplying the results by the peak width at half peak height. Test results are given in Table 3.

Preparation of Alkylbenzenes. - Alkylation experiments were conducted using the 170° to 300°C fraction of the urea adduction product as the alkylating agent. Benzene was alkylated on a semimicro scale using established procedures (11). Benzene and anhydrous AlCl_3 were charged to a 150 cc flask equipped with stirrer, thermometer, and separatory funnel for the addition of the alkylating agent. The straight-chain olefin-paraffin mixture was added over a 30-minute period. Additional catalyst was added at 10-minute intervals following initiation of reaction to maintain a maximum reaction temperature of 55°C. Following the addition period, 15 minutes was allowed for stirring and completion of the reaction. The acidic mixture was cooled to room temperature and neutralized by the addition of 20 pct NaOH solution. The catalyst and benzene-rich layers were then separated by successive water washings in a separatory funnel, after which the product was fractionated into three cuts on a 10-inch Vigreux column. The cuts included benzene, an intermediate composed of paraffins and unreacted olefins, and alkylbenzenes. The alkylbenzene fraction was analyzed by infrared spectrophotometry, and the presence of alkylbenzenes was confirmed; no alpha olefins were detected. Yields calculated from distillation data are reported in Table 4.

Sulfonation of Alkylbenzenes. - Liquid SO_3 was vaporized into a metered air stream, and the mixture was introduced into a 100 cc flask containing alkylbenzenes (8). The flask was equipped with a thermometer and submerged gas-inlet and outlet tubes; agitation was provided by the SO_3 -air flow. The SO_3 (14 g) was bubbled into the alkylate (40 g) for approximately one hour. External cooling was necessary to maintain a reaction temperature of 50° to 60°C with an air rate of 1,350 cc/minute. The reaction mixture was neutralized with 60 cc of 10 pct NaOH solution producing a light tan slurry.

Figure 2 is a simplified flow diagram for preparing the C_{10} to C_{16} alkylbenzene sulfonate. The percentage figures given in the flow diagram are the weight-percent of the product versus the input feed to each individual processing step. Fifty pct of the n-olefin-paraffin mixture is within the desirable range of C_{10} - C_{16} . The remaining 50 pct is concentrated chiefly in the high boiling fraction (>300°C) and consists of a mixture of C_{17} - C_{20} olefins and paraffins. Investigations are in progress to increase the yield of usable alkylbenzenes. These include the thermal cracking of the high-boiling paraffins to give C_{10} - C_{16} olefins and the direct conversion of the olefins to alkylbenzenes by eliminating the urea adduction step. When these results are available, an economic study of the process will be made.

Biodegradability Tests. - A sample of the alkylbenzene sulfonates was submitted to the United States Testing Company, Inc., Hoboken, N. J., for determination of its biodegradability. The test procedure used was that adopted by the West German Government (6) as no standard has been prescribed as yet by the United States. This procedure for evaluating surfactant biodegradability calls for the use of a continuous activated sludge waste-water treatment test.

RESULTS AND DISCUSSION

The percent decomposition of the methylene blue active substance (MBAS) was calculated daily. These values are given in Table 5 and shown graphically in Figure 3. A summary of the results is given in Table 6. The presence of 5.6 pct soap found in the test sample undoubtedly represents sample contamination. The biodegradability of the sulfonate sample averaged 99.52 pct. The West German law specifies that decomposability of acceptable anionic detergents must be at least 80 pct (arithmetic mean) (4).

CONCLUSIONS

Straight-chain olefins and paraffins were extracted from a low-temperature lignite tar neutral oil fraction by urea adduction. Infrared analysis of the adducted product revealed no urea contamination and a strong concentration of alpha olefins with only a trace of branch-chain olefins. The 170° to 300°C fraction (C₁₀-C₁₆) of the olefin-paraffin mixture was used to prepare a mixture of alkylbenzenes which, upon sulfonation, gave a synthetic detergent that was 99.52 pct biodegradable.

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TABLE 1. - Urea adduction of straight-chain aliphatics from neutral oil

<u>Charge,</u> <u>g</u>	<u>Methanol,</u> <u>cc</u>	<u>Urea,</u> <u>g</u>	<u>Ether/H₂O,</u> <u>cc</u>	<u>Pure product,</u> <u>wt pct</u>
75	20	45	50/150	12.0
17.5	445	87.5	50/150	12.7
500	300	500	150/500	15.0

TABLE 2. - Retention times of pure olefins and paraffins

<u>Compound</u>	<u>Retention time¹</u> <u>(minutes)</u>	<u>Relative retention¹</u> <u>(to n-dodecane)</u>
n-Decane	1.59	0.43
1-Decene	1.77	0.48
n-Undecane	2.43	0.66
1-Undecene	2.70	0.74
n-Dodecane	3.66	1.00
1-Dodecene	4.05	1.32
n-Tridecane	5.52	1.51
1-Tridecene	6.12	1.67
n-Tetradecane	8.34	2.28
1-Tetradecene	9.24	2.52
n-Pentadecane	12.63	3.45
1-Pentadecene	13.89	3.80
n-Hexadecane	19.02	5.20
1-Hexadecene	21.06	5.75

¹ Corrected for air.

TABLE 3. - Quantitative analysis of C₈ to C₁₆
α-olefins and paraffins

<u>Compound</u>	<u>Vol., pct</u>
Trimethylpentane	Trace
n-Octane	Trace
1-Octene	Trace
n-Nonane	0.8
1-Nonene	0.9
n-Decane	3.5
1-Decene	3.9
n-Undecane	5.5
1-Undecene	6.5
n-Dodecane	7.2
1-Dodecene	8.0
n-Tridecane	7.6
1-Tridecene	8.8
n-Tetradecane	7.7
1-Tetradecene	8.6
n-Pentadecane	8.3
1-Pentadecene	8.4
n-Hexadecane	8.1
1-Hexadecene	6.3
	<hr/> 100.0
Paraffins	48.7
Olefins	51.3

TABLE 4. - Synthesis of alkylbenzenes

<u>Wt ratio,</u> <u>benzene/feed</u>	<u>AlCl₃ catalyst,</u> <u>wt pct</u>	<u>Reaction conditions</u>		<u>Yield, pct¹</u>
		<u>Temp., °C</u>	<u>Time, min</u>	
4.6 ²	1.8	40-55	45	89.5
4.6 ³	2.1	50-55	45	45.0

¹ Weight-percent, alkylbenzene/feed.

² Commercial C₁₁ to C₁₅ alpha olefins.

³ Olefin-paraffin mixture (neutral oil 170° to 300° C) (C₁₀ to C₁₆).

TABLE 5. - Percent MBAS biodegraded per day

<u>Day of test</u>	<u>MBAS biodegraded, pct</u>	<u>Day of test</u>	<u>MBAS biodegraded, pct</u>
8	95.4	19	100.0
9	94.0	20	100.0
10	100.0	21	100.0
11	100.0	22	100.0
12	100.0	23	100.0
13	98.8	24	100.0
14	100.0	25	100.0
15	100.0	26	100.0
16	100.0	27	100.0
17	100.0	28	100.0
18	100.0	29	100.0
		30	100.0

Decomposability mean value,
99.48 pct

TABLE 6. - Summary of biodegradability tests

	<u>Percent</u>
MBAS in alkylbenzene sulfonate	66.3
Soap in sample	5.6
Average of decomposability values for 23 consecutive days following break-in period.	99.48
Decomposability of the detergent (including soap ¹) in the sample	99.52

¹ Calculated from Part I, No. 7, Specification of
West German Government Ordinance.

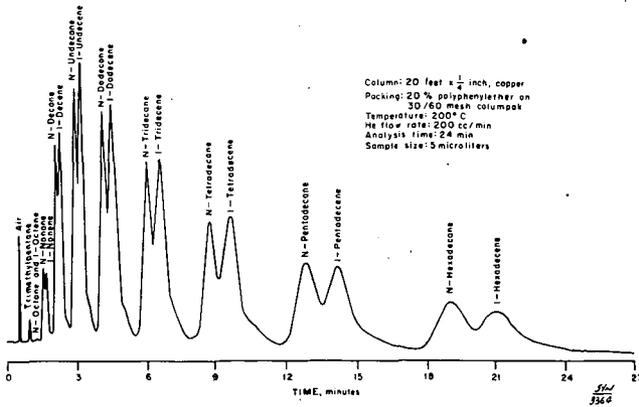


FIGURE 1. Chromatogram of C₈-C₁₆ olefin-paraffin mixture.

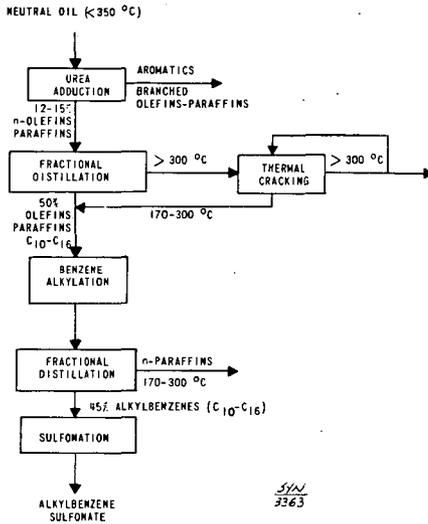


FIGURE 2. Proposed process for utilization of normal olefins in low-temperature tar.

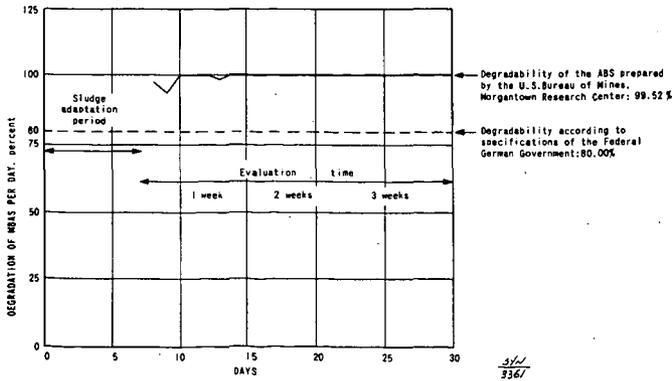


FIGURE 3. Degradation of methylene blue active substance.