

Fig. 3. Corrected optical density versus p.p.m. BHA in known samples: A, curve for hardened lard samples; B, curve for lard samples.

relationship when this method is applied to the determination of BHA in lard samples. With fats much softer than lard the accuracy of this method falls off rapidly on account of their increased solubility in the solvent. When measures are taken further to decrease their solubility, the solubility of BHA is also reduced but not to a reproducible level. It is therefore a necessary restriction of this method that the fat samples under investigation not be softer than lard or rather that they do not contain more lower-melting, more-soluble triglycerides.

This method was used to determine how effectively BHA is removed from lard or hardened lard during deodorization. In the deodorization process steam is bubbled through the fat, which has been heated to a temperature of 220°C. at 1-mm. pressure for 4 hr. Under these conditions the steam distillable BHA should be completely removed from the fat. Thirty p.p.m. of BHA were added to hardened lard both before and after deodorization, and samples of each were then analyzed by the present method. Table II compares these results with a control as well as the analysis of these samples by the 2,2'-bipyridine-ferri-

TABLE II

BHA Content of Hardened Lard Before and After Deodorization

	BHA recovered (p.p.m.)	
	Present method	Colorimetric method (1, 9)
1. Control (no BHA added).....	0	0
2. 30 p.p.m. BHA added to control.....	29.3	20
3. Sample 2 after deodorization.....	0	0
4. 30 p.p.m. added to Sample 3.....	29.6	20

chloride method. The colorimetric procedure for analysis gives low results, and while it does indicate the complete removal of BHA during deodorization, the results cannot be considered reliable for low concentrations of BHA. The use of borax-2,6-dichloroquinonechlorimide (9) is under optimum conditions capable of the qualitative detection of BHA. However this method is of little practical value to the processor who has to restabilize a deodorized stabilized lard (11).

It was observed that, on re-examination of the hardened lard-BHA test samples after 40 and 100 days of storage at room temperature, there was a decrease in the antioxidant level. After 40 days there were 68 p.p.m. and after 100 days 57 p.p.m. for the 100-p.p.m. BHA sample. This decrease was found to be proportional at all BHA concentrations at each time interval, thus exhibiting a continued linear relationship. We can attribute this to the oxidation of BHA in its role as an antioxidant with the loss of its characteristic phenol-grouping. This loss through oxidation is not thoroughly understood, but it is thought that the isomeric phenoxy radicals will rearrange to give a semiquinone structure (8) or, as in the case of the oxidation of butylated hydroxytoluene (4), undergo some degree of dimerization. Either path would result in the observed decrease of BHA.

Summary

A direct spectrophotometric method for the determination of butylated hydroxyanisole has been presented. This procedure allows good precision in the analysis of lard and hardened lard containing from 0 to 100 p.p.m. of BHA and is more reliable than existing colorimetric techniques, especially in the lower range of antioxidant concentrations.

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[Received January 9, 1959]

Analysis of Surfactant Mixtures. I.

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MOST SCHEMES for characterizing or analyzing surfactants rely on specific reactions of the hydrophilic part of the molecule (e.g., sulfate, sulfonate, or polyethoxyethanol groups). Much additional useful information can be obtained by also

identifying the hydrophobic raw material used in the manufacture of the surfactant. Identification of the hydrophobic portion of the molecule is very difficult on the intact surfactant and can be accomplished much more easily if it can be decomposed into a

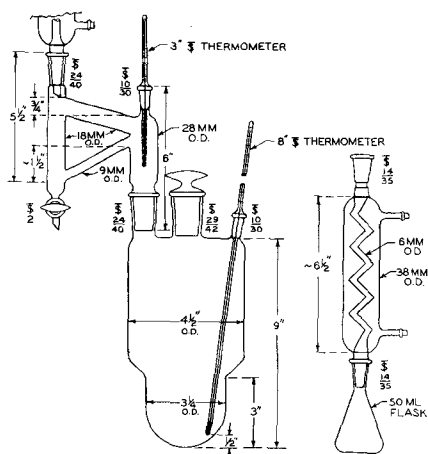


FIG. 1. Apparatus for decomposition with phosphoric acid.

characteristic nonsurface-active hydrophobic oil. This is true for individual surfactants, also for mixtures, because it is much simpler to separate and identify the derived oils than the surfactant mixture itself.

Surfactants containing ester, amide, or sulfuric acid ester groups can be easily decomposed into characteristic hydrophobic oils by hydrolysis in dilute acid or alkali. However surfactants, such as aromatic sulfonates or those containing polymerized ethylene oxide without the weak linkages mentioned above, generally decompose only under more severe conditions. For example, ethylene oxide condensates of alkylphenols or alcohols react with hydrobromic acid (11) or hydrochloric acid (3) to give the corresponding aromatic or aliphatic halide. Hydriodic acid (5) also decomposes these surfactants to the corresponding aromatic iodide and an alkyl iodide or olefin. A well-known method of recovering a characteristic oil from aromatic sulfonates is desulfonation at elevated temperatures (2, 4). This is generally accomplished by treating the sulfonate with 60–70% sulfuric acid and superheated steam at 140–190°C. or with concentrated hydrochloric acid in a sealed container at 150–200°C. Another procedure involves the use of hot, concentrated phosphoric acid (1, 8, 9). Ease of desulfonation varies greatly; the sulfonic acids of polyalkylbenzenes, phenols, or aromatic amines are much more reactive than the sulfonic acids of the monoalkylbenzenes.

Desulfonation of detergent-range alkylbenzenesulfonates is not reported in the literature but is effectively carried out by using phosphoric acid. This technique was also found to be successful for decomposing most other common surfactants into characteristic recoverable oils. It involves steam-stripping a mixture of the surfactant and phosphoric acid at 215°C. for 90 min. Subsequent analysis of the recovered oil provides much useful information, both for individual surfactants and mixtures, such as retail washing-products. Phosphoric acid is the preferred decomposing medium because it permits the reaction to be carried out at atmospheric pressure and because it causes less charring than sulfuric acid.

In this investigation emphasis was on developing a quick routine decomposition method that would apply to as many surfactant species and mixtures as possible. Many of the surfactants give recovered oils, which are essentially identical with the starting hydrophobic raw material. In other cases the recovered

oils are characteristic of the hydrophobic raw material but possess a different functionality. Two surfactant types, *alpha*-sulfo fatty acids and alkanesulfonates, do not yield a recoverable oil by this procedure. This method is very useful for characterizing hydrophobic raw materials of commercial surfactants and also for analyzing surfactant mixtures.

Experimental

Decomposition Reaction and Oil Recovery. About 5 g. of surfactant and 20–30 carborundum boiling chips (Carborundum Grit No. 10RA, 8 to 14 mesh, Carborundum Company) are added to 250 ml. of specially prepared phosphoric acid (boiling point = 215°C.) in the reactor (Figure 1). The mixture is heated until the phosphoric acid begins to boil. The water trap is filled, and the heating rate and return water-flow are adjusted to maintain the pot temperature at 215°C. \pm 2°C. with a rapid condensation rate (60–80 drops of condensate per minute). The reaction mix is refluxed for 90 min. after the overhead thermometer indicates a vapor temperature of 100°C. (If excessive foaming occurs, normal antifoaming procedures, such as additives or hot surfaces, are helpful.) Then the oil and water in the trap are quantitatively transferred to a 125-ml. separatory funnel, using about 5 ml. of water and 5 ml. of acetone.

Acetone is added until the aqueous layer is 70-volume percentage of acetone, and 20% KOH is added to the mixture until a blue color is formed with Gramercy Universal Indicator. The solution is then extracted twice with a 10-ml. and once with a 5-ml. portion of isopentane. Additional 70% acetone may be required if fatty acids salts separate from the solution. The aqueous layer is saved. The isopentane extracts are combined, washed twice with 10-ml. portions of water, and filtered through a small, fluted, filter paper, collecting the filtrate in the 50-ml. tared Erlenmeyer flask (Figure 1). To insure a quantitative transfer the separatory funnel is rinsed with a few milliliters of isopentane; and the filter paper is washed thoroughly with a fine stream of isopentane until the dark color of the absorbed oil is removed.

The neutral hydrophobic oil is obtained by removing the isopentane through the Vigreux column (Figure 1) on a steam plate at 130–140°C. surface temperature for 30 min. The isopentane content of the residual neutral oil (5–10%) may be determined by gas-liquid partition chromatography,¹ as described below.

The acidic oil fraction is obtained by acidifying the aqueous-acetone layer and extracting with two 10-ml. portions of isopentane. The combined isopentane extracts are washed with two 5-ml. portions of 3 N HCl and filtered through filter paper, as described above. (Dry diethyl ether may be used to wash the filter paper if the acids begin to crystallize on the paper.) The isopentane can be completely removed from the acidic oil by careful heating on the steam plate without the Vigreux column.

Preparation of Methyl Esters. A 100-mg. sample of the recovered acidic oils is placed in a 50-ml. Erlenmeyer flask along with 25 ml. of anhydrous methanol and two drops of concentrated sulfuric acid. The solution is allowed to reflux for 30 min., cooled, and neutralized with 20% KOH after diluting with

¹ In the remainder of this paper the abbreviation GALIPA is used in place of gas-liquid partition chromatography.

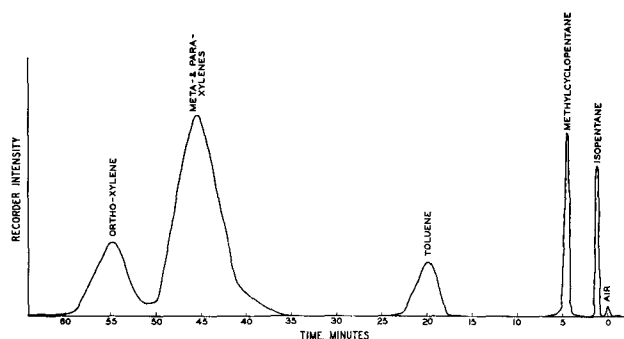


Fig. 2. Gas-chromatography curve for low-boiling components—Column 1.

TABLE I
Relative Retention Times of Known Compounds
(Column 2—260°C.)

Compounds	Relative retention time
Diisobutylene.....	0.04
1-Octene.....	0.05
1-Decene.....	0.11
Tertiary dodecyl mercaptan.....	0.11 to 0.13
Commercial tetrapropylene polymer.....	0.11 to 0.15
1-Dodecene.....	0.24
1-Tetradecene.....	0.50
1-Hexadecene.....	1.00
1-Octadecene.....	2.05
1-Octanol.....	0.15
1-Decanol.....	0.34
1-Dodecanol.....	0.71
1-Tetradecanol.....	1.58
Diisobutylene phenol.....	1.54
Commercial tetrapropylene benzene	
Peak 1.....	0.74
Peak 2.....	0.89
Peak 3.....	1.04
Peak 4.....	1.23
Peak 5 (Inflection).....	1.35
Peak 6.....	1.45
Peak 7.....	1.62
Peak 8.....	1.86

50 ml. of water. The mixture is then extracted with two 10-ml. portions of isopentane, and the esters are recovered from the isopentane layers by use of the Vigreux column as described above.

Gas-Liquid Partition Chromatography (GALIPA). The three columns used in this work are described below. Column No. 1 is used to analyze for isopentane by adding a weighed amount of methylocyclopentane as an internal standard. Column No. 2 is used for the C_8 to C_{18} olefins, C_8 to C_{14} alcohols, and commercial detergent alkylates. Column No. 3 is used for the methyl esters of fatty acids and the C_{14} to C_{18} alcohols. Relative retention times for known compounds relative to 1-hexadecene or 1-octadecene are pre-

TABLE II
Relative Retention Times of Known Compounds
(Column 3—300°C.)

Compounds	Relative retention time
Methyl laurate.....	0.54
Methyl myristate.....	0.82
1-Octadecene.....	1.00
Methyl palmitate.....	1.17
Methyl stearate.....	2.04
1-Dodecanol.....	0.44
1-Tetradecanol.....	0.810
1-Hexadecanol.....	1.69
1-Octadecanol.....	3.36

sented in Tables I and II. Figures 2 to 5 present typical curves obtained on the pure materials.²

Column No. 1. Temperature, 90°C.; 40 g. of didecylphthalate per 100 g. of Johns-Manville C_{22} crushed brick (20–30 mesh); 6½ ft. by ¼-in. OD copper tubing; 24-g. packing in column.

Column No. 2. Temperature, 260°C.; 40 g. of 85/100 penetration paraffinic Middle East asphalt per 100 g. of Johns-Manville C_{22} crushed brick (20–30 mesh); 10 ft. of ¼-in. OD copper tubing; 36-g. packing in column.

Column No. 3. Temperature, 300°C.; 40 g. of Dow Corning High Vacuum Silicone Grease per 100 g. of Johns-Manville C_{22} crushed brick (20–30 mesh); 12 feet of ¼-inch OD copper tubing; 36 g. of packing in column.

Ion Exchange Resin. A batch ion exchange method (6) was used to prepare the anionic surfactant-resin complex.

Discussion

Alkylbenzenesulfonates. Detergent-range sulfonates, such as tetrapropylenebenzenesulfonate, are very resistant to decomposition in hot phosphoric acid. This is shown by the fact that only 1–2% decomposed in 90 min. at 185°C. (Table IV). The rate increases rapidly as the temperature rises however. Charring also increases with temperature so that the 90-min. yield of alkylbenzene is less at 225°C. than at 215°C. The rate of formation of alkylbenzene is directly proportional to the amount of sulfonate in the reaction mix during the early stages of the reaction (first 30–60 min.) but generally slows down later. This was found true for commercial alkylbenzenesulfonates as well as for sulfonates made from monoalkylbenzenes of known structure. At 215°C. the 90-min. recovery of detergent-range alkylbenzene is about 70–80% of theoretical, and the ultimate recovery is about 85%. The percentage of alkylbenzene recovered in 90 min. is not sensitive to the amount of sulfonate charged

² The temperatures may be changed to improve the resolution of the Columns 2 and 3. However these temperatures were chosen to allow identification of as many hydrophobic materials as possible on two columns in 60 minutes' time or less.

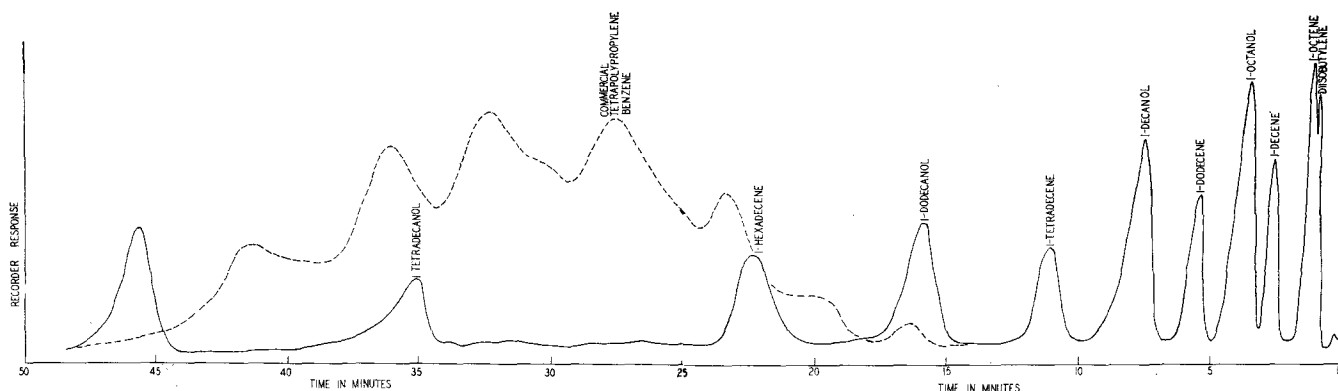


Fig. 3. Gas-chromatography curves for olefins, alcohols, and detergent alkylate—Column 2.

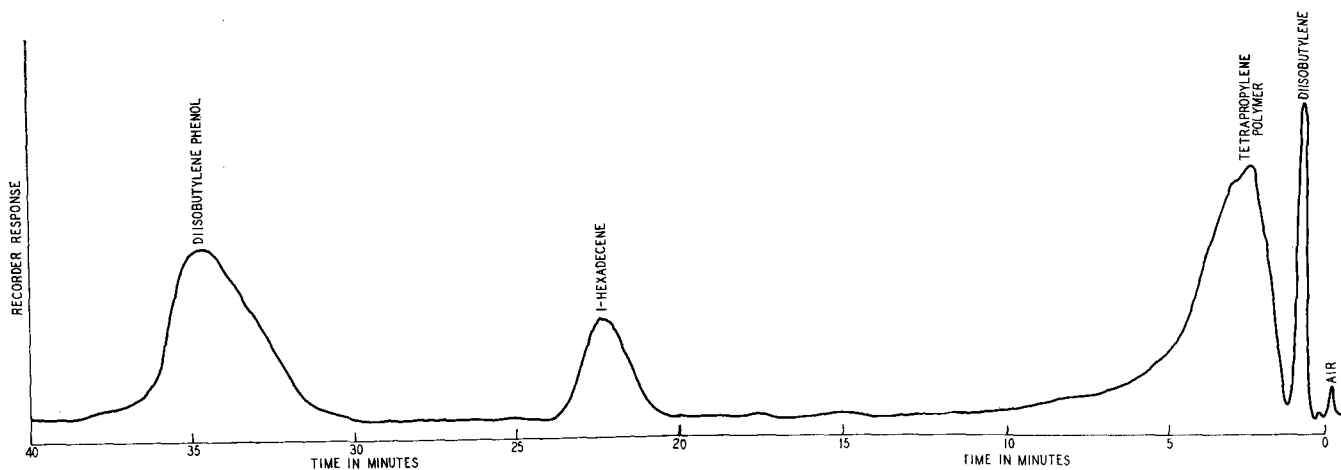


FIG. 4. Gas-chromatography curve for olefin polymers—column 2.

TABLE III

High-Molecular-Weight Portion of the Mass Spectra of Desulfonated Tetrapropylenebenzenesulfonate

M/e	Relative intensity ^a		M/e	Relative intensity ^a	
	Before Sulfonation	After Desulfonation		Before sulfonation	After desulfonation
198	0.5	241	Tr	0.5
199	Tr	1.0	242	Tr	0.5
200	Tr	0.6	243	0.6	1.5
201	2.1	6.5	244	1.2	2.6
202	1.1	2.3	245	1.0	1.5
203	15.6	17.1	246	14.5	17.1
204	3.5	3.7	255	0.2
212	0.2	256	Tr	0.2
213	0.9	257	0.1	0.6
214	0.4	258	0.6	0.9
215	1.4	5.1	259	0.4	0.7
216	1.0	1.9	260	4.2	4.1
217	13.4	16.5	271	Tr	0.3
218	4.7	4.9	272	Tr	0.2
226	0.2	273	0.2	0.6
227	1.0	274	0.9	1.0
228	0.4	285	0.2
229	1.4	3.6	286	Tr	0.2
230	1.2	2.4	287	Tr	0.6
231	3.8	4.2	288	0.3	0.5
232	9.9	9.7	301	Tr	0.2
			302	0.1

^a Relative to 1,000 for the 119 (M/e) peak.

or to the presence of inorganic materials, such as sodium sulfate and silicates, which are commonly present in retail products.

The rate of desulfonation increases with the decreasing molecular weight of the alkyl group. Preliminary data indicate that the sulfonate from *n*-butylbenzene desulfonates at a rate about 15 times as fast as that from *n*-decylbenzene and that sulfonate from ethylbenzene is about 20 times as fast as the decyl compound. Differences in rate become less in the higher

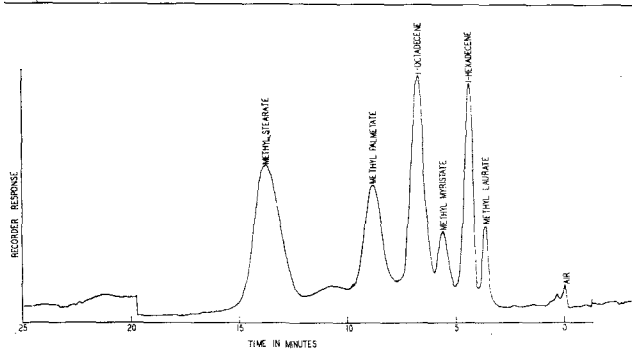


FIG. 5. Gas-chromatography curve for high-boiling components—Column 3.

molecular weight region constituting detergent-range alkylates. Use of a 90-min. reaction time essentially eliminates selectivity caused by differences in desulfonation rates because even the higher-molecular-weight species present in commercial products decompose almost to the ultimate recoverable limit in that time. This is borne out by comparing the high-mass spectral fragmentation patterns of tetrapropylenebenzene before sulfonation and after subsequent sulfonation-desulfonation treatment. These data (Table III) show that little change occurs in the relative amounts of the parent masses although some degradation occurs, as shown by the presence of new peaks in the spectra of the recovered oil.

There is apparently little change in either molecular weight or structure of monoalkylbenzenes during sulfonation or desulfonation. This was indicated by analyses using GALIPA, infrared spectra, and high-mass spectra. GALIPA and mass spectral analysis indicated a small amount (less than 1%) of degradation to lower boiling materials with little or no change in general fragmentation pattern. Infrared spectra indicated no detectable change except for the formation of small amounts of olefinic unsaturation or oxidation products. Alkylbenzenes tested in this manner include commercial detergent alkylate, 1-phenyl-decane, 2-phenyl-dodecane, 2-phenyl-2-methylundecane, 1-phenyl-5,7,7-trimethyloctane, and 2-phen-

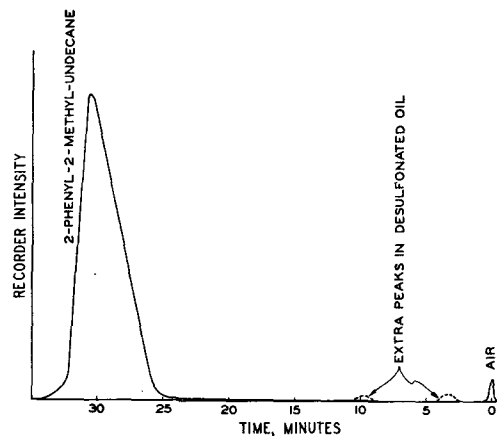


FIG. 6. Gas-chromatography curves for 2-phenyl-2-methylundecane and recovered oil from 2-phenyl-2-methylundecane sulfonate.

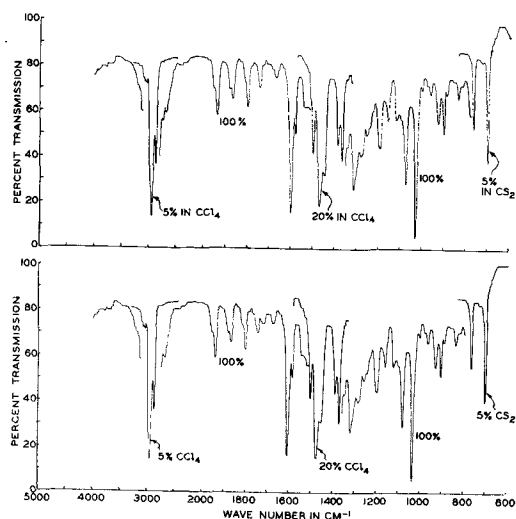


Fig. 7. Infrared spectra of 2-phenyl-2-methyl-undecane (upper curve) and recovered oil from 2-phenyl-2-methyl-undecane sulfonate.

yl-2,6,10-trimethyl-undecane. Typical comparisons by GALIPA and infrared are shown in Figures 6 and 7 for 2- ϕ -2-methyl-undecane.

For surfactant mixtures (especially liquid detergent compositions) the analysis is simplified somewhat by separating the anionic and nonionic components from each other prior to phosphoric acid treatment. Methods have been reported (6, 10) for carrying out this separation, involving tying the anionic to an appropriate ion exchange resin. However no method has been reported for recovering the anionic from the resin. As shown in Table IV, the yield of alkylbenzene from the resin-sulfonate complex is only slightly less than that obtained from the sodium sulfonate alone.

TABLE IV
Effect of Certain Variables on the 90-Minute Yield of Oil from Commercial Sodium Dodecylbenzenesulfonate (348 Avg. MW)

Sulfonate charged, grams	Temperature °C.	Additive grams	Recovered oil
			Yield % theoretical
1	185	1-2
1	190	25
1	200	49
2	215	78
11	215	78
1	224	49
2 ^a	215	68-71
2	215	Sodium sulfate, 2	79
2	215	Sodium sulfate, 5	79
2	215	Sodium silicate, 1	82

^a Sulfonate charged as the complex formed from 20 g. of Dowex 1-X2 ion exchange resin plus 2 g. of the sodium sulfonate.

Other Surfactant Types. Table V presents results of decomposing surfactants other than monoalkylbenzenesulfonates with hot phosphoric acid. Although the temperature used was 215°C., most of these materials will also decompose at 185°C., a temperature that does not decompose detergent-range aromatic sulfonate surfactants. The starting materials in these reactions were commercial surfactants, purified as nearly as possible to a 100%-active state. Where possible, theoretical yields are indicated in Table V.

In the case of the straight-chain alkyl sulfates, alkylbenzenesulfonates, and fatty acid-based surfactants, fairly good yields of the original hydrophobic

oils were obtained. However recovered oils obtained from the branched alcohol-based surfactants and from the ethylene oxide condensates of commercial lauryl alcohol, tridecyl alcohol, dodecyl mercaptan, and diisobutylene phenol were different from the original hydrophobic materials. For example, sodium dioctyl-sulfosuccinate gave approximately an equal mixture of octyl alcohols (GALIPA retention time of 0.16) and octenes (retention time of 0.06).

The lauryl and tridecyl-based ethylene oxide adducts gave only olefins derived from the alcohols; the former were predominantly *trans*-olefins (strong infrared absorption peak at 970 cm⁻¹) and the latter branched olefins. (The presence of absorption at 810 cm⁻¹ is attributed to trisubstituted olefin since peroxides were found to be absent.) GALIPA analysis showed two peaks with retention times of 0.51 (unbranched tetradecenes) and 0.26 (unbranched dodecenes) for the lauryl alcohol-based product and a peak at 0.21 (branched tridecyl olefins) for the tridecyl alcohol-based product. In addition, some lower and higher olefins are formed in small amounts. The mercaptan product decomposed mainly to branched olefins derived from the mercaptans; the GALIPA analysis showed a large peak at a retention time of 0.12. This is the same retention time found for the mercaptans. However the products are not soluble in 30% ethanolic sodium hydroxide as are the mercaptans. Although the alcohol-based surfactants are completely converted to the olefins, some mercaptans are recovered unchanged from the mercaptan condensate decomposition.

The alkylphenol condensate decomposed extensively, apparently giving a mixture of olefins, conjugated olefins, and alcohols formed by cleavage at and rupture of the aromatic ring. The ultraviolet spectrum of this product showed a strong absorption peak in the 240-250 m μ region, which is typical of conjugated systems. However the ultraviolet spectra did not show typical aromatic absorption peaks over the 260-290 m μ region. GALIPA analysis showed the presence of two major peaks with relative retention times of 0.16 and 0.04 to 0.08. These times correspond to those observed for branched dodecenes and octenes, respectively. In addition, the infrared spectra show that an appreciable amount of the product contains an alcohol group.

TABLE V
Recovery of Oils from Phosphoric Acid Decomposition at 215°C. (90 Minutes) (Purified Commercial Surfactants)

Surfactant (2-g. charge)	Average yield— wt. % of charge % theoretical		Br. No. of rec. oil, Br./cg. oil
	Neutral	Acidic	
Tetrapropylenebenzenesulfonate.....	53 (78)	0
Xylenesulfonate.....	40 (79)	0
Tallow alcohol sulfate ^a	52 (72)	0
Lauryl alcohol sulfate ^a	53 (80)	0
Lauroyl isethionate ^a	0	59 (96)
Lauroic-myristic diethanol amide ^a	0	64 (91)
N-methyl-N-oleoyl taurate ^a	0	58 (88)
Dioctyl sulfosuccinate ^a	29 (.....)	0	82
Ethylene oxide condensates:			
Coconut acids + 15 moles EO ^a	3 ^b	21 (89)
Lauryl-myristic alcohols + 3 moles EO ^a	49 (92)	0	85
Tridecyl alcohols + 9 moles EO ^a	30 (94)	0	80
Tert. dodecyl mercaptans + 9 moles EO ^a	24 (.....)	5 (.....) ^c	82
Diisobutylene phenol + 9 moles EO ^a	13 (.....)	1 (.....) ^d	77

^a These materials are also decomposed at 185°C. without a decrease in yield of oil.

^b Infrared analysis indicates that this material is a small amount of volatile, low-ethylene-oxide-content ester.

^c This fraction is predominantly tert. dodecyl mercaptan.

^d Ultraviolet analysis indicates that this material is nonaromatic but contains conjugated systems.

Surfactant Mixtures. The decomposition product is normally the same in mixtures of surfactants as that obtained separately. However, as might be expected, the presence of a relatively stable, strong acid, causes dehydration of alcohols to give olefins. For example, decomposing a mixture of alkylbenzenesulfonate and lauryl sulfate in phosphoric acid gives alkylbenzenes plus dodecenes. As can be seen from their relative retention times (Table I), these olefins are readily analyzed by GALIPA.

Depending on the complexity of the mixture, it may not be possible to separate all major species in the decomposition oil by GALIPA. In these cases, several other conventional analytical techniques may be useful individually or in combination. Some examples of useful techniques are urea clathration, solvent partition or crystallization and liquid-phase chromatography. It appears possible to decompose most other surfactant types selectively in the presence of detergent-range alkylbenzenesulfonates at 185°C. Excessive foaming is the chief problem in this technique but can be minimized by lowering the amount of alkylarylsulfonate charged to one gram and employing conventional defoaming procedures.

For example, a mixture of lauryl sulfate (2 g.) and commercial tetrapropylenebenzenesulfonate (1 g.) was heated for 60 min. in 185°C. (BP) phosphoric acid. Water was then removed from the trap, and the reaction mixture was heated for another 60 min. at 215°C. A normal yield of 0.90 g. of dodecenes was obtained at 185°C. and a normal 65-min. yield of 0.45 g. of alkylbenzene was recovered at 215°C. In another experiment a mixture of straight-chain olefins and polypropylenebenzene was obtained by decomposing a mixture of tallow alcohol sulfate and alkylbenzenesulfonate. Because GALIPA will not resolve these products, the olefins were separated from the alkylbenzene by forming and recrystallizing the urea adduct. Although the olefins were recovered in a pure state, the alkylbenzene recovered from the filtrate was contaminated with some olefin. However this separation was sufficient to identify the olefins as probably derived from tallow.

Phosphoric acid decomposition does not furnish a single analytical scheme for all conceivable mixtures of surfactants. The products however are more amenable to classical analytical tools than are the starting surfactants. Further work on the conditions of the decomposition reaction or subsequent analytical

procedures may increase the general applicability of this method to complex surfactant mixtures.

Summary

Some data on the use of 93% phosphoric acid as a reagent for recovering the hydrophobic portion of surfactants are presented, and their application to the analysis of surfactant mixtures is discussed. Aromatic sulfonates, straight-chain alkyl sulfates, fatty acid amides, and fatty acid esters decomposed to give good yields of the starting hydrophobic materials. Dioctylsulfosuccinate gave a mixture of octyl alcohols and olefins while the ethylene oxide condensates of lauryl alcohol, tridecyl alcohol, and tertiary dodecyl mercaptan gave olefins derived from the starting hydrophobic materials. Diisobutylene phenol-ethylene oxide condensate decomposed to olefins, conjugated olefins, and alcohols formed by rupture of the aromatic ring. The products are characteristic of the hydrophobic oils, and in most cases products from mixtures of surfactants can be separated by known analytical methods. *Alpha*-sulfo fatty acids or alkane sulfonates do not give recoverable oils by this treatment.

Acknowledgment

The authors wish to acknowledge the contributions made during this investigation by members of the Analytical Division of the California Research Corporation, especially C. F. Spencer and F. A. Elder for gas chromatography and high-mass spectral determinations, respectively, and H. M. White for infrared and ultraviolet analyses. They also wish to express their appreciation to the Oronite Chemical Company for their interest and funds provided for this investigation.

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[Received October 22, 1958]

Distribution of Water in the United States as a Function of Hardness

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IT is a well known fact, especially by the American housewife, that synthetic detergents will perform better than soap in hard water since they do not form the insoluble soaps which lead to poor detergent. The syndets do not have the inherent undesirable characteristic of leaving a ring in bath tubs and sinks or producing "tattle-tale gray" on fabrics as

do soaps. A fact that is not generally known by the public, but well known by the detergent industry, is that synthetic detergents themselves have different performance characteristics in soft and hard water.

Many of the synthetic detergents used in washing dishes and doing light hand-laundry are prepared from surface-active agents derived from petroleum