Qualitative and Quantitative Analysis of Mixtures of Surface-Active Agents with Special Reference to Synthetic Detergents

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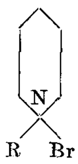
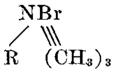
FOR a better understanding of performance evaluation results, obtained with commercial detergents, for product control, etc., a qualitative and (or) quantitative analysis of their surface-active agents is necessary. Accordingly, an identification scheme has been developed which permits in general their detection and determination.

Important types are, for instance:

Anion-active compounds	
(1) alkylaryl sulphonates	R aryl SO_3Na (Nacconol, Oronite)
(2) fatty alcohol sulphates	$ROSO_3Na$ (Duponol, Gardinol, Fab)
(3) sec. alkyl sulphates	$ROSO_3Na$ ("TEEPOL")
(4) fatty acid amide sulphates	$RONHROSO_3Na$ (Echfalon)
Non-ionics	
(5) alkyl phenol ethylene oxide derivatives	R phenol $(C_2H_4O)_n$ (Stergene)
(6) polythylene glycol	$(C_2H_4O)_n$ (Carbowax)
Cationics	
(7) alkyl pyridinium compounds	 (Fixanol C)
(8) quaternary ammonium compounds	 $\overset{NBr}{R \quad (CH_3)_3}$ (Lissolamine A)

Mixtures of (1) and (2) or (1) and (3) are very common [Tide (U.S.A.), Omo (Holland), Perr (Holland), Esi (Switzerland), Fama (Switzerland), Pon (Switzerland)]. Mixtures of anionics and non-ionics also occur.

Linsenmeyer (1) is one of the first who developed a system (1940) for the qualitative analysis of the most important products marketed at that time. He divides them into eight groups on the basis of solubility of their calcium salts and according to their acid resistance. This method does not cover the many types now on the market and cannot be used for quantitative analyses. Moreover mixtures of base materials cannot be detected.

Van der Hoeve (2), who has done a great deal of work in this field, has developed an analytical method that is easy to apply to individual substances although a somewhat simpler structure of the scheme would seem possible. His system is not suitable for mixtures either. Various specific reactions, first applied for this purpose by Van der Hoeve, have been incorporated in the scheme described in the present paper. Bergeron *et al.* (3) have developed a method for the qualitative analysis of anion-active detergents. They divide 24 types into three classes on the strength of their acid stability. The procedure is unsuitable for mixtures.

Of the investigators who have tried to include mixtures in their systems Berkowitz and Bernstein (4) should be mentioned. They analyze mixtures of fatty acid soap and a synthetic detergent quantitatively. Their method to determine the syndet as the difference between the alcohol-soluble part and the sum of the fatty acid soap, sodium chloride, and traces of soda present in the alcoholic extract does not seem fully to meet the requirements and can certainly be improved by using the method combined with that developed by Epton (5) for syndets. Moreover it does not identify the type of synthetic detergent. Gilby and Hodgson (6) divide the detergents into four groups on the strength of a qualitative determination of C, H, O, N, and S and use this scheme combined with a modified Linsenmeyer system. There is no primary division into anionics, cationics, and non-ionics. For the quantitative analysis use is made of Epton's titration method. In the case of a mixture of fatty acid soap and a synthetic detergent the latter is determined indirectly as the difference between total alcohol soluble and soap + fatty matter. However, although some mixtures of syndets can be qualitatively identified, the method is unsuitable for quantitative determinations.

Attempts were made by the present authors to develop a scheme for general application which at the same time is suitable for qualitative and quantitative analyses of surface-active agents and their mixtures.

As in the methods of Wurzschmitt (7, 8) and Gilby and Hodgson (6) the reactions or determinations are to be carried out after removal of the inorganic constituents from the mixture.

The scheme makes use of the main division into anion-active substances, cation-active substances, and non-ionic substances.

It should be emphasized that the separations into an alcohol-soluble and an alcohol-insoluble part, as described below, and some identifications (namely, those based upon the presence of nitrogen) can only be carried out when the cation is an alkali metal or an alkaline-earth metal. Where NH_4^+ is present as a cation it can easily be identified, *e.g.*, by means of Nessler's reagent, and subsequently be removed by means of alkaline bromine (reagent 6) as follows:

Ten g. of sample are dissolved in 50 ml. of water, after which 100 ml. of alkaline bromine solution are added. The mixture is allowed to stand for 1 min. at room temperature. (After this time a drop of Nessler's reagent at a glass rod should no longer show a brown discoloration). To determine whether salts of amines are present, 50 ml. of 30% NaOH are added, and the mixture is boiled for two hours under reflux. The vapors are tested for the presence of amines by means of red litmus paper. If the paper turns blue, the mixture contains amines.

When organic cations are present (ethanol amines, guanidine, morpholine), there is no point in an al-

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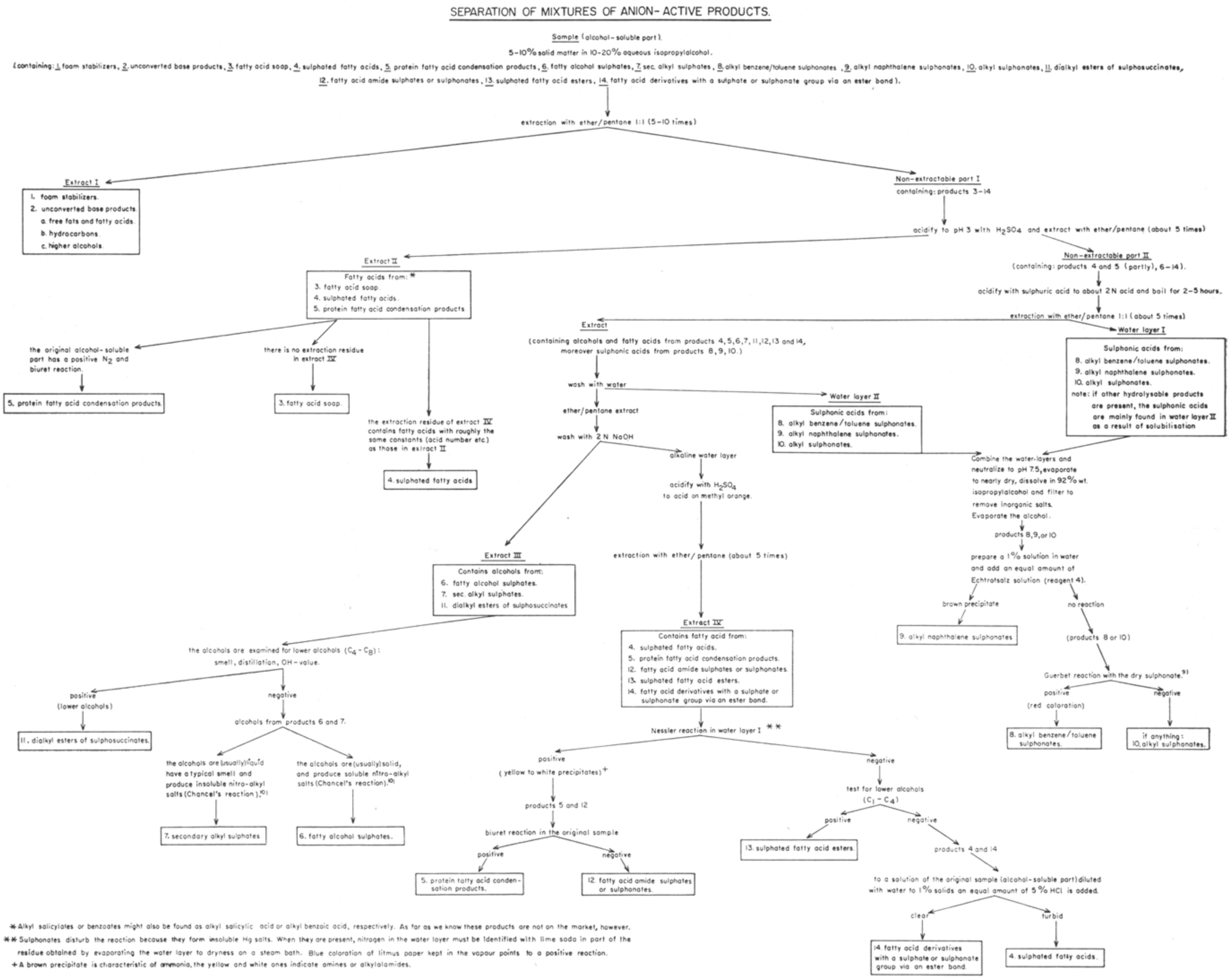
[1] Translation of an article published by the same authors in Chem. Weekblad, *49*, 341-8 (1953).



* Alkyl salicylates or benzoates might also be found as alkyl salicylic acid or alkyl benzoic acid, respectively. As far as we know these products are not on the market, however.

** Sulphonates disturb the reaction because they form insoluble Hg salts. When they are present, nitrogen in the water layer must be identified with lime soda in part of the residue obtained by evaporating the water layer to dryness on a steam bath. Blue coloration of litmus paper kept in the vapour points to a positive reaction.

\+ A brown precipitate is characteristic of ammonia, the yellow and white ones indicate amines or alkylolamides.

FIG. II.

cohol separation, on account of the solubility of the corresponding salts of the inorganic anions in the alcohol. The test for amino-nitrogen with Nessler's reagent mentioned in Figure 2 must then be replaced by a quantitative nitrogen determination; in that case only a more extensive analysis can give a decisive answer as to the type of surface-active compound present.

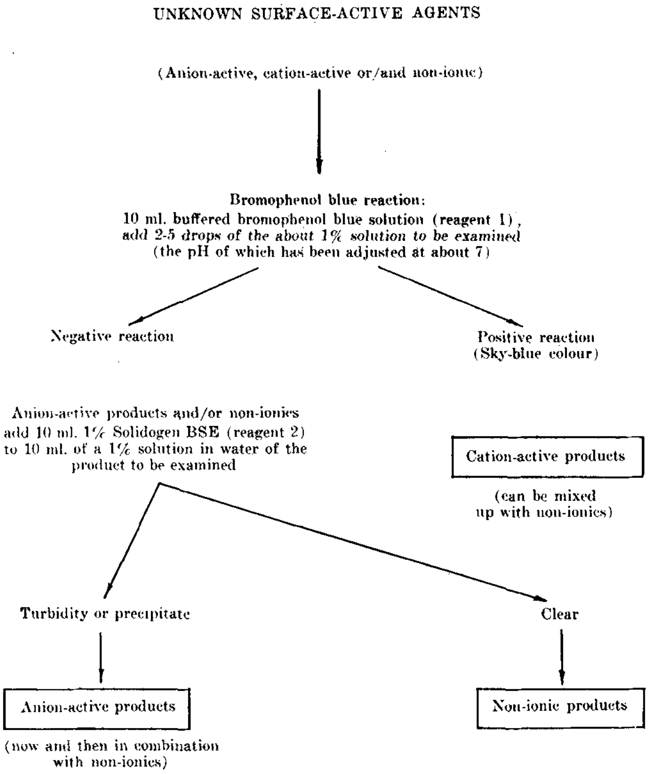


FIG. I.

1. ANALYTICAL SCHEME

The analytical scheme used is based on the following classification:

I. *Anion-active products*

These products are divided into three main groups:

1. products still containing compounds in which the only hydrophilic group is the COOMe group (Me = metal;
2. products which can be split up by boiling with mineral acid, with formation of higher alcohols or fatty acids;
3. products which cannot be split up by means of mineral acid.

II. *Cation-active products*

1. quaternary ammonium bases
2. pyridinium compounds
3. hydrochloric salts of high molecular weight amines
4. sulphonium compounds

III. *Non-ionic products*

1. ethylene oxide polymerization products
2. esters of polyhydric alcohols

Chemicals Required:

1. Solidogen BSE (cation-active substance, supplied by Cassella Farbwerke, Mainkur, Frankfort-am-Main, Fechenheim, Germany, and prepared by the action of dimethyl sulphate on the condensation product of polyethylene diamine with chlorinated paraffin wax).[2]
2. Echtrotsalz AL[3] (diazotized α-amino anthraquinone).

Reagents Required:

1. Buffered bromophenol blue solution:
   7½ ml. of sodium acetate 0.2 N.
   92½ ml. of acetic acid 0.2 N.
   2 ml. of bromophenol blue 0.1% in alcohol 96%.
   The pH of this solution must be between 3.6 and 3.9.
2. 1% solution of Solidogen BSE in water.
3. Nessler's reagent (5 g. KI in 5 ml. H_2O. Add a $HgCL_2$ solution [1:20] until the precipitate remains. Filter over glass wool, add a solution of 15 g. KOH in 30 ml. H_2O and add H_2O to 100 ml.).
4. Diazo reagent: Echtrotsalz AL, 2% solution in water.
5. Naphthol reagent: 0.1% β-naphthol in 1 N NaOH.
6. Alkaline bromine solution: 31.2 g. of bromine + 15.6 g. NaOH per litre of water.
7. *Spacu's reagent* (9): dilute solution of cupric acetate to which some drops of 10% potassium thiocyanate solution have been added.
8. KI_3 reagent: 1.27 g. I_2 + 2.0 g. KI per litre.

2. LIST OF TESTS FOR QUALITATIVE ANALYSIS

Reaction I. *Anion-active products*

To 10 ml. of a 1% solution of the surface-active agent in water, 10 ml. 1% Solidogen-BSE solution (reagent 2) or another cation-active substance is added. Turbidity or a precipitate points to the presence of anion-active products.

Reaction II. *Cation-active products*

To 10 ml. of a buffered bromophenol blue solution (reagent 1) 2-5 drops of the about 1% solution to be examined (the pH of which has been adjusted at about 7) are added. Cation-active products give a sky-blue color. If they occur, anion-active products will be absent in consequence of the mutual reactivity of anion-active and cation-active products, resulting in the formation of compounds practically insoluble in water.

Reaction III. *Non-ionic products*

When the two preceding reactions are negative, the surface-active material present belongs to this class, which is formed by the polyethene oxide condensation products and the esters of polyhydric alcohols. The former are the more frequent ones and can easily be identified by adding some drops of the solution to be examined to 10 ml. of a KI_3 solution (reagent 8). A discoloration from orange to red or reddish brown or the formation of dirty greyish brown-colored precipitates reveals their presence.

Reaction IV. *Nitrogen*

200 mg. of the dried product are mixed with 800 mg. of sodium hydroxide in a reaction tube, after which a plug of glass wool is placed on top. The tube is gently heated above a small flame or in a sand bath at 200°C.; a red litmus paper is kept over it (the gases can also be passed into water via a tube). Blue coloration (or coloration of the Nessler reagent) points to nitrogen.

Reaction V. *Nitrogen (Biuret reaction)*

To 10 ml. of a 1% aqueous solution of the original alcohol-soluble part of the product to be examined are added 1 ml. of 10% NaOH and 0.5 ml. $CuSO_4$ 5 aq. (0.3%). The mixture is heated gently. When a violet color appears, the reaction is positive.

Reaction VI. *Nitrogen (Nessler reaction)*

The sample to be tested is made alkaline by the addition of a concentrated NaOH solution. When Nessler's reagent (reagent 3) is added, ammonia nitrogen produces a brown color. Yellow and white precipitates are formed when amines are present.

Reaction VII. *Naphthalene rings*

When a 1% solution of an alkyl naphthalene sulphonate is mixed with an equal amount of the Echtrotsalz AL reagent (reagent 4), a brown precipitate is formed. The solution under test has to be neutral since alkaline solutions invariably give brown precipitates.

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[2] Theoretically, any cation-active agent will do, but some of them only give turbidities while others produce a precipitate. The latter group is the most suitable for our purpose. Cationic materials which, according to v. d. Hoeve (2), may be substituted include "Solidogen FFL" (Cassella Farbwerke, Mainkur), "Fixanol VR" (Imperial Chemical Industries), and "Liovatin E" (Sandoz).

[3] Fast Red Salt AL is stated to be the equivalent (2) (General Dyestuffs Corporation).

Reaction VIII. *Detection of one-ring aromatics* [*Guerbet reaction* (11)]

The following procedure was used, which is somewhat different from that cited:

a) Mix 100 mg. of dry active matter with 2-3 ml. of fuming nitric acid and heat to dryness on a sand bath (200°C.); care should be taken that no carbonization takes place.
b) Add to the residue 2 ml. of concentrated hydrochloric acid and 5 ml. of absolute alcohol. Stir and heat on a water bath with 0.5 g. of zinc dust till the alcohol has almost evaporated.
c) Place the mixture in a separating funnel, dilute with water to 20 ml., and extract twice with ether.
d) Dilute the water layer with water to 40 ml., add 30% sodium hydroxide solution to dissolve the zinc hydroxide, and extract twice with ether. Combine the ether extracts of c) and d) and shake with 5 ml. of 3 N hydrochloric acid. Discharge the acid and dilute with 10 ml. of water.
e) Add 5 ml. of 1% sodium nitrite to 5 ml. of the acid solution, cool in ice for 5 min. Then stir the mixture into 7 ml. of ice-cooled 0.1% β-naphthol solution (reagent 5). Take care that this solution gives an alkaline reaction. Alkylaryl sulphonates give an orange-red color, the dye formed is extractable with chloroform.

Reaction IX. *Detection of secondary higher alcohols* (10)

As a result of the action of HNO_3 on secondary alcohols, acid-reacting nitro-alkalanes are formed, which produce characteristic K and Ag salts. Transfer 1 ml. of the alcohol under test, together with an equal volume of HNO_3 (spec. grav. 1.35), into a test tube, heat, and dilute with water when the reaction is complete. Then shake out with ether. The ether layer is separated and evaporated. The residue is taken up in alcohol. Finally, alcoholic KOH is added, and the mixture is left undisturbed for some time. Secondary alcohols then give yellow prisms of the nitro-alkyl salts. Primary alcohols, when treated in the same way, form neutral esters of nitric and nitrous acid, which do not precipitate when KOH is added.

Reaction X. *Detection of pyridinium compounds* (9)

The sample under test (in about 5% aqueous solution) is made just acid with concentrated acetic acid. Add an equal amount of Spacu's reagent (reagent 7). Pyridinium compounds produce a dirty green color due to the formation of copper pyridinium rhodanide.

3. Pretreatment of an Unknown Product for the Analysis

The present commercial products vary widely in their active matter content; moreover complicated "builder" compositions are often found, especially with detergent powders. It is therefore desirable, before starting the investigation proper, to have some ideae of the active matter content. As far as products of the anion-active type are concerned (which constitute a great majority), this can easily be obtained by the so-called methylene blue titration (5), a method carried out in a two-phase system where methylene blue is used as indicator and a cation-active substance as standard solution. For conversion into a percentage wt. an equivalent weight of 350 can be taken. It is clear that this method gives only a rough indication of the active matter content; no non-ionic products and fatty acid soap are found.[4] This "pre-analysis" is very useful for the further investigation, however.

4. Removal of Inorganic Ingredients

To remove the majority of the inorganic salts possibly present, enough isopropyl alcohol is added to the aqueous solution of the sample to be examined so that the final concentration of this alcohol is about 92% or more. Powders are mixed with some water to form a paste and are boiled up after the addition of the alcohol. After filtration the filter residue is treated[5] once more in the same way and is then almost free from active matter. The quantity still remaining in the salt can, if desired, be determined by the methylene blue titration (5).

The alcohol solution is now made just alkaline to phenolphthalein and then distilled under moderate vacuum (pressure about 2-10 cm. Hg), water being added until an aqueous solution containing 5-10% solid matter and 10-20% alcohol is obtained. In view of the low heat stability of some substances and the consequent possibility of acid formation, it must occasionally be ascertained if the solution still shows an alkaline reaction to phenolphthalein; if necessary, a drop of sodium hydroxide must be added. The quantity of organic matter required for a total quantitative analysis greatly depends on the composition of the components and amounts to not more than about 15 g.

5. Division of the Unknown Types of Active Matter, Cation-active and non-Ionic Compounds (Figure I).

The scheme is based on the primary separation into:

I. Anion-active products
II. Cation-active products
III. Non-ionic products

Anion-active products are present if the solution under test gives a precipitate or if it becomes turbid on addition of a cation-active substance (reaction 1).

Cation-active products, on the other hand, give precipitates with anion-active substances. Moreover they change the color of some indicator solutions. With a buffered bromophenol blue solution a sky-blue color is obtained (reaction 2).

Non-ionics, when belonging to the ethylene oxide derivatives, can be identified by their reaction with a solution of iodine in KI, resulting in dark red colors or brown to grey precipitates (reaction 3). Since this type of compounds is sometimes blended with anion-active products, it is desirable also to carry out this reaction when the presence of anion-active compounds has already been demonstrated. It should be remarked that this method is sensitive to a concentration of about 0.05% in the solution to be examined.

6. Subdivision of the Anion-active Compounds

When in the solution under test anion-active compounds have been detected, a type of separation can take place by repeated extraction as indicated in Figure II while the presence of admixtures such as higher alcohols, fatty acid amides, and fatty acid alkylol amides (which are sometimes present as wash- and foam-promoters) can also be determined.

In order to ensure quantitative separations, particularly between the surface-active agents and any wash- and foam-promoters present, the concentration of surface-active material in the sample (alcohol-soluble part) should not be higher than 10% wt. since in a more concentrated solution the solubility of the above promoters is too great. Even if this condition is fulfilled some wash- and foam-promoters are difficult to remove. It is therefore advisable to repeat the first extraction with ether/pentane 5 to 10 times, each time with 50 ml. of solvent, in a separating funnel.

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[4] A method for the quantitative determination of ethylene oxide products has lately been reported by N. Schönfeld in Nature, *172*, 820 (1953) Potassium ferro cyanide is added in excess to the solution to be analyzed, and, after filtering off the precipitate, the amount of potassium ferro cyanide in the filtrate is determined by titration with zinc sulphate.

[5] Care should be taken that the pH of this solution does not decrease to below 7.5 during this treatment; if necessary, a drop of alkali can be added.

This treatment can also be carried out by means of a suitable continuous extractor (about 4 hrs.).

The ether/pentane extract is once washed with water (washings to be added to the extracted solution) and dried on anhydrous sodium sulphate, after which the solvent is distilled off.

Extract I. This extract may contain, in addition to the above-mentioned wash- and foam-stabilizers, fats and fatty acids (*e.g.*, from superfatted soap) and hydrocarbons generally originating from surface-active agents prepared from hydrocarbons. From a determination of the acid value, saponification value, hydroxyl value, nitrogen content, molecular weight, boiling range, etc., it can in most cases be inferred whether certain products are present or not.

Extract II. This extract can only contain fatty acids originating from products with a carboxyl group as the only hydrophilic group, *viz.*:

1. Fatty acid soap
2. (Low) sulphated fats or fatty acids (*e.g.*, some types of Turkey-Red Oil)
3. Protein/fatty acid condensation products (*e.g.*, Lamepon A).

Extract II. contains all of the fatty acids of product (1), those of products (2) and (3) only as far as they are not sulphated or bound to the disintegrated proteins.

The first method to distinguish between these three types is testing them for nitrogen (reaction IV.), using a sample of the alcohol-soluble part of the product to be examined, which sample has been evaporated to dryness. The presence of nitrogen and a positive Biuret reaction (reaction V.) point to the presence of protein-fatty acid condensation products.

The separation is continued with the non-extractable part II. already present (see Figure II). (Low) sulphated fatty acids are present if in extract IV fatty acids are obtained with the same or almost the same constants (acid value, saponification value) as those of extract II.

If further separation no longer yields any fractions, fatty acid soap is present as the only surface-active agent.

It should be remarked that possible mixtures of protein-fatty acid condensation products with fatty acid soap or sulphated fatty acids are characterized, either by an unusual fatty acid/nitrogen ratio, or by the additional presence of sulphur as a hydrolysable sulphate.

Mixtures of fatty acid soap with fatty alcohol sulphates or sulphosuccinic esters are characterized by the presence of alcohols in extract III. If the fatty acid soap is mixed with other, more complicated fatty acid derivatives, fatty acids are again found in extract IV., but in that case the constants of these fatty acids generally differ from those obtained in extract II. Besides the fatty acids in extract II., mixtures of fatty acid soap and sulphonates give sulphonic acids in water layer I or II.

In the hydrolysis of the non-extractable part II, the conditions of which are so rigorous that as a rule the products which are difficult to hydrolyse (*e.g.*, Igepon T) are also decomposed, a mixture of higher alcohols and fatty acids can be formed while sulphonic acids may also be present. The sulphonic acids can be removed from this mixture by washing with water. A wash with 2 N caustic solution is an attractive method of separating alcohols from fatty acids, by which it is possible to determine the constants of the products obtained.

Extract III. now only contains alcohols originating from:

1. Primary alkyl sulphates (Gardinol, "Sulphonated Lorol")
2. Secondary alkyl sulphates ("TEEPOL")
3. Sulphonated succinic esters (Aerosols)

Extract IV. This extract contains fatty acids[6] originating from the following compounds:

1. Fatty acid amide sulphates or sulphonates (Oratol, Igepon T, Humectol CX, Echfalon)
2. Sulphated fatty acid esters (Calsolene oil)
3. Fatty acid derivatives linked with a sulphate or sulphonate group *via* an ester bond (Igepon A), sulphated fatty acid monoglycerides (Vel Beauty Bar)
4. (Highly) sulphated fatty acids
5. Protein-fatty acid condensation products.

Water layers I. and II. Sulphonates, if present in the product to be examined, give rise to sulphonic acids in water layers I. or II., dependent on the composition of the product. When they occur in water layer I., neutralization with NaOH to pH 7 gives a mixture of sulphonates and, for instance, sodium sulphate.

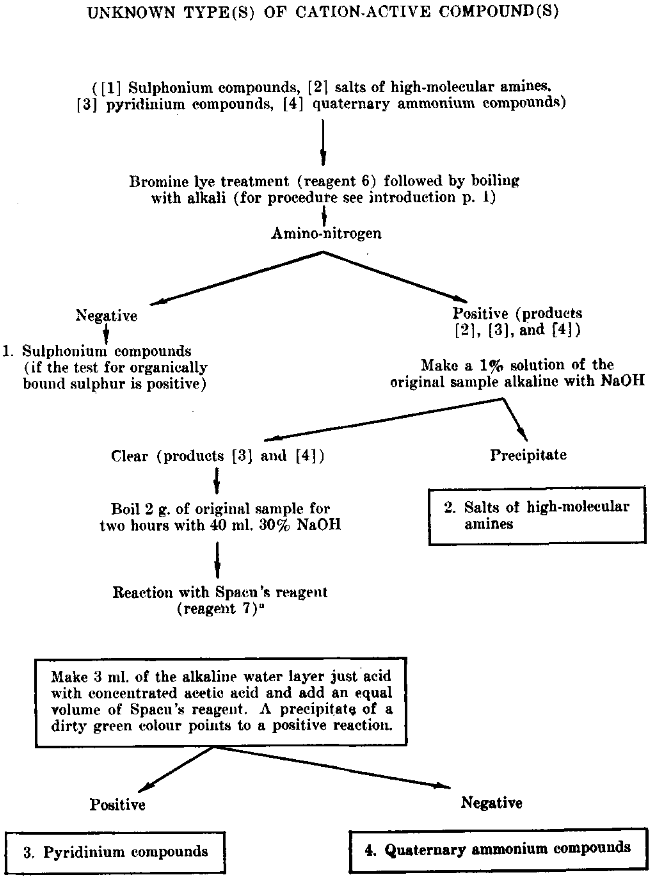

FIG. III.

[a] The test with Spacu's reagent can only be used for a qualitative analysis. It should be added that:

(a) If pyridinium compounds are found, the presence of quaternary ammonium compounds is not precluded.

(b) If salts of high-molecular amines have been found and it is desired to ascertain wheter there are still other cation-active compounds that contain nitrogen, the separated amines should be removd by extraction with ether before carrying out the reaction with Spacu's reagent. A negative reaction with Spacu's reagent may in this case also mean that there are no such compounds. To verify this, the solution from which the high-molecular amines have been removed should again be tested for the presence of nitrogen and cation-active substances.

If a further quantitative separation is desirable, this can be done by precipitation of the Na_2SO_4 with alcohol, filtration, and evaporation. The value found by means of the methylene blue titration (5) combined with the weight of the amount of alcohol solubles gives the equivalent weight of the sulphonates.

The following are the most usual types: alkyl naphthalene sulphonates (*e.g.*, Nekal BX), alkyl benzene sulphonates (*e.g.*, Oronite), and aliphatic sulphonates (mersolates).

The *alkyl naphthalene sulphonates* can immediately be recognized by the brown precipitate produced when Echtrotsalz AL (reagent 4) is mixed with an equal volume of a 1% active-matter solution prepared from water layer I. or II. (reaction [VII]). This solution must not be alkaline however since in this case the reagent invariably gives a brown precipitate.

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[6] The term "fatty acids" to be taken in a wide sense.

The alkyl benzene sulphonates and other one-ring sulphonates can be identified by means of the Guerbet reaction (11). When they are present, an orange-red color appears (reaction VIII).

Aliphatic sulphonates only give a light-yellow discoloration. Another characteristic difference between aliphatic and alkylaryl sulphonates is their absorption of U.V. light The latter have a very marked absorption between 2,200-2,400 Å.

Finally, alkylaryl sulphonates in a 0.5% solution produce turbidity or precipitates when they are mixed with an equal volume of 1 N potassium hydroxide. A solution of aliphatic sulphonates remains clear.

7. SUBDIVISION OF THE CATION-ACTIVE PRODUCTS

The group of the cation-active products comprises: quaternary ammonium bases (Lissolamine A); pyridinium compounds (Fixanol C); hydrochloric salts of high-molecular amines; and sulphonium compounds.

The fourth group is distinguished from the others by the absence of nitrogen (any ammonia nitrogen present having been removed by a treatment with alkaline bromine solution). The hydrochloric salts of high-molecular amines, when reacted with alkali, give a separation of the amines; the two other groups can be distinguished on the basis of their behavior with respect to copper acetate (potassium thiocyanate solution) (Spacu's reagent, reagent 7). The above is elucidated in Figure III.

8. SUBDIVISION OF THE NON-IONIC PRODUCTS

In Section 2 it has already been noted that the two types of non-ionic products are polyethylene oxide condensation products and the mono-esters of polyhydric alcohols. They can be distinguished by means of the KI_3 reaction (reagent 8). If this reagent is added to the ethylene oxide condensation products, a red discoloration or even a brown precipitate appears. This group can be subdivided on the basis of the difference in stability of the various components in an acid medium.

When a sample (about 2 g.) is boiled for an hour with 40 ml. of 10% hydrochloric acid, a top layer of fatty acids is obtained if they were linked to polyethylene oxide. Fatty acid amide derivatives also give fatty-acid separation.

Polyethylene oxide and condensation products of ethylene oxide with fatty alcohols and of ethylene oxide with amines remain almost clear.

Figure IV gives a picture of the further separation in this group.

UNKNOWN TYPE(S) OF NON-IONIC DETERGENT(S) OF THE POLYETHYLENE OXIDE GROUP

1. Fatty acid alkylolamide polyglycol ether, 2. fatty acid ester of polyglycol ether, 3. alkyl naphthol polyglycol ether, 4. alkyl phenol polyglycol ether, 5. amino polyglycol ether, 6. fatty alcohol polyglycol ether, and 7. polyglycol ether.

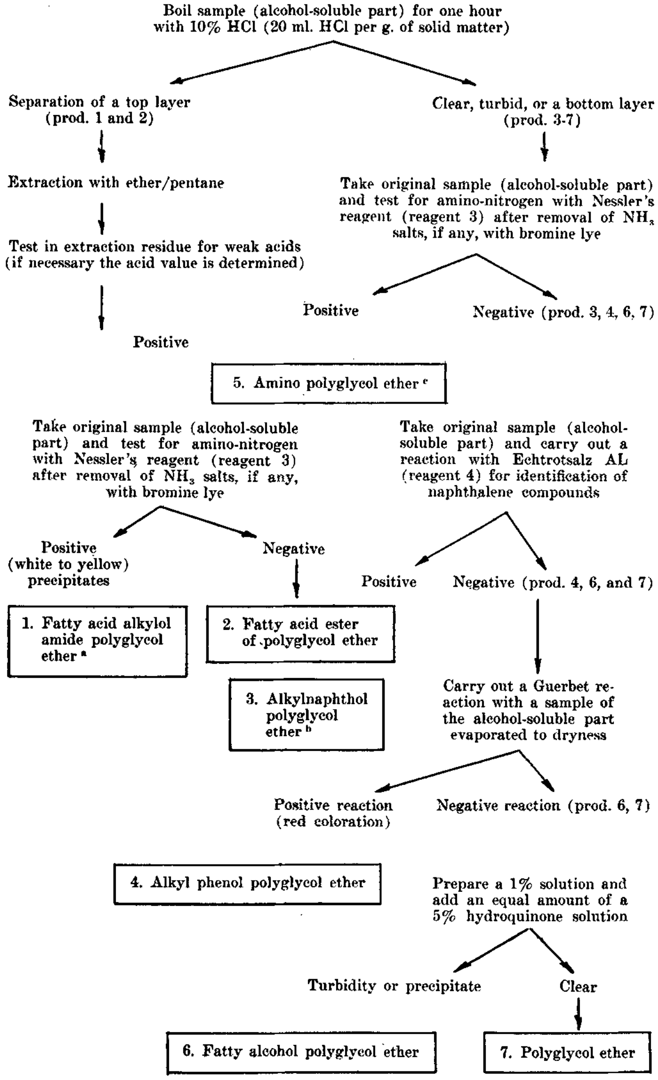

FIG. IV.

[a] Possibly mixed with a fatty acid ester of polyglycol ether.
[b] Possibly mixed with products 4, 6, and 7.
[c] Possibly mixed with products 3, 4, 6, and 7.

Discussion

The above-mentioned system has been successfully applied in our laboratory for a long time. Below follows an analysis on a qualitative and quantitative basis of a mixture prepared from two "syndets" and fatty acid soap in the presence of some builders.

The figures show that analysis according to the new scheme gives results accurate enough for a "commercial" analysis. Of course, mixtures are conceivable which cannot be completely analyzed according to this scheme, *e.g.,* mixtures of fatty acid soap, highly sulphated fats, and another fatty acid derivative; but so far we have not come upon such mixtures in our practice. In this case, working according to the scheme described in this paper, fatty acids would be found in extracts II. and IV. of Figure II. Sulphate, nitrogen, or other determinations might then serve for further analysis, which might ultimately lead to a probable composition.

It goes without saying that, in a field where so many combinations are possible, occasional extension of the scheme will be necessary. In the last few years the scheme has proved to be useful for the analysis of a great number of commercial products.

Physical methods can also be used in the analysis of detergents. In section 6 reference was made to a method of distinguishing between purely aliphatic and alkylaryl sulphonates by means of the U.V. absorption spectrum.

A method of analysis using infra-red absorption has been developed by Delsemme (12), who thus de-

Components	Composition % (theoretical)	Types of organic compounds found	Percentage found
Coconut fatty acid isopropanol amide	0.8	Fatty acid alkylol amide	0.5
Na-palmitate	1.5	Fatty acid soap	1.5 (average number of C atoms per molecule 16.5)
Alkyl benzene sulphonate	1.9 (mol. wt.=342)	Alkyl benzene sulphonate	2.2 average mol. wt. 352
"TEEPOL" (sec. alkyl sulphates)	3.9	sec. alkyl sulphates	3.9
Builders: soda ash, Na-CMC, sodium pyrophosphate and sodium sulphate	4.9	....	....
Water	87.9	....	87 (determined according to Dean and Stark ASTM D 95-46)

termines not only the different types (alkyl sulphates, alkylaryl sulphonates, polyethene condensation products) but also the degree of branching of the alkyl sulphate, the chain length of non-ionics based on polyethene oxide and, for the anion-active compounds, the cation present. In addition, this method can be used for quantitative analyses.

Recently Sadtler (13) has also suggested analyzing synthetic detergents by means of infrared absorption.

Both Delsemme's and Sadtler's method may be valuable to those who have an apparatus for infrared spectrography. An advantage of these methods is that the spectra can be filed so that new products can immediately be compared with previous ones.

Acknowledgment

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Summary

An identification scheme for surface-active agents is given which enables these agents or their mixtures to be detected in commercial products. Use is made of the acid resistance of the various types, which make it possible to separate the different compounds step by step from the mixture.

An important feature of the method is that it can be used also for quantitative analyses by weighing the extraction residues obtained and determining their physical and chemical constants.

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Bisphenol Derivatives as Antioxidants for Carotene

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PHENOLIC antioxidants have been shown to possess marked ability to prolong the induction period of autoxidizing paraffin wax (4) and, under certain conditions, to protect carotene similarly (1). The success achieved in these tests with several compounds related to the bisphenols prompted a more extensive investigation of these materials and related compounds as antioxidants for carotene during storage. As far as possible, the compounds tested were chosen to permit observation of change in activity with systematic change in structure. The present report deals with the results of these stability tests.

Experimental

Stability of Oil Solution. The effectiveness of the antioxidants for the protection of carotene in oil solution was first determined. The substrate used for testing the antioxidants was a solution of purified crystalline carotene in a highly refined mineral oil.

The details of the stability test for carotene in oil solution have been published previously (6). It consists of a determination of the time required for breakdown of 20% of the carotene in the oil solution stored as a thin layer at 75°C. under specified conditions. As in previous work (1), the antioxidants were incorporated on an equivalent molecular basis rather than on a weight basis in order to facilitate the comparative evaluation of the antioxidants in the oil solution.

Stability in Alfalfa Meal. To test the effect of the antioxidants on the stability of carotene in alfalfa meal, a rapid, simple method of incorporating the antioxidant was employed. This involved spraying a Cellosolve (ethylene glycol monoethyl ether) solution of the antioxidant on a 200-g. sample of meal while it was tumbled at 12 r.p.m. in a rotary mixer. Samples were then stored for 2 weeks at 65°C. Results so obtained were comparable to about eight months' storage at 25°C. Details of this technique have been described fully in an earlier report (5).

Results

Bisphenol Derivatives in Mineral Oil Solution. Since all of the experiments reported here followed