Conclusions

1. The oven drying method for the determination of water in sodium alkyl aryl sulfonates results in incomplete removal of water and may result in the loss of unsulfonated oil and other volatile products.
2. The determination of water in sodium alkyl aryl sulfonates by desiccation over concentrated sulfuric acid results in incomplete removal of the water.
3. The determination of water in sodium alkyl aryl sulfonates by azeotropic distillation and subsequent measurement of the water distilled is not recommended because of the operational difficulties and lack of sufficient accuracy.
4. The azeotropic distillation of Suter (6) is applicable for the determination of water in sodium alkyl aryl sulfonates, but comparable results may be determined more readily by the proposed Karl Fischer method.
5. The determination of water in sodium alkyl aryl sulfonates by the Karl Fischer method is the most satisfactory of the methods investigated.

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Some Observations on the Solubility of Sulphonated Castor Oil in Organic Solvents

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RESEARCH on the solubility of soap in organic solvents plus water and the study of different phases encountered has made much progress in recent years (1). The study of the solubility of sulphonated castor oil (commercially known as turkey red oil) has not progressed in a similar manner. This subject however is of great practical importance for the textile industry. The author has undertaken some experimental work on these lines. Results of these experiments may help to initiate further research on this subject.

It was found that the solubility of most commercially available turkey red oils in organic solvents of the aromatic type such as benzene, xylene, and toluene, and of the paraffinic type, such as kerosene and light petroleum fractions was rather poor. The reason for this was that the water content of most commercial products was much higher than 30%. In order to obtain better results a sulphonated castor oil with water content below 30% was specially prepared in the laboratory and the experiments carried out with this product. This highly concentrated turkey red oil is as easily prepared on a plant scale as the more dilute types.

Experimental

150 g. castor oil were sulphonated with 37.5 g. sulphuric acid at a temperature not exceeding 30°C. After the sulphonation was completed, which took about 30-45 minutes, the mixture was allowed to stand for about 20 hours. The sulphonation product was washed free of uncombined sulphuric acid with 150 g. of a 10% sodium chloride solution. After another period of 12 hours' settling the wash solution was drained off and the washed sulphonation product neutralized with 60 g. of a 20% caustic soda solution. The final product was a viscous clear liquid with pH about 7.5 in 1:1 dilution with distilled water. The product has a water content of 28%, organic SO_3 content of 9.0%, and 58.0% total fatty matter.

This sulphonated castor oil was the material with which all solubility tests were carried out. The first observation was that in all solvents used in the experiments the sulphonated oil was more soluble when less solvent was used for dilution. This observation was quite in accordance with similar observations with triethanolamine oleate, which is not completely soluble in gasoline below 2% (2).

Results

Petrol Ether as Diluent. 100 g. sulphonated oil were completely soluble in 50 ml. petrol ether (boiling range 50-70°C.). When 100 g. sulphonated oil were diluted with 66 ml. petrol ether, the mixture became turbid. On standing for 10 hours, a clear liquid separated at the top of the mixture (40 ml. = 24% of the total).

Kerosene as Diluent. 100 g. sulphonated oil were completely soluble in 66 ml. kerosene (140-230°C. boiling range with about 18% aromatic and olefinic constituents). A mixture of 100 g. sulphonated oil with 100 ml. kerosene became turbid and after 10 hours a clear liquid separated on top (80 ml. = 40% of the total).

Benzene as Diluent. 100 g. sulphonated oil were completely soluble in up to 400 ml. benzene. A mixture of 100 g. sulphonated oil and 500 ml. benzene became turbid and a clear liquid separated after 10 hours' standing (110 ml. = 18.3% of the total).

Xylene as Diluent. 100 g. sulphonated oil were completely soluble in up to 400 ml. xylene. A mixture of 100 g. sulphonated oil with 500 ml. xylene became turbid and a clear liquid separated on top of the mixture on standing for 10 hours (120 ml. = 20% of the total).

Toluene as Diluent. 100 g. sulphonated oil were completely soluble in up to 500 ml. toluene. A mixture of 100 g. sulphonated oil in 600 ml. toluene became turbid and a clear liquid separated on top after 10 hours' standing (280 ml. = 46.5% of the total.)

Conclusions

It was observed that sulphonated castor oil (with 28% water content) is miscible with much greater volumes of aromatic solvents than with solvents of the paraffinic type. Separation of the mixture at high dilution ratios shows that it is likely that a miscellar structure exists between the solvent, the sulphonated oil, and the water contained in the sulphonated oil. This miscellar structure is disrupted at higher dilution ratios. Furthermore it was generally observed that mixtures where the sulphonated oil was completely dissolved in the solvent gave stable milky white emulsions on dilution with water. The latter fact is of great practical importance.

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Relationship Between Nickel Content of Soap and Conversion to Polymer in Manufacture of Synthetic Rubber (GR-S)[1]

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COLLABORATIVE research under the Soap Development Program for GR-S of the Rubber Reserve Company revealed that the polyunsaturated fatty components of tallow soap emulsifiers acted as retarders in the emulsion polymerization of GR-S. Reports of this work (3, 6) presented data showing that selective hydrogenation of the fat stock eliminated this difficulty and that spectrophotometric methods (4, 5) of analysis for residual polyunsaturation could be used as a means of production control. Moreover the solution of this problem facilitated conversion of polymerization plants to a continuous process.

In operation of the continuous process for the emulsion polymerization it soon became apparent however that other undesirable substances were sometimes present in the soaps. Variability in plant reactions occurred when some soaps were used which were satisfactory in polyunsaturate content. Although this variability could be overcome to some extent by adjusting the proportion of modifier, there are several valid objections to this adjustment in the practical and economical operation of plants. A study was therefore started in 1946 to determine the cause of this further difficulty.

Rubber Reserve Company plants accumulated data on plant reaction that involved several selected batches of soap having both satisfactory and unsatisfactory characteristics in the continuous polymerization process. Fourteen of these soaps from hydrogenated fats, supplied by four soap manufacturers, with plant polymerization data from three Rubber Reserve Company plants were received by this laboratory for examination.

The soaps were examined spectrophotometrically (4, 5) for polyunsaturated constituents. Table I shows the results of these analyses. Also shown in Table I are conversion as well as amended conversion figures, which have been compensated for variations in polyunsaturated content of the soaps. The corrections introduced for these variations were calculated by use of the formula (3):

$$\text{Drop in conversion} = 1.3 \times \%\ \text{linoleic} + 4\ (\%\ \text{linolenic} + \%\ \text{arachidonic}) \qquad (1)$$

Since in the plant conversions are subject to variations with the amount of modifier used, the amended conversion figures in Table I need a further adjustment to reflect a uniform basis of 0.40 part of modifier. This further adjustment is made on the assumption that a 1% drop in conversion is equivalent to a decrease of 0.01 part in charge of modifier. This assumption is reasonably valid for the narrow range of variations in modifier involved. Table I also shows these adjusted conversion data.

Wide variations in the adjusted conversion data indicated that undesirable substances other than polyunsaturates were present in the system. Various considerations indicated that the undesirable activity of certain soaps might be associated with their heavy metal content. Accordingly the soaps were analyzed quantitatively for nickel, copper, and iron. The methods of analysis are described below.

Method of Analysis

Preparation of Samples. Approximately 500 g. of each sample of soap was ground in a mortar to an extremely fine powder. Each powder was then thoroughly mixed by rotation in a glass jar, from which subsequent samples for analyses were drawn.

Ashing. Ashing was done under conditions carefully designed to prevent loss of metals. Duplicate 10-gram samples were transferred to 100-ml. platinum dishes. The samples were heated under infrared lamps until thoroughly charred. The dishes were removed and cooled, and 3 ml. of 1:1 sulfuric acid was added. The dishes were rotated in such a fashion that all the charred soap was wetted, and the infrared heating was repeated until sulfuric acid fumes ceased to be evolved and the soaps were carbonized. This required about 14 hours. The carbonized soaps were then ashed in a muffle furnace, where the temperature was raised gradually by 100° increments from room temperature to 600°C.; the 600°C. heating continued for 18 hours (over-night). To destroy the remaining trace of carbonaceous material, 3 ml. of concentrated sulfuric acid was added, followed by

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