Since it is not possible to determine from the experimental evidence that the isolated hydroxyalkyl peroxides are intermediate products of the secondary reactions of autoxidation, the possibility that these peroxides represented end-products of side reactions induced by the experimental set-up must be considered. Should this be the case, the reactions postulated by Walsh (15) for the oxidation of hydrocarbons would serve for an explanation of the isolated oxidation products. Aldehydes and alkyl-free radicals are formed from the decomposition of the initial hydroperoxides. Hydroxyalkyl hydroperoxides and peroxides may then be produced in the traps by the reaction of the scission aldehydes with hydrogen peroxide in a manner analogous to the synthesis of these peroxides.

The alkyl-free radical could react with further oxygen and after acquisition of a proton yield a primary hydroperoxide. The latter would decompose into an alkoxy and a hydroxy radical. The alkoxy radical, which is of a highly unstable nature, could produce an aldehyde or formaldehyde. The latter would react with further oxygen to produce formic acid.

**Summary**

Methyl oleate, oleic acid, and cis-9-octadecene were oxidized at 80° with a stream of air, and the volatile decomposition products were collected in dry ice traps. The volatile material consisted of an aqueous fraction and water-soluble substances, an oil fraction, and a crystalline product. The substances in the aqueous fractions were characterized as formic and acetic acid, and their formation was studied during the autoxidation of the various substrates up to 21 days. The crystalline material was purified, and its properties were examined. The purified crystals showed chemical and infrared properties very similar to a sample of synthesized bis-(hydroxyheptyl) peroxide. Formic and acetic acid were also shown to be produced during the decomposition of hydroxyalkyl peroxides.

**REFERENCES**

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**The Measurement of Lime-Soap Dispersion**

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Numerous tests have been proposed to measure the lime-soap dispersion properties of synthetic surface-active agents. These tests generally fall into two classes: nephelometric (i.e., tests designed to measure a decrease in turbidity of soap-dispersant solutions); and what may well be termed titrimetric (i.e., tests which measure the quantity of undispersed lime soap by difference titration following removal of the undispersed material by filtration or centrifugation).

Examples of the former are methods of Dupin and Reutenauer (1) and the method reported by Baird, Brown, and Perdue (2) while titrimetric methods are typified by the technique recently described by Harris (3), a modification of one due to Ramachandran, Uppal, and Venkataraman (4).
These tests serve to compare the lime-soap dispersing power of two or more agents by measurements made on lime-soap oleates. Thus they do not measure the dispersive ability of a particular agent in a particular formulation. This makes the tests highly artificial. As will be shown, lime-soap dispersion by a particular agent is a complicated function of the soap base employed and of the concentration of the agent as well as of the particular use concentration employed. Furthermore, since dependence of the effectiveness of an agent on its concentration varies from agent to agent, a test carried out at a fixed soap-dispersant ratio will often lead to erroneous conclusions about the relative (or, as will be shown later, even absolute) value of a given dispersant.

Obviously, what is required is a test that gives a practical measure of the lime-soap dispersion in a particular dispersant-soap formulation. Such a test is described in this paper. It is designed for the interpretation of data on combination detergent-soap toilet bar preparations; slight modification makes it suitable for other applications.

**Experimental**

**Solutions Required.**

a) A stock solution of the formula to be tested is made up at a concentration of 0.30% by weight in distilled or deionized water.

b) Artificial hard water at 250 p.p.m. as CaCO₃ is prepared by a hundred-fold dilution of a 25,000 p.p.m. stock solution. The latter is prepared by dissolving 45.0 g of CaCl₂·2H₂O in enough distilled or deionized water to make one liter, and similarly dissolving 40.0 g MgCl₂·6H₂O. These are mixed to give two liters of 25,000 p.p.m. solution.

c) 0.008 N HCl.


**Procedure.** The test is carried out at room temperature (ca. 80°F.). The stock dispersant-soap solution is diluted by means of volumetric equipment to give solutions at concentrations of 0.20%, 0.15%, and 0.10% by weight. Ten milliliters of the 0.30% stock solution and of each of the three dilutions are transferred by volumetric pipette to 20 x 150-mm. test tubes. To each solution 10 ml of the 250 p.p.m. hardness solution is added rapidly from a pipette. The procedure thus leads to the preparation of a series of solutions at dispersant-soap concentrations of 0.05%, 0.75%, 0.10%, and 0.15% by weight, and at a hardness of 125 p.p.m. as CaCO₃.

The solutions thus prepared are immediately filtered through a small plug of glass wool¹ (supported in the apex of a long-stem 60°-funnel) into a 125-ml Erlenmeyer flask. The test tube is rinsed with about 10 ml of distilled deionized water, and the rinsings are used to wash the glass-wool filter and thus are combined with the original filtrate.

To the filtrates is then added 10 drops of methyl purple indicator, and the filtrate is titrated with the standard acid to the methyl purple end-point. The addition of ten ml of ethanol to the filtrate prior to titrations has been found to sharpen the end-point.

Ten milliliters of the original solutions are also transferred to 125-ml Erlenmeyer flasks, diluted to approximately 50 ml, and titrated as above. The amount of soap in the form of gross lime-soap curd for each of the dispersant-soap concentrations is then calculated as follows:

\[
\text{% Soap as curd} = \frac{V_o - V}{V_o} \times 100
\]

where \(V_o\) is the volume of standard acid required to titrate 10 ml of the original dilutions of the stock-dispersant soap solutions, and \(V\) is volume of acid required to titrate the filtered solution, following the addition of hardness. The results are reported to the nearest percentage: the reproducibility of the experimental data is of the order of ± 3%.

It is important that the stock soap or dispersant-soap solutions be used when quite fresh. Discordant results are obtained with aged solutions, possibly as the result of the formation of acid soaps. Some modification of the technique is required in the evaluation of built formulations since a blank correction for the alkalinity of the builder will have to be made. Other hardnesses (e.g., 50 p.p.m. or 300 p.p.m.) may be studied by appropriate dilutions of the stock hardness solution.

**Discussion**

Data typical of those obtained by this test are shown in Figure 1. In this series the effect on the lime-soap dispersion of soda soap (made from 25% coconut oil and 75% tallow) by the substitution for

![Graph of experimental data](image)

FIG. 1. Effect of concentration of dispersant (sodium H-coco monoglyceride sulfate). 1. 100% soap. 2. 95% soap/5% dispersant. 3. 85% soap/15% dispersant. 4. 75% soap/25% dispersant.

the soap of varying percentages of an anionic detergent (sodium H-coco monoglyceride sulfate) was studied. These data usefully illustrate some important points in the use and interpretation of the test.

1. **Method of Plotting Data.** In the interests of simplicity in handling the data, they are plotted in a way which could lead to some confusion unless the user is forewarned; with this forewarning the method is completely useful and practicable. It will be noted that the abscissa is given in units of weight percentage of the composition being treated; on the other hand, the ordinate gives the soap retained on the glass-wool filter in the form of gross curd in units of percentage of total soap. Thus, for example, if a

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¹It is important that Pyrex brand glass wool (Corning Cat. No. 800) be employed. Wool made from soft glass possesses a residual alkalinity which interferes with the determination.