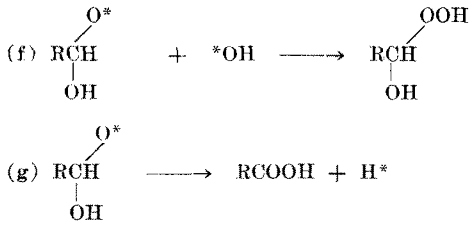
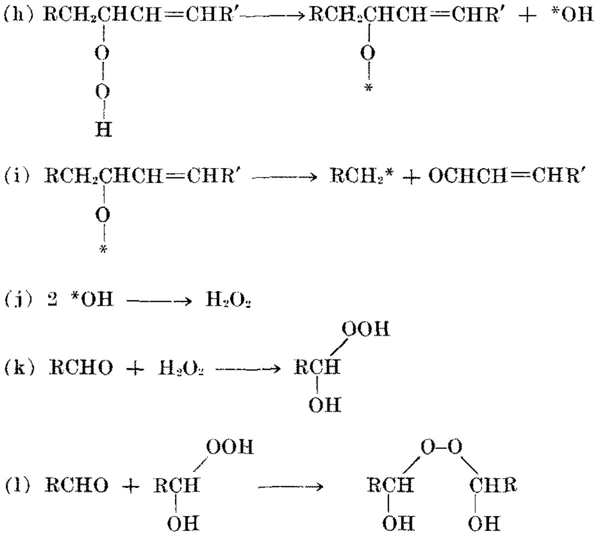


$$(f)\ \underset{\textstyle OH}{\overset{\textstyle O^*}{RCH}} + {}^*OH \longrightarrow \underset{\textstyle OH}{\overset{\textstyle OOH}{RCH}}$$

$$(g)\ \underset{\textstyle OH}{\overset{\textstyle O^*}{RCH}} \longrightarrow RCOOH + H^*$$

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.



$$(h)\ RCH_2\underset{\textstyle O-O-H}{CH}CH{=}CHR' \longrightarrow RCH_2\underset{\textstyle O^*}{CH}CH{=}CHR' + {}^*OH$$

$$(i)\ RCH_2\underset{\textstyle O^*}{CH}CH{=}CHR' \longrightarrow RCH_2^* + OCHCH{=}CHR'$$

$$(j)\ 2\ {}^*OH \longrightarrow H_2O_2$$

$$(k)\ RCHO + H_2O_2 \longrightarrow \underset{\textstyle OH}{\overset{\textstyle OOH}{RCH}}$$

$$(l)\ RCHO + \underset{\textstyle OH}{\overset{\textstyle OOH}{RCH}} \longrightarrow \underset{\textstyle OH}{RCH}-O-O-\underset{\textstyle OH}{CHR}$$

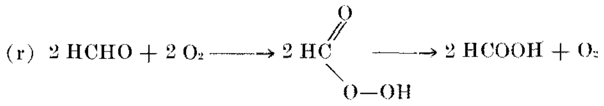
The alkyl-free radical could react with further oxygen and after acquisition of a proton yield a primary hydroperoxide. The latter would decompose into an alkoxy and a hydroxy radical. The alkoxy radical, which is of a highly unstable nature, could produce an aldehyde or formaldehyde. The latter would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

(m) $RCH_2^* + O_2 \longrightarrow RCH_2OO^*$

(n) $RCH_2OO^* + RCH_2R' \longrightarrow RCH_2OOH + \underset{*}{RCH}R'$

(o) $RCH_2OOH \longrightarrow RCH_2O^* + {}^*OH$

(p) $RCH_2O^* \longrightarrow RCHO + {}^*H$
or
$\longrightarrow R^* + HCHO$



$$(r)\ 2\,HCHO + 2\,O_2 \longrightarrow 2\,HC\begin{matrix}{=}O\\-O-OH\end{matrix} \longrightarrow 2\,HCOOH + O_2$$

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.

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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 formulation 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 $CaCO_3$ 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 $CaCl_2 \cdot 2H_2O$ in enough distilled or deionized water to make one liter, and similarly dissolving 40.0 g. $MgCl_2 \cdot 6H_2O$. These are mixed to give two liters of 25,000 p.p.m. solution.

c) 0.008 N HCl.

d) Methyl purple indicator (supplied by Fleischer Chemical Company, Washington 4, D.C.).

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 $CaCO_3$.

The solutions thus prepared are immediately filtered through a small plug of glass wool[1] (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:

$$\% \text{ Soap as curd} = \frac{V_0 - V}{V_0} \times 100$$

where V_0 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 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.

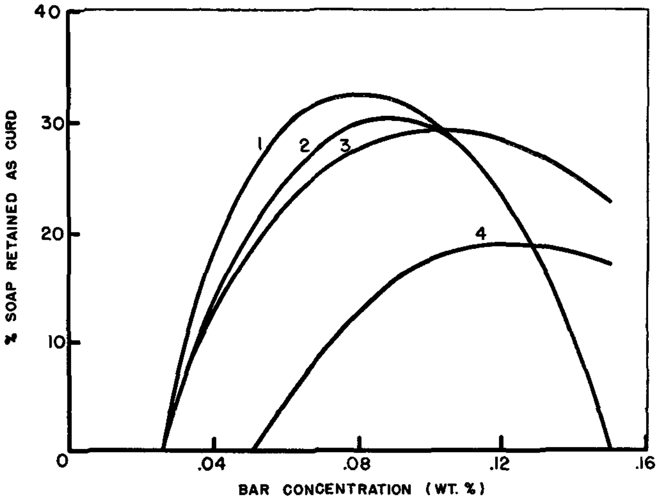

FIG. 1. Effect of concentration of dispersant (sodium H-coco monoglyceride sulfate). *1.* 100% soap. *2.* 95% soap/5% dispersant. *3.* 85% soap/15% dispersant. *4.* 75% soap/25% dispersant.

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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[1] It 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.

pure soap gives, at some use concentration, a value of, say, 40% as gross curd while a 90 soap-10 detergent combination shows 30%, the actual mass of curd in the second case is not 0.75 of that in the first but $0.90 \times 0.75 = 0.675$. This could, of course, be corrected for by adjusting the percentage of lime-soap curd figure to take into account the amount of dispersant present; by plotting the abscissa in units of the soap concentration rather than that of the composition concentration; or by doing both.

Obviously, such corrections require considerable additional manipulation of the data. Furthermore there is a most pertinent objection to plotting the abscissa in terms of soap concentration above. Since this test is designed to compare and evaluate formulations (rather than dispersants, *per se*), it is appropriate to compare them at equal use concentrations. By the same token it is felt that comparison in terms of the percentage of total soap present remaining undispersed affords a truer picture of relative effectiveness.

2. *Results of High Concentrations.* A remarkable feature of the data in Figure 1 is the behavior of the lime-soap-dispersion curves for 15% and 25% dispersant at the higher use concentrations. As can be seen, at concentrations higher than 0.104% in the former case, and higher than 0.126% in the latter, the soap-dispersant composition is actually poorer in performance than the soap alone.

This may be partly understood by the consideration of the lime soap-dispersion curves for soap alone (0% dispersant). As can be seen, beginning at the lowest concentrations,[2] there is a constant increase in the percentage of soap found as gross curd until a concentration of about 0.075% is reached, whereupon the amount of lime-soap curd begins to decrease, reaching a zero value at about 0.150%.

This behavior is entirely in accord with what one would expect; 0.075% represents approximately the soap concentration which will completely titrate the hardness of 125 p.p.m., and beyond this point there is excess soap, which in itself acts as a dispersant, causing the rapidly falling portion of the curve. It is true that, as a result of the method of plotting the data, some decline in the curve would be found even in the absence of dispersion; however a simple calculation will show that the observed drop-off is considerably in excess of what can be ascribed to the plotting artifact.

With this in mind consideration may be given to curves for the system containing 15% and 25% dispersant. In interpreting these curves, it should be kept in mind that while these agents are surface-active materials and hence dispersants, they are also strong electrolytes and hence coagulants. What is observed therefore is a result of balancing of these two opposed effects. Thus, at lower total concentration, the dispersant effect is found to predominate whereas at the higher concentrations (where the absolute concentration of dispersant is appreciably higher) the coagulant effect becomes more important.

Fortunately the higher concentrations are rarely found in actual use; probably not more than one in 50 bathtub users will have a final concentration higher than, or as high as, 0.10%. Thus a very large percentage of users of a composition consisting, say, of 25% of this monoglyceride sulfate dispersant in soap, will note a real improvement in the hard-water performance over soap alone.

If the above interpretation is correct, we should expect that non-ionic dispersants would prove to be more effective on a weight basis than the anionics and that the coagulant effect at high concentrations should be missing or slight.[3] Furthermore the addition of a strong electrolyte should change the shape of the dispersion curve for the non-ionic to one resembling that for the anionic dispersant.

That this is the case is shown in the data of Figures 2 and 3. In this case the lime-soap dispersion curves for a commercially available non-ionic surface-active material (Pluronic L44) are plotted at concentrations of 0 and 5% relative to the soap (Figure 2). As can be seen, even at 5%, this composition is approximately equivalent to one containing 25% of the anionic previously considered. Figure 3 portrays the effect of the addition of a strong electrolyte (sodium chloride) at concentrations of 5% and 10%, based on the amount of dispersant. It is evident that the expected effect occurs to a small extent even at low concentrations (and to the same extent for both salt concentrations), and to a somewhat larger extent at the higher total concentrations.

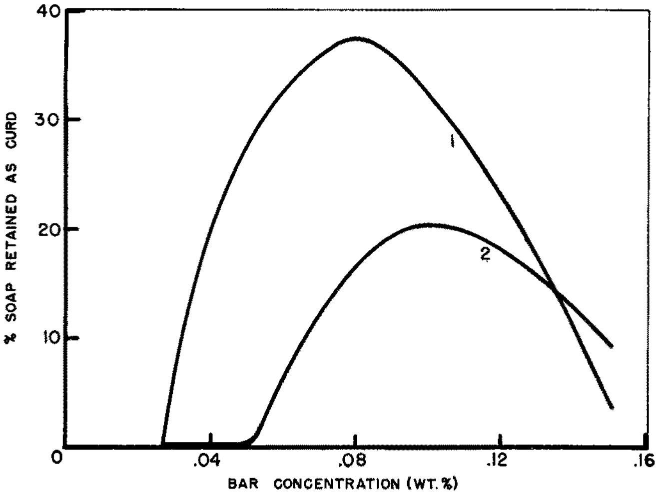

FIG. 2. Effect of non-ionic dispersant (Pluronic L-44). *1.* 100% soap. *2.* 95% soap/5% dispersant.

The interplay between the dispersant and coagulant properties of anionic dispersants may serve to explain why certain materials which have in the past been reported as being very good dispersants (on the basis of tests employing one arbitrary use concentration) have turned out to be relatively ineffective in actual use and when evaluated in this test. Certain of the Igepon series fall into this category.

It is of interest to note that this test serves to demonstrate the effect of composition and structure on lime-soap dispersion. For example, Figure 4 portrays the self-lime-soap dispersion of a series of soda soaps of varying compositions. As one might expect, the dispersion improves with increasing coconut oil con-

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[2] It should be pointed out, parenthetically, that at the worst, no more than 35–40% of the total soap is ever found in the form of gross lime-soap curd. This last statement may be modified to the extent that there undoubtedly exist coagulant agents (as opposed to dispersants) which, added to soap, would have the effect of increasing the curd percentage, *e.g.*, an inordinately high concentration of sodium chloride.

[3] In some cases we may expect the presence of traces of electrolyte impurities.

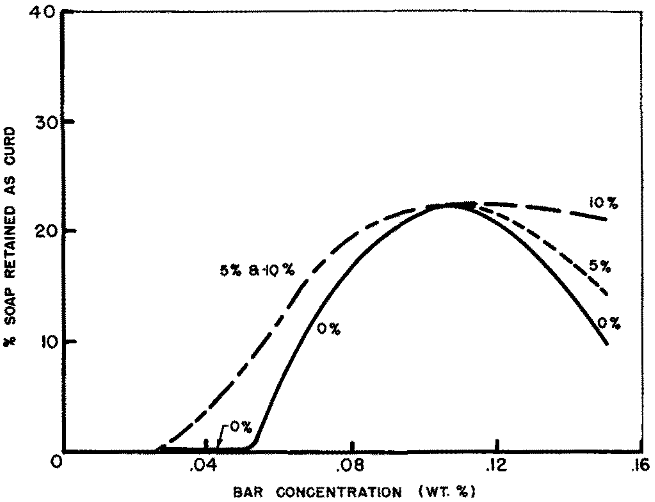

FIG. 3. Effect of added electrolyte on lime-soap dispersion by non-ionic. Dispersion of 95% soap/5% dispersant in the presence of 0%, 5%, and 10% NaCl, based on dispersant concentration.

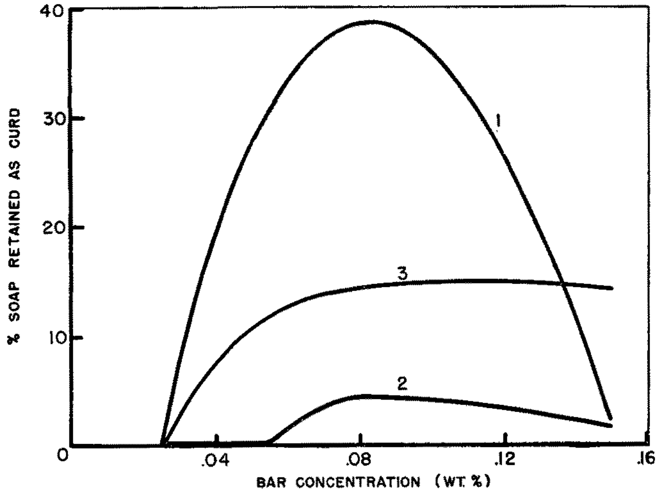

FIG. 4. Effect of coco/tallow ratio on self-dispersion of soda soaps. *1.* 25% coco/75% tallow. *2.* 35% coco/65% tallow. *3.* 50% coco/50% tallow.

tent since this results in a preponderance of more soluble short chain and unsaturated lime soaps being formed. However it is to be noted that the composition containing 35% coco is considerably better in lime-soap dispersing power than any of the others. This is a somewhat surprising result, but it has been borne out by observation in practical use tests.

There is also evidence that the effect of structure on lime-soap dispersion can also be demonstrated with this test. For example, in a series where a fixed hydrophobic group is modified by a hydrophilic group of varying activity (*e.g.*, a series of polyoxyethylene derivatives), it can be shown that optimum dispersion is to be found at quite specific hydrophilic-hydrophobic ratios.

Summary

A new titrimetric method for the measurement of lime-soap dispersion is described. This method differs from previously reported ones in that it is a practical method, *i.e.*, it measures lime-soap dispersion for formulations over a range of water hardness. It is specifically designed for the study of toilet-bar formulations but may be applied to any soap-dispersant formulation. This method also makes manifest the coagulant (as opposed to dispersant) properties of anionic agents at high use concentrations, which may explain why dispersants reported satisfactory by previous tests have been found unsatisfactory in practice. The test is also capable of demonstrating the effect of composition of the formulation and the structure of the dispersant on the lime-soap dispersion.

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Solubility and Heat Stability of Fat-Soluble Derivatives of Vitamin B_6[1,2,3]

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A WHITE CRYSTALLINE COMPOUND, pyridoxine hydrochloride, has served as a commercial source of vitamin B_6. So-called "fat soluble" derivatives of vitamin B_6 have been prepared by esterifying pyridoxine with the short chain fatty acids, acetic (1, 2, 3, 4, 5, 6) and propionic acid (4). These compounds have two disadvantages for practical use in the fat industry. First, they are completely or almost insoluble in fats. Second, they are readily destroyed by heat at the temperature which is usually applied to frying purposes. Witting *et al.* (7) have recently shown that in certain cases the need for vitamin B_6 is increased when heated fats are included in the diet. Their observations have thus necessitated synthesis of a fat-soluble vitamin B_6 preparation which is stable toward heat.

The synthesis of fat soluble derivatives of the vitamin B_6 group (8) and their biological activity has recently been investigated (9). These long chain fatty acid esters were fully active as a source of vitamin B_6 when tested with rats.

Experimental

Synthesis of Fat-Soluble Derivatives of Pyridoxine. Pyridoxine-5-monopalmitate and the fully

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[1] Portion of a thesis presented by T. Sakuragi as partial fulfillment of the requirement for the degree of Doctor of Philosophy in Food Technology.

[2] This work was supported by research grant No. A-257 from the National Institute of Health, U. S. Public Health Service, Department of Health, Education and Welfare.

[3] Presented at the 29th annual meeting of the American Oil Chemists' Society, Oct. 10–12, 1955, Philadelphia, Pa.