

necessary: acetaldehyde, acetone, acetyl chloride, amyl acetate, amyl nitrate, benzoyl chloride, *n*-butyl ether, diethyl ether, methylene chloride.

The solvent or disintegrating action of the following was sufficient to prevent or greatly hinder the use of the lubricant: aniline, acetic acid, tertiary amyl alcohol, benzyl alcohol, *n*-butyl alcohol, tertiary butyl alcohol, ethyl alcohol, methyl alcohol, diethylamine, ethylene chlorohydrin, ethylene glycol, formic acid, propionic acid, pyridine, quinoline, water and solvents containing water. In general, therefore, water, alcohols, aliphatic acids and to a lesser extent certain amines and nitrogen containing heterocyclic compounds prevent the use of the lubricant.

Before lubricating a stopcock with this preparation, petroleum and rubber grease should be entirely removed by means of benzene or acetone and the stopcock should be thoroughly dried. After applying a thin film of the lubricant, a stopcock will remain gas tight even when frequently turned in the presence of solvents of the first group mentioned above. With a liquid-air trap in the line to remove any water vapor evolved, a stopcock lubricated as described will hold a good vacuum. In gas analytical operations where the presence of petroleum grease was thought to cause error by absorbing constituents such as ether vapor, the glycerin-dextrin-mannitol lubricant has been used with success. Water dissolves the lubricant readily and may therefore be used to remove it when desired.

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The Probable Non-Existence of Normal Tribasic Aluminum Soaps Such as Aluminum Tripalmitate

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Aluminum soaps are articles of commerce used in several industries; they are even listed in most catalogs of pure reagents, and they have frequently been employed in scientific work.¹ Nevertheless, after repeated purchases and attempts to prepare aluminum tripalmitate and other tribasic aluminum soaps, we have come to the conclusion that the product is a mechanical mixture from which an appreciable proportion of free fatty acid is at once dissolved by ether, leaving behind a monobasic or at most a dibasic soap such as a dipalmitate, even when prepared and extracted in the complete absence of moisture. For example, Kahlbaum's aluminum tripalmitate yielded 50% of its fatty acid content to ether dried over sodium. A sample of aluminum palmitate obtained from Eimer and Amend contained only one equivalent of fatty acid to three equivalents of aluminum.

Aluminum soaps are usually prepared from aqueous solution by pre-

¹ For example, in emulsions of water with other solvents, in studies of swelling, etc.

cipitating a soluble soap with aluminum salt. The precipitate is then taken to be the tribasic aluminum soap. Consideration of the elementary theory of aqueous solutions (compare, for example, aluminum sulfide) would lead one to expect a doubtful or negative result on account of the extensive hydrolysis of a salt of a weak fatty acid with a base at once so weak and insoluble as aluminum hydroxide.

Preparations of Oleates, Stearates, and Palmitates from Aqueous Solutions.—When aluminum sulfate solution was added in excess to an aqueous solution of a sodium or potassium soap, the P_H of the soap solution changed during precipitation from about 8.5 to about 4.5. The precipitates were washed with water, alcohol and ether or with acetone, and aluminum was determined by ignition as Al_2O_3 . They contained from 5.5 to 6.7% aluminum for palmitates and from 5.0 to 6.2% for stearates and oleates. This indicates a gross composition slightly nearer to dibasic rather than monobasic soap, which was confirmed by a determination of fatty acid present. Preparations made when the P_H was kept equal to 8.5 with sodium bicarbonate gave similar results. With P_H between 3 and 4.5 the product contained little more palmitic acid than corresponded to monopalmitate.

Preparation of Palmitates in Non-Aqueous Media.—Preparations made in 95% alcohol and in absolute methyl and ethyl alcohols gave results no nearer the tripalmitate. Diamyl ether, a good solvent for aluminum soap, was used with palmitic acid and freshly prepared aluminum hydroxide washed with alcohol and ether. The soap from this solution was no better. Similar procedures with chloroform left as much as 14% of aluminum in the soap even when the solution had become clear.

Finally, we turned to the reaction between aluminum ethoxide and palmitic acid and benzene which had been dried over sodium. Of 2.6 g. of Kahlbaum's ethoxide, 2.0 g. dissolved on refluxing with benzene. When the theoretical amount of Kahlbaum's best palmitic acid was added, the resulting solution was clear and fluid, but after evaporation to dryness a large amount of fatty acid or fatty anhydride was extracted at 40° by dry ether, yielding palmitic acid 92.2 and 93.5% and aluminum 5.10 and 5.15%. This corresponds closely to an anhydride or ethoxide of aluminum dipalmitate (there was no water present at any time for formation of $AlPal_2OH$).

Further experiments in the same direction have been made in the Department of Chemistry, University of Nevada, Reno, by S. Allan Lough and E. L. J. Randall. The Kahlbaum palmitic acid used was found to be 99.9% pure as determined by titration with standard alkali. The ethoxide by ignition indicated a content of 45.28% although only 40% was extracted with benzene, leaving the alumina behind. Another sample of benzene extract contained 88% of material removed from the

crude ethoxide after filtering through surgical absorbent cotton. After reaction with more than the theoretical amount of palmitic acid and extracting the dried (at 45°) product with ether, the aluminum content was 4.8% as compared with the 5.1% already quoted. In a final experiment with dried benzene which had dissolved 77% of the crude ethoxide the product was dried in four portions at 25, 45, 55 and 75°. The crude material contained between 2.85 and 3.00% of aluminum and after hydrolysis with sulfuric acid yielded fatty acid determined by titration in alcoholic potash corresponding to from 78.96 to 94.84% of palmitic acid. These four products after extraction with sodium-dried ether contained, respectively, 5.38 and 4.43, 5.36 and 5.34, 5.29 and 5.20, 5.24 and 5.33% of aluminum, whereas aluminum tripalmitate would contain only 3.400% of aluminum. These results again indicate that not more than the dibasic palmitate is attained even under these unusually favorable conditions.

Our conclusion is that aluminum soaps are commonly a mixture of uncombined free fatty acid with either a monobasic or a mixture of mono- and dibasic soaps. Normal tribasic aluminum soaps have never been prepared even in completely anhydrous media.

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THE DETERMINATION OF IODINE IN BUTTERFAT

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The estimation of iodine in carbonaceous materials such as oil or butter is generally regarded as the most difficult of all estimations of minute amounts of iodine in natural products. The most recent method that has been described is that of McClendon, Remington, von Kolnitz and Rufe,¹ in which melted butter (as much as 500 g. in one sample) was sprayed from an atomizer into a silica tube and burnt with a current of oxygen in the presence of a catalyst. This process obviates the difficulty inherent in the much simpler method of combustion with alkali, namely, that the low iodine content of the material necessitates so large a sample being taken for analysis that the use of an excess of potash is out of the question. This leads to loss of iodine, and in addition there is a pronounced tendency for the products of saponification of the butter to froth up during combustion in an uncontrollable fashion.

However, in the micro-titration method devised by the author for the

¹ J. F. McClendon, Roe E. Remington, Harry von Kolnitz and Redding Rufe, *THIS JOURNAL*, **52**, 541 (1930).