Metallic Soaps*

A Discussion of Occurrence, Uses and Properties

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WE think of soaps as the alkali salts of the acids contained in fats. These acids in combination with glycerine occur naturally in vegetable and animal oils and fats, and when treated with caustic soda or potash become soaps in the common acceptance of the term, with liberation of glycerine as a by-product of the process we call saponification. We do not concern ourselves with the fatty acids of the same series of lower molecular weight, as acetic, formic, propionic, but with oleic, stearic, palmitic and lauric chiefly. With soda, potash and ammonia, their products are soluble in water, produce lather in abundance and are detersive in action.

However, there are other salts of the same acids, which are for the most part insoluble in water, do not lather and do not clean. They possess, however, properties that set them apart in a class by themselves, have acquired considerable commercial value in the past and are destined to play a greater role in the future. They are the soaps of the alkaline-earths and of the heavy metals, very interesting compounds of wonderful possibilities.

Metallic Soaps as Driers

Some of them have been in use for ages without the knowledge at first of their composition, only of some of their properties, learned of through accident rather than research. They are the siccatives or so-called driers of the paint and varnish industries. At first, the oxides, carbonates or inorganic salts of such metals as lead, cobalt and manganese were added to oils like linseed and tung to assist in their oxidation or drying. At ordinary temperature, these oils set too slowly for most purposes. Hence the use of boiled oils in paints. Later, the soaps themselves were prepared and added, as the linolenates, linoleates, resinates and 'tungates.' These soluble driers act as catalysts or oxygen carriers, permitting the entire body of the oil to dry in a few hours where formerly a day or two was required. It is found that those salts are the most effective whose metals form lower and higher oxides, which is in accord with the theory of catalysts propounded. On this subject an extensive literature and research have grown up. It is, therefore, needless to go further into the application of metallic soaps to the paint and varnish industry, as being too familiar and comprehensive a subject to discuss here.

A description of the manifold uses to which metallic soaps are put show to what extent they have already established their importance; and wherever I can, I shall indicate the places where they may apply to further advantage or point out possible uses for the future.

The zinc, iron, nickel, cobalt and chromium soaps are used for waterproofing leather and canvas and in coloring varnishes. The aluminum and magnesium soaps go to waterproofing textile goods. Aluminum

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soaps are especially important, finding extensive employment in the waterproof sizing of papers, in substitutes for leather, in celluloid, rubber and insulating materials, in mordanting, in oil-emulsions like oil-dag, solidified oils or solid lubricants, floor waxing compounds, polishing preparations, etc. The oleate is particularly useful as an oil thickener.

Pharmaceutical Uses

In the pharmaceutical line, the mercury, lead and zinc compounds have long been known, chiefly as ointments and plasters. The strontium soap of dibromobehenic acid is a substitute for potassium bromide. Zinc stearate is familiar to you as a facial or dusting powder for the skin. Lead oleate has great antiquity, having been known to Dioscorides, the Greek physician and authority on Materia Medica. Copper oleate is used in granulation and in ulcers. The soaps of pharmacy are prepared by trituration of lard or suet, or of oleic acid, with the oxides of the metals and therefore are chiefly mixtures of the consistency of pastes or ointments. The pure soaps themselves, however, are beginning to find a field of their own in the dry state. The saturated fatty acid salts of mercury should find use as antiseptic and germicidal dusting powders for wounds, without the toxic effects of the usual mercury compounds. Iron soaps may replace to advantage in pill or in emulsion form the various preparations of peptized iron for internal use. Silver soaps, likewise, may be substituted for preparations like argyrol that stain or for the cauterizing of raw surfaces in place of the caustic nitrate or in lieu of the silver caseins, proteins or vitellins. Research along these lines should reveal an astonishing number of places where the soaps may be employed dry, or emulsified and incorporated with other ingredients.

Copper and mercury soaps are useful in fungicide sprays for trees and plants, in disinfectants and in anti-fouling paints. The latter applied to ship-bottoms prevent the growth of barnacles by their poisoning action, or protect the metal from corrosion by causing these parasites to slip off of their own weight. Small amounts, added to the usual alkali soaps, are employed as antiseptics.

In wool scouring, lime is at times thrown into the waste suds to settle out the fat with the insoluble soap formed. Salts of magnesium and iron are likewise used to carry down the fatty acids as soaps together with the neutral portions of the wool fat. The mass is subsequently extracted with acetone or preferably the higher ketones, dissolving out the neutral fat for further refining to the final lanolin of the drug trade.

Dry-cleaning Applications

Metallic soaps are going to be used considerably more in the dry-cleaning line. At present magnesium oleate in petroleum benzine is added to the solvents of the dry cleaner to prevent spontaneous firing from the static electricity generated by the withdrawal of silk goods from the bath. In my own experiments, I have found that a few metallic soaps—nickel for example—in benzol or certain of the lacquer solvents, will produce good lathering and detergent effects. They are, therefore, of possible use in the cleaning of such fabrics as are injured by water soluble alkali soaps—as in the cleaning of silk and chamois.

Occurrence in Oils

Of frequent occurrence are the lime and iron soaps in our own oil industries, though fortunately seldom to the extent of causing serious annoyance. Yet at such times, their formation accidental or incidental to manufacturing processes, forced desired attention to their presenec, their properties and the means of their removal. Otherwise we would never know about them. In olive oil foots, for example, lime soaps occasionally occur in sufficient amount to warrant rejection of shipments. Being soluble in carbon bisulphide or warm ether, the soaps pass through the filtration media concealing their presence on the usual form of analysis for moisture and impurities and soap color required by the trade. The appearance of the foots reveal large amounts by their sliminess, pastiness or semi-solidity when they should be practically liquid. As a rule, foots show normally only a bare trace of lime, giving on ignition one tenth or two tenths of one per cent of ash, which should be practically all iron oxide. Abnormal content of lime soap arises possibly from the use of lime oxide or carbonate in the last pressing of the olive marc to reduce the acidity of the commercial oil obtained, and the subsequent carbon bisulphide extraction of the residue for sulphur oil or foots; the lime soaps produced dissolving and remaining in the oil.

Tanks, drums, pipelines, etc. will furnish under careless conditions the rust to combine with oil to produce iron soaps that darken the color of oils, at times sufficiently to affect acceptance of delivery. With favoring conditions of high temperature, moisture and long contact even with low acid oils, the oxides become suspended in the oil partly mechanically, partly colloidally, and there is partial solution as soap as well. In the latter case, we say that the color of the oil has been fastened. Filtration will, therefore, not lighten the color in the severe case. Partial saponification with soda ash or lye will remove this, as will the use of hydrochloric, oxalic or phosphoric acids. In our laboratory, we have had a few shipments of palm-kernel oil, sold on color as one consideration, thus darkened by iron soaps. It is surprising what an insignificant amount of iron soap will do to discolor an oil. I have had a few instances of edible olive oil also darkened by iron in solution, through the use of inferior drums. On long standing, the oil clarified somewhat because of the settling of iron oxides, originally in such a fine state of suspension as to be invisible, but the soap in solution rendered the oil too dark for other than technical purposes unless capable of being treated by harmless methods.

Lime soaps are also to be found in inedible tallows and greases, and we as chemists determine their amount as soluble impurities by ignition, and calculation of the ash back to the soap basis.

Metallic Soaps as Emulsifiers

In the hydrogenation of oils, small amounts of nickel soaps are formed from the reaction involved at high temperature. It has been suggested to use nickel soaps, and also mixtures of nickel and iron or copper soaps of fatty acids as catalytic agents to promote intimate contact between catalyst and oil in this process.

One of the most important properties of soap is its ability to form emulsions. The alkali soaps have been used extensively for such. Of the insoluble soaps, lime and aluminum are thus chiefly employed. The textile industry draws on the former for softening agents, the petroleum industry on the latter type for lubricants. I have found that ordinary soda soap will emulsify its weight or over of free stearic acid to which water can be added in large amount, and the resulting product will stand up as a silky paste, 'gel' or emulsion according to the dilution. This emulsion is quite durable and fails to break under severe conditions.

The usual emulsions are of oil dispersed in water with a small amount of water-soluble soap to keep the globules of oil from coalescing. With metallic soaps, we may reverse the procedure and disperse water in oil. Solidified oils, solid lubricants and cutting compounds may thus be formed.

I remember in connection with lubrication, the solicitude with which a petroleum oil was once examined for saponifiable matter, because it was then believed that animal or vegetable fats present in such an oil would cause gumming under friction, and the acid present or produced by hydrolysis would corrode bearings and the metallic parts of contact. Research into what constitutes the 'oiliness' of oils, whereby they lubricate, has evolved the so-called 'germ' process in lubrication, based on studies of capillarity and surface tension. It is no longer thought that a saponifiable fat is objectionable, but on the contrary it is held advantageous. So now, we incorporate fatty compounds or better still, smaller amounts of fatty acids in proper proportions for the various types of lubricants, as steam turbine, cylinder, cup, etc. These help to spread the oil into minute places and wet surfaces that were not so efficiently reached before. It was a known though peculiar fact that the fatty oils were better lubricants in general that the mineral oils, though why was then unknown.

To overcome the objection that still persists to a small degree of the corrosive and gumming effects of saponifiable fats, even with the increased lubrication that now results from their inclusion, metallic soaps may be substituted in part or entirety for the fats. As emulsions with mineral oils, they maintain continuous and permanent films, wetting the surfaces of contact and spreading better, due to the decreased interfacial tension between oil and metal because of their presence. Hence, I look for a greater future for the metallic soaps in lubricants.

To the analyst, encumbered with the conventional tests of an undecisive nature due to the ingenuity with which adulteration and admixture are now practiced, the use of metallic soaps in his work should come as a godsend. The tearing down of oils into their constituent fatty acids and the determination of their ultimate composition are his final and almost inevitable resort; for no longer do iodine values, etc., give him the substantial evidence needed to adjudge an oil. By preparing the metallic soaps of the mixed acids and separating them by the appropriate solvents, he is in a fair position to prove adulteration and put the oil bootlegger in a tighter position than his relative of another line.

Develop New Chlorophyll

The firm of Dr. F. Wilhelmi, Taucha Bez, Leipzig, Germany, has succeeded in producing a water soluble powdered Chlorophyll which is now being manufactured commercially. In this form, the chlorophyll is said to be three times as strong as is the usual paste form now in general use in the oil and allied industries.