# Chemical Problems in the Manufacture of Soap

### Fundamental Principles of Soap Making Discussed

THE study of soap-making from a chemical point of view presents many interesting problems. Like many other industrial operations, the manufacture of soap has gradually developed from very rude beginnings, by accumulated experience, to become a highly specialized branch of chemical manufacture.

It was well known that when an oil or fat is mixed with a solution of caustic alkali—soda or potash—and allowed to stand for some little time, at a moderate temperature, a solid product, or soap, is formed. This, in short, was the "cold process" of producing soap, but in this operation any excess of alkali, also any impurities contained in the alkali and the fat, as well as the glycerine, remained with the soap, which was, therefore, a variable and far from pure product. It was also known that saponification could be accelerated by heating the oil and alkali solution and bringing them into intimate contact by agitation, and when it was discovered that the soap could be "salted out" or separated by addition of common salt, the removal of impurities, together with the glycerine, become possible, and better qualities of soaps could be produced.

These operations of the soap maker, although simple in appearance, depend for their success upon an intimate knowledge of the raw materials and the careful adjustment of the working conditions, since without such knowledge and attention to details it would be a matter of luck if a satisfactory finished product resulted, and the regular production of a standard quality of material would be altogether out of the question.

### Composition of Oils and Fats

The composition of fats and oils was established on a scientific basis by the researches of Chevreul, described so clearly and accurately in his remarkable work, "Recherches Chimiques sur les Corps Gras d'Originie Animale," 1823. He showed that when a fat or oil is heated with an alkali two very definite products are always formed, viz., a soap and glycerine (the latter previously discovered by Scheele, in 1779, by heating lard with lead oxide and water in the preparation of lead plaster). He proved that fats are combinations of fatty acids with glycerine—or, rather, with its radicle glyceryl—and that on heating with alkali the latter combines with the fatty acids to form salts, or soaps, while thus replacing the glycerine which appears in the free state.

Chevreul was able to identify several fatty acids in various oils and fats; he separated and analyzed these acids and examined many of their compounds, and he also demonstrated that natural oils and fats are composed of mixtures of the simple glycerides, olein, stearin, etc., in various proportions; the nature and relative quantities of these governing the properties of the product.

On separating the two constituents—fatty acids and glycerine—and weighing them, it was found that their combined weight was greater than that of the original fat taken, which is explained by the fact that the elements of water are taken up during the reaction, and he concluded that saponifiable fats have a composition exactly similar to that of the compound ethers, the alcohol in this case being glycerine, which is capable of uniting with fatty acids with the elimination of water and the formation of the esters (triglycerides or fats).

The conclusions arrived at by this great investigator 100 years ago have been amply confirmed by numerous later workers, who have also added considerably to our knowledge. Berthelot extended the work, and showed that fats can be produced artificially by the direct union of fatty acids and glycerine under heat and pressure with elimination of one, two, or three molecules of water and the formation of what we now know as mono-, di-, and tri-glycerides, respectively.

Although it is possible to prepare these three kinds of glycerides artificially, the glycerides found in natural fats are, probably without exception, entirely those known as tri-glycerides, i.e., triolein, tripalmitin, tristearin, etc., or mixed triglycerides, such as oleo-dilaurin.

From the different characters of the various oils and fats it is evident that they do not all possess the same composition; in fact, there are no two alike, and no natural fat or oil consists of only one glyceride; usually four or five glycerides are present; sometimes even more. Perhaps the nearest approach to a pure glyceride is castor oil, which contains nearly 95 per cent. of triricinolin. Recent investigations have however, shown that the glycerides are compound, i.e., two or three fatty acids may be in union with the same molecule of glycerine, forming what are known as mixed glycerides, and quite a number of these compounds have been isolated and examined. The possible number of these molecular compounds is infinite, and their influence upon the properties of oils and fats has only recently been realized.

The crude oils and fats are never neutral, a proportion of free acids being always present. The amount of free fatty acids depends upon the nature of the original raw material, and also upon the method of extracting the oil. Animal fats and oil usually contain little free acids, but vegetable oils often contain a very large proportion; thus, the free fatty acids in tallow rarely exceed 5 per cent., whereas olive oil sometimes contains 25 per cent. and palm oil may contain as much as 80 per cent.

### Fat-Splitting Enzymes

If the original raw material is damp or mouldy then the oils extracted therefrom contain a high percentage of fatty acids, the latter being liberated by the enzymic action of moulds and bacteria, the glycerine liberated at the same time being to a large extent destroyed, with consequent low yield of that commodity in the glycerine extraction house. Several seeds contain also active principles known as "lipolytic" or fat-splitting enzymes, which are liberated when the seeds are crushed, and these, assisted by moisture, warmth, and a slight acidity, are capable of converting neutral fats into fatty acids and glycerine completely, and in very short time. Castorseed is a notable example of a seed containing a lipolytic enzyme or "lipase," the application of this seed in a crushed state for fat-splitting being the basis of several patents by Connstein, Nicloux, and others. Palm fruit pulp and olive pulp also contain fat-splitting enzymes, which accounts to some extent for the high percentages of fatty acids in the oils from these sources, but these oils are to a large extent prepared from more or less decomposed material, in which moulds and bacteria also generate enzymes of a similar character.

## Unsaponifiable Matter

The unsaponifiable matter in fats and oils, consisting, for the most part, of cholesterol or phytesterol and their esters, plays no definite part in soap-making, since the amount present is so small, in most cases, rarely amounting to more than one per cent.; but certain oils contain high proportions of unsaponifiable matter. For instance, sperm oil contains about 45 per cent. of alcohols, which appears as unsaponifiable matter, and certain shark liver oils have been found to contain unsaponifiable hydrocarbons in such quantities as to render them entirely unsuitable for soap-making.

It is a well-known fact that in the manufacture of soap by the boiling process strong solutions of caustic soda are unsuitable in the first stages, since the oil and alkali do not mix; that is, the interfacial tension between the two is so high that there is practically no interpenetration, any action which takes place being possible only at the surfaces in contact or bv violent agitation; the strong soda solution, behaving in a similar manner to common salt in salting out any soap which may be formed, also interferes with the saponification. It is, therefore, necessary to employ weak solutions of alkali at first through which the oil can be disseminated in a finely divided condition in the form of an emulsion. In emulsions the oil globules are reduced to extremely minute dimensions, and thus they expose an enormous surface to the hydrolytic action of the alkali. At the same time, the soap formed lowers the interfacial tension between the oil and the water, so that the oil globules are still further comminuted and saponification proceeds more rapidly, the soap, in this case, remaining in solution, the alkali is free to exert the maximum action consistent with the conditions.

In this direction, the presence of free fatty acids in the oil is a distinct advantage, since the combination of these with the alkali is almost immediate, and no external energy is required to bring it about; the saponification of the oil is thus accelerated by their presence.

## Rate of Saponification

The rate at which saponification proceeds will vary with the nature of the oil or fat used, the temperature, and the strength of the solution of alkali. All fats and oils are not equal in the ease with which they can be saponified. Coconut oil is very quickly saponified, and so is castor oil, but olive oil not so readily and tallow still less easily; but by blending oils which are readily saponified with those that are not, the saponification of the mixtures is rendered easier.

The question has arisen as to whether certain glycerides in oils are saponified before others, or whether the oil is saponified as a whole, and also whether the saponification, once started, proceeds direct to the formation of soap or in three stages, with the formation of diglyceride, monoglyceride, and then soap. These problems will have to be dealt with later.

There is every reason to believe that some glycerides are more readily saponified than others; the glycerides of the lower fatty acids, for instance butyric, caprylic, etc., up to myristic acid, appear to be more readily saponified than the glycerides of the higher acids, e.g., palmitic, stearic, etc., but they are so combined with one another in the natural fats that the individual glycerides are not selectively hydrolyzed, the fats being apparently saponified as a whole.

In the manufacture of commercial soaps it is usual to blend two or more oils together to obtain particular results.

Tallow or stearin forms an extremely hard soap, which does not readily dissolve in water, forms a stiff paste with water, and does not readily lather, although the lather, once formed, is a lasting one. On the other hand oils usually yield softer soaps which are more easily soluble, form thin solutions, and readily lather, although the lather is not very permanent. By blending tallow with oils a fairly hard soap is obtained, which dissolves moderately easily in water, forms a thicker solution, which lathers easily, and the lather is more permanent.

Palm oil forms a soap which is intermediate in its properties between that of tallow and the oils, and forms a useful third material for blending the others together.

It may be noted that oils, such as olive oil, containing fatty acids belonging almost entirely to the oleic series form very good hard soaps, whereas those containing a high percentage of the more unsaturated acids—linolic, etc.—i.e., cottonseed oil, linseed oil, fish oils, etc., form pasty soaps, and are unsuitable to be used alone, except for soft-soap making. Castor oil forms a hard soap, but the solutions are very thin, it gives very little lather, has very little detergent properties, and does not hydrolyze like other soaps when dissolved in water.

### The Quantity of Alkali

It has been stated that saponification is never complete unless the alkali is in excess, but this is not correct; complete saponification can be brought about with the theoretical quantity of alkali, provided the right conditions are ensured. Excess of alkali is more likely to retard saponification than is a deficiency. In cold saponification, in which a strong solution of alkali is stirred into the warm oil and the mass kept at a temperature of 70° to 80° F., 95 to 99 per cent. of the oil will be saponified in 48 hours, and if the temperature of the oil be raised to about 160° F. and the solution of alkali is well stirred in, the saponification is so rapid that the whole mass will set to a stiff translucent jelly in about half an hour.

### Salting Out

After the saponification is almost complete, we have in the boiling process a mixture consisting of a solution of soap and glycerine, some free alkali, and some unsaponified fat. Since soaps are hydrolyzed by water, there will be free alkali and an acid soap, or perhaps free fatty acids. On addition of common salt the soap becomes much more viscous, and at a certain concentration of salt two layers are formed, a concentrated solution of soap on the surface containing the unsaponified fat and a salt solution below containing the glycerine. There may be a third intermediate layer, containing a proportion of all the constituents. If the salt is added in sufficient quantity soap curds will be formed. This action takes place not only with strong solutions of soap, but with comparatively weak ones also. Caustic soda has the same effect as common salt, and is even more effective; it also forms curds. Carbonate of soda and sulphate of soda also will salt out soap, but they are not so effective, and they behave in a somewhat different manner, forming two liquid layers, the upper soap layer setting to a gelatinous mass on cooling. Sulphate of soda is the least effective.

### Effect of Salt

The effect of the salt is, however, not merely that of separating the soap in the form of a paste or as curds. There are in the kettle, besides neutral soaps, the products of dissociation—free alkali and an acid soap or free acids—which are caused to recombine by the addition of the salt; that this is the case may be demonstrated by estimation of the free alkali before and after such addition.

The writer has been able to touch upon only a few points in the present article. As time goes on, other problems will be dealt with, and, no doubt, there will be opportunities for treating upon these subjects in a fuller manner. *Oil and Color Trades Journal.*

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# The Detection of Extracted Olive Oils

## Organic Silver Salts Exhibit Marked Reactivity to Sulphur

By M. F. LAURO

THE various tests for extracted oils are based on reactions with traces of the solvents left in the oils after extraction. On Olive Oil Foots or Industrial Olive Oil, extracted from olive pulp by means of carbon bisulphide, sufficient solvent is always present to be easily ascertainable, by almost any of the methods used for the detection of sulphur or sulphur compounds. When, however, such oils are bleached, refined and blended with pressed oils, the percentage of solvent present is considerably reduced, generally to a point where it becomes quite a problem for the chemist to determine its presence.

### Metallic Silver Method

The so-called "Coin" test is the one most often used in the United States for the detection of carbon bisulphide in olive oil. The suspected oil is heated, with a bright new dime or piece of silver foil suspended half-way in the oil, in a test-tube immersed in an outer oil bath to prevent scorching. The heat is gradually carried up to 210°C. taking from fifteen to twenty minutes, then held at that temperature for another fifteen minutes. The silver is examined to see if blackened. A black stain on the silver indicates the presence of sulphur or its compounds. At times the metal is stained a coppery hue, rather than black, in