THE MANUFACTURE OF TOILET SOAPS

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The manufacture of any soap is the solution of a problem in practical fat chemistry. The problem posed is this: what chemical reaction, physical and mechanical treatment, what additions of auxiliary materials are necessary to convert a given fatty glyceride (or mixture of glycerides) into a soap of the desired chemical and physical properties (including odor, color, luster, etc.), of the requisite chemical stability (i.e., keeping qualities), while incidentally permitting the recovery of glycerine.

A fatty acid has in general the formula

$CH_3.CH_2$ . . . COOH, which may be written—FOH

in which F represents the acidyl group $CH_3.CH_2....CO$:

The formula for a simple triglyceride is then

$$C_3H_5(OF)_3,$$

and our problem is to so carry out the principal reaction:

$$C_3H_5(OF)_3 + 3NaOH = 3NaOF + C_3H_5(OH)_3$$

as to obtain the required result indicated in our first paragraph. The equation, while it represents the chemistry of our problem in a superficial manner, is by no means the complete answer to our problem, which is how is soap manufactured. As in every other industry the technic of the laboratory is merely the basis of the manufacture and is not of itself sufficient to indicate the manufacturing process. The chemist with an ordinary university laboratory training could no more produce a marketable soap than the graduate of an engineering course could with his university training alone design a battleship or a watch.

The manufacture of toilet soap is in many respects chemically the simplest soap manufacturing process known, starting as it does with the purest raw materials and yielding as its product the closest approach to pure soap which is marketed commercially. However, the physical and mechanical processes involved are quite complicated and will serve to indicate how profound an effect physical conditions have on our simple chemical reaction.

It is hardly necessary to recall the facts of soap manufacture, but this is done merely to bring out the chemistry of the processes involved. Soap manufacture consists essentially in

(1). The saponification of the fat.

(2). The separation of the soap formed from the glycerine liberated, from the impurities and the by-products.

(3). The physical treatment of the soap (including coloration and perfuming) to give it the requisite physical characteristics.

The saponification of fat is not by any means as simple an operation as the equation for the chemical reaction indicates it to be. The questions of maximum yield of soap, maximum recovery of glycerine and the varying speeds of saponification of the oil complicate matters. Cocoanut oil saponifies very readily with the evolution of much heat, while tallow is much more difficult to saponify as are also the hardened (hydrogenated) oils. The separation of the soap from its solution is brought about by the commonly used method of organic chemistry, the salting out by the use of a salt with an ion in common, in this case common salt, NaCl, to salt out soap, NaOF. Hardened whale oil requires a brine of 1.06 specific gravity to salt out the soap formed from it, while cocoanut oil or palm-kernel oil soap requires a brine of 1.125 specific gravity for complete salting out.

In all modern soap practise mixtures or blends of fats are used as the raw material for soap. This is advantageous from several points of view. In the first place the soaps produced are better. They combine advantageous properties such as quick lathering with retention of the lather in a manner not possible for the product of a single fat. Saponification is easier in general; the hardened fats saponify much more easily when added to a partially saponified charge which causes rapid and easy emulsification; on the other hand cocoanut oil and palm-kernel oil tend to swell and boil over unless added similarly to a partially saponified charge.

Each operation in soap boiling (that branch of soap manufacture which deals with the production of the pure soap from the original fat) is known as a change. Soap production by the old cold process can actually be carried out as one step; namely, the treatment of a fat (cocoanut oil) with the requisite amount of caustic solution to produce a soap mass of the correct water content and to retain all the glycerine. This is still sometimes used by very small scale manufacturers of specialties such as shampoo pastes or even shaving creams; but it plays a part of negligible importance as compared to the great soap manufacturing industry.

On a somewhat larger scale soap boiling may be conducted with as few as two changes (strong change and fit) or three changes (brine change, strong change and fit); but the manufacture of a high grade toilet soap is a process involving six changes. They are:

1. *First brine change:* In this the charge is saponified and then grained (or salted out) by salt, allowed to settle over night and the spent lye drawn off.
2. *Second brine change:* In this the charge from the first brine change is closed (i.e., redissolved in hot water), more alkali and fat may be added, the charge is again grained with salt, allowed to settle and the spent lye drawn off.
3. *Resin change:* In this the charge is again closed, grained with salt and the resin soap added.
4. *First strong change:* In this the charge is again closed and is

opened (salted out) with caustic soda, allowed to settle and the half spent lye drawn off. This is essentially a washing process to remove impurities, especially those of color-producing character.

5. *Second strong change:* This is similar to the first strong change.

6. *Fit:* This is the final operation yielding the pure soap.

The ideal strength of caustic soda is 1.300 specific gravity. The details of quantity of water added (as such or as steam) the rate of feeding in the fat (melted, if solid at ordinary temperature) and caustic soda, the maintenance of suitable temperatures, etc., play an important role in the saponification but will not be considered in this brief review. The salt is added by sprinkling in the requisite weight while the charge or "pan" is boiling smoothly. The soap rises or grains, the brine with most of the glycerine forming the lower layer. The stronger the brine the harder is the curd or separated soap; a moderately soft curd is desirable as it permits better separation of the spent lye. The charge from the first change is settled over night and the spent lye is analyzed in the morning. If too much alkali is present the charge must be heated up again and corrected by the addition of more oil or of fatty acids. If satisfactory the sludge cock is opened and the spent lye drawn off. The sharper the separation the more successful the subsequent operations. Indeed sharp separation of the soap from the impure liquors after every change is a fundamental necessity for the production of high grade soap in good yield.

In the second change the soap is boiled up with steam, water added until the charge is closed and fairly thin. In some cases only about two-thirds of the fat is saponified in the first brine change so that the additional third and the requisite caustic are now added. Graining is produced as before, followed by settling and drawing off the spent lye.

These two changes and the resin change which follows have as their function the complete saponification of the charge and the washing out of the glycerine and impurities. The removal of all glycerine is economically impossible and the finished soap will contain 0.2-0.4 per cent of absolute glycerine.

The amount of spent lye is about equal in weight to the soap produced. The spent lye from the first change contains 4-6 per cent of glycerine, the second spent lye 2-4 per cent of glycerine, and the brine from the resin change about 1 per cent or less of glycerine. It is claimed by some that the slightest trace of resin will ultimately appear in the distilled glycerine. The spent lye from the first two changes should not ordinarily be higher than 1.105 specific gravity and will usually contain 10-15 per cent of common salt. The spent lyes are allowed to cool before being sent to the glycerine department and some soap separates out. The skimming off of this soap and its return to the process tends to increase the yield somewhat and to prevent difficulties in the glycerine department.

For the resin change the charge is closed with as little water as possible, the necessary salt for graining is added, and then the resin as such or as resin soap. If added as resin it should be the finest water white and sufficient caustic is added to form the resin soap. Resin or resin soap is never added to a closed pan but always to a grained pan. It is added after most of the glycerine has been removed (by the spent lyes of the first two brine changes) as the resin soap even in small quantity tends to retain glycerine. When the resin soap is formed separately soda ash is used and the resin soap may be salted out once or twice to cleanse it of impurities before adding to the soap pan. After the addition or formation of the resin soap the pan is allowed to settle out. This is fairly rapid requiring only about 5 hours. As the process of graining represents driving an equilibrium to completion in one direction, i.e., the salting out of the soap, the addition of a new component, sodium resinate, may affect this equilibrium and cause the partial closing of the previously grained charge. In such a case additional salt is added to restore complete graining. The spent lye goes to the glycerine department.

The charge is now subjected to the strong changes. It is closed with water and then grained with caustic soda solution of 1.300 specific gravity. The function of this operation is to remove salt which is more harmful in subsequent operations than caustic soda and to wash the soap clean of impurities. After overnight settling the half-spent lye is drawn off. It is generally dark in color and should be used only to saponify dark colored charges (for laundry soap) as its use for saponifying fats intended for light colored toilet soaps is likely to cause darkening of the final product.

For the second strong change closing should be carried out with a minimum of water and the graining with the least possible quantity of caustic soda which will accomplish the desired result. After overnight settling the half-spent lye is drawn off to storage. If the operations have been carried out so far with care and precision the pan will be low in salt and other impurities, will contain the lowest practicable amount of half spent lye mechanically (or chemically) held in the soap and will be entirely free from unsaponified fat. It is now ready for the fit.

The fit is the most important operation in the boiling of pure toilet soaps. The desideratum is the maximum yield of pure soap. The pan is first closed by the smallest possible amount of water. The less sodium salts in solution (salt and caustic soda) the smaller the amount of water necessary. This is vitally important to a degree not required in the other changes as will be seen. Then it is grained with caustic soda in the minimum possible amount. The fitted soap separates into two layers, a bottom layer containing all the impurities (the nigre) and a top of pure soap. So far as the fit is concerned, the nigre, which is rich in soap, is a waste product. It may be reworked for toilet soap, but should be used for darker charges if possible. A fitted soap after complete settling should contain 61-63 per cent fatty acids and up to 0.2 per cent caustic soda.

After fitting comes the cleanse or removal of pure soap. Four days at least should be allowed for complete settling of the charge and separation of the nigre, a longer time if possible. The maximum time permissible is determined by the rate of cooling (the final temperature should not drop below 150° F.) ; the larger pans used in modern practise permit longer and more efficient settling. The top of the fitted and settled soap is covered with a thin, hard spongy layer of "fob" which is removed by a long handled spade, leaving a clean surface of neat soap. The still hot soap is drawn off by the skimmer pipe to a feed tank, crutcher or frame.

In the manufacture of household soaps, which is similar to the above, the charge may be bleached somewhat in the fitting by the addition of a pound of zinc dust per ton of soap, but the stock used for a good toilet soap should render this unnecessary.

The yield of pure soap (as compared to total soap in the fitted charge) may be 60-85 per cent depending on the previous separation of half spent lye and the time available for the final settling. The remaining 15-40 per cent of soap in the nigre is recovered by reworking in one way or another.

The crutcher is a steam jacketed kettle with a stirrer. In this the slight excess of alkali in the soap is neutralized by the addition of cocoanut oil, clean fatty acids or sodium bicarbonate. Perfume and coloring matters are added at this stage to soaps which are not to be milled. They are always added in solution to ensure homogeneous mixture. In the older practise the soap was run from the crutcher into frames where cooling took place very slowly. Modern practise cannot permit this time-consuming and space-consuming method and has replaced it by the water cooled press type of frame. This saves time, space and labor, produces less scrap and for most purposes actually a better product. The blocks of soap from the press are cut into slabs, bars, and finally stamped into cakes. Many so-called toilet soaps receive practically this kind of processing including a surface drying, but the true toilet soap is the milled product.

A household soap should be slightly translucent and the rapid cooling tends to create just this translucency. The fact long known to soap makers has received theoretical consideration and investigation at the hands of McBain and his co-workers who have shown a physical difference to exist between the structures of rapidly cooled and slowly cooled soaps. Toilet soaps should be as opaque as possible. Slow cooling produces opacity but it is in general not permissible. The old frame cooling method yielded the best type of opaque soap.

In practically every case modern soap works cool their toilet soap for milling by running the warm soap over a series of rotating water cooled cylinders from the last of which the soap is scraped as a solid ribbon which drops on to a belt conveyor leading to the dryer. In some cases bars obtained by water cooled press processes are chipped. The product in both cases is pure soap free from fat, free fatty acids, salt and all except a few thousandths of a per cent of caustic soda.

Toilet soaps must be hard so as not to use up too quickly and this is accomplished by reducing the water content in the dryer. The best drying temperature is about 100° F., but higher temperatures are sometimes used. The final dried product should contain 80-81 per cent of fatty acids. A good toilet soap must be hard, opaque yet lustrous, uniform in texture, entirely free from material injurious to the skin. Its color (if any) should be resistant to light, its perfume should be stable and unaffected by standing. The dried flakes or chips are subjected to certain mechanical operations which will be considered later, but certain considerations may be taken up now.

The titer value of the fatty acids of the stock should not be too high; 38-40° is best, it should never exceed 40° nor drop below 37°. If the titer value is below 37° it may be necessary to dry to 82-83 per cent fatty acids to get the requisite firmness. In the case of soap flakes for sale as such the titer value is preferably a little higher, namely, 42°.

Tallow is the principal constituent of milled soaps but since the titer value is 40-46°, low titer value oils must be used in conjunction with it. For colored soaps palm oil is satisfactory, but it gives at least a creamy color to the product.

For white soaps the best white stock must be used. This includes 50-70 per cent of finest white tallow, varying amounts of cocoanut oil, lard, palm kernel oil, etc. A few per cent of castor oil tends to improve the finish of the cake. Colored toilet soaps may be made from almost any stock of the proper titer value with a color not darker than buff; no hypochlorite bleached oil must be used as this affects the dyes added and may give a chlorine odor on lathering. Half spent lyes are never used for high grade soaps as they tend to return some of the colored impurities the removal of which is one of the principal objects of the very elaborate changes of the soap boiling process. And even for colored soaps half spent lyes tend to prevent uniformity of color.

Tallow soap gives a slow but lasting lather, cocoanut oil soap a quick but very temporary lather; the mixture is ideal. Small quantities of resin tend to fix the perfume.

To return to our soap flakes or chips. As they emerge from the dryer they are chilled by a current of cold air as they must be cold when entering the mill and cooling does not easily occur in the storage bin.

The object of milling is to crush the chips into a more or less plastic, homogeneous condition while completing the incorporation of the perfume and coloring materials. The color and perfume are added as concentrated solutions in the mixer which acts as feeder to the milling machine. Some toilet soaps are superfatted at this point. Fats may not under any circumstances be added; the superfatting is accomplished by adding 1-5 per cent of lanolin or soft petroleum jelly (melted!) during the mixing preliminary to milling. They tend to give a lustrous finish and to impart a velvety softness in use. Sometimes zinc oxide is added to the soap in the crutcher to help increase the opacity of the final product but excessive amounts tend to impart a putty-like appearance.

The mill consists of steel or granite rollers revolving at different speeds. The flakes are crushed, kneaded together again and finally emerge as homogeneous ribbons. Heating up in the mill must be prevented as rise in temperature causes loss of perfume and a diminution of opacity.

The milled soap must now be converted to cake form. This is accomplished by means of a plodding machine which is essentially an Archimedes screw squeezer so arranged as to exert great pressures. The soap is extruded as a hard continuous bar which is automatically cut into correct lengths for stamping into cake form by a suitable machine.

The compression cylinder of the plodder is water cooled to remove the heat generated which would tend to make the soap less opaque. The extrusion orifice or nozzle is gas heated so as to polish the bar which emerges.

Thus we have converted the fat into commercial soap. Numerous chemical and physical problems have not been touched on as space forbids. There is the working up of the glycerine, the production of caustic solutions, the preliminary treatment of low grade or rancid fats, the use of fillers, the addition of medicaments, the use of suitable colors and perfumes, the control methods employed throughout the soap-making process, the analysis of soap and finally that most interesting branch of chemistry, the theory of soap action.

We have considered the conversion of fat into soap, the separation of the soap from its accompanying impurities and the obtaining of a high yield whilst producing and retaining the particular kind of physical characteristics deemed desirable. The whole process is thus broadly analogous to what the chemist is always attempting to achieve in the laboratory: a high yield of pure product from a raw material available at a low price.