Soaps from Fatty Acids

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ONE of the present trends in soap making is the increasing use of fatty acids in place of the fats and oils formerly used. While it is only in recent years that appreciable amounts of fatty acids have been consumed by the soap industry, the idea of soap from fatty acids is not new. In 1825 a French patent on separating fatty acids recommended using the solid acids for manufacturing candles and the liquid acids in soap making (1). For many years after this the only fatty acid used for soap was this crude oleic acid by-product of stearic acid manufacture. Then a process was developed for recovering fatty acids from certain wash water obtained in textile mills. This material was known as "fullers' fat." By about 1900 the Twitchell, Autoclave, and Enzyme splitting processes were in use, and fatty acids were relatively plentiful with a consequent increase in their use in the soap industry. However even these acids were relatively low in quality, and only recent developments in fat splitting and distillation processes have given the high quality fatty acids now used in soap making.

These new techniques for the production and purification of fatty acids are one of the chief reasons for their expanded use in the soap industry. Additional impetus was provided by government restrictions and raw material shortages during World War II (2). One government regulation curtailed the use of fats and oils in soap processes from which glycerine was not recovered. Since glycerine cannot be recovered from potash soaps made by the saponification of fats and oils, this regulation could be complied with only by the use of fatty acids. A wartime shortage of olive oil foots brought about the use of red oil as a replacement in making textile soaps. Another war measure was the use of acidulated foots from alkali refining, necessitated by the need to conserve edible oils. While fatty acids in all of these cases were being used as substitute raw materials, many soap manufacturers found advantages in them which led to their continued use even when oils were once again available.

Advantages and Disadvantages of Fatty Acids

Some of the advantages of using fatty acids in soap manufacturing are given as follows (3).

Because the reaction between fatty acid and alkali to form soap is a simple neutralization, it takes place immediately on contacting the reactants. Complete neutralization is achieved without the long boiling time or the large excess of alkali needed to completely saponify an oil. This, in itself, gives an appreciable saving in operating time and steam usage. In addition, the lack of glycerine in fatty acid soaps makes unnecessary brine washing for the recovery of glycerine as is required with soaps made from oils. Also, the alkali content of the final product made from fatty acids can be controlled by a simple titration of the soap and addition of the small amount of alkali or fatty acid required for the adjustment.

The rapid, complete reaction between fatty acid and alkali to form soap allows the use of simpler equipment than is required for the saponification of oils. In place of the large kettles normally used for soap making fatty acids can be neutralized in relatively small crutchers. Crutcher neutralization also allows incorporation of other ingredients as part of the same operation. The neutralization can even be carried out continuously, with a large production volume possible from a unit occupying very little factory space.

Preparation of soap from fatty acids permits considerably more variation in moisture content of the soap than can be obtained by kettle saponification of fats. In conventional kettle boiling the final neat soap obtained after settling and separating the nigre layer has a moisture content which must be maintained at a fairly set value if the excess salt and alkali are to drop out in the nigre as desired. The moisture content is usually in the range of 30% water in the neat soap. When neutralizing fatty acids in a crutcher, the moisture content can be higher or lower than this value. The actual moisture required is fixed only by the need to maintain the soap in a physical state which will allow it to be handled satisfactorily.

The use of fatty acids often allows upgrading of stocks with a consequent saving in money. Thus a low grade fat stock unsuitable for use in a given product can be split and the resulting acids distilled to give considerable improvement in color and odor. It will often be found that the split and distilled acids will be cheaper than the high grade fat stocks they replace despite the additional processing costs. An example of this is the use of acidulated foots from alkali refining. Splitting and distillation also make possible more uniform raw materials for soap making than are obtained by the usual refining and bleaching of fat stocks, and the soaps made from them are accordingly more uniform.

An additional cost advantage in using fatty acids for soap production is that sodium carbonate can be used for the reaction in place of the more expensive sodium hydroxide. This is possible because the fatty acids will react with a fairly weak alkali while glycerides require strong alkali for saponification. In the case of potash soaps the carbonate is more expensive than the hydroxide, and this advantage is not realized.

A final benefit gained in using fatty acids, and one of the most important, is that it permits the precise selection of both the fatty acid and the alkali to give desired properties in the product. Lauric, myristic, palmitic, stearic, and oleic acids, which are the major constituents of the fats and oils commonly used in soap making, are sold commercially in purities of 90% or better. Also singly and doubly distilled acids from individual fats and oils such as coconut, cottonseed, soybean, tallow, etc., are available. Since soaps of the different fatty acids have different solubility, foaming, and detergency properties, it is possible by blending acids to obtain a product which gives best performance for a given use. Likewise, in using fatty acids, the alkali can be varied in a manner not possible in saponifying fats and oils. Sodium, potassium, and amine soaps free of glycerine can be prepared, each type having its own distinctive properties. Mixed alkalies can also be used. It can be seen from the foregoing that fatty acids, far from being a substitute raw material, are necessary for making many soaps which cannot be made directly from oils.

While there are many advantages to using fatty acids rather than oils, some disadvantages should also be noted. The storage and handling of fatty acids require some precautions which are not necessary with oils. Fatty acids cannot be handled in carbon steel equipment because of their somewhat corrosive nature, and stainless steel or aluminum is generally used. Prolonged contact with carbon steel will lead to color darkening as a result of iron pick-up. Fatty acids are more easily oxidized than oils, and when stored in contact with air at temperatures high enough to melt them, they will again tend to darken in color. Distilled fatty acids generally cost more than their corresponding oils although there are many exceptions to this, usually acids made from the refining foots of edible oils. All three of these objections are based on economic considerations since the first two involve increased equipment costs. If the increased cost can be carried by the product, fatty acids would appear to be the raw material to use in soapmaking. This assumes, of course, a new installation with no existing fat and oil saponification equipment.

Choice of Raw Materials

As previously mentioned, an important point in using fatty acids is that both the anion and cation of the soap can be specially selected to give the properties desired. For choosing the raw materials the following information can be used. In varying cations, sodium soaps are found to be generally hard, easily salted out of solution, and with relatively low solubility compared to potassium soaps. The potash soaps are generally soft, cannot be salted out, and foam slightly better than sodium soaps. They are especially suited for use as liquid soaps and shampoos. Ethanolamine soaps have better oil and water solubility than either sodium or potassium soaps but have somewhat poorer detergency. They are mild, having a pH of only 7.5-8, and are used in shaving creams and cosmetics.

Soap properties also vary widely with the fatty acid chosen. The acids generally used in soapmaking range from C_{12} to C_{18}. Below C_{12} the high water solubility leads to poor surface activity, and above C_{18} the solubility is too low for practical use. The following table gives an indication of the relative solubilities of various sodium and potassium soaps (4).

Relative Solubilities of Sodium and Potassium Soaps

	Temp. for 5% Soln.	Temp. for 10% Soln.	Temp. for 20% Soln.
	°C.	°C.	°C.
Sodium Oleate (C_{18} unsat.).	23	24	26
Sodium Laurate (C_{12}).........	31	37	41
Sodium Myristate (C_{14}).......	48	52	57
Sodium Palmitate (C_{16}).......	60	64	69
Sodium Stearate (C_{18}).........	72	74	77
Potassium Myristate (C_{14})...	7	8	9
Potassium Palmitate C_{16}).....	29	30	31
Potassium Stearate (C_{18}).....	48	49	49

It can be seen that as the fatty acid molecular weight increases it is necessary to increase the temperature to get good solubility. Thus for low temperature solubility potash soaps of oleic, lauric, or myristic acids and the soda soap of oleic acid would give best results. The foam has been found to increase to a maximum at C_{14} and then decrease as the molecular weight increases. The oleates however give foam similar to the laurates or myristates. The palmitates and stearates give foam somewhat inferior initially but with greater stability than that given by the laurates, myristates, and oleates. The C_{16} and C_{18} acids, including the unsaturated, give better detergency than the shorter chain acids (5).

For shampoos coconut fatty acids, which contain mostly lauric and myristic acid, give the rapid and profuse lather desired. For toilet soaps the sodium soap of a blend of coconut and tallow acids gives a firm, attractive bar. This combination, containing all five of the individual fatty acids discussed, gives good foam and detergency in a fairly wide temperature range. The lower molecular weight fatty acids present in small amounts in coconut oil are believed to cause skin irritations, and these light ends are often removed from the coconut acids by fractional distillation before using in toilet soap. Liquid soaps are made from potassium hydroxide and the various vegetable oil fatty acids high in oleic and linoleic acids. These include cottonseed, soybean, corn, and peanut fatty acids. These materials give highly water-soluble soaps which can be used as concentrated solutions. Since linoleic acid, because of its high unsaturation, is somewhat unstable, a high grade liquid soap will use only the oleic acid as its raw material.

For commercial laundry and textile operations sodium soaps are generally used even when low temperature solubility is desired. The fatty acids chosen depend on the temperature of the operation in which the soap is to be used. For cottons and linens where high temperature treatment is permissible, tallow fatty acids (stearic, palmitic, and oleic) give a soap with good high temperature solubility and detergency. For silks, woolens, and synthetics where low temperatures are used, a red oil soap gives the desired low temperature solubility and detergency. For operation at intermediate temperatures mixtures of tallow acids and vegetable oil fatty acids high in oleic give the desired properties.

Shaving soaps and creams use potash soaps of stearic acid to obtain good solubility along with stable foam. Some coconut oil may also be used to help the lathering ability.

While many of the soaps just described can be made only from fatty acids, some can be made from either oils or fatty acids. However working with fatty acids allows the soap manufacturer to use a few basic raw materials as blending stocks for a wide variety of soaps having different properties. This is of great value to the small manufacturer of industrial soaps.

Soap Making Procedures

Processes for making soap from fatty acids vary from the regular kettle boiling technique used with fats and oils to the newer methods for continuous neutralization.

In the kettle boiling procedure the equipment and operation are essentially the same as in the saponification of oils. For sodium soaps the fatty acid is "killed," using a lye containing salt and excess alkali and, because there is no glycerine present to be removed by washing, the soap can then be taken directly through the "half-finish" and "finish" steps. Once the half-finish stage is reached, the soap is handled in the same way as in a normal saponification, with the product being a settled neat soap from which a nigre has separated. During the killing step some boiling lye should be present in the kettle initially, and the fatty acid and remaining lye are then run in together keeping on the alkaline side at all times. The purpose of this method of addition is to avoid the formation of lumps of soap containing unneutralized fatty acid at their centers since these lumps are very difficult to eliminate once formed. Either sodium hydroxide solution or a concentrated sodium carbonate solution can be used in this method, but if carbonate is used, the rate of addition of fatty acid during the neutralization must be regulated to avoid boiling over the kettle because of carbon dioxide evolution. After the neutralization with carbonate is complete, boiling with open steam must be continued until the carbon dioxide has been removed.

Liquid soaps can also be made in a kettle, using an open steam coil for agitation and closed steam for any additional heat required. Potassium hydroxide is used as the alkali, and no salt is used in the lye since potash soaps cannot be grained. No nigre is separated from a finished liquid soap, and the final product contains everything charged to the kettle. Accordingly, only enough caustic is used to give a slight excess of alkali in the finished soap, and enough water is added either in the caustic or separately to give approximately the desired soap concentration. For a liquid soap using a 50:50 or 75:25 coconut acid to red oil charge stock, a solution containing approximately 35% soap is common. As with sodium soaps, a portion of the lye is charged to the kettle initially, and the rest is added with the fatty acid. Since there is little chance of lump formation in making liquid soaps, no harm is done if the batch is on the free fatty acid side during the introduction of the raw materials. After everything is charged, agitation with open steam is continued until the neutralization is complete. The batch is then checked and adjusted with fatty acid or alkali to the desired final free alkali content. This normally runs approximately 0.05% free alkali as KOH for liquid hand soaps and somewhat higher for scrub soaps. A final adjustment of soap concentration may be made at this time by adding water. The batch is then pumped away for final finishing which may include addition of perfume, color, and stabilizers, and clarification by filtration.

It is not uncommon in making liquid soaps to use coconut oil rather than coconut fatty acids along with the red oil. The procedure is essentially the same as given previously, except that the coconut oil is completely saponified first with a large excess of potassium hydroxide. The red oil and additional KOH are then added and the batch completed as before. This soap, of course, will contain some glycerine from the coconut oil.

Both sodium and potassium soaps can be made in crutchers as well as kettles. For the potash soap the equipment need be only a tank provided with either a jacket or coil and a slow speed mixer. Mechanical agitation replaces the open steam used in the kettle procedure, and any heat required to start the reaction is provided by closed steam. At the completion of the neutralization the batch can be refrigerated by running brine through the jacket or coil and then clarified by filtration.

With sodium soaps a heavy duty crutcher must be employed for neutralizing fatty acids. Many techniques and many types of equipment have been used successfully to make soap in this manner. Either sodium hydroxide or sodium carbonate can be used for the neutralization, but the former is generally preferred because of the shorter batch time possible with no need to eliminate carbon dioxide from the soap. The sodium hydroxide solution is made up to a concentration which will give the desired moisture content in the soap, allowing for the water formed in the neutralization. Thus, the charge for a typical toilet soap using 80% tallow fatty acid and 20% coconut fatty acid would be:

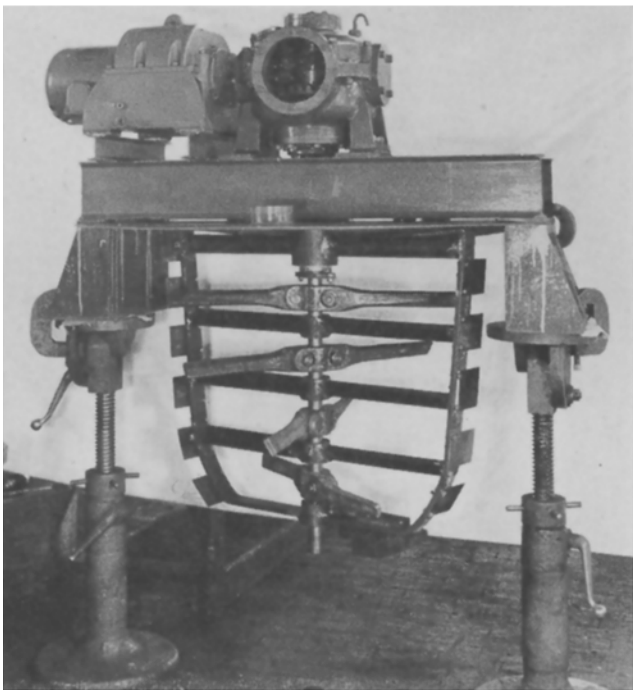
Tallow Fatty Acid	51.6%
Coconut Fatty Acid	12.9%
28.7% NaOH Solution	35.5%

This formula gives a soap with 30% moisture and 0.1% free alkali as Na_2O, approximating neat soap in composition except for a lack of salt. Salt can be added as part of the lye if it is desired. The soap produced by this method is treated in the same way as neat soap as far as the finishing operations are concerned.

The actual neutralization operation consists simply of charging the fatty acid and caustic soda solution to the crutcher and mixing until uniform. A sample of the soap is then checked for free alkali and an adjustment made with caustic or fatty acid as needed. The order of addition of the raw materials varies. It is desirable to charge the caustic solution to the crutcher first, warm it, and then add the fatty acid while mixing. This minimizes the possibility of forming lumps of soap containing fatty acid. However when this procedure is followed, the soap formed at the beginning of the fatty acid addition is "grained" by the large excess of alkali, and a very stiff mixture, difficult to agitate, is formed. If sufficient power is available in the crutcher this, of course, is no problem. With an efficient crutcher it is possible to charge all of the caustic and fatty acid with no agitation and then turn on the mixer to get rapid neutralization with a minimum of lump formation. In this case precautions must be taken to avoid boil-overs because of the heat of neutralization. If fatty acid at 140°F. and caustic at 80°F. are used, there should be no excessive vaporization of water. When operating facilities allow it, the best addition procedure to follow is that used in the kettle neutralization: charge some of the caustic initially, and then slowly add the remaining caustic and fatty acid together with the mixer on. The batch can then be kept on the free alkali side without enough excess caustic present to grain the soap.

For best results the crutcher used in preparing sodium soaps from fatty acids should have a heavy duty agitator which scrapes the sides of the vessel and gives maximum shear with minimum introduction of air. It should also have a jacket provided with steam and water connections. The scraping action is needed to prevent any of the reactants from collecting on the vessel walls where they cannot be drawn into the reaction mass. It also improves the heat transfer to or from the soap. Shearing action is desirable for obtaining rapid breakup of fatty acid lumps which may form during the neutralization. Aeration is to be avoided because it leads to increased batch volume with possible overflow from the vessel, and it increases the viscosity of the soap with resultant lower mixing efficiency. The presence of air in the soap may also cause difficulty in the subsequent processing. The jacket is used to provide heat at the start of the neutralization and may also be used for cooling, if required.

An example of a crutcher which fits these requirements is a jacketed Dopp crutcher with a double-motion, positive-scraping agitator (6), shown in Figure 1. This agitator has two sets of horizontal paddles



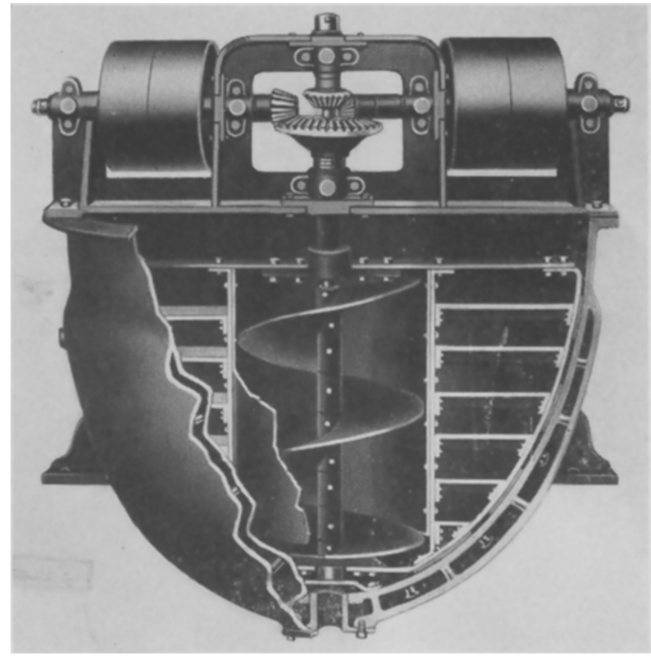
Courtesy of Buflovak Equipment Division of Blaw-Knox Co.

FIG. 1. Dopp Mixer Style "D"

which revolve in opposite directions. The extremities of one set of blades are joined to form a sweep running close to the walls of the vessel and provided with blades which scrape the walls. The sweep is driven from its top by a short, hollow, vertical shaft extending down through the uppermost cross member. Within the hollow shaft is a solid vertical shaft carrying the second set of paddles. One set of paddles gives a lifting action, and the other forces the material down. The net effect is a shearing action which is very effective in making a uniform product. The sweep with scrapers is driven at about 15 rpm and the inner paddles at 25-30 rpm.

A less complex piece of equipment which has given satisfactory results in neutralizing fatty acids is a horizontal paddle crutcher. This consists of a horizontal cylindrical vessel with a shaft containing vertical paddles running through it. In operation these paddles intermesh with stationary baffles set in the vessel to give considerable shearing of the material being mixed. The moving paddles extend close to the crutcher walls, giving some of the desired scraping action. This type crutcher should be run full to avoid aeration of the soap during the mixing.

The classic soap crutcher, consisting of a jacketed vessel containing a helix or screw agitator in a draft tube, does not always give satisfactory results in soap making by fatty acid neutralization. It provides neither the scraping nor the shearing action that are needed and does not give efficient removal of lumps.



Courtesy of Buflovak Equipment Division of Blaw-Knox Co.

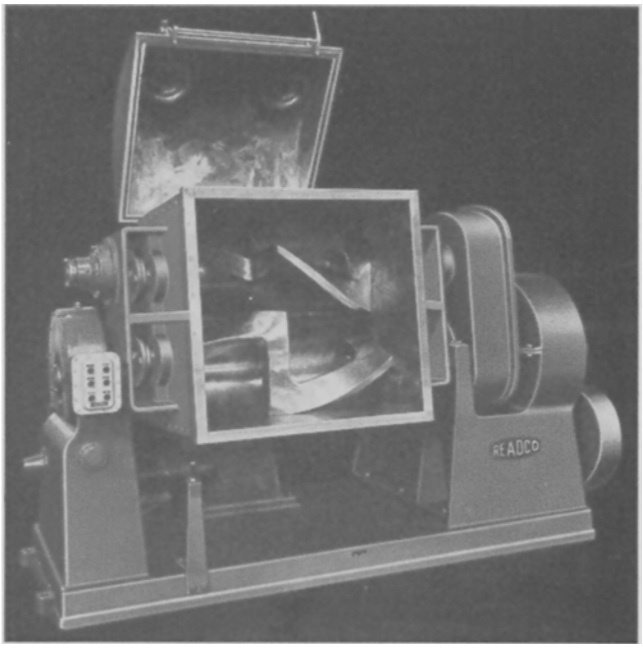
FIG. 2. Dopp Mixer Style A-D

Also, if a heavy, grained soap is present in the crutcher, the screw cannot circulate it and revolves in the soap mass without causing any mixing. If the helix is used as the inner mixer of a double-motion agitator, with the outer mixer containing horizontal paddles and a positive-scraping sweep, as shown in Figure 2, better results can be obtained. This still does not give as much shearing as the first type crutcher discussed.

A final piece of equipment which can be used for soapmaking is the kneader or dough-mixer shown in Figure 3. This is a horizontal vessel containing two heavy blades rotating at slow speed in opposite directions. The blades are so shaped that they intermesh and give a shearing action. The clearances between the blades and the sides and walls of the vessel are small, resulting in no dead spots in the mixer. The shearing action in this type unit is not as efficient as in the Dopp or the paddle crutcher, and there is considerable aeration during the mixing operation. However, for soft soaps such as shave creams, where no hard lumps form, the kneader gives satisfactory operation.

The ultimate in soap-making from fatty acids is the continuous process. This consists basically of a system for metering the fatty acid and caustic streams in the proper ratio into a contactor which thoroughly mixes them to form soap. As in batch crutching, the caustic concentration is adjusted to give the moisture content desired in the finished soap, and the caustic to fatty acid ratio is set to give a small amount of free alkali in the product. A process such as this would be used where production of large quantities of one or two products is to be carried out. Frequent formula changes are undesirable because they cause the production of a large amount of off-grade transition material. Small scale operation is impractical because of the high overhead cost of such an installation.

The major problem in continuous neutralization is maintaining the proper caustic to fatty acid ratio.



Courtesy of Read Machinery Co. Inc., York, Pa.

FIG. 3. "Readco" Tilting Bowl-Double Arm Mixer

To make a soap in which the free alkali content varies by ± 0.04% as Na_2O it is necessary to hold the caustic to fatty ratio within ± 0.5% of the set point. This can be done in several ways. One successful process uses piston type proportioning pumps for feeding the reactants (7). The pumps have the same drive with a variable speed adjustment between them for minor ratio adjustments. The two streams pass through a high speed mixer, and the soap leaving is run into a blend tank with a one-hour holdup. In this tank the soap is mixed and then withdrawn for further processing. The mixing assures a uniform product despite any small variations in pump rates or caustic concentration. The effluent from the neutralizer is checked for free alkali at intervals and any necessary ratio adjustments made.

Another process (8) in use regulates the flow of the caustic and fatty acid by means of flow control valves, as shown in Figure 4. Both streams pass through flow meters which transmit impulses to the ratio controller. With the caustic flow regulated manually, the ratio controller adjusts the fatty acid flow to give the desired ratio. The Askania orifice meter system or the Fisher and Porter Flowrator metering system are satisfactory for use as the ratio controller. In the case of both this flow control system and the positive displacement metering system it is necessary to maintain the caustic and fatty acid at constant temperatures for accurate control, since a weight ratio is being controlled by volumetric means. The streams of reactants leaving the ratio controller pass through a high speed mixer and then go directly to storage with no blending necessary. Again the soap is checked periodically for free alkali content. With a unit such as this it is possible to make as much as 10,000 lbs./hr. of soap with control on the free alkali of ± 0.04% as Na_2O and no unreacted free fatty acid.

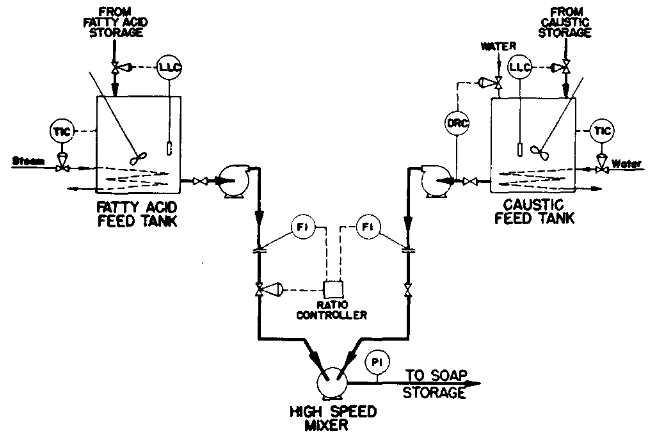


FIG. 4. Flow Diagram for Continuous Neutralization of Fatty Acids

Conclusions

It can be seen from the foregoing discussion that fatty acids are an important factor in the present production of high quality soaps. The wide variation possible in properties of soaps made from them and their rapid and complete reaction with alkali give them advantages over fats and oils in many applications. With improvements in fatty acid processing still being made, it is to be expected that the use of fatty acids in soapmaking will continue to expand in the years to come.

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