

# LECTURES OF THE 1963 SHORT COURSE ON ADVANCES IN SOAPS AND DETERGENTS

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## A Review of Several Available Continuous Saponification Processes

A. L. SCHULERUD, Colgate-Palmolive Co., New Brunswick, New Jersey

IN THIS DAY of synthetic detergents people are inclined to feel that soap is a thing of the past, but in toilet soap alone over 500,000,000 lb a year are sold. While this is small compared to the heavy duty laundry detergent business, it can still bring a tidy profit to those companies who keep up with the improvements and economies that can be deduced from today's advancing technology. Because many of our present day professionals have had little contact with basic art or science of soap making, this article will begin with some fundamental definitions and descriptions of the kettle soap making process.

Figure 1 represents the various steps in a counter-current kettle process. Soap making fats and oils are usually triglycerides of fatty acids ranging from C-12 to C-18 with some free fatty acids in them unless these have been removed by alkali refining. When these fats are heated and mixed with a solution of sodium hydroxide, the fats are split to form glycerine and fatty acids. The acids then combine with the sodium hydroxide to form the sodium salt or soap. For mechanical reasons the solution of NaOH also has some sodium chloride in it to keep the mixture more

fluid by salting out the less soluble sodium soaps. When agitation is stopped, this mixture of soap, sodium hydroxide, sodium chloride, glycerine and water will, if the concentrations are right, separate into two layers. The top layer contains most of the soap and is called "curd soap" if the low layer contains enough electrolyte so that very little soap is dissolved in it. Such a lower layer is called a "lye." The act of hydrolyzing a fat and neutralizing the fatty acids formed is called "saponification" or "killing." In actual kettle practice this may be done in two steps taking off a neutralizing lye or "change" when the fat is about 95% saponified by allowing the kettle to sit quietly for several hours thus separating a lye rich in glycerine and sodium chloride and almost free of sodium hydroxide. This is called a glycerine lye. The second or "killing change" completes the saponification of the fat and establishes the proportion of salt and alkali to soap to give the kind of "fit" or "finish" desired.

Because glycerine used to be a valuable by-product of soap making, it is standard practice to boil the curd soap with a lye consisting of water, sodium

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SCHEMATIC DIAGRAM OF COUNTER CURRENT SOAP-LYE SYSTEM

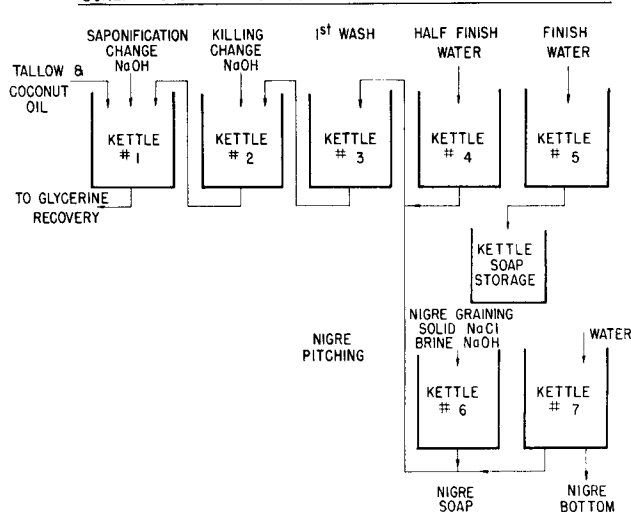


FIG. 1

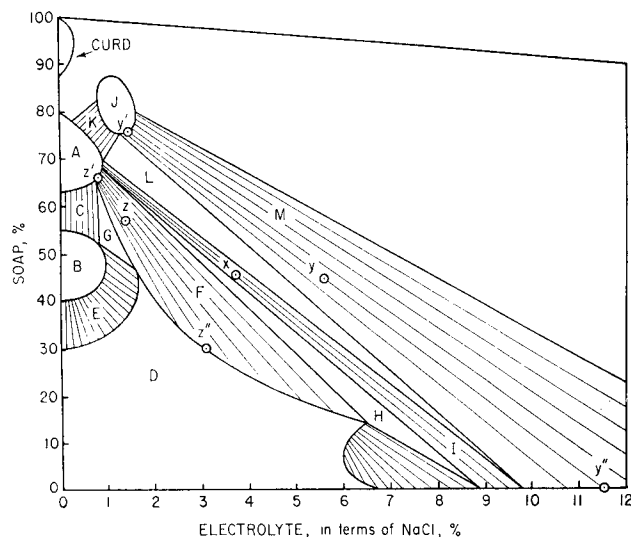


FIG. 2

chloride and sodium hydroxide (12–18° Bé with 3.5 to 6%  $\text{Na}_2\text{O}$ ) and little or no glycerine so that the lye will wash out entrapped glycerine from the curd and concentrate it in the wash lye. Countercurrent contacting of the soap from more recent saponification batches with lyes from preceding batches reduces glycerine in the soap to desired levels while concentrating the glycerine in the wash lyes. One wash change has been indicated in Figure 1 for simplification. Actual practice may have as many as three or four “washes” with or without increasing the NaOH content as the “killing” change is approached. Actually, with today’s glycerine market the killing lye should probably be taken off at “half finish” concentration (about 10° Bé with 1.7 to 1.9%  $\text{Na}_2\text{O}$ ) so that the time and labor of putting on the washes could be saved. If the kettle is thoroughly boiled on the neutralization and killing change and during the fitting operation, a neat or kettle soap should be obtained with less than 1% glycerine in it. The fitting or finishing of a kettle is accomplished by adding water to the agitating mass to reduce the electrolyte concentration until the soap curd or grain softens to an almost homogeneous condition that a skilled soap boiler recognizes by the way the soap “sheets” off a trowel or other flat smooth piece of metal that has been warmed and coated with the soap mass. When the kettle has been properly “finished” and allowed to settle for a sufficient time, it will have separated into two or possible three layers. The top layer is “Soap Boilers Neat Soap” or more commonly “kettle soap.” The lower layer or middle one, if there are three layers, is called the “Niger” and the bottom layer the “Niger Lye.” In general, fitting conditions are usually used that avoid the formation of niger lye. After sufficient time has elapsed so that no further appreciable separation will occur, the kettle soap containing about two thirds of the soap formed from the original oils used is pumped to storage for further processing into various finished products. The crust of frozen kettle soap, plus the true niger, is then boiled with the addition of strong electrolyte in the form of solid salt (new or from glycerine purification), strong salt solution, strong sodium hydroxide solution or a combination of any of them to “grain” the niger by raising the sodium ion concentration in the total boiling mass and creating a condition like we had when a wash was taken off the complete boil as de-

scribed earlier. Settling this mass gives us a grained soap curd as in our washes and a lye which is the beginning of the wash lye that progresses up through the various stages and batches of the countercurrent washing system to finally be removed to glycerine recovery on the neutralizing change. Additional salt, sodium hydroxide or water may be added to it to give the desired ratio of lye to fat charged often referred to as the “bulk of lye” or “lye bulk.” The grained niger soap after the lye has been removed is boiled up with steam and sufficient water added to give it a rough fit when agitation is stopped with a total electrolyte slightly higher than when the complete kettle was fitted as described earlier. This treatment of the niger is known as “pitching” and gives another two layer separation of niger soap and niger bottom upon settling. The top layer is returned to a succeeding boil on the last wash before half finishing. The niger bottom is used in lower grade soaps because it contains a concentrate of aldehydes, ketones, dicarbonyls—degradation products of the fatty materials used—that can adversely affect the color and odor of higher quality soap products such as toilet soaps.

Figure 2 is a partial representation of a McBain modified Phase Diagram for Commercial Sodium Soap (1). This is shown only for purposes of illustration. The critical compositions and phase boundaries shift with changes in composition of the fat stocks used and with temperature. However, by using the diagram without getting too specific, we can visualize what was happening during the various operations involved in practicing the kettle boiling process and also when practicing various continuous saponification processes because they all use minor variations of the standard batch process adapted to continuous operation.

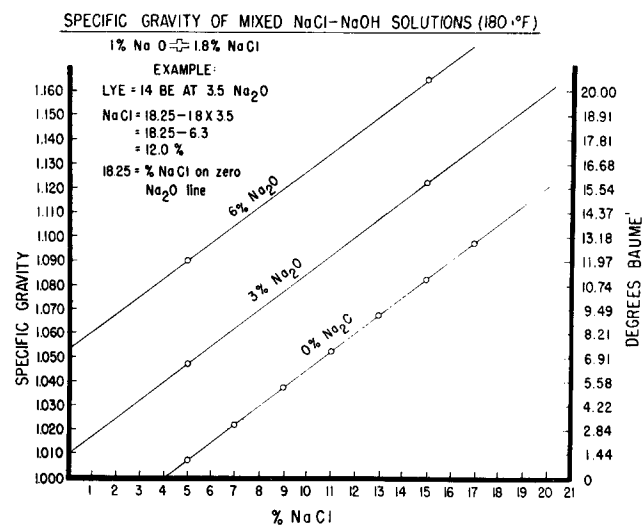
You will note that the weight per cent anhydrous soap is plotted along the vertical axis, and the weight per cent of sodium chloride or electrolyte is shown as the horizontal axis. The weight per cent of water is then 100 minus the sum of the anhydrous soap and electrolyte. You may have noted that I am using the term electrolyte instead of salt or sodium chloride. This is because, as already pointed out, the lyes used in many of the parts of the process are mixtures of sodium chloride and sodium hydroxide. When we wish to identify these mixtures on a Modified McBain Diagram such as in Figure 2, the per cent electrolyte is found by adding the weight per cent of sodium

chloride to 1.3 times the weight per cent of sodium hydroxide expressed as  $\text{Na}_2\text{O}$ . The actual value of the constant I have used as 1.3 is controversial with values presented ranging from about 1.25–1.5. The glycerine present in the system has been shown (2) to behave like water in these systems.

In this diagram there are four one-phase regions: A, B, D, and J representing, respectively, neat (kettle) soap, middle soap, niger (isotropic solution) and kettle wax (curd). There are six two-phase regions, represented by C, E, F, I, K and M. These have a shaded appearance from the tie-lines that have been drawn in them. When operating in these regions, the composition of each phase separating is represented by the ends of the tie-line passing through that particular composition. The amount of each phase present can be estimated by measuring the distance from the total composition point along the tie-line to the ends of that tie-line. For instance, if we have established a composition represented by  $y$ , we will separate kettle wax and lye phases having compositions represented by  $y'$  and  $y''$ , respectively. The fraction of kettle wax will then be equal to  $yy''/y'y''$  and the fraction of lye will be equal to  $yy'/y'y''$ .

In normal soap boiling practice we should avoid compositions represented by B, C, E or G because all of these have the surety of forming more or less middle soap. This middle soap is what is referred to as "waterlogged soap" or a "horsed" kettle in soap boilers' parlance. It is encountered when the electrolyte is largely caustic soda and the proportion of fat present has gotten far enough ahead of the lye portion so that the saponification reaction has used up most of the electrolyte. When a countercurrent wash system is used, this condition seldom occurs because of the fairly high proportion of sodium chloride present at all times. This high sodium chloride plus excess caustic when it is present keeps the saponification charge somewhere in the regions I, L or M, while fats and spent killing lye plus sodium hydroxide are being charged to the kettle and desirably somewhere near the composition represented by  $x$  when charging is complete and agitation is stopped. It will be remembered that the lye that separates from the neutralizing charge is practically free of sodium hydroxide when the charge is properly applied. To assure this, the caustic soda added is controlled so that the fat charge is not completely saponified but contains some 5–10% unreacted fatty material. Boiling is continued in the presence of this excess fat till the soap mass when tasted no longer will "bite" the tongue. This condition occurs at about 0.1% free  $\text{Na}_2\text{O}$ . When boiling a charge containing 20% coconut oil and 80% tallow, the lye separated will have a specific gravity of 10–12 Bé (as shown in Fig. 3).

In practical kettle boiling, the condition of the kettle at any time is checked by separating the lye and titrating it to obtain the  $\text{Na}_2\text{O}$  content (using a phenolphthalein indicator) and its specific gravity determined (hot) using a Baumé hydrometer for liquids heavier than water. Thus, we find the various stages of the process defined by specifying that the lye from that step will have an  $\text{Na}_2\text{O}$  content and Baumé between certain limits. I suppose if I were able to use my Physical Chemistry, I could calculate the per cent NaCl present from these two figures. However, I have found it easier to make the few determinations necessary to draw the graph shown in Figure 3 so that I may check my actual compositions against those anticipated by the McBain diagrams. The graph was



made by preparing known concentrations of sodium chloride and checking the specific gravity at 180F to obtain the several points on the 0%  $\text{Na}_2\text{O}$  line. This procedure was repeated using a constant 3%  $\text{Na}_2\text{O}$  with varying NaCl to get the 3%  $\text{Na}_2\text{O}$  line and with a constant 6%  $\text{Na}_2\text{O}$  to get the third line. With this data, we can easily determine that 1%  $\text{Na}_2\text{O}$  has an effect on specific gravity equal to 1.8% of NaCl. From this figure we can calculate the sodium chloride content of any given lye analysis as in the example in the graph. Of course, in lyes with fairly high glycerine content such as the neutralizing lye we were just discussing, we have a further complication. The glycerine at about 8% in the lye also increases the specific gravity roughly as much as 2% of  $\text{Na}_2\text{O}$ . So the 10–12° Bé with 0%  $\text{Na}_2\text{O}$  would say the neutralizing lye should have about 14.5% NaCl, but correcting for the glycerine content reduces this to 9 to 10% NaCl actually present. Referring to Figure 2 following the tie-line from point  $x$  to the intersection with the horizontal axis, we find that the lye should contain 9.2% NaCl. Also, measuring the length of the tie-line from point  $x$  to the neat soap phase boundary and the length of the tie-line from the intercept with the abscissa to the neat soap phase boundary and dividing the first figure by the second we find that the lye separated will be 34% of the total weight in the batch before separation. Similarly, the neat phase layer will be 66% of the total weight in the batch. The anhydrous soap will be about 66% of that or about 44% of the batch. Reducing this to original fats charged gives about 40 parts fat charged to 34 parts of glycerine lye removed. This shows that the diagram we are using was designed for a system having a lye bulk (ratio of glycerine lye removed to fat charged) of 1:0.84. The kettle practice that is being referred to in this discussion is based on a usual lye bulk of 1:1.

This matter of lye bulk is not particularly critical, as might be deduced from studying the modified McBain diagrams and, as is demonstrated by the practice of using "split washes" in the industry. The practice of split washing seems to have developed from the desire to remove as much glycerine from the soap as possible while carrying the greatest fat charge possible in a given size kettle. From the discussion above, in which we found the lye bulk upon which our diagram was based, it can be seen that the fat charged plus the glycerine lye removed accounts for roughly 75% of the total material in the batch at that point.

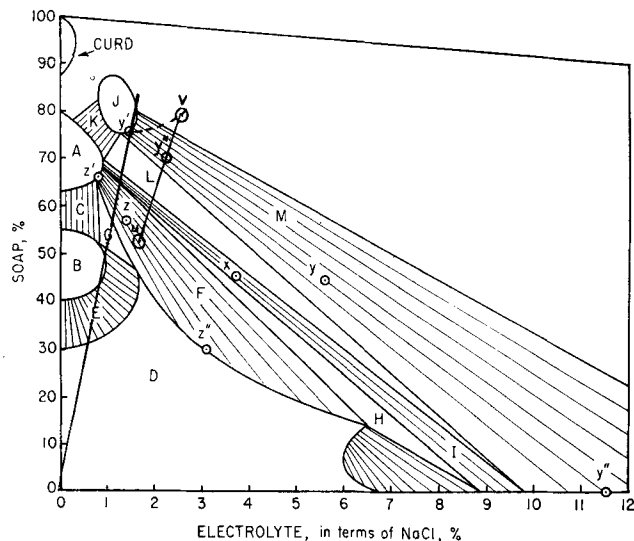


FIG. 4

The other 25% is mostly water that is picked up from the lyes upon which the saponification takes place so the wash lyes (and to a great extent the killing lye) must contain this much more water than the saponification lye. This means that in the changes after the neutralizing change we will have up to 125 lb of material in the batch we are working for every 100 lb handled on the neutralizing change and about 50% of it will be lye. So, if you use the maximum charge you can handle in the kettle you have on your neutralizing change, that kettle will not be large enough to handle a complete wash charge on the subsequent changes unless you use only part of the lye you are bringing up through your countercurrent washing system. It seems logical to assume that this kind of reasoning led to the practice of using only half of the total lye to be processed on any given cycle and calling it the 1st first wash or the 2nd first wash, etc. There are two other good reasons for split washes if you are trying to remove the last trace of glycerine from your soap. First, as every organic chemists knows, if you want to do an efficient extraction with a certain amount of solvent you use it in several small portions rather than one large one. Second, the lye obtained by combining the half finish lye and the niger graining lye has to be increased with fresh brine and caustic to make enough lye for a 1:1 bulk. The half finish and niger graining lyes contain some glycerine so the most effective glycerine removal from the soap would be achieved by using the fresh materials free of glycerine as the 2nd half of the last wash before the half finish change.

As suggested earlier, with today's glycerine prices it would be well for any company producing soap to have a hard look at the need for washes that are made for the purpose of removing glycerine. Labor, inventory and steam savings are possible through the marked reduction in cycle time that can be achieved as well as space saving by retiring unnecessary kettles and lye holding tanks. If you happen to need expanded capacity, this is a way to get increased capacity without added capital investment.

In my effort to more completely define and make understandable the terms and practices found in boiling soap, I have strayed a bit from the modified McBain diagram. We had just settled a glycerine lye that was 34% of the total weight of the neutralizing change. After the kettle has settled for about an

hour, this lye is removed from the system by drawing it from the bottom of the kettle. This leaves a mass of soap in the kettle having a composition of roughly 66% anhydrous soap, 0.9% sodium chloride and 33% water. Up to this point theory and actual practice coincide fairly well, but from here on the art of soap boiling has full rein. Theory says you add salt or brine to the upper layer from the previous change to approach the point y on the diagram. However, in practice we still have unsaponified fat in the upper layer left from the neutralizing change so we must add enough caustic to be sure all the fat is saponified. We also find that using open steam for agitation we must add heat through closed steam coils to keep from getting too much condensation and, if the soap is too closed or low in electrolyte, the steam does not break through the contents of the kettle but causes it to swell instead of boil. Because of these considerations many variations in wash concentrations may be found in industry. When labor is cheap and excess capacity is available, the older method of boiling with little steam at low electrolyte content and taking days to weeks to complete the final delivery of finished kettle soap may be followed. In this method, the soap boiler seldom works to the right of region I on the diagram. Since the 1930's, however, there has been a tendency until recently to work with the kettle tightly grained with high electrolyte content lyes that approach the right hand side of region M until we reach the finish. This allows very rapid boiling and vigorous agitation while promoting fast separation of phases when settling because of the greater difference in density between them.

That is also why a half-finish lye is taken so that the electrolyte in the kettle can be reduced enough to keep from settling a very large proportion of niger. At this point it should be noted that the diagram shown on Figure 2 does not define area J in terms that correlate with actual experience. This may be because separations in practice are not as complete as those used in forming the diagram or the boundaries are not as precisely fixed as shown in Figure 4. In any event, if this diagram were correct, adding water to any composition on the kettle wax boundary to the right of y' would not change the composition or proportion of the neat and niger phases obtained at any point fixed in the F region of the diagram. This is readily seen by drawing a straight line from any point on the boundary of area J from point y' to the junction with the right hand boundary of area M through the origin of the diagram. All points fall very nearly on the same line. Experience would suggest that the kettle wax boundary should follow somewhere near the location of the dotted line that I have superimposed on the diagram with the tie-lines spread out more to the right as in the kettle wax area for sodium stearate shown in Figure 5 (3). If this postulation were accepted, then it is easy to see why adding water from point v to y'' in Figure 4 plus settling and removing a half finish lye would make a noticeably smaller portion of niger than if water were added to reach point u without taking off the half finish lye.

As suggested a few minutes ago, in recent years there has been a trend to a middle ground in electrolyte content of the wash lyes because it has been found that lower electrolyte throughout the boiling process promotes desirable soap bar properties such as firmer texture at higher moisture content, more rapid solubility without increased sloughing tendency, and the production of Beta phase without modification

of milling or plodding equipment or hydrogenation of the fat stocks used to prepare the kettle soap.

The "fit" or finish that produces kettle soap and niger is arrived at by adding water to an upper layer represented by point *y'* or some point slightly to the left of it arrived at by separating a lye containing about 10% electrolyte. This "fitting" operation is quite critical because too "fine a finish" (too much dilution) gives neat and niger phases with such a slight difference in density that the phases will not separate with gravity settling. On the other hand, if too little dilution is made, the neat soap that separates will be undesirably high in electrolytes. If too much water is added, it is possible to back-track by adding a little brine unless you have actually formed middle soap; but this is undesirable because it forms a greater proportion of niger. Of course, as in the De Laval automatic finish it is possible to reach a finish by adding a dilute solution of sodium chloride or mixed chloride and hydroxide. This, too, will give a greater proportion of niger than plain water, but makes the amount used less critical. By exploring the various points along the water addition line in the F region, it can be seen that a "fine" (more water) fit will give about 17% niger while a more "rough" or "coarse" fit may give 8% niger or less. At first glance to anyone acquainted with soap making in kettles, these figures seem very low. A rule-of-thumb in the industry says that one-third of your fat charge will be in the niger and the soap concentration in the niger will be around 30%. The proportions found from the diagram are the equilibrium proportions at a temperature of 180F or higher with a closed system that prevents evaporation of water. In kettles handling 200,000 lb min charges of fat stocks, it is not uncommon to let them settle for 96 hr or more. During this time a great deal of neat soap freezes on the sides of the kettle and as a crust over the top of the mass. This, obviously, is not part of the fluid kettle soap that is finally removed from the kettle, but gets handled as part of the niger. This immediately suggests that a centrifuge should make it possible to recover most of the neat soap formed thus increasing the kettle soap output from each batch and markedly reducing the niger to be re-worked. This has been done in some installations, but there are some complications. If you try to pump the mass from a freshly boiled kettle, you flash steam in the bowl of the centrifuge which prevents good separation of neat and niger. If you let the mass cool some, you have started to drop the niger and so have a non-uniform feed which complicates the operation of maintaining a good separation. You may drop niger fast enough that you will be pumping niger phase only for a while. This has led to the practice of settling the kettle overnight and pumping off the settled niger before centrifuging. You may often find there is very little niger left to separate by centrifugation, but you also achieve the removal of most of the small dirt and scale particles that can give problems in finished products made from the kettle soap.

In the 1958 short course, Mr. Jones of the Sharples Corp. reviewed several continuous saponification processes (4). Of the ones he discussed, the Sharples and the De Laval are still very much available. Both of these processes use centrifuges for making the phase separations after saponification, washing or fitting. These processes require a rather large capital investment because of the number of centrifuges required. Since most of the separations can be made quite

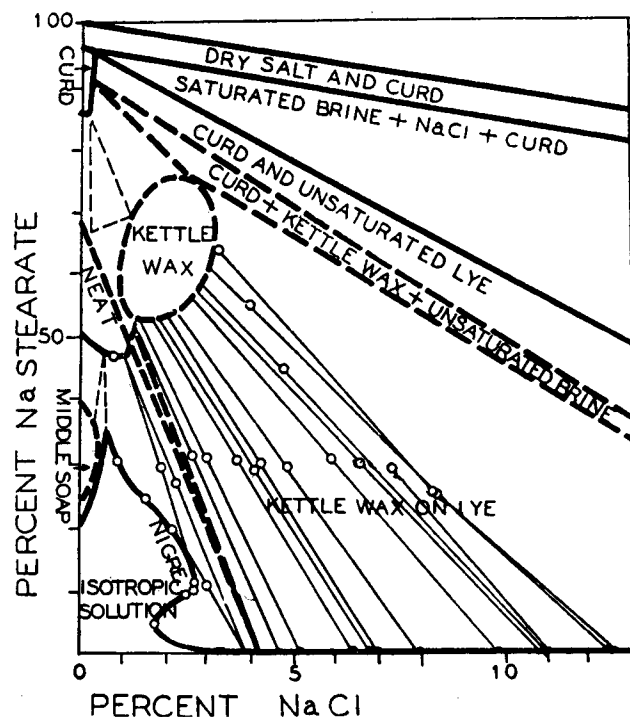


FIG. 5

rapidly by gravity settling, two Italian firms, Meccaniche Moderne and G. Mazzoni—both located in Busto Arsizio—have developed and are selling fairly similar continuous processes using heat exchangers to obtain optimum settling conditions and continuous settlers to make the separations. They both have the same problem as the Mon Savon process described by Jones in that gravity settling to make a continuous separation neat and niger is too slow to coordinate well with the rest of the operations. It would seem that one centrifuge at this point might complete an efficient and economical continuous saponification process.

Let's look at these four processes in a little more detail. Figure 6 shows a De Laval Centripure process consisting of their saponification stage, two counter-current washing stages, and a fitting stage. The saponification stage consists of an internally baffled column with two recycle systems to promote efficient agitation and dispersion of the fresh raw materials, fat and caustic. The fat feed is held at a constant rate while the caustic is varied through the action of a differential pressure meter sensing the pressure difference across the main recycle pump. De Laval has determined that this pressure difference bears a direct relationship to the per cent of electrolyte as it influences the viscosity of the recycle stream. Actually, at the neutral point the viscosity is high. As electrolyte is increased the viscosity decreases to a minimum and then starts to rise rapidly again. They like to operate on the higher electrolyte content just past the point of lowest viscosity. Control is reported to be very good. They use a similar type of control to arrive at their automatic finish. Since washing is less critical of the proportion of washing solution to soap adjustable proportioning pumps give adequate control. As you can see in Figure 6, the wash system is countercurrent with the fresh wash lye contacting the previously washed soap before continuing on to contact the more glycerine rich feed from the saponification stage and then going on to glycerine recovery.

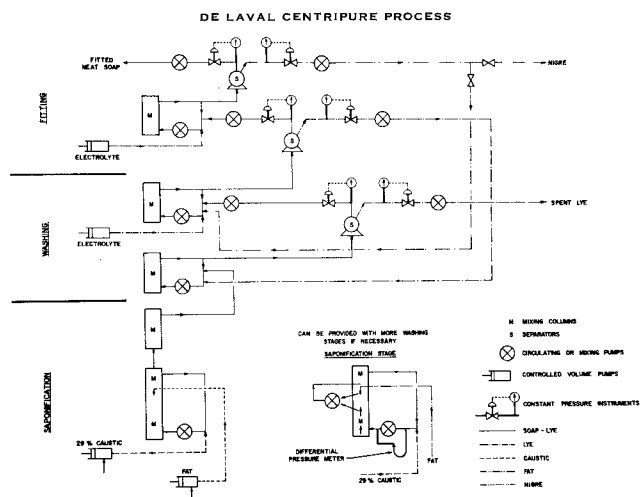


FIG. 6

Figure 7 depicts the Sharples process. Here the Kettle Process that we have already discussed is followed rather exactly. The fresh fat is mixed with the caustic strengthened glycerine rich wash lye that has come up through the several stages of the process in the presence of a recycling mass of already saponified material. This promotes emulsification and rapid reaction of the reactants. The mixture is drawn off the saponification vessel to maintain a constant level in it and the reaction completed in the first stage mixer to give a glycerine rich spent lye with 0.1% NaOH or less when separated from the soap layer. The soap layer contains from 10-2% of unreacted fat. This soap layer is mixed with the second stage wash lye that contains enough sodium hydroxide to complete the saponification and enough salt to provide a two-phase washing system that is separated into kettle wax and lye, etc. to the fitting stage where a dilute fresh wash is used to obtain a "finish" in the neat soap-lye region so that no niger is separated at any time.

Figure 8 is a diagram of the Meccaniche Moderne Process. In spite of the apparent complexity of the process, it is practically a duplicate of a Sharples plant except for the modifications necessary to substitute heat exchangers and settler for centrifuges. Also, they fit with water only to give a finish that separates kettle soap and a niger. A unique feature of this process and the Mazzoni Process is the German made proportioning pump used. This pump is actu-

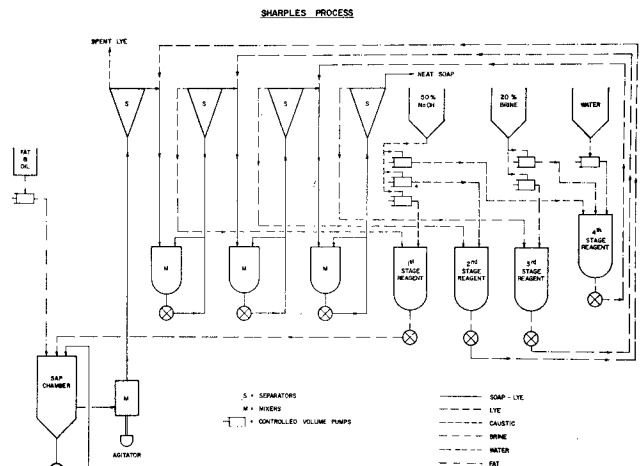


FIG. 7

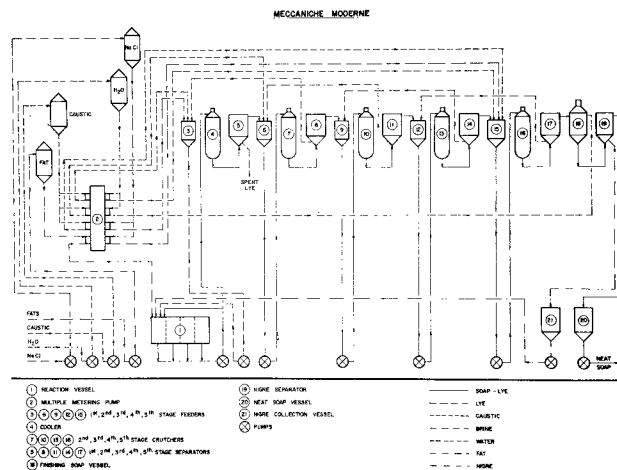


FIG. 8

ally eight pumps driven by the same motor. Each pump is capable of individual adjustment to balance its stream with the others and once all pumps are adjusted you are supposed to be able to stop and start the system without the problem of rebalancing streams unless a new feed stock is introduced. The lye concentrations are controlled so that at temperatures around 200F the soap is in solution, but upon cooling the two phases appear allowing separation of a soap upper layer and lye lower. This kind of system would provide ideal contact for glycerine removal, if concentrations required were not too critical to be readily maintained. However, even if it were found necessary to always have two phases present in the wash stages, a satisfactory washing should be obtainable. As mentioned earlier, the continuous separation of neat and niger by gravity settling is slow and, so far as we have ever heard, rather uncertain. This might mean that large batch settling tanks or a centrifuge would have to be substituted for the continuous gravity settler.

Figure 9 shows the Mazzoni Continuous Saponification Process. A little study will reveal that this process is very similar to the Meccaniche Moderne one just discussed. When first presented for sale, the main difference was in the handling of the washes to effect the separation into two phases. Mazzoni used external heat exchangers to heat to the homogeneous phase and cool to get the two phases for separation while Meccaniche Moderne did the heating and cooling in a complex two-section tank that served as a hot mix tank in the top section and a cool settler in the bottom one. More recently this unit has been separated into two so that there is very little difference even in the equipment today.

In the United States, and probably in most parts of the world, if you already have a going kettle house, it is very difficult to justify on a straight cost savings the switch to any continuous saponification system especially if you modernize your kettle house along the following lines:

1. If you are using 100% filtered fat stock, you may be able to shorten the settle after fitting to 16 to 24 hours, thus freezing very little neat soap and increasing your yield from each kettle.
2. With some experimentation, you can reduce the wash lye bulk to about 0.5 to 1 thus producing a glycerine lye with close to 20% glycerine with a consequent saving in evaporation costs in glycerine recovery.

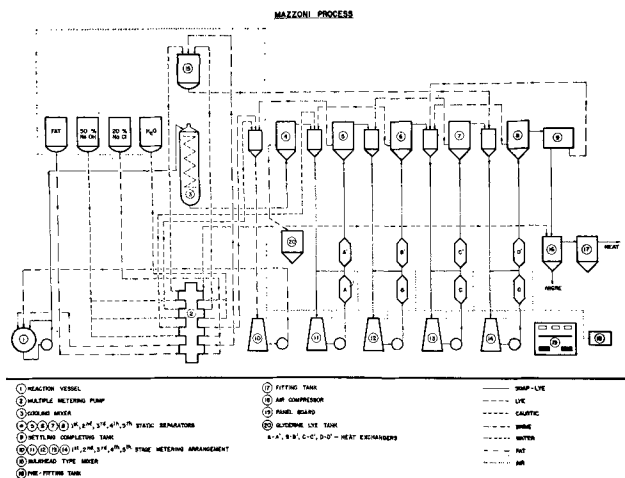


Fig. 9

3. Finally, with glycerine prices declining you should examine the cost of putting on wash lyes. It is feasible to completely eliminate the wash lyes and the half finish without changing the glycerine recovery greatly.

If new production facilities are needed, then consideration should be given to installing one of the continuous saponification processes. They require about one-tenth the usual kettle house space for equal production. They require a little more electricity for pumps and mixers, but save a great deal of steam. All of them are producing acceptable soap in some part of the world. The De Laval process is probably the best from the point of view of ease of getting on stream and adjusting to variations in composition of fat stocks, but it is the most expensive and, as presented here, is more costly than the others to operate because of the excess caustic in the glycerine lyes. With all the continuous processes you may find a difference in the odor of the soap produced because of the lack of steam distillation during processing and either the separation of no niger or recycling without taking off a niger degrading.

REFERENCES

1. Bailey—Industrial Oil & Fat Products, 2nd edition, p. 844.
2. Ferguson, R. H., Oil & Soap, 14, 115-118 (1937).
3. Davidsohn, Better, and Davidsohn, Soap Manufacture, Vol. 1, p. 82.
4. Jones, L. D., JAOCS, 35, 630 (1958).

# Manufacture of Soap from Fatty Acids

A. B. HERRICK and ERIC JUNGERMANN, Soap Research and Development Dept., Armour & Company, Chicago, Illinois

SOAP MANUFACTURE via the fatty acid route has been practical only since the development of continuous fat-splitting equipment of the countercurrent type in the 1930's and 1940's by workers at Colgate-Palmolive-Peet Company, Emery Industries, and Procter and Gamble (1,2,3).

The two general methods of making soap, 1) direct saponification of fat and 2) fat splitting followed by distillation and saponification, both have some advantages and disadvantages. The many features of direct saponification of triglycerides by batch and continuous methods are covered by another paper (4) presented at this Short Course.

It is the purpose of this paper to describe the processes and equipment involved in manufacturing soap from fats via fatty acids in some detail, and to discuss the advantages and disadvantages of the various soap making procedures. A simplified schematic diagram of the process being described is shown in Figure 1.

### Fat Splitting

A number of excellent reviews have been written on fat splitting (5,6,7) and fatty acid distillation. Essentially, the hydrolysis of triglycerides to fatty acids and glycerine by reaction of water and fat under conditions of high temperature and pressure is a simple chemical process. To obtain high yields of fatty acids, the reverse reaction in the equilibrium must be repressed by countercurrent washing to remove the glycerine from the reaction zone. A simple diagram of a fat splitter is shown in Figure 2. The rate of the reaction is controlled by the temperature in the splitter and by the amount of catalyst used.

An important feature in the design of the fat

splitter and auxiliary equipment is whether a catalyst is to be used or not. The catalyst most often employed in commercial splitters is zinc oxide. Others tried include NaOH, KOH, LiOH, MgO, Ca(OH<sub>2</sub>). The zinc catalyst is converted to zinc soaps before the fat enters the splitter. This catalyst was found by Lascaray (8) and was the most effective one tried. The function of this catalyst is to assist in emulsifying the triglyceride oil with water to permit the hydrolysis to begin without the lengthy induction period otherwise required. When a certain amount of hydrolysis to fatty acid has occurred, the solubility is greatly increased and the reaction proceeds rapidly.

If a catalyst is employed, additional equipment is required to mix the zinc oxide with the fat and get it into solution before the fat enters the splitter, and also to remove it from still bottoms after distillation.

Without a catalyst, a larger splitter is required to obtain the same rate of throughput at the equivalent extent of reaction (97-99% split). Since other aux-

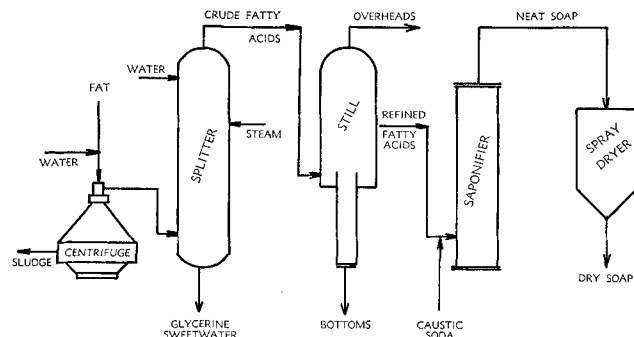


FIG. 1. Schematic diagram of fatty acid route to soap.