Continuous and Automatic Saponification of Fatty Acids

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MODERN DEVELOPMENTS in the field of synthetic detergents and their consequent emphasis in technical literature have, to some extent, overshadowed the advances in the older but still very important field of soap manufacture. The new developments in this industry, characterized initially by the general adoption of continuous finishing process, a typical example of which is the Mazzoni Process for the vacuum cooling and drying of soap, have now been extended in ever increasing volume to the saponification process.

Many continuous processes for the saponification of glycerides and of fatty acids, each of which has its own advantages and disadvantages, have been developed over a period of many years. The use of split distilled fatty acids derived from low grade garbage fats and acid oils can be of considerable financial interest to the soapmaker; the improved glycerine yield, colour and odour upgrading of the fatty acids and in many cases the further valorization of the low mol wt fatty acids recovered in the topping distillation process, are also vital points of interest.

The continuous saponification of fatty acids is the logical culmination of the soap-making method based on the fat splitting and distillation of fatty acids. The studies carried out in this field by the Mazzoni Company have led to the development of two processes: the SC process for the saponification of fatty acids with caustic alkali and the SCC process, where the main part of the fatty acids is preneutralized with soda ash, followed by the completion of saponification with caustic alkali. This second process is of interest when the use of soda ash is more convenient, economically speaking, than the use of a caustic alkali.

Notwithstanding that the saponification of fatty acids is, chemically speaking, a simple reaction, its technological conversion into an industrial and continuous process has involved the solution of various problems in order to comply with the practical necessity of ensuring a definite constancy in the soap composition and, in the case of the preneutralization with soda ash, to ensure in the finished soap the presence of only small traces of carbonates.

It is the purpose of this paper to describe the features of the two saponification processes and the equipment involved, and to discuss in some detail the method employed for the automatic control of the soap alkalinity. Some attention will also be paid to the handling of distilled fatty acids and saponification lyes, in order to obtain an acceptable soap without further processing, such as washing and fitting.

SC Process

The process is illustrated in Figure 1. Fatty acids and caustic lye flow by gravity from feeding tanks 1 and 2 through the strainers 3 and 4 and the preheaters 5 and 6 to the constant level tanks 9 and 10, equipped with float-type level controllers. The preheaters are heated by means of low pressure steam and preheating temp in normally maintained between 50C and 60C (122F–140F) and the controlled by the pneumatic controllers 7 and 8. The constant level tanks feed the pumps which form part of the proportioning unit 11. For each reactant there are two pumps which operate as a "duplex" system to smooth the flow and which pulsate in rhythm with the pumps for the other reactant. The pumps have the same drive with a variable speed adjustment to regulate the plant output, while each pump is capable of individual adjustment of the stroke length.

The reactants are metered into the reactor 13, which is a multistage centrifugal mixer, and they are dispersed in a soap stream coming from the mixing tank 15 and recirculated by the pump 12. This recirculated soap plays the role of reaction vehicle and acts as a damper. From the reactor the soap enters into the mixing tank 15 where an intensive circulation of the mass is maintained. The recirculated soap passes through the flow chamber 14 where an electrode assembly is installed that acts as a device for measuring the

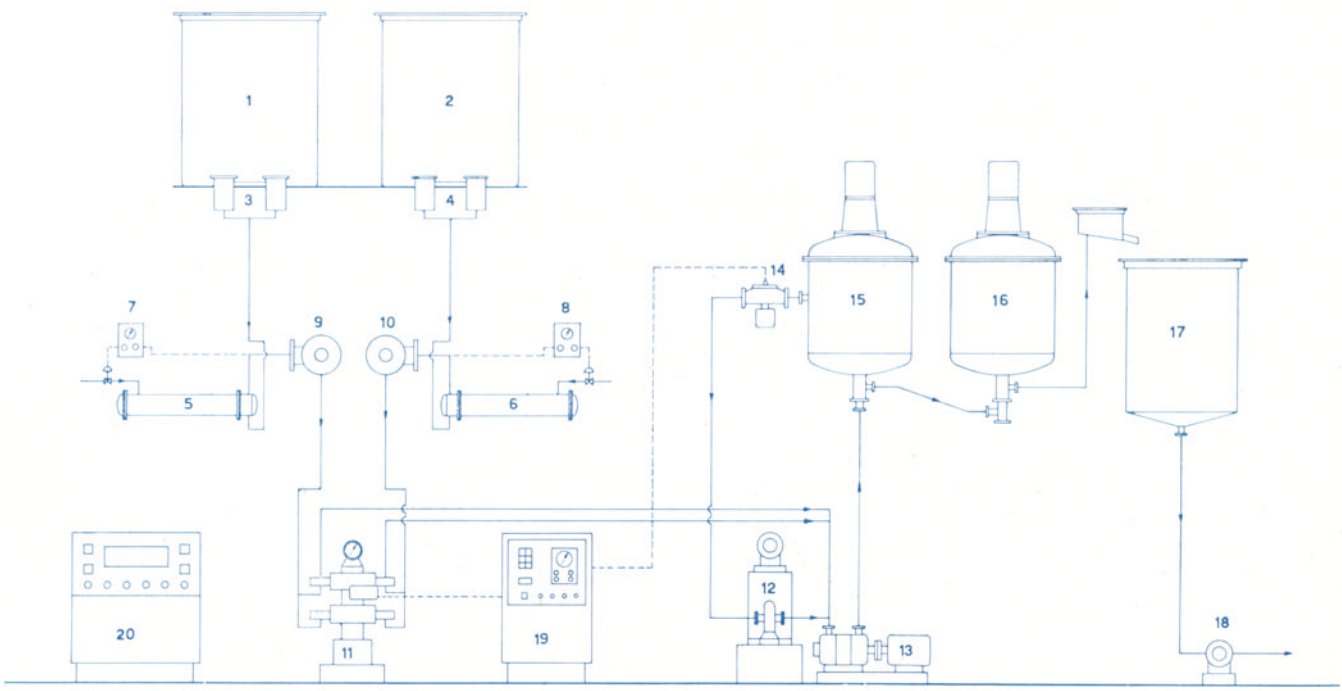

FIG. 1. Schematic diagram of "SC" continuous fatty acid saponification with caustic lye.

soap alkalinity. The signal obtained by the electrodes is transmitted to the board 19 from which an amplified signal emerges to correct the stroke length of one of the caustic pumps of the proportioning unit 11. The characteristics of this alkalinity control will be further described. A quantity of soap, equal to the sum of fatty acids and caustic entering into the process, passes continuously from mixing tank 15 to blend tank 16 where the saponification is completed and a uniform soap composition is obtained despite any small variation in mixing tank 15. The saponified and constant product flows continuously into the holding tank 17. The saponification temp is normally maintained at about 90C (194F) and it is controlled by the preheating temp of the reactants.

The unsaponified content of the soap leaving the plant is normally between 0.03 and 0.08%. The presence of about 10% of neutral fat in the fatty acids mixture does not cause an appreciable diminution in the degree of saponification of the soap leaving the plant. Normally caustic soda solution is used as saponifying agent, but it is possible to use also caustic potash, or other alkalies or mixtures of alkalies. As an example, the addition of a small percentage of caustic potash to the caustic soda solution imparts special properties to the finished soap, notably an increase in plasticity and improved solubility.

The strength of the saponifying lye determines the fatty acids percentage in the finished soap which can be varied from 60–70% and even higher. The necessary brine can be added either in the saponification lye or it may be metered by a separated pump. Furthermore, the sodium chloride percentage of the soap can be varied within suitable limits to provide the desired characteristics to the soap; as an example, a low sodium chloride content (from 0.1–0.2%) together with a reasonably low free alkali content is conducive to obtaining translucent soaps by milling and plodding.

SCC Process

As illustrated in Figure 2, the fatty acids and the carbonate solution (at about 25–27% concn) contained in feeding tanks 1 and 2 are fed by gravity to the metering pumps of the proportioning unit 7, whose features are similar to those of the proportioning unit of the SC process. Through the preheaters 8 and 9 the metered reactants are fed to the neutralizing reactor 12, which is a high speed flow mixer. The mixture obtained by the reaction passes into the mechanical centrifugal separator 13, where the carbon dioxide is removed and neutralization is completed. The resulting acid soap passes to the saponification section which is identical to the SC plant previously described. In this section saponification is completed by means of an addition of caustic lye from tank 3 to the reactor 15 by means of a pump which forms part of the proportioning unit 7. The stroke length of this pump is adjusted by the automatic alkalinity control system. The necessary brine can be mixed with the carbonate solution or can be fed separately to the process by an individual metering pump.

While in the neutralization of commercial fatty acids mixtures for soap making with caustic lye, there is a heat development of about 9.5 Calories per mol of mixed fatty acids, the neutralization with solution of soda ash is appreciably endothermic: the heat absorption is about 4 Calories per mol of mixed fatty acids. In addition to this, a certain quantity of water is flashed off from the reaction mixture to assist in the carbon dioxide removal. From the foregoing, it is apparent that the heat input is larger in the case of carbonate saponification than in saponification with caustic lye and this is obtained mainly by preheating the soda ash solution to a temp of about 120C (248F), while the fatty acids are preheated at a temp not over 100C (212F). The contact of the reactants in the neutralizing reactor causes a sudden fall in the temp due to the endothermic process.

The neutralization reaction of fatty acids with carbonate in aqueous medium occurs with the evolution of carbon dioxide and is a reversible one. For instance at low temp, carbon dioxide is able to react with diluted soap solutions with formation of sodium bicarbonate and liberation of free fatty acids. For this reason, the reaction of fatty acids with sodium carbonate proceeds quantitatively only if conditions are provided that assure the complete removal of carbon dioxide. Such conditions are:

1. temp near to the boiling point of water;
2. low partial pressure of carbon dioxide;
3. high concn of the acid soap mass;
4. relatively low pH (i.e., relatively high free fatty acids content of the acid soap mass).

The mechanical centrifugal separator is in fact a film reactor where the viscous acid soap mass, after removal of the major portion of carbon dioxide undergoes on a cylindrical wall very intensive shearing actions, and at the same time, the action of heat to evaporate some of the water from the aqueous soap. These combined actions greatly facilitate the decomposition of the last traces of bicarbonate by inducing a rapid reaction with fatty acids and lowering the partial pressure of the resulting carbon dioxide which is thus re-

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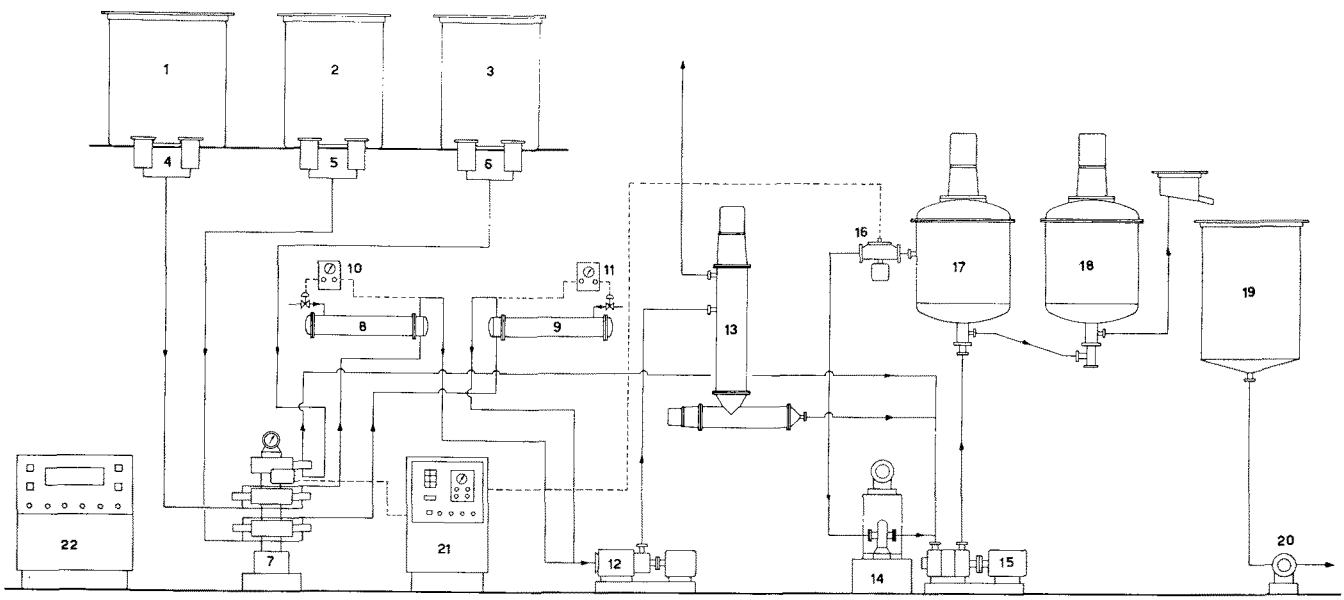

FIG. 2. Schematic diagram of "SCC" continuous fatty acid saponification with soda ash and caustic lye.

Saponification .

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moved. The reaction is carried out at about 95C (203F) and at atmospheric pressure with a holding time in the neutralizing system of a few seconds.

For a fatty acid mixture suitable for toilet soap and with a preneutralization degree of about 80%, the residual quantity of sodium carbonate in the finished soap averages 0.05%. Due to the removal of all the gas traces, the resulting neat soap leaving the plant is completely transparent and has the appearance of clear liquid honey. Moreover, a substantial quantity of volatile odour bodies is stripped by the carbon dioxide–steam mixture during the degasifying step of the process. Figure 3 represents a partial view of the SCC plant.

The SCC plant can also be operated by employing caustic soda solution alone as saponifying agent.

Soap Alkalinity Control

Differing from the soap graining and fitting stages of the conventional soapmaking methods (where the separation of the curd soap from the lye, or of the neat soap from the nigre, is determined by the total content of electrolytes and where, therefore, the control of the sodium chloride percentage has the same importance as the caustic control), in the continuous saponification of fatty acids the major problem is in maintaining the proper ratio of reactants, i.e. fatty matter and saponification lye, by means of the control of the soap free alkalinity. The neutral electrolytes, as sodium chloride, introduced in small quantities in to the soap mass, normally from 0.1–0.5%, can be easily controlled by means of any standard volumetric proportioning device.

The automatic control of both SC and SCC continuous saponification plants is based on the continuous potentiometric measurement of the soap alkalinity in the primary saponification zone. The measurement is carried out directly on the low hydrolized concd soap by means of an electrode-assembly formed by a metal-metal oxide electrode sensitive to the OH ions and a reference electrode in a particular disposition. This is a peculiar application where, differing from the standard pH measures, the electrode potential is directly related to the free NaOH content of the soap determinable by titration. This application has been made possible by the fact that in the homogeneous concd soap phase, the OH ions have a very high activity, and this determines a high sensibility of the electrodes potential against the variations of the free alkalinity. In reality the potentiometric measure can detect the neutralization ratio over an extended range, from soaps containing considerable amts of free fatty acids to soaps having a fair excess of free alkali. The relation between the electrode potential and the free alkalinity is shown in Figure 4. The pattern of the potential curve is of the same type found in the potentiometric titration of a weak monobasic acid with a strong base. Actually the measuring takes place in a portion of the right branch of the curve, corresponding to a neat soap alkalinity comprised between 0:05 and 0.15% NaOH.

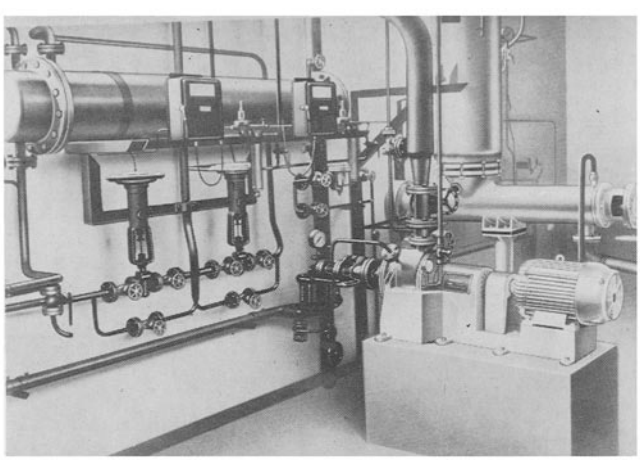

FIG. 3. Partial view of an "SCC" Plant showing the preheater for the carbonate solution, the neutralizing reactor of fatty acids with carbonate, the lower part of the mechanical centrifugal separator and film reactor with the screw to feed the acid soap to the saponification section.

The potentiometric method of alkalinity measurement fulfills perfectly the requirements of the continuous saponification of fatty acids. In fact, for example, soap viscosity is dependent upon its total electroylte content, and this viscosity, in the range of concns of interest in the practical control, varies in accordance with "U" shaped curve, while the electrode potential depends only on the soap alkalinity and it varies accordingly with this, following a continuously rising curve. Practically it results that the measured potential depends exclusively on the soap alkalinity. Even very large variations of moisture and sodium chloride percentages in the soap or in the composition of the fat stock do not influence this measuring. Furthermore, this is dependent of variations in plant output or of the quantity of soap recirculated through the flow chamber and reactor. The variations of the electrode potential due to temp changes are automatically compensated.

For the purpose of continuous measurement a robust electrode assembly has been developed, suitable for operation under severe conditions of alkalinity, viscosity and temp, without alteration to the active electrode surface and without causing disturbing potential (1). The apparatus ensures the maximum operating safety and a long life of the electrodes. The electrode potential is transformed into an amplified output signal, used for reading, recording and for the automatic control of the process. Recent advances in the electronic field have permitted the use of transistorized circuits for various functions, such as signal amplification and control, so that this apparatus presents no maintenance problem.

Figure 5 is the photograph of a portion of the recorder chart of a continuous saponification plant for fatty acids. As the measuring instrument is of potentiometric zero setting type, the zero point (centre of the chart) corresponds with the control value which, in this case was 703 mv. With this control system, the free alkali content of the soap manufactured with these plants can be very easily maintained within limits of plus or minus 0.01% NaOH. As this type of control is used in conjunction with a capacitative reaction system, its performance is very steady even when external disturbances are present; for example, variations in the saponifying lye strength. In the SCC plants the proportioning system of caustic lye with automatic control of the soap free alkalinity simultaneously acts as a device for the continuous titration of the free fatty acids content of the acid soap. In other words, the stroke length of the caustic lye metering pump is directly related to the free fatty acids content of the acid soap.

Soap Quality and Handling of Raw Materials

The neutralization and saponification, in both the described plants, take place in enclosed vessels away from air contact and always at temps under 100C (212F), so that there are no oxidation reactions nor structural alterations to the fatty acids.

In the soap-making method via fatty acids, the purification of raw materials consists of two main steps, i.e., the treatment of fats before splitting, and the fatty acid distillation. The quality of soap depends on the removal of the colour and colour-forming bodies as well as of the odour in these purification stages. Moreover, it depends on using freshly distilled fatty acids or protecting them against atmo-

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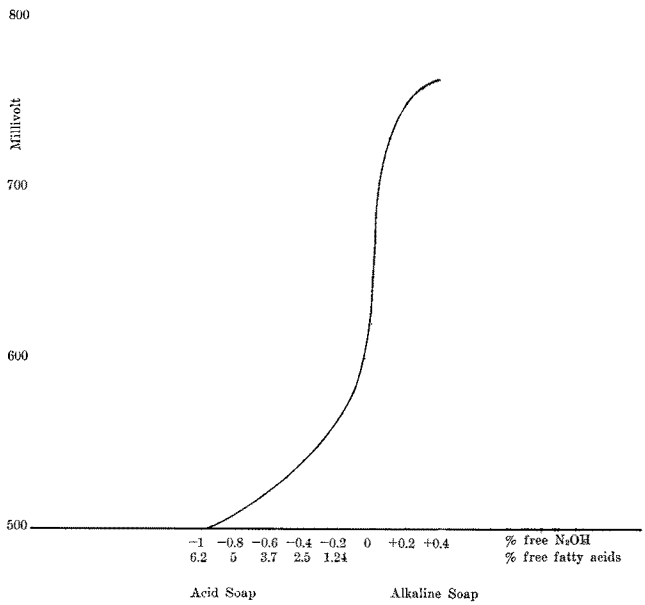

FIG. 4. Electrode potential vs. free NaOH and free fatty acids of concentrated commercial soap 62–67% total fatty acids.

spheric oxidation before saponification. In other words, fatty acid oxidation has a deleterious effect on the soap quality and particularly on the soap colour.

It is now well established that the hydroperoxides of polyethenoid fatty acids are the main cause of colour reversion at the saponification stage of fatty acids that have been subjected to atmospheric oxidation (2). For this reason selective hydrogenation improves resistance against the reversion of distilled fatty acids, but, generally speaking, it is definitely more economical to eliminate the external causes of oxidation by well cooling the fatty acids before they leave the distillation plant, as well as by protecting the fatty acids against the action of atmospheric oxygen either by immediate use or by storage under an inert gas blanket. Also the addition of antioxidants as well as of metal scavengers has proved to be a satisfactory method of protection of distilled fatty acids.

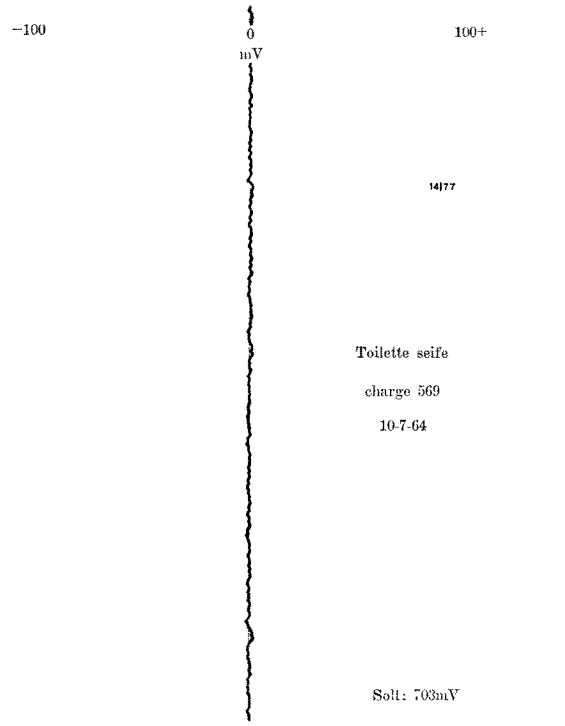

FIG. 5. Photograph of a portion of the chart recorder of a continuous saponification plant for fatty acids.

Another important condition for obtaining white soaps with good keeping colour and odour is the use of saponifying lyes with a very low ion content. A very simple method is to add the chelating agent (EDTA), normally used for soap protection, directly to the saponifying lye, in order to inactivate any traces of heavy metals present.

In certain cases, such as the saponification of undistilled fatty acids or of fatty acids affected by long or indifferent storage, the SC and SCC plants can be manufactured with ancillary parts for the continuous bleaching and also for the continuous washing and fitting of the produced soap.

Economics

The utilities consumption per ton of 63% fatty acids soap, produced with a three tons per hour plant, is:

	SC	SCC
Steam kilograms	40	150
Electricity kwh	8.5	13
Labour hours	0.33	0.33

The overall manufacturing costs for steam and electricity are much lower than the cost of steam alone in the saponification of fatty acids by means of the kettle method. The savings obtainable with these continuous processes are even more obvious if the losses of fatty acids, caustic and brine in the lyes are considered, as well as the degrading of nigres, characteristic of the kettle process.

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