stearic acid and magnesium α-sulfostearate, were the best detergents.

A concentration of 0.1% is considerably below the c.m.c. for neutral monovalent metal α-sulfopalmitates [$C_{14}H_{29}CH(SO_3M)CO_2M$]. At 0.25%, nearer the c.m.c., the ΔR value for ditriethanolammonium and disodium α-sulfopalmitate increased to 27.8 and 31.7, respectively.

Wetting Properties. Wetting properties were measured as the time in seconds required to sink a standard binding tape (6) suspended by means of a 1-g. hook and a 40-g. anchor in 500 ml. of a 0.1% solution. The wetting time values were as follows:

Triethanolammonium α-sulfopalmitic acid	50
Magnesium α-sulfopalmitic acid	32
Ditriethanolammonium α-sulfopalmitate	56
Magnesium α-sulfopalmitate	25
Triethanolammonium α-sulfostearic acid	66
Ditriethanolammonium α-sulfostearate	51

The value for disodium α-sulfopalmitate lies in this range.

Foaming Properties. Foaming properties, measured by the Ross-Miles pour-test (5) on 0.1% solutions in distilled water at 60°, are recorded in Table III.

TABLE III
Immediate Foam Height (5), mm., of Acid and Neutral Salts of α-Sulfopalmitic Acid and α-Sulfostearic Acid; 0.1% Solutions in Distilled Water at 60°.

Cation	α-Sulfopalmitic		α-Sulfostearic	
	Acid	Neutral	Acid	Neutral
Ammonium	175	190	....	....
Triethanolammonium	160	100	160	190
Lithium	190	....	205	....
Sodium	175	25[a]	75	15
Potassium	200	125	....	....
Magnesium	220	215	160	220
Calcium	220	....	125	....

[a] Foam height = 175 mm. at 0.25% concentration.

Most of these salts had better foaming properties than the sodium salt. The acid and neutral magnesium salts of α-sulfopalmitic acid, magnesium α-sulfostearate, and calcium α-sulfopalmitic acid had the highest and most stable foams. This may explain the better foaming properties of the sodium salt in hard water. Here again a concentration of 0.1% is below the c.m.c. for salts such as disodium α-sulfopalmitate, and an increase to 0.25% concentration improved the foam height.

Summary and Discussion

Of the several salts of α-sulfopalmitic and α-sulfostearic acid prepared, salts of adequate purity with measurable or considerable solubility in water are naturally those of greatest interest. These are, in general, the ammonium, triethanolammonium, lithium, sodium, potassium, magnesium, and calcium salts. A study of the wide variation in their aqueous solubility leads to an explanation of corresponding differences in surface-active properties. Outstanding differences were observed in the comparison of the slightly soluble acid sodium and potassium salts with the highly soluble acid triethanolammonium and lithium salts. At room temperature sodium and potassium salts appear to have the properties of a simple electrolyte and crystallize from solution as their ionic solubility is exceeded while at this concentration acid triethanolammonium and lithium salts exist in micellar solutions.

Each salt seems to have a critical temperature, somewhat similar to the Kraft point of soaps, above which crystalline properties give way to colloidal properties. This critical temperature appears on a solubility curve as a sharp increase in solubility. Dilithium α-sulfostearate is the only salt in this group which does not show marked increase in solubility below 100°. Acid magnesium and acid calcium salts, and dipotassium α-sulfopalmitate show marked solubility increases at temperatures lower than for corresponding sodium salts. Neutral magnesium salts exist in colloidal solution at concentrations lower than the solubility of corresponding neutral ammonium, sodium, or potassium salts. Salts of the divalent metals appear to form complex solutions which may not contain exclusively the same anionic species as corresponding salts of the monovalent metals. In general, salts forming micellar solutions at lower temperatures have better detergent and foaming properties.

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Continuous Soap Washing and Finishing, Using Multistage, Countercurrent, Centrifugal Contactors

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THIS PAPER PRESENTS a significant advance in soap technology, consisting of a process for continuous washing and finishing of soap employing multistage, countercurrent, centrifugal contactors.

Introduction

Soap boiling, although known for many hundreds of years, has been generally considered an art rather than a science until approximately the last 30 years. The work of Martin Fischer in 1921 was the first serious attempt to explain the physical chemistry of the various soap phases encountered in soap-boiling operations (1). This was followed by the important work of J. W. McBain and others (2, 3). But even with this present well-developed knowledge soap boiling is still largely an art in many of the soap plants.

Soap can be produced by the saponification of neutral fats and oils or the neutralization of fatty acids. Saponification of the first type is better known and more widely used and is the only process considered in this paper.

Several different methods of operation are used in practical soap-making (4). The oldest is called the direct-wash, lye system or direct flow system. In this all operations of soap boiling are carried out in a single kettle. These operations, commonly called "changes," include saponification, washing, and finishing. The kettle is generally equipped with open and closed steam coils, stock, lye and water lines, and a swing pipe for withdrawing products at different levels.

An improved modification of the direct flow system is the counterflow system. Several kettles are used in series, and the individual boiling steps are handled as in the direct wash system. After saponification, in place of using fresh liquid for each washing change, lyes from previous boils of soap of the same grade are used. These are worked through "weak" to "strong" changes and at each step become richer in glycerine. The counterflow lye system is an approach to the ideal situation of countercurrent extraction where a series of small washes are more effective than a single large wash of the same volume.

In recent years several methods have been developed and have come into commercial use for the continuous manufacture of neat soap from neutral fats and oils. These processes use the same fundamental soap-making steps as the kettle process.

One of these processes substitutes centrifugal separation for each of the four stages of the countercurrent kettle operation. With the large amount of complicated auxiliary equipment required, this process does not lend itself readily to interrupted operation. To obtain best results the installation must be operated continuously for at least five days.

A second process for the continuous manufacture of neat soap from neutral fats and oils employs a countercurrent, gravity-type of column having several separate chambers. After saponification the soap mass is passed through the various chambers for mixing and settling, countercurrent to wash brine.

The various kettle processes and the continuous processes described thus far have advantages and disadvantages when considered from the view-point of practical soap-boiling operations. For kettle boiling the advantages include: relatively simple equipment; low cost of repairs; long life of equipment (generally 30–50 years); and flexibility.

Disadvantages of the kettle boiling process include: need of skilled labor requiring a master soap boiler and assistant; concentration glycerine lye when using the direct flow system; long process time—four days are generally a minimum requirement for a kettle based on a 24-hr., boiling schedule; relatively large inventory of material in process; non-uniformity of product—quality of production can vary from kettle to kettle; some iron contamination is possible even when using stainless steel kettles; and relatively large consumption of steam.

The continuous systems offer certain advantages in attempting to make the soap-boiling process completely automatic, thereby striving for maximum uniformity in conjunction with maximum production. For continuous mechanized systems the advantages include: less space required; relatively short processing time; small inventory of soap in process; less iron contamination; greater uniformity in quality; lower labor costs; more concentrated glycerine lye; and lower steam costs.

Disadvantages of continuous mechanized systems are technical supervision required, higher repair costs, reltively higher initial cost, "round-the-clock" operation for most systems, costly starting and stopping operations for some types of mechanized systems, and higher electrical energy costs.

The use of Podbielniak countercurrent, centrifugal contactors in soap-boiling operations incorporates the advantages of kettle saponification with those of the continuous mechanized systems.

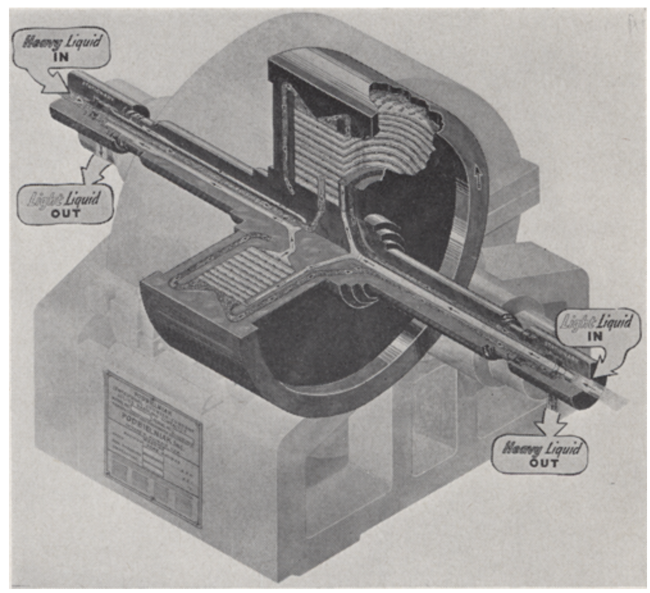

FIG. 1. Diagram illustrating flow of fluids through Podbielniak solids handling centrifugal contactor.

General Principle of Operation

A photo-diagram (Figure 1) illustrates the flow of fluids through the centrifugal extractor. The contacting and separating of two liquid phases, either of which may contain suspended solids, is effected continuously and countercurrently in the "contact elements" of the spinning rotor. The lighter of the two liquid phases is pumped to a position near the outer diameter of the rotor while the heavier phase is pumped to a position near the inner diameter. The heavy phase flows outward, displacing the lighter phase and causing it to flow toward the center. The action of the contacting elements within the rotor is intimately to mix and separate in multistage fashion. "Quiet" zones, near the center and at the large diameter, provide clarification of both streams as they leave the rotor.

Hydraulically balanced pressure-tight seals at each end of the shaft separate the entering liquids from the effluent liquids and prevent leakage of the process materials to the atmosphere. Centrifugal force ranging from 2,000 to 5,000 times gravity (depending upon rotor diameter and r.p.m.) permits satisfactory handling of phases with as little as 0.02 specific gravity difference and insures positive intimate mixing of the two countercurrently contacted phases to produce as many as 10 theoretical stages of extraction in a single compact rotor.

By suitably adjusting the back pressure of the "light liquid out" the relative volumes of the rotor hold-up or the primary interface can be maintained constant and independent of flow ratios. The high gravities produce centrifugally clarified "raffinate" and "extract" phases at high ratios of through-put to volume hold-up.

Flow Sheet for Continuous Glycerine Washing and Fitting

Figure 2 describes a typical flow sheet for continuous glycerine washing and fitting of soap, using two centrifugal contactors in series operation. Saponified kettle soap is pumped and metered into a Soaprazon extractor, where it passes countercurrently

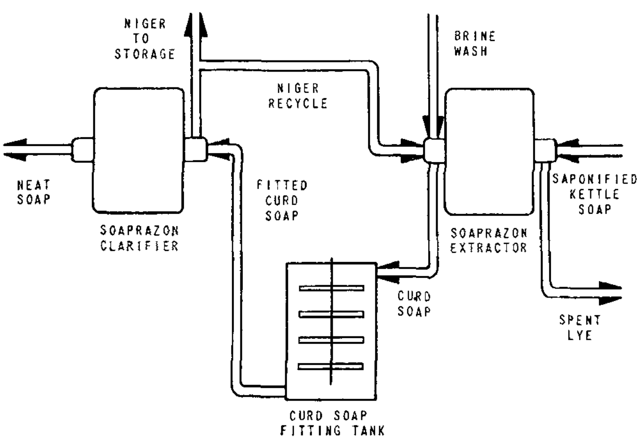

FIG. 2. Continuous soap washing and finishing, using multistage, countercurrent, centrifugal contactors.

to brine wash of proper concentration. The soap and brine are intimately mixed and separated many times inside the rotor as previously described. This equipment is designed to extract the glycerine with an efficiency equal to at least four theoretical stages. Spent lye leaves the extractor as the heavy liquid phase and is sent to the glycerine-recovery system.

Curd soap from the extractor is passed into a reaction chamber, where it is continuously fitted to permit proper separation of the neat and niger soap phases. The type and amount of fitting solution can be varied, depending on the characteristics of the curd soap. The fitting chamber is sized to allow approximately ½-hr. retention time for the curd soap, based on maximum rated through-put for the entire installation. Paddle-type mixers, rotating slowly, provide adequate contacting of the curd soap and fitting solution.

The fitted curd soap is pumped through a Soaprazon centrifugal clarifier, where the niger phase is separated from the neat soap phase. The clarifier is generally similar in design to the contactor, whose flow characteristics have been described. It is also similar to the Podbielniak Duozon, which has been successful in the commercial degumming and refining of vegetable oil (5). Its high efficiency clarification elements and 180°-phase separation provide maximum separation and clarification of the niger and neat soap phases. The ability to adjust the point of inlet of the fitted curd soap permits the clarifier to handle many different types of soaps.

The entire installation is interconnected by automatic flow and ratio controllers, thereby permitting continuous operation with minimum labor requirement.

All viscous soap phases are pumped and metered by constant displacement pumps, powered by variable-speed drive units equipped with air cylinders for automatic speed regulation. Brine wash and fitting solution pumps are the constant-speed turbine or centrifugal type.

The Soaprazon contactors are driven by variable-speed drive units which permit operation at any desired speed up to approximately 2,400 r.p.m. Special features are included in the drive units, which provide rapid braking of the rotor during shut-down operation.

Adjustment of the brine wash and fitting solution concentrations is accomplished by continuous blending equipment. Provision is made for rapidly changing the phase ratio if this is indicated by a change in the characteristics of the curd soap.

Capacitance-type, liquid-level controllers used in conjunction with pneumatic air regulators control accurately the liquid level of material in the curd-soap fitting tank and niger-recycle tank.

Automatic pressure controllers and diaphragm-type valves maintain the primary interface at any desired level in each Soaprazon contactor. The degree of clarification can be established accurately by a simple adjustment of a pressure controller mounted on a panel board. The entire mechanical operation can be started, operated, and shut down from a console type of graphic panel board. All soap lines and tanks are steam traced or jacketed and insulated. The rotor housings are heated by closed steam coils. For shut-down purposes all soap lines can be cleaned by blowing soap to a receiving tank, using high pressure steam.

Operation and Maintenance

Before starting the washing operation, all lines and tanks handling soap are heated by steam. A small flow of hot soap from the kettle is passed through the lines and rotors for additional heating, during which time the Soaprazon contactors are brought up to operating speed. For installations of approximately 10,000–15,000 lbs. per hour neat soap this entire operation can be completed within 20 min. The soap flow-rate required to bring the installation to operating conditions can be approximately 1,000 lbs. per hour; therefore only 500–1,000 lbs. of soap need be recycled or reworked because of starting operations.

Countercurrent extraction operations are started immediately upon reaching operating speed. Brine wash and saponified soap flow-rates then are adjusted for desired production capacity.

Shut-down of the plant requires only 20 to 30 min. Consequently less than 1,000 lbs. of soap need be reworked because of the shut-down of an average-sized plant. This makes the described countercurrent centrifugal process particularly desirable where operation covers only one or two shifts per day.

Initial setting of the process variables can be based on a preliminary test of each new batch of saponified kettle soap. In addition, the soap chemist or shift operator can adjust the variables properly according to the appearance of the curd soap in the fitting tank. Periodic tests for caustic and salt in the fitted curd soap also insure that operations are proceeding under the proper conditions.

Niger soap leaving the Soaprazon clarifier is collected in a receiving tank, equipped with a capacitance type of liquid-level controller. From this tank the niger can be recycled in any desired proportion to the Soaprazon extractor. The portion not recycled may be sent to an empty saponification kettle for use in the next batch of soap or collected in a storage tank.

Niger soap recycled to the extractor may be admitted into the rotor at any one of several different radial locations. This adds flexibility in that the niger phase may be introduced into the main extraction mass at any desired position from approximately the first to the fourth theoretical extraction stage.

The contactors are generally self-cleaning. Foreign particles, dirt, and other impurities usually collect in the heavy-liquid, effluent phase and leave with the spent lye or niger phase. No time-consuming disassembly or spare rotors are required. If necessary, a short, back-flushing operation, using hot brine, can be used completely to clean the rotor. During back-flushing operations it is not necessary to shut down the entire plant but necessary only to slow down the centrifugal contactor to approximately one-half speed. Back flushing for 10–15 min. is generally sufficient for most operating conditions. For an extraction plant properly erected and operated, back flushing should not be required more than once in 7–10 days of continuous operation.

Maintenance on the contactor is low as there are no moving parts other than the rotor bearings and mechanical seals. Heavy-duty ball or roller bearings are used and provided with forced-feed lubrication systems. Bearing assemblies are designed to be sealed completely against the corrosive atmosphere generally found around soap plants.

The balanced type of mechanical seals, especially designed for this process, are used to keep the inlet and outlet streams separated. These seals have demonstrated excellent service and long life. When necessary, replacement of seals is simple and rapid.

Auxiliary equipment associated with the extractors requires only the usual maintenance of pumps, electric motors, and automatic control instruments.

Specifications and operating conditions will vary according to the type of raw material handled and the product desired. Each Soaprazon installation is designed to the customer's specific requirements. Figure 3 shows the type of performance which can be demonstrated on most soap systems now used commercially.

A.	Electrolyte Range for Fitting Operation	
	Caustic	0.15–0.25%
	Sodium chloride	1.0 –1.2 %
B.	Average Neat Soap Specifications	
	Caustic	0.10% or less
	Sodium chloride	0.50% or less
	Glycerine	0.50% or less
	Water	29.5–30.5%
	(Based on soap containing 15–20% coconut oil)	
	Lye/soap ratio	1.0 (maxi'm)
	Glycerine in spent lye	9–11%

FIG. 3.

Conclusions

There are many advantages in the use of Podbielniak multistage, countercurrent, centrifugal contactors for continuous glycerine washing and fitting of soap produced by saponification by the usual kettle method. These advantages are:

1. The operation is flexible, permitting rapid change of stock.
2. Volumetric hold-up in the extraction installation is small so that only a small amount of stock need be reworked after starting, stopping, or change-over.
3. The extraction efficiency in removing glycerine from soap is high, and the clarification of phases in each step is complete.
4. The volume of niger soap produced is lower; generally 15% as compared to usual 20%.
5. With little increase in space requirements, it allows great increase in production from existing kettles. Very small space is required for contactors and auxiliary equipment. Generally no new building construction or remodeling is required. Equipment with a capacity of 10,000 to 15,000 lbs. of neat soap per hour occupies an area of less than 200 sq. ft. and 8 to 10 ft. in height.
6. The operation is simple, not requiring highly skilled operators.
7. The start-up is rapid and equilibrium conditions quickly attained. Generally, after starting, neat soap meeting product specifications can be made in 20 to 30 min.
8. The compactness of the installation and high capacity of the equipment permit economical use of stainless steel and other corrosion-resistant materials.
9. The ability to use automatic control minimizes manpower requirements so that one operator per shift is adequate for any plant of reasonable size.
10. Efficient operation is possible either for a plant running only one or two shifts per day, or for a plant operating continuously.
11. The Soaprazon requires little maintenance. It is generally self-cleaning, and no disassembly or manual clean- is needed.

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