highly chlorinated oils. It is apparent from Table II that the degree of chlorination is directly related to the thermal stability of the composition. Also the physical properties observed are directly related to the degree of chlorination, and values tend generally to show an increase with increasing amounts of chlorine in the oil.

Heat stability measurements at 350°F. on highly chlorinated compositions indicate greater reflectance loss during the initial 30 min. than that observed for a DOP plasticized composition, 50% as against 25%, respectively. Beyond this point the results favor DOP only slightly. At room temperature no observable color change of these compositions was detected after a period of three months.

The over-all results indicate that highly chlorinated tung oils are effective in lowering the milling temperatures of polyvinyl chloride copolymers, but the products are not very flexible at room temperature.

Summary

The chlorination of tung oil was investigated, and certain chlorinated products were screened as plasticizers for polyvinyl chloride resin. Chlorine readily added at low temperatures (0 to 20°C.) as well as at higher temperature (75°C.). The chlorination was highly selective for triene conjugation as the disappearance of triene closely paralleled the amount of chlorine added during early stages of chlorination. Considerable conjugated diene is formed as indicated by characteristic ultraviolet absorption in the diene region. In later stages of chlorination considerable substitution occurs as evidenced by the fact that products containing more than 40% of chlorine could readily be obtained. All the products were more or less unstable, evolving hydrogen chloride and darkening at room temperature. The chlorinated tung oils were screened as plasticizers, at the 30% level, for polyvinyl chloride by using butyl epoxystearate as a stabilizer. Products containing small proportions of chlorine (less than about 20%) were not compatible with polyvinyl chloride; products containing moderate amounts (about 30%) were compatible and had some plasticizing effect but decomposed excessively on milling. Those products containing the highest proportion of chlorine (more than 40%) were compatible and did not decompose on milling or molding. These highly chlorinated tung oils lowered the milling temperature of polyvinyl chloride copolymer but showed little, if any, ability to product compositions which are flexible at room temperature.

Acknowledgments

The authors wish to express their appreciation to V. P. Whitley for the chlorine analyses, to E. T. Rayner for the diene value determinations, to R. R. Mod for assistance in the plasticizer screening tests, and to R. T. O'Connor for helpful discussion concerning interpretation of ultraviolet and infrared absorptions.

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A New Approach to Continuous Soap Making—Constant Composition Control[1]

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THE MANUFACTURE OF SOAP is one of the oldest industrial processes known in chemical technology. The art of making soap depended upon the skill of the soap boiler and was based upon many years of practical experience. During the past 50 years the rapid development of pure and applied chemistry, especially in the field of colloids, has made it possible to understand many reactions on a scientific basis. Based on this knowledge, soapmaking has now developed from an art into a scientific procedure.

The Centripure Process (1) of continuous soapmaking is an example of the successful application of scientific knowledge to the continuous operation and automatic control of a chemical process basically known since the days of antiquity.

In this process the production of soap from neutral fats is carried out continuously in three stages, each having its importance: saponification of the neutral fatty oils with lye; washing of the soap mass with brine to recover the glycerine released in the process; and fitting of the soap in order to effect further purification.

The Saponification Stage

As is well known, the initial reaction velocity in the saponification of neutral fatty oils with lye is very slow because of the immiscibility of the components. However the reaction may also be regarded as autocatalytic since the soap produced is capable not only of dissolving lye but also of dispersing neutral fatty oils into a colloidal suspension (2, 3). In this way a considerable enlargement of the contact surface re-

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sults, and the saponification is greatly accelerated. When carried out in accordance with the conventional kettle process with its unsatisfactory mixing of the components, soapmaking is characterized by a limited saponification velocity. It will thus take a considerable time before the reaction is completed.

However in this continuous process the main principle is to utilize the catalytic effect of the soap in the saponification reaction by feeding the neutral fatty oils into the soap already present. Here the oil is immediately dispersed and dissolved.

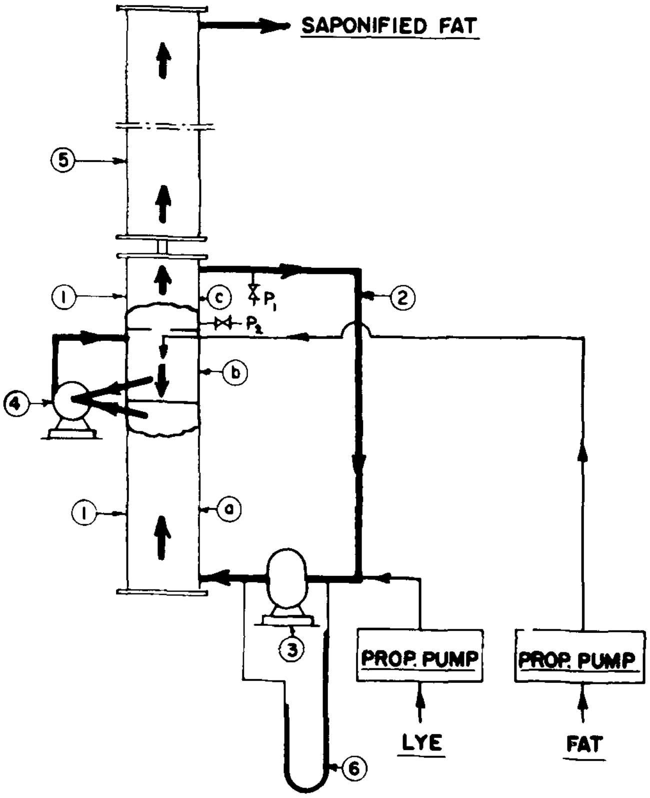

FIG. 1. Saponification section.

The operation of the saponification column is shown in Figure 1. A circulating pump brings the soap into the saponification column while the neutral fat and the lye required for saponification are conveyed to the column by proportioning pumps. The soap in the lower portion of the column always contains a certain excess of lye, hence the saponification of the neutral oil introduced in the column will start immediately.

The excess lye also makes it possible to avoid formation of certain less desirable soap phases of low electrolyte content, such as middle soap and acid soap. For the same reason it is very important to maintain a high recirculation velocity in the saponification column.

The fat is introduced into the middle section of the saponification column and mixed with the soap already present by means of a centrifugal pump. Although the passage through this part of the column is a matter of only two minutes, analytical tests have shown the degree of saponification to be as high as 99.8%. When leaving at the the top of the column, the soap is actually 99.95% saponified.

As has already been mentioned, a definite excess of lye is extremely important not only completely to saponify the neutral fatty oils but also to make sure that the correct soap phases are formed (4). This makes it necessary to have complete control of the lye-to-oil ratio at all times. It is well known to every soapmaker that the physical characteristics of the soap, particularly the viscosity, will vary considerably under the influence of excess lye. Detailed investigations of these factors have shown the viscosity variations of the soap to be useful not only in a qualitative but also in a quantitative sense.

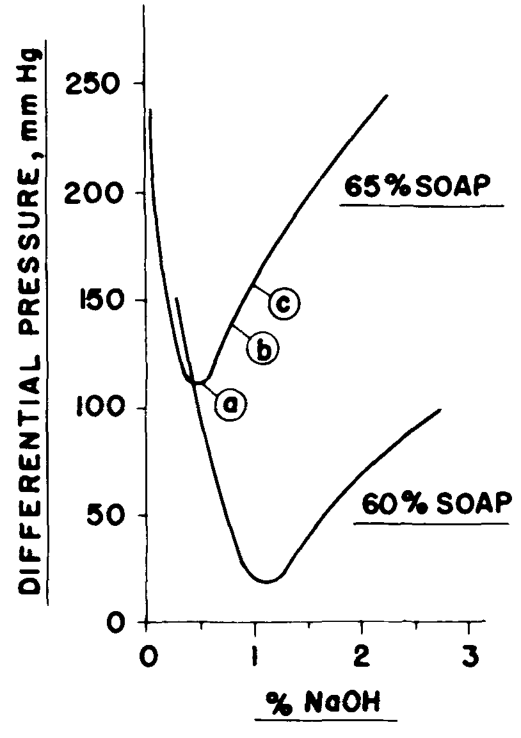

FIG. 2.

Figure 2 illustrates the relationship of electrolyte content to viscosity, where the viscosity is expressed in terms of differential pressure. At an initial low electrolyte content the soap in question will be extremely viscous. As the electrolyte content increases, the viscosity will decrease and, after passing a minimum, will again rapidly increase. Points a, b, and c illustrate increasing viscosity with increasing electrolyte concentration.

The relationship may further be illustrated by the use of a McBain (5) diagram for a particular soap. Figure 3 illustrates a typical diagram with the important phases enlarged. Area A indicates the neat soap phase, Area F the nigre soap and middle soap (not marked), Area G a mixture of neat soap and nigre soap, Area I represents a three-phase region of neat soap, nigre soap, and spent lye, and Area J represents neat soap and spent lye. Also on this diagram are shaded areas indicating regions of equal viscosity.

The point of minimum viscosity (Figure 2) corresponds very closely with the boundary zone between neat soap and nigre (point a). The right-hand branch of the viscosity curve first corresponds to a mixture of neat soap and nigre and, at higher viscosities, to a mixture of neat soap, nigre, and spent lye (point b). At still higher viscosities a phase has

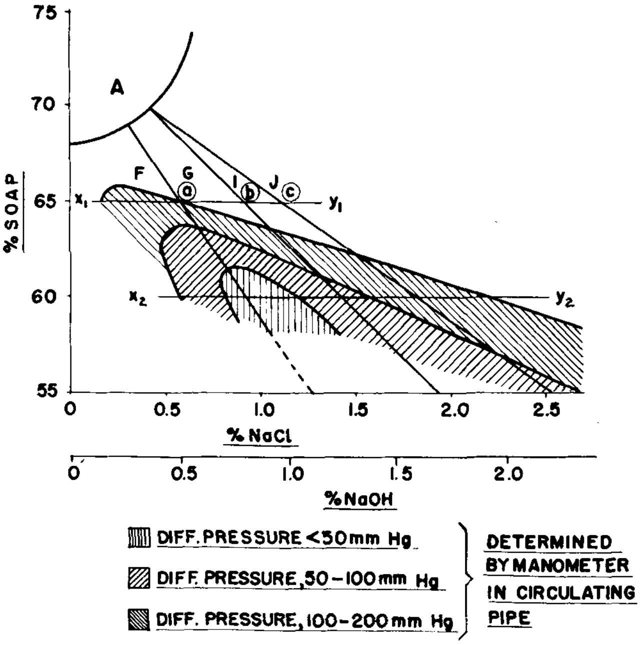

FIG. 3.

been established between neat soap and spent lye, for example point c.

An important feature of the McBain diagram with its characteristic phase equilibria is that every point in the shaded area corresponds to a well-defined viscosity and *vice versa.* Consequently the changes in viscosity may be used for the automatic constant-composition control of the lye-fat ratio. In actual production practice the viscosity of the soap in the saponification column is determined by measuring the pressure drop across the circulating pump. While the feed pump for neutral fat is set at a constant through-put corresponding to the actual through-put of the entire soap plant, the through-put of the lye pump may be varied. Any change in the viscosity of the soap, which indicates either a deficiency or excess of lye in the saponification stage, would automatically result in a compensating change in the lye flow.

The accuracy that may be obtained in the setting of the excess of lye not only depends on the accuracy of the instruments and the character of the fatty charge but also on the portion of the curve (Figure 2) that corresponds to the operating conditions. Under certain conditions it may be possible to obtain an accuracy of ±0.01% in the excess of lye. Although it is true that the composition of the fatty material exerts a certain influence on the shape of the viscosity curve, the glycerine content of the initial material is of much greater importance in the manufacture of most standard toilet soaps. A high glycerine content in the initial material, which would occur when using neutral fatty oils, would result in the displacement of the viscosity minimum on the curve (Figure 2) to the left, which would apparently indicate a low electrolyte content. With a low glycerine content in the initial material, for example, when using higher percentages of fatty acid, the viscosity minimum would be displaced towards the right and would indicate an apparent higher electrolyte content.

However these matters are of negligible importance in the practical application of automatic constant-composition control since, with a given starting material, it is quite easy under normal conditions to determine the position of the minimum. In practice, when carrying out operations at some point on the left branch of the curve in Figure 2, there will be an immediate drop in viscosity when the fat pump is momentarily stopped. The drop in viscosity willl continue until the minimum has been reached and the viscosimeter pointer begins to move up again. The shape of the viscosity curve for the fat mixture in question will, hence, be well-defined and there will be no difficulties in finding a suitable point of control for the regulation of the fat-lye ratio.

The unique relationship between the viscosity of the soap and the equilibrium of its phases offers an opportunity of using viscosity measurements for the continuous control of the saponification process. This puts an end to time-consuming chemical analyses and also the risk of treating any considerable quantities of soap in an inadequate manner.

The Washing Stage

To recover the glycerine the soap is washed countercurrently by an aqueous electrolyte solution. The solution most generally used is brine (NaCl). The soap is mixed with brine (electrolyte solution) in each washing step; the phases are formed, that is, fitted neat soap and spent lye, then are separated in a Hermetic centrifuge. It is of great importance that the electrolyte concentration be carefully adjusted. A high electrolyte concentration can result in the formation of a grainy soap phase that occludes spent lye containing glycerine. Therefore the presence of this grainy soap phase will impair the efficiency of the washing stage and must be avoided. At too low an electrolyte concentration, nigre may occur, and this will mean an unnecessary loss of soap. Generally an electrolyte concentration of 12–14% as NaCl is maintained.

It is, of course, possible to judge the properties of the different phases occurring in the washing stage by examining samples taken from the separators. However the use of instruments to determine the phase conditions offers a most important means of facilitating the control work. The same viscosity-indicating system as in the saponification stage is used to provide the information necessary concerning the phase conditions of the fitted neat soap.

The amount of brine necessary for the washing is set by adjusting a variable-speed proportioning pump. Pure water and concentrated brine are fed to the suction side of the pump. The spent lye-to-soap ratio (generally some 35–50 kg. spent lye to every 100 kg. of fitted neat soap) is preset by adjusting the pump flow rate. The concentration of the brine is adjusted by varying the quantity of water by means of a rotameter in such a way that the desired phase conditions of the soap are established. This may easily be checked by the viscosity readings at the instruments. It is possible to arrange the adjustment of the electrolyte concentration along completely automatic lines if desired. The concentration of free alkali in the spent lye is dependent to some extent on the operating conditions and the excess lye in the saponification stage. Generally the excess lye ranges between 0.1% and 0.3% in the saponification stage.

The glycerine yield and the glycerine concentration in the spent lye as well as the glycerine content of the finished soap depend upon a number of factors. The most important are as follows: the amount of glycerine in the initial material that may be recovered theoretically; the soap-to-spent lye ratio; and the number of washing steps.

Assuming that the recoverable glycerine content of the initial fatty charge amounts to 10% and that some 40–45 parts of spent lye are used for every 100 parts of washed soap, the glycerine recovery in a soap plant comprising three washing stages and one fitting stage will be 90–95%. The glycerine concentration in the spent lye would be 14–16%, and the glycerine content of the fitted soap would be approximately 0.5%.

The Fitting Stage

Although glycerine, water-soluble color pigments, and other impurities are removed by the washing operation, the washed soap still contains various fat-soluble impurities, such as hydroxy fatty acids and low-molecular-weight fatty acids. Under certain conditions these impurities may impair the quality of the finished soap. The fitting operation has been included so that these impurities may be removed and milling properties of the soap improved.

Every soapmaker knows the difficulties that are often associated with a correct fitting operation. It is therefore a matter of great importance that the continuous soap process permits automatic regulation in the fitting stage. The underlying principle of this constant-composiiton control system has already been mentioned in the description of the saponification stage. Its function in the fitting stage may be readily illustrated by Figure 4. As may be seen, the soap in the fitting stage has its lowest viscosity in the central portion of fitting area G. A study of the fitting operation of a soap mixture containing 65% soap will show the following picture. At low electrolyte concentrations the soap is a mixture of nigre and middle soap, possibly also containing some neat soap (area F). At 0.83% electrolyte content (point a) the fitting zone is entered, and the soap now comprises two phases, nigre and neat soap. As the electrolyte content increases, there is a drop in viscosity. The minimum viscosity at this soap concentration is at an average electrolyte content of about 1.1%. As the electrolyte content increases, there is an increase in viscosity, and at 1.25% electrolyte (point b) the boundary of the three-phase area is reached. At higher electrolyte content the soap mass is comprised of three phases which are neat soap, nigre, and spent lye. This would occur on the diagram of electrolyte contents between 1.25% and 1.38%, that is between points b and c.

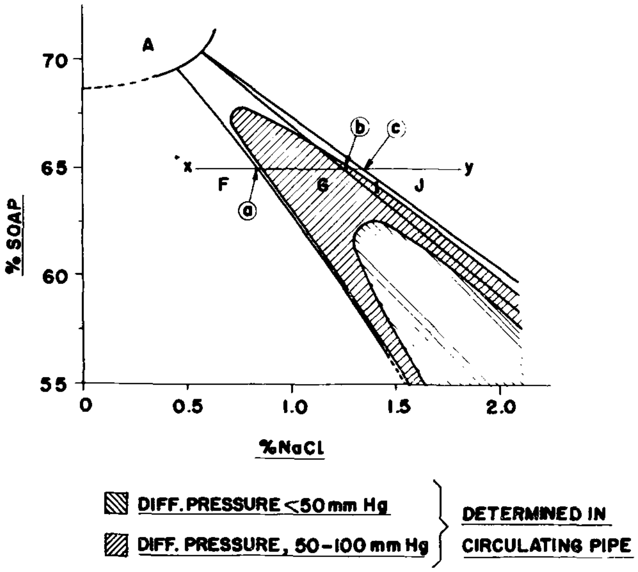

Fig. 4. Phase diagram with isobars.

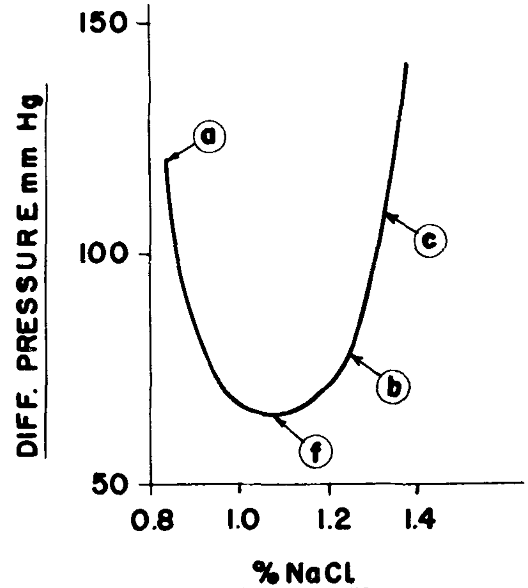

Fig. 5.

When carrying out the fitting operation two variables must be fixed. One is the soap content of the entire soap mass. This is adjusted by means of the proportioning pump for the fitting electrolyte. The other is the desired composition of the nigre. This factor is set by means of the electrolyte concentration. It is controlled from the changes in viscosity.

A typical viscosity curve of a fitting operation is shown in Figure 5. When soap is to be fitted from a fatty stock of unknown composition, a high electrolyte concentration in the salting-out area, or three-phase area, is used initially. The electrolyte concentration is then quickly reduced until the minimum point on the viscosity curve has been reached. A suitable point of operation is then adjusted on the right-hand branch of the control curve.

If a nigre of high soap content is desired, the working point is established near the minimum of the control curve (point f). If a "hard" fitting is desired, that is a nigre with low soap and high electrolyte content, the working point is established farther up the control curve between points f and b.

Experience has shown that in practice it is best to carry out the fitting operation along the right-hand branch of the viscosity curve. When working on the left branch of the control curve, between points a and f, the nigre obtained has a high soap content and a small electrolyte content. This type of nigre is very difficult to separate from the neat soap. The nigre under these conditions has a very high viscosity. In addition, the density difference between this type of nigre and neat soap is very low, making centrifugal separation of neat soap and nigre very difficult.

As mentioned, at low over-all electrolyte content, the nigre produced contains a comparatively large amount of soap. When operating along the right-hand branch of the viscosity curve however, the nigre phase will decrease in soap content and increase in electrolyte as the viscosity increases. At high electrolyte contents the conditions of the fitting operation begin to resemble those of the washing operation, and the desired improvement in the qualities of the neat soap can no longer be obtained.

The relationship between the over-all electrolyte content of the soap and its viscosity is almost independent of the composition of the initial fatty charge as far as the fitting stage is concerned. In the saponification stage this was not the case since the glycerine content of the raw materials exerts a strong influence on the viscosity curve. In the fitting step where there is almost no glycerine present, small changes in the soap because of variations in the feed stock have very little effect on the viscosity. At all times the fitting is thoroughly controlled by the automatic constant-composition instruments. The neat soap is produced at the precise degree of fitting desired, and the quantity of nigre formed is accurately controlled.

In the manufacture of toilet soap with its severe demands on the over-all electrolyte content of the finished soap, it is extremely important to use a highly efficient centrifugal separator in the fitting step. The over-all electrolyte content of the finished soap is dependent on the composition of the original fatty charge, particularly on its content of low-molecular fatty acids. From our numerous tests it is felt that the values obtained under practical plant-operating conditions will be only 0.03% over the theoretical values. For the majority of toilet soaps this would correspond to an over-all electrolyte content of 0.38% to 0.43%.

It is possible to set the NaOH-to-NaCl ratio, within certain limits, by choosing a suitable fitting electrolyte. The free NaOH content may be kept as low as 0.02% without difficulty.

To avoid increasing concentrations of hydroxy acids and low-molecular fatty acids, a certain part of the nigre is continually bled off from the system. Normally up to 10% of the nigre is sent to the slop tank for rework while the rest will be returned to the last washing stage.

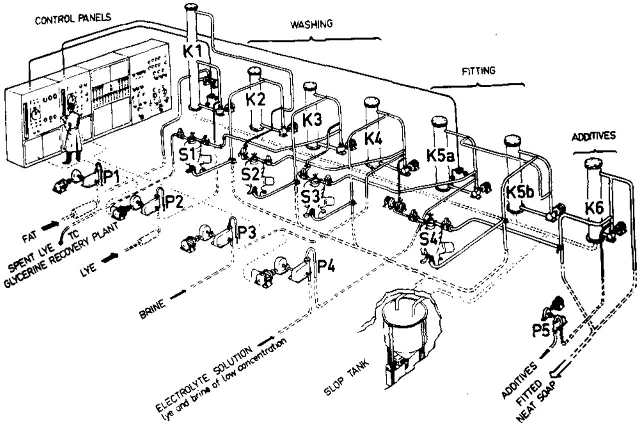

Fig. 6.

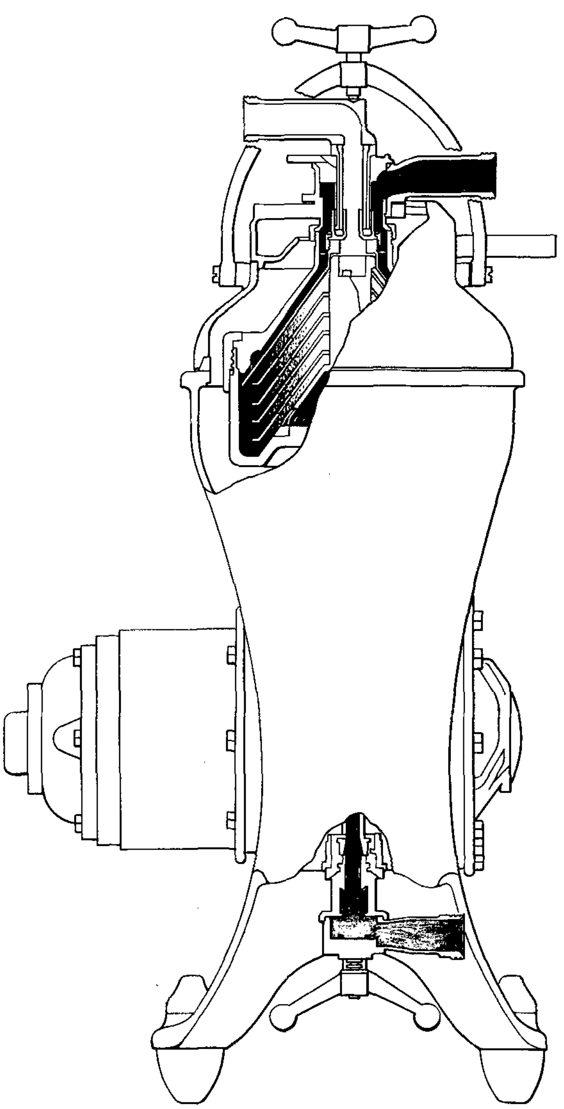

Fig. 7. De Laval "hermetic" separator.

The Plant Operation

This process consists of a hermetically closed, completely automatic system controlled from one instrument panel. The over-all process is illustrated in the flow sheet shown in Figure 6.

The raw fatty material and caustic soda solution enter the saponification reactor by means of pumps P1 and P2, respectively. The completely saponified soap leaving reactor K1 then flows to the washing section. Here the soap is countercurrently washed with electrolyte and after each wash is centrifugally separated. The mixing towers of the washing section are shown as columns K2, K3, and K4. The Hermetic centrifugal separators for the washing section are designated as S1, S2, and S3, respectively.

The completely washed soap leaving the washing section then enters the fitting section. After reaching phase equilibrium for the fitting in columns K5a and b, the fitted neat soap is separated from the nigre in the Hermetic centrifuge designated as S4.

The fitted neat soap then may go to the additive section, designated as column K6, where the soap may be mixed with certain fillers.

As mentioned, this process is continuously operated under automatic constant-composition control in a completely air-free hermetic condition. This is accomplished by utilizing Hermetic pressure centrifuges for all separation in the various stages. The centrifuge used is of the type shown in Figure 7 (6). The material to be separated enters the bowl through the hollow spindle. At the inlet to this hollow spindle is a special feed pump mounted directly on the spindle. By means of this built-in pump the material is forced to the separating zone of the centrifuge bowl. Here separation of the light component (soap) from the heavy component (spent lye or nigre, depending on the stage) occurs. These components then flow respectively to the next processing stage without the need of intermediate booster pumps.

Summary

A new continuous process for the manufacture of soap is described, detailing the three main operations in soapmaking, that is, saponification, washing, and fitting.

In the new process all operations involved in the production of soap are carried out in a hermetically closed system. The amounts of lye necessary for the saponification as well as of brine for the washing and fitting operations are regulated by the automatic constant-composition control system, which eliminates the older method of control of the soapmaking process by cumbersome chemical analyses.

The process is based on the use of the Hermetic separator, a centrifuge of special design which allows the regulation of the separation efficiency during operation and which prevents any admixture or contact of the soap with air and consequently any oxidation of the product during processing.

All types of soap, high grade toilet soap as well as laundry soap and industrial soaps, can be produced by this process, which is characterized by high flexibility, low operation-costs, and a high quality of the finished product.

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X-Ray Diffraction Study of Some Normal Alkyl Thiolesters of Long Chain Acids

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RECENT PUBLICATIONS (2, 3) described the preparation of some normal alkyl thiolesters of long-chain acids. Many of the thiolesters of long-chain fatty acids are solid crystalline materials at ordinary temperatures, suitable for characterization by X-ray diffraction. In this paper long spacings taken from X-ray diffraction powder data are reported for 39 *n*-alkyl thiolesters of normal long-chain aliphatic acids containing an even number of carbon atoms, namely, lauric, myristic, palmitic, and stearic acids. The length of the *n*-alkyl groups attached to sulfur varied from 7 to 18 carbon atoms, with individual groups containing even or odd numbers of carbon atoms.

Experimental

The thiolesters used were those prepared recently by Sasin and Sasin *et al.* (2, 3). The compounds used were crystallized from acetone at room temperature. X-ray diffraction measurements were made with a General Electric XRD-3 direct recording unit, using nickel-filtered CuKα radiation ($\lambda = 1.5405$ A), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, scanning speed 2° per minute, chart speed 60 in. per hour, linear scale, 2-second time-constant. The long-spacing values given in Table I were obtained from oriented unground samples. The unground samples were placed in a thin layer on a glass slide and firmly pressed to insure adherence. The exposed surface of the specimen on the glass slide was approximately 0.5 in. wide by 1.0 in. long. These long-spacing values are the average of at least seven orders taken from the oriented samples. The first and often the second and third orders were not included in the average because of the limited accuracy with which they could be measured. In general, the values given in Table I are precise at least to ± 0.05 Å.

Also included in Table I are the relative intensities of the first five orders of long spacing. The relative intensities were obtained as follows. All samples were carefully ground in an agate mortar to minimize orientation. The ground samples were placed in the recess of a plastic holder 1.0 in. long, 0.5 in. wide and 0.015 in. deep and were gently packed to insure adherence. The intensities of the diffraction lines were measured as counts per second at the maximum height minus counts per second of the background, then expressed on a relative scale (I_{Rel}) with the strongest line arbitrarily given a value of 1,000.

The complete X-ray powder-diffraction data for these compounds are not included herein because of the relatively large amount of space that this would require. However the data were sent to the Joint Committee on Chemical Analysis by Powder-Diffrac-

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[1] Submitted by D. A. Lutz in partial fulfillment of the requirements for the Master of Science degree at Drexel Institute of Technology.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.