

May 20, 1941.

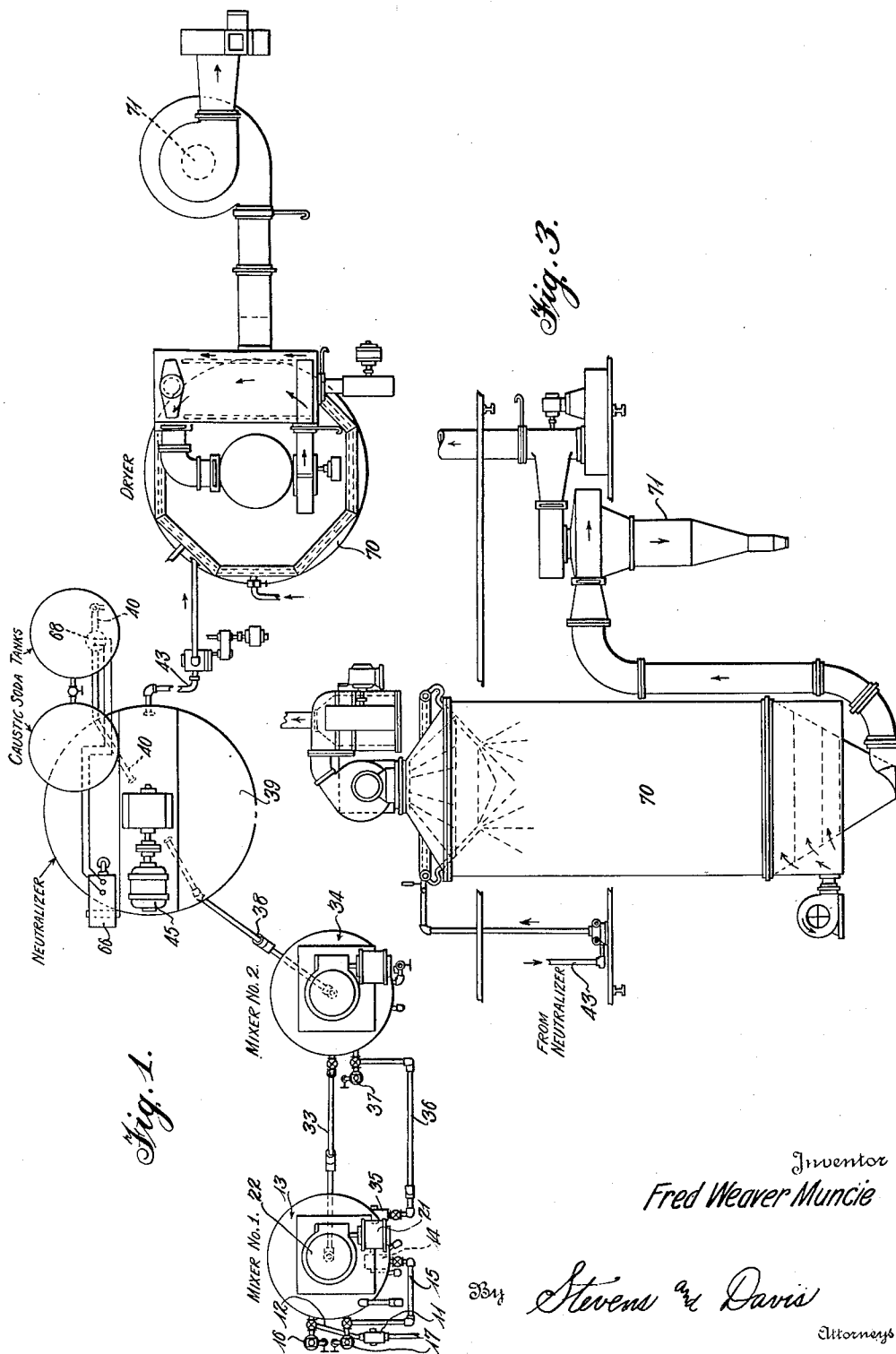
F. W. MUNCIE

2,242,979

DETERGENT

Filed Sept. 19, 1939

4 Sheets-Sheet 1



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4 Sheets-Sheet 2

Fig. 2.

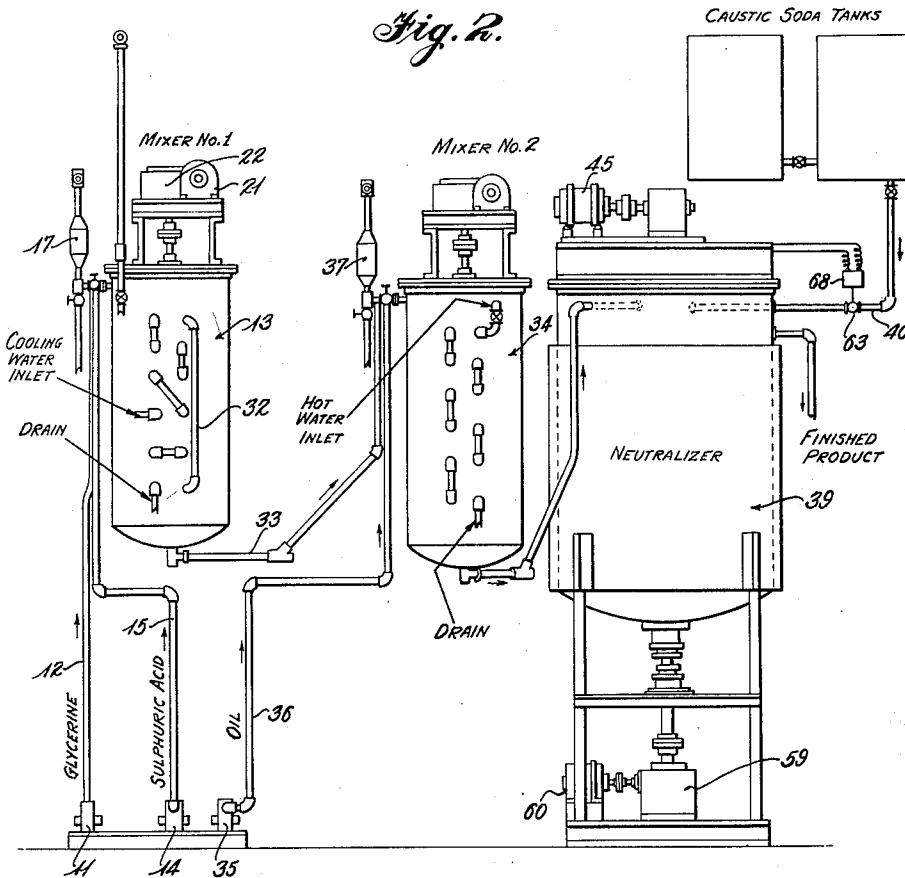
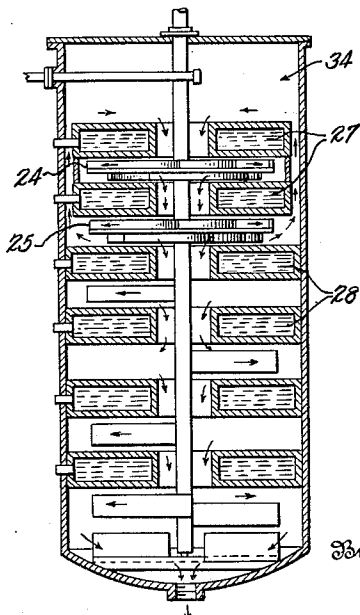


Fig. 6.



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Fig. 4.

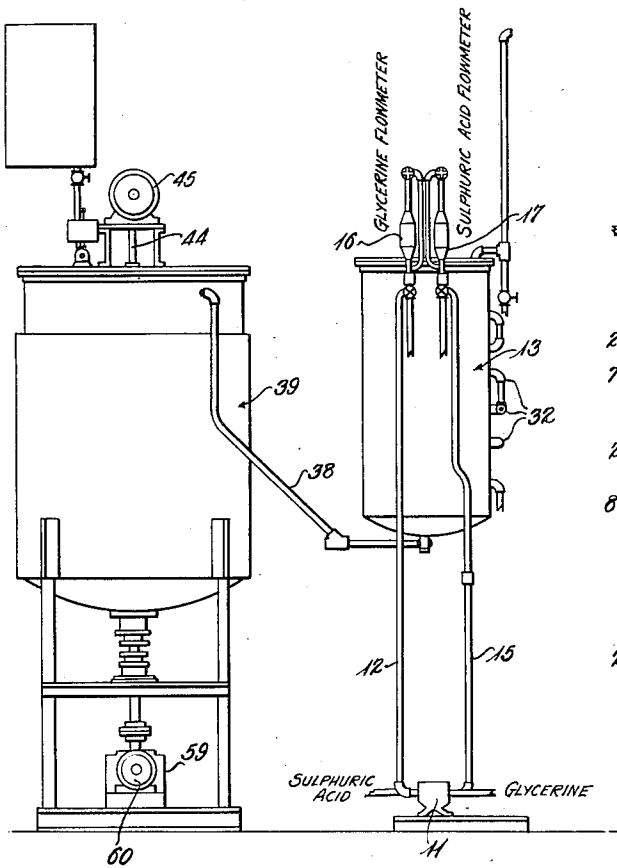


Fig. 5.

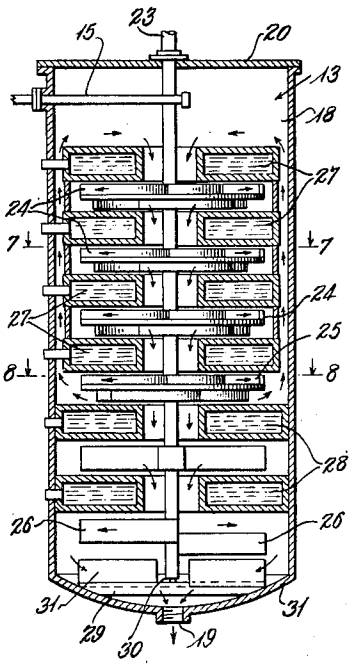


Fig. 7.

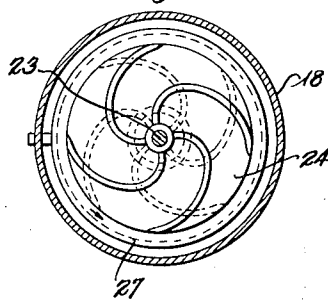
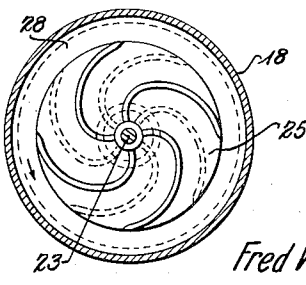


Fig. 8.



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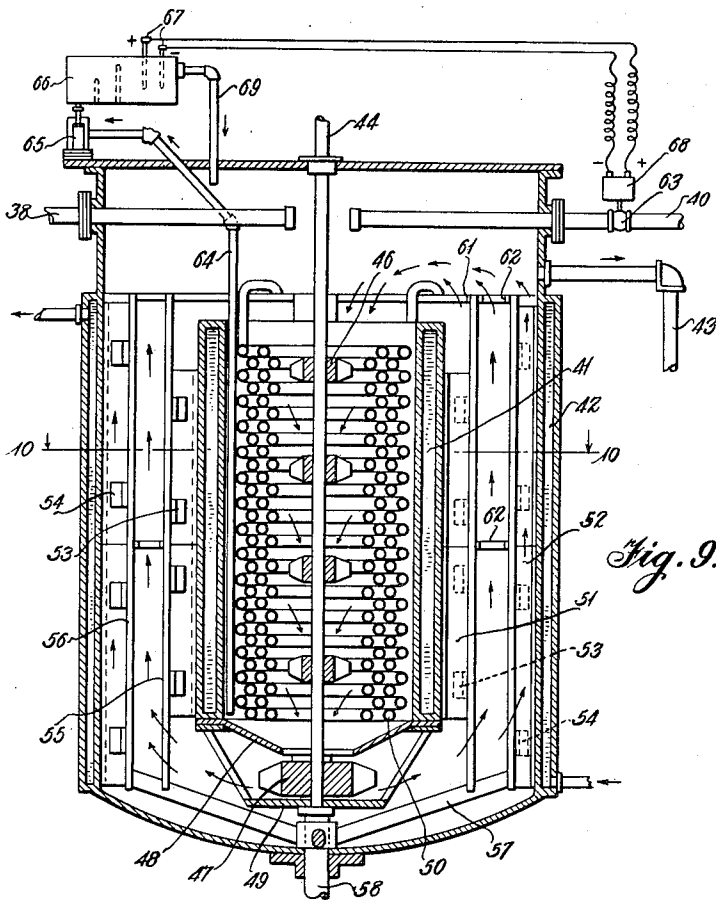
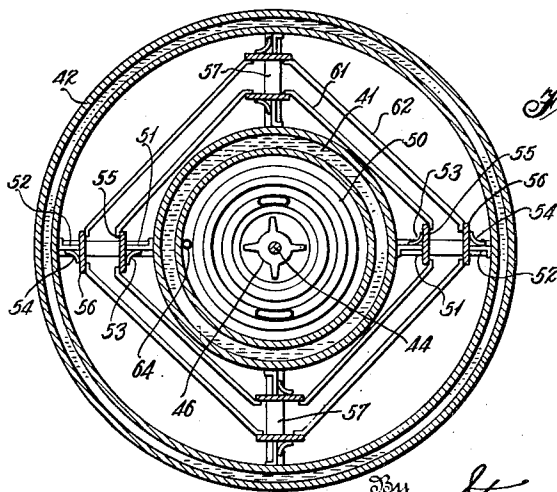
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4 Sheets-Sheet 4



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UNITED STATES PATENT OFFICE

2,242,979

DETERGENT

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Application September 19, 1938, Serial No. 230,675

19 Claims. (Cl. 260—400)

This invention relates to the art of washing or deterging. It concerns particularly, certain new, highly effective detergent materials, their use, and an improved process and apparatus whereby these materials may be manufactured speedily and economically by a continuous process if so desired. The new materials are far superior to ordinary soaps as detergents in hard water, and according to the present invention may be produced at a cost sufficiently low to enable them to compete on a direct price basis with ordinary soap for domestic use.

Ordinary soaps, that is, the alkali metal salts of the fatty acids, have been in use for many, many years, and consequently, the commonly used soaps and the processes of manufacturing them have become quite standardized. To supply the demand requires large soap manufacturing plants involving large initial investments and large upkeep expenditures, this being mainly due to the fact that the saponification process in large scale production requires kettles of enormous size and power sources of commensurate size to furnish the necessary heat for the reaction.

In a copending application by this inventor, Serial Number 28,712, filed June 27, 1935, now Patent No. 2,130,362 products of the general type of those adapted to be produced according to this invention are described in detail, and a process is there given by which they may be prepared. In copending application Serial No. 28,711, filed June 27, 1935, now Patent No. 2,130,361 there is given another method for producing an improved variety of the same general type of material, and also, apparatus for accomplishing the preparation of the new products economically and in a continuous manner. The products produced according to that process are somewhat improved over those produced according to the first mentioned application, although they are apparently of the same general type. This application is directed more especially to the apparatus disclosed in application Serial No. 28,711 and to details of the process intimately connected therewith.

As has been emphasized in the copending applications mentioned above, the business of merchandising domestic soaps has become highly competitive, particularly in recent years. To meet this competition many new detergent materials have been produced, most of which are sulphonates or sulphuric acid esters of organic compounds. The sulphonated alcohols are among the better known of these compounds.

While the sulphonated or sulphuric acid ester

products heretofore known have certain advantages over ordinary soaps in that they are not alkaline, do not form insoluble salts with calcium and other metals, and have a high detergent power, nevertheless, such products have not replaced ordinary soap for domestic use, primarily because they are too expensive to manufacture.

The purpose of the invention described in the copending applications is to provide a new type of product of this general kind, that is superior to soap in hard water, at a cost comparable to that of soap, whereby the new product may be sold in direct competition with ordinary soap for domestic use. This will give to the public a much improved detergent product at a price that will encourage the use of the new product despite the keen competition that now exists in the soap merchandising field.

According to the applications mentioned, the new products are formed by the interaction of a fatty oil, anhydrous glycerine, and fuming sulphuric acid, preferably in the approximate proportion of one molecular weight of fatty oil to two molecular weights of glycerine and in excess of three molecular weights of sulphuric acid. Preferably, the resultant product and the excess of sulphuric acid is then neutralized with a concentrated solution of caustic soda or a similar base. In the examples given in application Serial No. 28,712, the glycerine and fatty oil are first reacted by heating to around 175° to 205° C., in the presence of a small amount of caustic soda, or at 280° to 290° C., in the absence of caustic soda. The resultant product is thereafter treated with the sulphuric acid and finally neutralized.

According to application Serial No. 28,711, it has now been found that the preliminary reaction of fatty oil with glycerine is unnecessary. When the three ingredients, in the proportions given, are mixed at a temperature not greatly above room temperature, simultaneously, or in any desired order, an equilibrium results with the formation of the same type of product that is produced according to the examples in the copending application. It appears that the sulphuric acid, in the amount and concentration used, acts in a four-fold capacity; namely, as a hydrolytic agent toward the triglyceride, as an esterifying agent, to sulphate the composition, and for the absorption of the water of reaction. While all of the ingredients may be mixed simultaneously, the preferred mode of reaction is to mix the glycerine and sulphuric acid with cooling, and thereafter combine this mixture, at a slightly elevated temperature, with the fatty oil,

since by proceeding in this manner, less darkening is caused by the action of the sulphuric acid on the fatty oil.

This invention, in addition, provides a method by which solutions of the final neutralized material may be obtained at a concentration that allows the production of dry material economically and in the physical state desired for marketing. In the production of dry material by spraying, for example, a bead of satisfactory size and form is best produced by feeding the material to the spray tower in a concentration of 40% or greater total solids. Neutralization of the material at such concentration is practical only at temperatures above about 35° C. since otherwise the slurry is so stiff that satisfactory mixing and cooling cannot be obtained. However, when an attempt is made to neutralize the material at a sufficiently high temperature to make it as fluid as is necessary, difficulty is encountered because of decomposition of the product caused by the combination of high acidity or alkalinity and the heat of reaction. To prevent this, according to the present invention, neutralization at high concentration and at relatively high temperatures is accomplished by flowing one or more streams of the acid reaction product and one or more streams of a concentrated neutralizing solution directly into confluence, in the exact proportion required for neutralization. This is made practical on a commercial scale by the use of an automatic pH control device to regulate the amount of the neutralizing solution added. The result is that the neutralization takes place before the decomposition can be caused, and there is then no acidity or alkalinity to further the decomposition.

The neutralization may alternatively be carried out by the addition of slightly less than the proportion of alkali required for complete neutralization, in order to keep the mixture slightly on the acid side until a considerable quantity of material has accumulated, after which the whole may be brought to the exact pH desired. This procedure is sometimes desirable because of the greater resistance of the product to hydrolysis by acid than by alkali.

The mixing of glycerine and sulphuric acid and the reaction of this mixture with fatty oil being simple operations and requiring only a short time of contact, it has been found convenient to conduct the entire process continuously from the initial operation of mixing acid and glycerine to the drying of the product by spraying or over a heated roll.

In its preferred form, the present invention contemplates the continuous mixing of substantially anhydrous glycerine and fuming sulphuric acid in accurately measured proportions at a controlled temperature and the reacting of the combined acid and glycerine with an accurately measured proportion of fatty oil, also at a controlled temperature, but which temperature is usually different from that at which the glycerine and acid are mixed. Further, according to the present invention, the mixing of a neutralizing agent with the glycerine-acid-fatty oil product and the control of the amount of neutralizing agent added in accordance with the hydrogen potential (pH) of the final product may all be accomplished continuously. The invention also includes, if desired, the spray drying of the final product to form beads of a pure, white appearance that are readily soluble in either hot or

cold water. Alternatively, the material may be dried over a heated roll.

While the above process may be considered the preferred embodiment, manufacturing methods and particularly the neutralization step as described in this application may, within the scope of this invention, be applied to making this type of detergent, by the process described in the copending application. Thus, a process may be performed according to this invention by continuously mixing the glycerine and fatty oil with caustic soda in accurately controlled proportions, continuously subjecting the mixture to a controlled elevated temperature of around 175° to 205° C. (or around 280° to 290° C. in the absence of caustic soda) to effect the first reaction, thereafter continuously reacting the product with a predetermined proportion of fuming sulphuric acid; and subsequently, continuously neutralizing as before by passing the product into confluence with the neutralizing agent, the amount of neutralizing agent being controlled by the hydrogen ion potential of the final product. Alternatively, the reaction product of fatty oil and glycerine made by the batch process may be passed continuously into confluence with the fuming sulphuric acid and subsequently neutralized continuously by passing it into confluence with the neutralizing agent.

If desired, instead of using a continuous process, the new detergents may be made according to the new process of this invention by reacting the fatty oil, glycerine, and sulphuric acid in the desired proportions, simultaneously or in any desired order, by the batch instead of continuously, and the neutralization may also be performed by the batch. In such instances and also in the continuous process, it is preferred to mix the sulphuric acid and glycerine before contacting either with the fatty oil in order to prevent a darkening of the oil by the action of the acid. This, however, is not imperative and the reactants may, less desirably, be mixed in a different order.

As a specific example of a process of making the new detergents according to the present invention, 64 pounds of anhydrous glycerine (99.5%) have been mixed with 526 pounds of fuming sulphuric acid (102.8%) at around 30° C. and the mixture stirred with 216 pounds of coconut oil at a temperature of 50° C. or slightly less. Fuming sulphuric acid of 102.8% concentration contains about 12½% excess sulphur trioxide. The reaction completed itself within approximately 40 minutes, and the product was thereafter neutralized in the manner above described at a temperature of about 40° C., preferably to a pH of 6.0 to 7.0. If a 30% aqueous solution of caustic soda is used to neutralize the product, the resultant solution will contain about 46% total solids of which around 40% will be the organic reaction product, and around 60% sodium sulphate. This combination of organic reaction product and sodium sulphate has been found very satisfactory for use as a domestic detergent in place of soap, but the percentage of sodium sulphate may be varied by a change in the proportion of sulphuric acid used, or may be removed entirely, if desired.

In place of 216 pounds of coconut oil, given in the above example, 272 pounds of tallow or palm oil may be used, or a mixture of oils may be employed. Glycols may also be substituted for glycerine, due allowance being made for the difference in their molecular weights.

In deciding upon the amount and concentration of sulphuric acid to use in the preparation of the new compounds, it has been found that, in general, enough sulphuric acid should be provided to fulfill the molecular weight requirements given above, namely, three molecular weights for every two molecular weights of glycerine and one molecular weight of fatty oil, and in addition, there should be an excess of sulphuric acid sufficient to absorb one molecular weight of water for each molecular weight of sulphuric acid that is to enter the reaction. Since this water needs to be absorbed readily, it is preferable that the amount and concentration of the excess of sulphuric acid be such that after absorbing the water the concentration of the excess sulphuric acid will still be at least about 99.3%. From this information the amount and concentration of the sulphuric acid, which it is desirable to use, may be readily calculated.

In neutralizing the acid reaction product by flowing the acid and neutralizing material into confluence under closely controlled conditions according to this invention, it has been found possible to use even stronger neutralizing solutions than the 30% caustic soda solution mentioned in the first example and to conduct the neutralization at a temperature considerably in excess of 40° C. This is of advantage for it permits the direct manufacture of more concentrated solutions of the detergent material, from which the final products may be more easily made.

The solution of the neutralized reaction product may be dried either by the spraying method set forth in United States patent to Dallas R. Lamont No. 1,652,900, or by other well known soap drying methods. The dried material, as made by the process of the first example, contains around 60% of sodium sulphate and 40% of the organic material, and will form a dry, granular, non-hygroscopic powder at room temperature. When warmed somewhat or compounded with an appropriate amount of water, glycerine or mineral oil, it may be milled, plodded or pressed into cakes by the use of the usual soap molding machinery.

As has been said, the sodium sulphate or other sulphate formed by the neutralization can be removed, if desired, but this is not usually necessary, and, in fact, the presence of this inorganic salt in the final products, in many instances, appears to improve the desirability of the material, particularly for domestic use. The product made according to the first of the above examples will contain about 60% sodium sulphate. For some purposes, however, it may be desired to produce a detergent according to the present invention but free from the inorganic sulphates formed by the neutralization. To eliminate this sodium sulphate it has been found easier to modify the original process by which the material is produced than to attempt to remove the sodium sulphate, once it has been formed in the composition.

As an example of a process by which the new materials may be formed and freed of inorganic salts, the fatty oil, glycerine, and sulphuric acid may be reacted as in the first example above. Then, instead of neutralizing with caustic soda, about 400 pounds of hydrated lime may be added to the mixture as a 10% slurry. Calcium sulphate will be formed from the excess sulphuric acid and lime, and will precipitate. The calcium salt of the new detergent product is soluble,

however, and the mixture may be filtered to remove the calcium sulphate. Preferably, an amount of water equal to the amount of the solution is used to wash the calcium sulphate free of detergent product. The solution, containing the calcium salt of the new material, may then be treated with a solution of sodium carbonate or sodium phosphate or sodium oxalate or other suitable calcium precipitant in an amount slightly in excess of that required to replace all of the calcium in the detergent with sodium and precipitate the calcium as the carbonate, phosphate or oxalate, or other insoluble calcium compound. This precipitate may also be filtered off, and the remaining solution is then ready for concentration as desired.

In order to stabilize the new product, the solution may, if it is found necessary, be adjusted to a pH of 6.0 to 7.0. Thereafter, it may be concentrated by boiling until it has the correct solids content for whatever use it is required. The solution may be evaporated to form a solid product from a concentration of around 25% or over by spraying, or by the use of drying rolls, or by any other suitable method. The anhydrous product when warm is soft and flexible, but becomes quite hard and brittle at room temperature, and can be prepared as a powder. A 20% aqueous solution of the salt free product is liquid at temperatures above 10° C.

In some instances, it may be desirable to use the calcium salt of the new material directly without converting it into the sodium salt, and in other cases, it may be to advantage to form the corresponding ammonium, triethanolamine, magnesium, potassium or other salts. These may be formed in the same manner as the sodium salts, or ammonia or triethanolamine may be added together with carbon dioxide to precipitate the calcium, instead of adding their carbonates or oxalates, sulphates or phosphates.

The calcium salt may be dried over a heated roll. In this case, a low temperature of drying is desirable, since the product has a tendency to char. The use of vacuum with the roll is desirable, or the product may be mixed to a slurry with a filler, such as calcium sulphate, chalk, bentonite, pumice or clay, and dried by means of the roll.

A product free from inorganic salts may be formed from the product made according to the example, if so desired, by extracting the product with alcohol to remove the product and leave the inorganic salt. Alternatively, the product may be extracted before neutralization, but after sufficient dilution to prevent reaction, with butyl alcohol. The butyl alcohol solution is thereafter neutralized with caustic or the like to the proper pH of around 6.0 to 7.0. Other solvents can be used in place of the alcohol and butyl alcohol mentioned.

In order to aid in the identification of the new products and to demonstrate their effectiveness as detergents, certain tests have been performed upon a product made according to the example and containing 60% sodium sulphate, and upon the same product without the sodium sulphate. The sodium sulphate containing product gave 450 cubic centimeters of foam when 50 cubic centimeters of an aqueous solution containing 1% of the material (total solids) were shaken thoroughly in a 500 cubic centimeter closed, graduated cylinder. The surface tension of a 0.25% solution was measured as 31.5 dynes per cm. and a

0.125% solution registered 31.3 dynes. The du Nuoy tensionometer was used according to the du Nuoy procedure.

Using a 1% solution of the sulphate containing material (60% sodium sulphate) as solution #1 and a 1% solution of the sodium sulphate free material as solution #2, and adding there-to equal volumes of a number of reagents in 10% solutions and at room temperature, the following results were noted:

	Reagent	#1	#2
1	CaCl ₂ ·2H ₂ O	No precipitate.	No precipitate.
2	BaCl ₂	White flocculent precipitate.	Do.
3	(NH ₄) ₂ SO ₄	No precipitate.	Do.
4	KCl	Slight turbidity.	Slight turbidity.
5	MgCl ₂ ·6H ₂ O	No precipitate.	No precipitate.
6	AlCl ₃	do.	Do.
7	Pb(C ₂ H ₃ O ₂) ₂	White flocculent precipitate.	Do.
8	CuSO ₄ ·5H ₂ O	do.	Do.
9	FeCl ₃	do.	Do.
10	ZnCl ₂	do.	Do.
11	AgNO ₃	do.	Do.
12	HgCl ₂ (saturated)	do.	Do.
13	Sea water	do.	Do.
14	HCl	No turbidity.	No turbidity.
15	Hard water (600 ppm.)	No turbidity cold or hot.	No turbidity cold or hot.

A test was also made of the detergent power of several well known detergents and of the sodium sulphate containing product made according to the example. The Standard soil test was used and the following results obtained with a Pulfrich photometer:

Product tested	Relative detergent efficiency	
	Soft water 50 ppm.	Hard water 300 ppm.
1 Palm and olive oil soap	100.0	100.0
2 Sodium lauryl sulphate	106.9	123.6
3 Sodium oleyl methyl taurine	96.4	106.7
4 Present product	111.5	140.9

While cocoanut oil has been named in the above examples, it is to be understood that the use of other fatty oils will also result in satisfactory products, due allowance being made for the difference in molecular weights. Among the oils which have been satisfactorily used are tallow, soy bean oil, and palm oil. In fact, it has been found that oils ordinarily considered to be inferior for the purpose of making soap, may be used according to this invention to produce products of a very good grade, and the use of even such materials as fish oils and garbage grease is within the scope of this invention. Also glycol or other polyhydric alcohols may be substituted for glycerine, and other sulphating or even phosphating compositions may be substituted for sulphuric acid. Monoglycerides may also be formed by reaction with glycerine or fatty acids, naphthenic acids, abietic acid or the carboxylic acids produced by the air oxidation of paraffin hydrocarbons, and thereafter reacted with sulphuric acid substantially as indicated above.

The products formed according to this invention are generally similar in properties to those described in the copending applications, but show some advantage apparently due to the improvement in the method of their preparation. It has not been possible, however, to explain the improvements in the product on the basis of a

change in chemical structure, so no new theory of the structure will be here advanced.

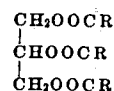
It is not desired in the present application to be in any way bound by the structural formula which the products herein described are believed to have, or by the chemical reactions which are thought to take place during the formation of the products. The oils from which the products are made are known to be of a complex nature, and the literature and researches upon the subject fail to give any absolute assurance as to the reactions that take place or the structural formulas of the compounds formed. Furthermore, since the oils are complicated mixtures of organic compounds, it is possible that the different compounds react differently with the glycerine and sulphuric acid, and it may be that this fact accounts for much of the value of the final product.

The following tentative explanation of the reactions and formulas are, therefore, given merely in order to aid in understanding this invention and with the reservation that they are but tentative.

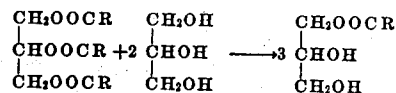
In the examples above given, cocoanut oil, glycerine, and sulphuric acid were specified as the main raw constituents. Cocoanut oil is comprised mainly of triglycerides; that is, glycerine esterified with three molecules of fatty acid per molecule of glycerine. The fatty acids present in these esters in cocoanut oil are usually about as follows:

Lauric acid	45%	CH ₃ (CH ₂) ₁₀	COOH
Myristic acid	20%	CH ₃ (CH ₂) ₁₂	COOH
Capric acid	10%	CH ₃ (CH ₂) ₈	COOH
Caprylic acid	9%	CH ₃ (CH ₂) ₆	COOH
Oleic acid	6%	CH ₃ (CH ₂) ₇	CH:CH(CH ₂) ₇ COOH
Palmitic acid	5%	CH ₃ (CH ₂) ₁₄	COOH
Stearic acid	3%	CH ₃ (CH ₂) ₁₆	COOH
Caproic acid	2%	CH ₃ (CH ₂) ₄	COOH

For every three molecules of fatty acid present there is, of course, approximately one molecule of glycerine, and when these fatty acids and the glycerine are combined, three molecules of water are dropped from the composition. The fatty acids in the oil may vary and, of course, will differ when the kind of oil is changed, but by using R as the fatty acid radical, the formula for the triglyceride may be considered to be

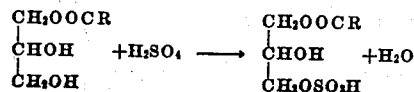


When one molecule of triglyceride of this formula is reacted with two molecules of glycerine, it appears that the following reaction may take place:



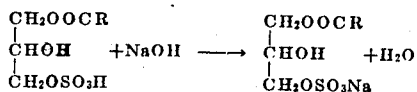
This reaction takes place upon the application of heat and is aided by the presence of caustic soda or other alkali, soaps, alcoholates, certain metals and other catalysts. The resultant products may be designated monoglycerides.

The addition of fuming sulphuric acid to the monoglyceride effects the formation of a new product, apparently according to the following reaction:



This product, when neutralized with caustic

soda, results in the final product apparently of the formula:



At the same time, any excess of sulphuric acid is converted into sodium sulphate.

According to the reactions and the formula given, the active ingredient in the final product is the monoglyceride sulphate of sodium, either with or without a quantity of sodium sulphate formed in the neutralization.

It is intended that the present products shall be used directly in place of the ordinary soaps, particularly for laundry, toilet uses and general domestic purposes, but it is possible to use the new products in combination, either with the ordinary type of soap or with other types of sulphated or sulphonated detergents or wetting agents. The new material may be compounded with sodium silicate, talc, pumice, whiting, feldspar, naphtha, phenols, titanium dioxide, barium sulphate or other materials commonly incorporated in soap.

The final products may be obtained by suitable manipulation in the form of cakes, powder, flakes or solutions and are adaptable for use as ingredients in shaving, facial or dental creams, liquid shampoos, mouth washes or cleansing solutions, shampoo or dental powders, as an addition to dye-stuff baths and for general detergent purposes, either alone or in admixture with soap. Since the products are not precipitated by mercury or silver, they may also be used to advantage in compounding antiseptic or germicidal detergents with mercury or silver salts. Furthermore, the product has a very much milder taste and odor than ordinary soaps prepared from the same oils and is, therefore, of particular value in dentifrices or mouth washes. Also, the material is not precipitated by sea water or hard water, and hence is particularly valuable where such waters must be used.

Additional details and advantages of the new process and of the apparatus specifically disclosed for performing the same will be apparent from a consideration of the accompanying drawings and from the following detailed description.

Figure 1 is a plan view of an apparatus adapted to perform the preferred process of this invention;

Figure 2 is a side elevational view of a portion of the apparatus shown in Figure 1;

Figure 3 is a side elevational view of the spray dryer shown in Figure 1;

Figure 4 is an end view of the apparatus shown in Figure 2;

Figures 5 and 6 are sectional views through the first and second mixers, respectively;

Figures 7 and 8 are sectional views taken on lines 7-7 and 8-8 of Figure 5, respectively;

Figure 9 is a vertical sectional view of the neutralizer; and

Figure 10 is a horizontal sectional view through the neutralizer, taken on line 10-10 of Figure 9.

The apparatus illustrated in the drawings is a plant installation adapted for the continuous performance of the preferred process of this invention. In describing the operation of this apparatus, reference will be made to sulphuric acid, glycerine, fatty oil or coconut oil, and caustic soda. It is to be understood, however, that these are used merely as preferred examples, and other equivalent materials or mixtures of materials may

be used instead. With this understood, it may be said generally that the apparatus operates, first, to mix the glycerine and the sulphuric acid, then to react the mixture with the fatty oil or oils, and thereafter to neutralize the glycerine-acid-fatty oil product with caustic soda.

According to the preferred mode of applying the principles of this invention, substantially anhydrous glycerine (around 99.5%) is supplied through a pump 11 and pipe 12 to the first mixer 13. At the same time, fuming sulphuric acid (around 102.8%) is supplied through a pump 14 and pipe 15 to the same mixer. The pumps 11 and 14, and a pump for the fatty oil which will be later described, are preferably geared together, so that each will supply its respective reactant in exactly the desired proportion. Numerous types of proportioning devices are known and any one of these which is found suitable may be used in place of the pumps shown. As an additional precaution to permit certainty with respect to the proportions of the reactants entering the mixer 13, volometers or flowmeters 16 and 17 may be connected to the glycerine pipe 12 and the sulphuric acid pipe 15, respectively, near the point where the pipes connect to the mixer. Volometers are calibrated vessels arranged to be filled and the time of filling noted by a stop watch so as to calibrate or adjust the proportioning mechanism. They drain back to the storage tanks after use.

As illustrated in Figs. 5, 7, and 8, the mixer 13 consists of a cylindrical shell 18, closed at the bottom except for a drain opening 19. The top of the mixer is closed by a cover 20 upon which is mounted a driving motor 21 and suitable gearing 22, shown in Figure 2. Through the top of the mixer a rotatably mounted vertical shaft 23 extends, and this shaft is connected to the motor 21 through the gearing so that it may be driven. A series of radially extending mixing paddles 24, 25 and 26 are carried by shaft 23, and these paddles are constructed for movement within spaces arranged between hollow annular members 27 and 28 positioned within the cylinder. Cooling water is circulated through the hollow members by means of pipe connections as shown in Fig. 2.

As illustrated, particularly in Figs. 5 and 8, the paddles and the annular cooling members vary somewhat in form. The four upper cooling members 27 are somewhat smaller in diameter than the inside of the shell 18, and are connected at their outer edges by cylindrical rings, so that a portion of the liquid in the mixer may flow upwardly from below the fourth member between the wall of the mixer and the peripheries of these upper annular members, and thus be mixed thoroughly with the fresh liquid as it enters the mixer. This action is aided by the construction of the paddles in the upper part of the mixer. Each of the three upper paddles 24 consists of a flat circular plate with four vanes extending helically above it to throw the liquid outwardly and four helical vanes below the plate to draw the liquid inwardly and propel it downward through the center opening in the underlying cooling element. The flat circular portions of the paddles completely prevent any of the liquid from passing directly downward along the shaft 23. All of the liquid is thus forced to travel out and around the edges of the circular portions of each of these three upper paddles. The fourth paddle from the upper end is an impeller 25 which must finally be passed by the liquid before

it enters the lower part of the mixer. This impeller is of similar construction to the first three paddles excepting that the four vanes above and the four vanes below the plate are all arranged to throw the liquid outwardly, and thus force a part of the liquid to return to the top of the mixer and induce a maximum mixing action.

The two lower cooling members 28 are fit snugly to the shell by ring members, and therefore, all of the liquid which passes these members must pass through the openings therein which surround the center shaft 23 and none can pass upwardly around the outside. The paddles 26 lying below the fifth and sixth cooling member are but double radially projecting arms fastened to the shaft 23. A cross member 29 is provided at the bottom of the mixer, and this cross member carries a pin 30 which enters an axial opening in the lower end of the shaft 23 to maintain the shaft in alignment. The cross member 29 is further provided with a pair of baffles 31 which retard any rotation of the liquid in the mixer and direct the liquid through the drain opening 19.

As will appear upon consideration of Figs. 4 and 5, the glycerine and sulphuric acid enter the mixer from pipes 12 and 15, and are released into the mixer at the top and near its center. They progress downwardly through the mixer as they become mixed, and the mixture passes out through the drain opening 19. As the glycerine and sulphuric acid are mixed, cooling water is circulated through the cooling members 27 and 28 to keep the temperature sufficiently low to prevent an appreciable darkening of the material. It has been found that a temperature of approximately 30° C. is sufficiently low for this purpose, although lower temperatures may be used and somewhat higher temperatures may be permitted without serious results.

Suitable pipes 32 are provided to supply water to the cooling members, the arrangement being such that the cooling water first enters the lower one of the four upper cooling members 27 from which it progresses upward to the top cooling member. It is thereafter conducted to the sixth or bottom cooling member 28, then to the fifth cooling member and finally discharged. This arrangement has been found to be especially desirable because it maintains a fairly even temperature throughout the mixture, the greatest cooling effect being produced in the upper portion of the mixer where the initial mixing takes place and the tendency for the compounds to react and evolve heat is greatest.

From the bottom of the mixer 13 the glycerine-sulphuric acid mixture is conveyed by piping 33 to a second mixer 34 at a point near the top. Fatty oil also enters this second mixer at a point near the top, being supplied by a pump 35 through a pipe 36. The pump, as already explained, is connected so as to supply a quantity of fatty oil accurately proportioned to the amount of glycerine and sulphuric acid supplied by pumps 11 and 14, respectively. As with the glycerine and sulphuric acid, a volometer or flowmeter 37 is provided for the fatty oil. This device is connected to the pipe 36 at a point near the second mixer, so that the proportion of fatty oil entering this mixer can be readily determined.

The construction of the second mixer 34 is substantially the same as that of the first mixer 13, so that it need not be described in detail although it has been shown in Fig. 6. The heat transfer members, which were cooling members in the first

mixer, are used as heating members in this second mixer, and hot water is passed therethrough to effect the heating. The hot water need not be circulated through the members in the order that the cold water was circulated through the cooling members in the first mixer, but instead, the water may first enter the top heating member and then progress downward through the next adjacent members in regular order to the lowest member from which it is discharged.

Furthermore, there are but two of the smaller sized heat transfer members at the top of this second mixer, and only one of the paddles has its vanes arranged to throw outwardly above and draw inwardly below the flat circular portion. All of the vanes on the second paddle throw outwardly. The lower part of the second mixer includes only heat transfer members fitting closely in the shell, and only double bladed radially extending mixing paddles are employed therebetween. Preferably, the average temperature in this mixer is around 50° C.

From the bottom of the second mixer the glycerine-acid-fatty oil reaction product is conveyed to the top of a neutralizer 39 by a transfer line 38. The neutralizer comprises a large cylindrical tank that contains mixing and cooling equipment sufficient to thoroughly mix, at a controlled temperature, the glycerine-acid-fatty oil product with a neutralizing material, which is preferably caustic soda. The caustic enters the upper part of the mixer through a pipe 40, preferably as a solution of 30% to 50% concentration, being discharged into the neutralizer at about the same point as the reaction product so that the two materials pass into immediate confluence and the process of neutralization begins at once. Upon the admission of the caustic and the reaction product into the neutralizer, the materials first pass downwardly through a cooling cylinder 41 and then upwardly between the outside of this cylinder and the wall of the neutralizer, which wall forms an additional cooling surface 42. Upon circulating to the upper end of the neutralizer, a part of the product is drawn off through a pipe 43 and conveyed to the drying equipment. The remainder is recycled with the incoming reaction product and caustic solution.

In order to thoroughly mix the caustic solution and the reaction product, agitation is provided in the form of a shaft 44 which extends downwardly through the top of the neutralizer and axially through the center of the inner cooling cylinder 41. This shaft is driven by an electric motor 45 through suitable gearing all mounted on top of the neutralizer. Shaft 44 carries a series of impellers 46 within the inner cooling cylinder and a larger impeller 47 just below the bottom of the inner cooling cylinder 41 for circulating the mixture. Appropriately shaped deflecting members 48 and 49 are provided to direct the mixture onto the large impeller member 47 so as to obtain a maximum circulatory effect. In the inner cooling cylinder 41, there is an axially extending, cooling coil 50 which provides additional cooling surface, and the cooling water is fed through this coil, into the bottom of the inner cooling cylinder and finally withdrawn from the top of that cylinder.

Between the inner and outer cooling cylinders 41 and 42 are a series of scrapers that continually remove any of the product that solidifies upon the cooling surfaces. As shown in Figs. 9 and 10, these scrapers comprise vertically extending strips

51 and 52, attached to the upright supporting members 55 and 56, and pressed against the inner and outer cooling cylinders, respectively, by springs 53 and 54. The supporting members are in turn mounted upon a spider 57 carried at the center of the bottom of the neutralizer tank upon a rotatable shaft 58 that extends through the bottom of the tank to suitable driving mechanism 59 and motor 60. The lower end of the agitator shaft 44 is rotatably received in a cavity in the upper end of this shaft 58. Braces 61 and 62 may be used to join the scraper supporting members 55 and 56, respectively, so as to make a more rigid construction.

In order to control the amount of caustic added, in accordance with the amount necessary to just neutralize the reaction product, a device is connected to the neutralizer for continuously measuring the hydrogen ion potential (pH) of the neutralized product, and this device controls an electrically operated valve 63 in the caustic line 40. The measuring device comprises a sampling pipe 64, through which a small amount of the mixed materials is continually withdrawn from a point near the bottom of the inner cooling cylinder by the action of a small pump 65. From the pump the material is discharged into a baffle tank 66 in which are electrodes 67 connected to operate the electrically operated valve 63 through an electrometric titration device 68. Thus the amount of caustic supplied is controlled so as to always be just sufficient to neutralize the reaction product, and the neutralized material may be kept accurately at a pH of around 6.0 to 7.0 which has been found highly preferable. The material flowing through the baffle tank is returned to the neutralizer by a pipe 69.

After the product leaves the neutralizer, it is preferably conveyed by the pipe 43 to a spray drying device such as shown in Fig. 3 and described in Patent 1,652,900 granted to Dallas R. Lamont on December 13, 1927. Since this part of the equipment is described in detail in that patent, it will be referred to here only in general terms. The neutralized reaction product of this invention, together with the considerable amount of water which still remains with it, is sprayed in a fine state of subdivision into a drying chamber 70 near the upper end. As it falls it is contacted by a large volume of air forced down through the chamber by suitable pumping mechanism. By the time the product reaches the bottom of the chamber it is dry and in the form of beads. These are drawn off in a current of air into a cyclone separator 71 where they are separated from the air in a form that is ready for packaging.

With the new product there appears to be considerable advantage to spray drying, although, of course, the product may be dried in other ways, if desired. However, if the product is spray dried, it forms beautiful, exceptionally white beads that dissolve instantly in water, either hot or cold.

While the apparatus described has been arranged to mix the glycerine and sulphuric acid prior to reacting them with the fatty oil, it is to be understood that this is only the preferred form and that other arrangements may be made. For example, the glycerine, sulphuric acid, and fatty oil may all enter one mixer together without any previous mixing, or the glycerine and fatty oil may be reacted as originally described in the copending applications or merely mixed, or the sulphuric acid may be mixed with the fatty oil prior to the addition of the glycerine. Also, lime

or other alkaline reagent may be used to effect the neutralization of the produce and suitable means provided to settle, filter or centrifuge the product to remove the precipitate formed.

Other features of the preferred apparatus and process, which have been described above, may be modified or omitted without departing from the broader scope of this invention. For example, the construction of the mixers may be changed so that one mixer accomplishes all of the mixing and reacting. Likewise the electrometric titration apparatus may be changed to any desired form, or even eliminated altogether.

I claim:

1. An apparatus for continuously forming a detergent product that comprises a mixer for reacting glycerine and sulphuric acid with fatty oil, heat transfer means within the mixer to maintain the desired temperature, and a neutralizer including an agitator, a cooling means and means to add a neutralizing solution in just sufficient amount to neutralize the reaction product.

2. An apparatus for continuously forming a detergent product that comprises a mixer for reacting glycerine and sulphuric acid with fatty oil, heat transfer means within the mixer to maintain the desired temperature, and a neutralizer including an agitator, a cooling means, scraper means for preventing the accumulation of solid material upon the cooling means, and means to add a neutralizing material in just sufficient amount to neutralize the reaction product.

3. An apparatus for continuously forming a detergent product that comprises a mixer for reacting glycerine and sulphuric acid with fatty oil, heat transfer means within the mixer to maintain the desired temperature, a neutralizer including an agitator, a cooling means and means to add an alkaline solution in just sufficient amount to neutralize the reaction product, and means to spray dry the neutralized product.

4. An apparatus for continuously forming a detergent product that comprises a mixer for reacting glycerine and sulphuric acid with fatty oil, means to continuously add glycerine, heat transfer means within the mixer to maintain the desired temperature, and a neutralizer including an agitator, a cooling means and means to add an alkaline solution in just sufficient amount to neutralize the reaction product.

5. An apparatus for continuously forming a detergent product that comprises a mixer for mixing glycerine and sulphuric acid, means to control the temperature within the mixer, a mixer for reacting the glycerine and sulphuric acid with a fatty oil, means to control the temperature within this mixer, and a neutralizer for mixing the reaction product with a caustic alkali solution, said neutralizer including an agitator, heat transfer surfaces and means to control the amount of caustic alkali added in accordance with the hydrogen ion potential of the resulting neutralized product.

6. An apparatus for continuously forming a detergent product that comprises a mixer for mixing glycerine and sulphuric acid, means to control the temperature within the mixer, a mixer for reacting the glycerine and sulphuric acid with a fatty oil, means for feeding constant proportions of the materials to this mixer, means to control the temperature within this mixer, and a neutralizer for mixing the reaction product with an alkaline solution, said neutralizer including an agitator, heat transfer surfaces and

means to control the amount of alkaline solution added in accordance with the hydrogen ion potential of the resulting neutralized product.

7. An apparatus for forming a detergent product that comprises in combination means for mixing a sulphonating agent with a polyhydric alcohol, means associated with said mixing means to maintain the desired temperature; means for reacting the mixture with one of the group consisting of fatty oils and fatty acids; means associated with said reacting means to maintain the desired temperature; means for neutralizing the reaction product with an alkaline solution in the presence of already neutralized material; means associated with the neutralizing means to maintain the desired temperature, and means for drying the neutralized product.

8. An apparatus for forming a detergent product that comprises, in combination, means for proportionally supplying a sulphonating agent and a polyhydric alcohol; means for mixing said proportions; means associated with said mixing means to maintain the desired temperature; means for proportionally supplying the mixture and one of the group consisting of fatty oils and fatty acids; means for reacting said proportions; means associated with said reacting means to maintain the desired temperature; means for proportionally supplying the reaction product and an alkaline solution; means for neutralizing said proportions in the presence of already neutralized material; means associated with the neutralizing means to maintain the desired temperature; and means for drying the neutralized product.

9. An apparatus for forming a detergent product that comprises, in combination, means for proportionally supplying according to weight a sulphonating agent and a polyhydric alcohol; means for mixing said proportions; means associated with said mixing means to maintain the desired temperature; means for proportionally supplying according to weight the mixture and one of the group consisting of fatty oils and fatty acids; means for reacting said proportions; means associated with said reacting means to maintain the desired temperature; means for proportionally supplying according to pH values the reaction product and an alkaline solution; means for neutralizing said proportions in the presence of already neutralized material; means associated with the neutralizing means to maintain the desired temperature; and means for drying the neutralized product.

10. An apparatus for forming a detergent product that comprises, in combination, means for proportionally supplying a sulphonating agent and a polyhydric alcohol; means for mixing said proportions; cooling means associated with said mixing means to maintain the desired temperature; means for proportionally supplying the mixture and one of the group consisting of fatty oils and fatty acids; means for reacting said proportions; heating means associated with said reacting means to maintain the desired temperature; means for proportionally supplying the reaction product and an alkaline solution; means for neutralizing said proportions in the presence of already neutralized material; cooling means associated with the neutralizing means to maintain the desired temperature; and means for drying the neutralized product.

11. An apparatus for forming a detergent product that comprises, in combination, means for proportionally supplying a sulphonating

agent and a polyhydric alcohol; means for mixing said proportions; means associated with said mixing means to maintain the desired temperature; means for proportionally supplying the mixture and one of the group consisting of fatty oils and fatty acids so that there is an excess of sulphonating agent equivalent to not less than about 99.3% sulphuric acid; means for reacting said proportions; means associated with said reacting means to maintain the desired temperature; means for proportionally supplying the reaction product and an alkaline solution; means for neutralizing said proportions in the presence of already neutralized material; means associated with the neutralizing means to maintain the desired temperature; and means for drying the neutralized product.

12. An apparatus for forming a detergent product that comprises, in combination, means for proportionally supplying according to weight a sulphonating agent and a polyhydric alcohol; means for mixing said proportions; cooling means associated with said mixing means to maintain the desired temperature; means for proportionally supplying according to weight the mixture and one of the group consisting of fatty oils and fatty acids so that there is an excess of sulphonating agent equivalent to not less than about 99.3% sulphuric acid; means for reacting said proportions; heating means associated with said reacting means to maintain the desired temperature; means for proportionally supplying according to pH values the reaction product and an alkaline solution; means for neutralizing said proportions in the presence of already neutralized material; cooling means associated with the neutralizing means to maintain the desired temperature; and means for drying the neutralized product.

13. A process for forming a detergent product which comprises proportionally mixing a sulphonating agent with a polyhydric alcohol within a mixing zone, controlling the temperature of said zone during the operation, proportionally reacting said mixture with one of the group consisting of fatty oils and fatty acids, within a zone of reaction, controlling the temperature during the reaction step, proportionally neutralizing the reaction product with an alkaline solution within a zone of neutralization in the presence of already neutralized material, controlling the temperature during the neutralization step, and drying the neutralized product.

14. A process for forming a detergent product which comprises proportionally mixing a sulphonating agent with a polyhydric alcohol within a mixing zone, cooling said zone to about 30° C. during the operation, proportionally reacting said mixture with one of the group consisting of fatty oils and fatty acids, within a zone of reaction, heating during the reaction step, proportionally neutralizing the reaction product with an alkaline solution within a zone of neutralization in the presence of already neutralized material, cooling during the neutralization step, and drying the neutralized product.

15. A process for forming a detergent product which comprises proportionally mixing a sulphonating agent with a polyhydric alcohol within a mixing zone, controlling the temperature of said zone during the operation, proportionally reacting said mixture with one of the group consisting of fatty oils and fatty acids, within a zone of reaction so that there is an excess of sulphonating agent equivalent to not less than about 99.3% sulphuric acid, controlling the tem-

perature during the reaction step, proportionally neutralizing the acid reaction product with an alkaline solution within a zone of neutralization in the presence of already neutralized material, controlling the temperature during the neutralization step, and drying the neutralized product.

16. A process for forming a detergent product which comprises proportioning a sulphonating agent and a polyhydric alcohol, combining the proportions within a mixing zone, controlling the temperature of said zone during the operation, proportioning the mixture and one of the group consisting of fatty oils and fatty acids, flowing said proportions into a zone of reaction, controlling the temperature during the reaction step, proportioning the reaction product and an alkaline solution, flowing said proportions into confluence within a zone of neutralization and in the presence of already neutralized material, controlling the temperature during the neutralization step, and drying the product.

17. A process for forming a detergent product which comprises proportioning according to weight a sulphonating agent and a polyhydric alcohol, combining the proportions within a mixing zone, controlling the temperature of said zone during the operation, proportioning according to weight the mixture and one of the group consisting of fatty oils and fatty acids, flowing said proportions into a zone of reaction, controlling the temperature during the reaction step, proportioning according to pH values the reaction product and an alkaline solution, flowing said proportions into confluence within a zone of neutralization and in the presence of already neutralized material, controlling the temperature during the neutralization step, and drying the product.

18. A process for forming a detergent product which comprises proportioning according to weight oleum and glycerine, combining the proportions within a mixing zone, cooling said zone to about 30° C. during the operation, proportioning according to weight the mixture and coconut oil so that there is an excess of sulphonating agent equivalent to not less than about 99.3% sulphuric acid, flowing said proportions into a zone of reaction, heating said zone during the reaction step, proportioning according to pH values the acid reaction product and caustic soda, flowing said proportions into confluence within a zone of neutralization and in the presence of already neutralized material, cooling the zone during the neutralization step, and drying the product.

19. An apparatus for forming a detergent product that comprises in combination means for mixing a sulphonating agent with a polyhydric alcohol, means associated with said mixing means to maintain the desired temperature; means for reacting the mixture with one of the group consisting of fatty oils and fatty acids; means associated with said reacting means to maintain the desired temperature, means defining a neutralizing zone, means for conducting reacted material from said reacting means to said neutralizing zone, means for supplying a neutralizing agent to said neutralizing zone, means for controlling the flow of neutralizing agent in said last named means responsive to the pH of material in said neutralizing zone and means associated with said neutralizing zone to maintain the desired temperature, whereby the supply of neutralizing agent is controlled directly by the pH of the material to which said neutralizing agent is added.

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