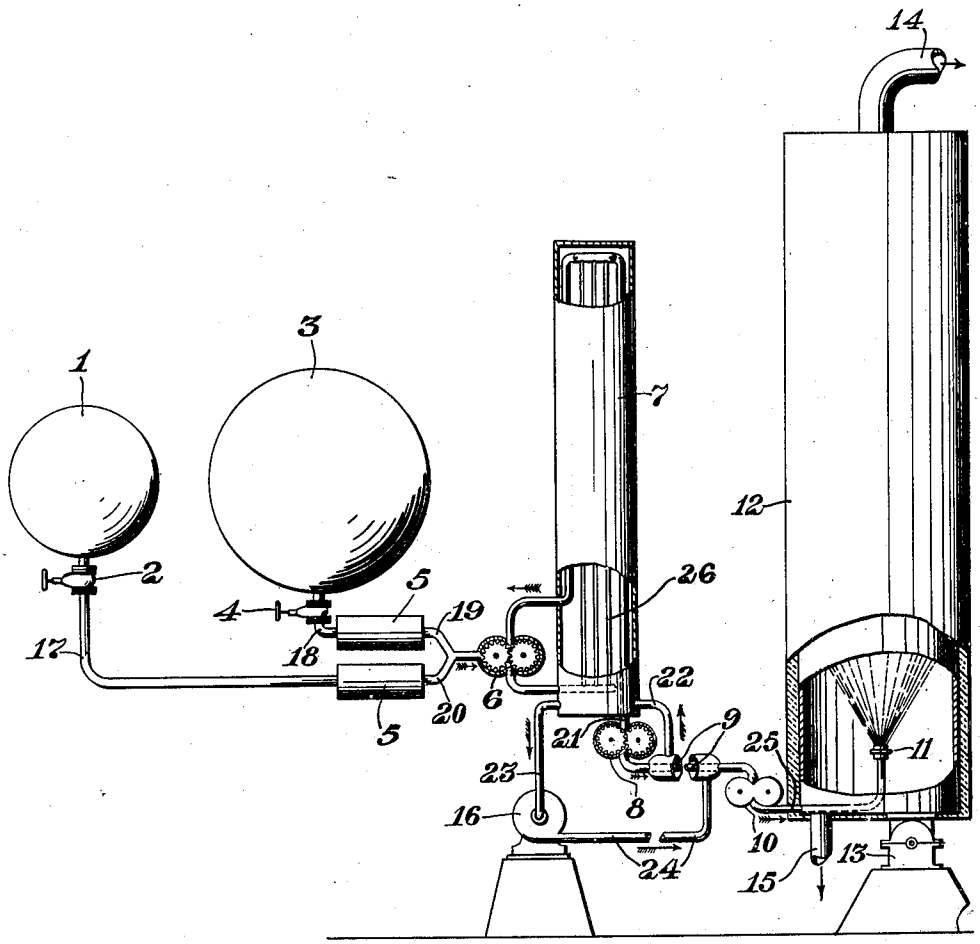
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SOAP-MAKING PROCESS

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SOAP-MAKING PROCESS

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This invention relates to the manufacture of soap. More particularly, this invention deals with that process of making soap wherein natural fats, consisting essentially of glycerine esters of higher fatty acids, are first converted into lower alkyl esters of said higher fatty acids, say the methyl, ethyl, propyl, or butyl esters, and the latter are then saponified with caustic alkali, liberating respectively methyl, ethyl, propyl, or butyl alcohol.

The foregoing process was referred to in U. S. Patent No. 1,701,703 of Joel Starrels, and described by me jointly with Walter C. Meuly in U. S. Patent No. 2,271,619. Certain modifications and improvements thereof are further described and claimed in U. S. Patent No. 2,360,844 by the two latter inventors. This process has numerous advantages over the old process of treating the glyceride of a higher fatty acid directly with caustic, among which is simple recovery of the glycerine by-product and the removal of impurities at the start instead of at the end of the soap process. The prior patents mentioned above were concerned primarily with procedures analogous to the traditional practice employed with the old processes, which procedures I have found possess several inherent disadvantages which reduce the economy thereof.

It is accordingly an object of this invention to overcome the disadvantages inherent in the lower alkyl soap process as heretofore described. Another object of this invention is to provide a practical, continuous method for carrying on the foregoing soap process on a commercial scale. Another object is to provide a process which can utilize lower alkyl esters of fatty acids which contain up to 10% free fatty acid, which may often be desirable, especially where esters made by an acid catalyzed exchange are available. A still further object is to provide for the economic recovery of the alcohol liberated. A still further object is to produce soap in a form which lends itself readily to plodding. A further object is to provide a method of manufacture which is free of objectionable foaming. A further object is to provide for the rapid initiation of the reaction of the starting materials and for their simple water-in-oil emulsification without having to supply steam for this purpose, or expensive outside mechanical energy. A further object is to dispense with heating, and yet deliver a cooled dried soap. Another object is to provide an apparatus of general utility in soap manufacture and treatment of oils and fats. It is a further object to produce soap of a character not hitherto attained, to-wit containing fats saponified 99.9%

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and no more than 0.1% free caustic, the soap being of an unexpectedly fine odor and as desired containing less than 0.05% sodium chloride, no glycerine and less than .05% free fatty acid.

The above paragraph is by no means exhaustive of the numerous objects and advantages of my invention, as will become evident later.

Among previous processes for making soap from lower alkyl esters of fatty acids is that disclosed in U. S. Patent No. 1,701,703 of Joel Starrels, where the alcohol produced in the saponification is removed as formed. In such a procedure there is great difficulty because of foaming. Also excess lye must be used to complete the saponification. Since there is no separation over a niger, as in the ordinary boiling process, a neutral soap is not produced. The other main difficulties with the aforesaid and all soap processes are the time and energy required. I have outlined below several discoveries about soap manufacture, which if taken into account, make possible the rapid manufacture of dry, neutral, salt-free soap from lower alkyl esters, with little energy input.

First, the conversion of an ester of a fatty acid to the sodium or potassium salt of that acid, that is to soap, really deports itself as though it consisted of two steps. In the first step there is a hydrolysis or taking up of water and splitting of the ester, and in the second step there is a neutralization by the caustic alkali of the free fatty acid formed by the first step, and the consequent release of water. The hydrolysis step and the neutralization step are exothermic. Theoretically about 75,000 calories per kilo are set free on treatment with caustic soda. Further, if these steps occur molecule by molecule, the reaction becomes of the chain type in that energy is passed on to adjacent molecules without first becoming evident as heat. In such a reaction the speed becomes extremely high. From a consideration of the above it is seen that if some heat is applied at the start, the reaction under proper conditions can be made very rapid.

Second, to enable the inception of the rapid chain type reaction it appears necessary that the water solution of caustic alkali be finely emulsified in the fat, that is, that a water-in-oil-type emulsion be formed. This is really a corollary of the first proposition in that hydrolysis water must be in the fat in the presence of a fat splitting catalyst, i. e., caustic soda. On mixing fat and a solution of caustic soda to produce soap the lye often causes a graining out of the soap just formed and causes a breaking of the emulsion essential to the reaction. The phases must

then be reunited by mechanical working under addition of heat. As the grained soap is present in discrete particles of low specific heat, it is slow and difficult to get the reaction started again. This breaking of the emulsion is a function of temperature, and concentration of the reactants. The higher the temperature the more likely is the emulsion to break, but the greater the saponification the less likely it is to occur. Also the more water there is present, the lower the temperature at which the emulsion will break. To secure the water-in-oil-type of emulsion it is necessary that there be present a certain amount of concentrated soap. This means concentrated alkali must be used. The concentration of the alkali, if a caustic soda solution, should not be much below about 35%, and the temperature of making the emulsion should be from a little above the melting point of the fatty material to about 65° C. On first mixing methyl esters of a fatty acid and caustic alkali, an oil-in-water emulsion is formed which is rendered unstable and finally inverted to a water-in-oil type as the concentration of soap becomes greater. A favorable content of soap for the water-in-oil type of emulsion is from 10% to 25%.

The formation of the first soap is aided by the presence of an emulsifier such as lecithin or by free fatty acid or by soap saponification catalysts, such as a phenol or fat-splitting catalyst. Unless properly handled a content of free fatty acid above 3% becomes troublesome, because saponification becomes so rapid, clots are formed with consequent non-uniform saponification. The belief that water must first be present in the fatty ester before saponification can start agrees with the fact that the soap catalysts phenol and thymol are very weak oil soluble acids which give off and take up water in the presence of caustic soda and under varying conditions. The lecithin and the fat-splitting catalysts tend to form water-in-oil emulsions. Also, the fact that saponification is aided by pressure and hindered by vacuum agrees with the theory that the saponification occurs in a water-in-oil emulsion.

Third, in the presence of alcohol of high enough concentration a neutral soap can be made. In any ordinary saponification in the presence of water there is an equilibrium short of complete saponification due to the fact that soap dissociates in water solution. In order that all the fat be saponified, from 5% to 10% excess alkali is required. This is the case in every soap process using water as a medium. In the "boiled" process most of this excess lye is removed in that the batch is allowed to form a 70% soap 30% water phase over a niger. In the "cold" process there is always used either an excess of caustic lye or an excess of fat. If there is an excess of fat rancidity is likely to develop in the finished soap since a good stable soap should not contain over 0.1% unsaponified fat. Accordingly, completely saponified neutral soap can be secured from lower alkyl esters of fatty acids, say methyl esters, by completing the saponification without removing the alcohol formed and by using a concentrated lye. This means the reaction ends in the presence of fairly strong alcohol.

Fourth, the rapid stage of a soap reaction where water is the medium ends with from 80% to 90% of complete saponification and occurs in a few minutes. Where a lower alcohol is the medium the rapid stage ends with nearly complete saponification and furthermore this nearly complete saponification will gradually complete itself in the space of 24 to 72 hours at ordinary temperatures while the soap is being worked up or even in storage as a finished product.

As hydrolysis is continually proceeding in the soap reaction there will be a certain amount of free fatty acids present at the end if there was an excess of oil at the start. Any superfatting secured by using an excess of fatty material at the start will therefore entail the risk of producing an unstable soap. This is because most soap making fats would yield some unsaturated acids which, if left in the free state in the finished soap, would tend to quickly decompose. Superfatting if desired, may be produced by adding an easily saponified ester of a saturated fatty acid, such as palmitic or stearic acid for instance pure methyl stearate or mono stearyl glyceride, at the end of the reaction. Such addition can also be made as a buffer to compensate for any error in the amount of caustic alkali or to allow for an excess of caustic purposely used. The lower the temperature at which the soap reaction is carried out and the quicker it is finished the less hydrolysis of excess esters will occur.

Another very important reason for keeping the temperature down during the reaction is to obviate oxidation. Other factors producing oxidation are presence of air and of oxidation catalysts such as salts of iron and copper. The starting materials should not contain air, and air should be excluded in the subsequent treatment.

It is particularly important also from the odor angle that the reactions incident to high temperature do not occur. The cost of perfume in a toilet soap ranges from one to two cents per pound of soap. A properly made soap from, say, methyl esters of fatty acids requires very little perfume.

In the light of the above it is now possible to detail a practical continuous pressure soap process. The objections to such a process hitherto have been the high temperature, from 200° to 300° C., required to attain the necessary speed of reaction, and the excess of alkali in the product.

In general I operate my lower alkyl soap process in a special three step procedure under autogenous pressure and temperature, which are comparatively low, and under substantially adiabatic conditions whereby all the reaction gases and practically all the heat developed in the process are retained in the reaction mass itself or in the reaction vessels until the third or cooling step.

In a practical application of my invention, a monohydric alcohol ester of a higher fatty acid, for instance the methyl ester obtained by alcoholysis of a natural fat (a glyceride) by the aid of an alkaline catalyst according to U. S. Patents No. 2,360,844 and No. 2,271,619, or with the aid of an acid catalyst, is partially reacted with concentrated aqueous sodium hydroxide solution in a suitable vessel or apparatus, where at the same time the reaction is initiated and a water-in-oil emulsion is formed. This emulsion is pumped into a long water jacketed and heat lagged pipe which constitutes the main reactor. The length of this pipe is governed by the reaction time desired and the conditions of heat interchange to the water jacket, and is usually about 100 feet. The diameter of the pipe determines the output capacity. The reaction in

the emulsifier is speeded by adding heat preferably by interchange from the water which has passed through the water jacket of the long reaction pipe. The reaction having started in the emulsifying apparatus and being about 25% completed therein, continues in the long pipe reactor as the materials move to the discharge end, the methyl alcohol liberated and about half the heat generated being retained thereby maintaining the mass in a plastic fluid state and under pressure. The heat transfer conditions in the reactor are such that the reaction has passed the critical emulsion breaking stage before the temperature is reached to cause such breaking. At the end of the reaction pipe the nearly completely saponified material contains enough heat to dry it to any degree depending on the absolute pressure into which it is discharged. The heat is sufficient, if 50% caustic soda has been used for saponification and if the starting materials were introduced at a temperature of about 40° C. and if the heat losses have not been above about 20%. The system as just described enables the ready addition of more heat by means of the heat transfer medium, if it is needed because of the use of more water in the composition or to speed up the reaction, or in the presence of other ingredients.

At the discharge end there is a throttling release so that the desired pressure is maintained in the reaction pipe. The discharged material may be passed through a spray nozzle into a vacuum chamber wherein a vacuum of about 27'' of mercury is maintained, with the result that as soon as the plastic soap emerges from the nozzle methyl alcohol and water are evaporated, puffing up the residual mass to a flaked porous solid. The gaseous methyl alcohol and water are led off through the top of the chamber through filters to a condenser, while the cooled fluffy soap particles of desired moisture content drop to the bottom of the chamber and may be continuously led off to a plodder, and eventually pressed into cakes. Alternatively the discharge may be to a continuous cooler to produce either puffed up or solid soap.

The above described practical application details a three step process. In the first step, in the space of five to ten minutes and without loss of heat, there is continuously produced a water-in-oil type emulsion having a temperature of about 35° to 65° C. and of about the following composition, if 50° caustic soda was used:

	Per cent
Methyl esters of fatty acids	55 to 63
Soap	24 to 16
Caustic soda	7.5 to 8.5
Methyl alcohol	2.5 to 1.5
Water	11 to 11

In the second step this emulsion is allowed to continue to react for up to 20 minutes under a pressure of about thirty pounds absolute and a temperature of about 100° C. to nearly complete saponification. In the third step the reacted mass is continuously discharged from the reaction pipe, when it may be handled in various ways including that of spray drying under a vacuum.

I shall now by reference to the accompanying drawing describe apparatus particularly suited for carrying out my invention. Referring to the drawing, the tank 3 contains a lower alkyl ester of higher fatty acids such as liquid methyl esters of tallow, and the tank 1 a saponifying agent, such as 50% caustic soda solution. These tanks are advantageously heated and lagged so as to supply materials of a uniform desired temperature. Valves 2 and 4 and pipes 17 and 18 connect the bottoms of tanks 1 and 3 to proportioning feeding devices 5 of any one of the suitable types well known to the art. The oil and caustic are continuously fed to the circulating stream of partially reacted and emulsified material by pipes 19 and 20. This stream of partially reacted material is kept in circulation by pump 6 which is of such size that it handles material at about 10 times the rate it is fed by the two proportioning feeders. The stream of partially reacted material is forced by pump 6 through the turbulent flow pipes 26. The system is jacketed by 7. The contents of this circulating system just described are such that the bulk of the reactants spends about five minutes circulating through the turbulent flow pipes and the pump 6. At the same time this material is circulated, it is subjected to heating action of the heat transfer medium which is flowing up and down through the jacket 7. This flow is such that at least no heat is removed from the circulating materials. Continually there is being pumped off from this system through pipe 21 by pump 8 partially reacted material equivalent to the feed by the proportioning feeders 5. Pump 8 feeds partially reacted emulsified and hot material to the jacketed reaction pipe 9. In the jacket of pipe 9 and counter current to the flow of the reacting material flows the heat exchange medium driven by pump 16. This medium flows from the jacket of pipe 9 through pipe 22 to jacket 7 and then by pipe 23 to circulating pump 16 and then by pipe 24 to jacket of pipe 9. Pipe 24 may pass through a heat exchange system for either lowering or raising the temperature of the heat exchange medium. The reacted material discharges through throttling pump 10 by which the desired pressure is maintained in the reaction pipe 9. The reacted material is forced through pipe 25 and spray nozzle 11 into the drying tower 12 from which the gases are sucked through outlet 14 by a vacuum apparatus which may consist of dust catchers, condensers, receivers and vacuum pump. The product falls to the bottom of the tower 12 and is continuously removed either by the soap plodder 13 or a sealed discharge 15. Additions to reacted stream can be made by a proportioning feeder ahead of pump 10.

The heat transfer medium circulating through jackets of the reaction pipe and the emulsifier may not always be essential to the process, from the economic standpoint, as will be seen from a consideration of the heat balance which follows in Example II below. Without great inconvenience these jackets could be insulated and any heat found necessary be supplied at tanks 1 and 3.

To make the invention clearer specific examples follow.

Example I

10,000 lbs. of tallow containing 20% free fatty acids was ester interchanged and esterified by using methyl alcohol and a mixed acid catalyst to yield 10,000 lbs. of a product having a saponification value of 195 and of about the following composition:

	Per cent
Methyl esters	86
Glycerides	8
Free fatty acids	6

The theoretical amount of caustic soda 100% required to saponify this is 1392 lbs. or 2784 lbs. of 50% caustic soda solution. About 20 lbs. extra lye was used. Tank 3 was charged with the 10,000 lbs. methyl esters and contents brought to a temperature of 40° C. Tank 1 was charged with the 2800 lbs. caustic soda solution which was brought to a temperature of 25° C. The proportioning feeders 5 were adjusted to feed 28 lbs. of the caustic lye and 100 lbs. of the methyl esters every 12 minutes. The temperature of the water in the heat exchange medium system was brought to 105° C. and the water circulated by pump 16 at a slow rate. Pump 6 was started operating at such a rate that it would handle 5,000 lbs. per hour of material and pump 8 was adjusted to handle 640 lbs. per hour or at such a rate that no pressure would be built up in the feed to pump 6. With the air release cocks open at the top of turbulent flow mixer the feed was started from the proportioning feeders and pump 8 started. As soon as system of pump 6 was filled samples of the emulsion were taken for quick analysis and control of the proportions. Pump 10 was started similarly to pump 8, and so as to maintain a pressure of about 15 lbs. gage in reaction pipe 9. A sample taken ahead of pump 10 showed more than 95% reacted. Pump 10 fed the spray nozzle which sprayed into chamber 10 in which was maintained a vacuum of 27". The sprayed soap was found to be cooled to a temperature of 50° C. and contained 3% methyl alcohol and 8% water. It was plodded to pellets and stored for two days and then milled and plodded to bars and cut and stamped to cakes. The finished soap contained .05% free caustic soda and less than 0.15% methyl alcohol.

Example II

Similarly were treated 19,500 lbs. of methyl esters of mixed tallow and coconut oil containing about 7.5% glycerides and having a saponification number of 205.7. Hence they required 2866 lbs. 100% caustic soda for saponification or 5732 lbs. of 50% lye. After saponification there was produced a mixture containing:

20,055 lbs. (9050 kilos) of soap figured as anhydrous
169 lbs. (77 kilos) of glycerine
2,134 lbs. (966 kilos) of methyl alcohol
2,866 lbs. (1300 kilos) of water

This mixture at the spray nozzle had a temperature of 105° C. and the dried cooled material had a temperature of 50° C. and the following composition:

	Per cent
Soap, 20,055 (9050 kilos)	87.33
Glycerine, 169 (77 kilos)	.73
Methyl alcohol, 658 (299 kilos)	2.87
Water, 2,082 (944 kilos)	9.07
	100

There was evaporated 667 kilos of methyl alcohol and 356 kilos of water. The heat required to do this is

	Calories
667,000×250	166,200,000
356,000×540	192,240,000
	358,440,000

In dropping from a temperature of 105° C. to 50° C. the soap lost this heat:

Material	Kilos	c.	Drop	Calories
Soap	9,050	0.7	55°	348,400,000
Methyl alcohol and glycerine	1,043	0.57	55°	32,640,000
Water	1,300	1.00	55°	71,500,000
				452,540,000

In the above batch 19,500 lbs. of fat or 8844 kilos were saponified. The heat set free was 8,844,000×75 equals 663,300,000 calories. The heat needed by the process was as follows:

	Calories	Value
Raise 8,844 kilos Fat, 25° C. to 40° C	66,330,000	$.332
Raise 8,844 kilos Fat, 40° C. to 60° C	88,440,000	.442
Raise 1,303 kilos Caustic, 25° C. to 60° C	31,924,000	.160
Raise 1,303 kilos Water, 25° C. to 60° C	45,005,000	.226
Raise Batch, 60° C. to 105° C	371,260,000	1.856
Heat for 20,000 lbs. soap equals	602,959,000	3.016

It is evident that without the addition of outside heat the temperature will not reach 110° C. If steam costs $.70 per 1000 lbs. and there is obtained for heating 320 calories per gram then 2,000,000 calories are worth 1 cent. If about 400,000,000 calories were put into the process of Example II the soap at spray nozzle would have a temperature of 155° C. and no vacuum would be required to dry it. The sprayed soap however would have a temperature of about 100° C. and require cooling. The quality of the soap would not be as good as that made at the lower temperature. Considering all factors the temperature should be kept under 140° C.

Example III

10,000 lbs. of methyl esters of fatty acids which contained 4% free fatty acid and about 28% methyl oleate and had a saponification value of 192 were similarly treated with about 3% excess or 3150 lbs. of 45% caustic soda lye. The temperature in the reaction pipe was made to go to 140° C. by using outside heat on the system. Just ahead of pump 10 there was continuously forced into the reaction stream a supply of liquid mono-stearic acid ester of glycerine equal to 1.5% of the mixture passing. The vacuum in the spray tower was held at about 20" of mercury. The finished soap, when analyzed two days later, showed less than 0.1% free caustic alkali and less than 0.1% free fatty acid.

Example IV

There was similarly treated a mixture of 9700 lbs. methyl esters of tallow and 300 lbs. stearic acid. The tallow methyl esters had an acid value of 5.7 and a saponification number of 194. The caustic alkali used was 3570 lbs. of a solution containing:

	Pounds
Potassium hydroxide	1940
Potassium carbonate	60
Water	1570
	3570

The fat and the alkali had both been brought to a temperature of 45° C. before feeding to the proportioners 5. The product from the reaction pipe 9 was fed directly to a cooler instead of to the spray tower.

It is plain from the above that the procedure

for initiating the reaction may vary widely. However, the factors of especial moment have been discussed and their application is illustrated in the examples. The simplest and easiest way of insuring the proper initiation is to have present a certain amount of free fatty acid and to have starting materials at about 40° C. Some alkyl esters like those from coconut oil will generally start very readily at room temperature. However, a very pure dry alkyl ester will not start readily. This is because the naturally occurring lecithin emulsifier and the 0.1% to 0.2% water usually present in seed oils are absent.

Many times it will be desired to add to the fat and alkali other ingredients. As these other ingredients will have a certain specific heat, there should be compensation in the heat balance for their presence. In general there should be enough total heat in the reacted mass so that its temperature reaches about 100° C. Example IV illustrates supplying outside heat. In this example the starting materials were raised to 45° C. This was advisable because of the extra water present in the caustic potash solution over that which would have been present if caustic soda were used.

Above I have given preferred examples of procedures. However, it is to be understood that the invention includes variations within the scope of the claims which follow.

I claim:

1. A continuous process for producing soap, which comprises continuously forming a water-in-oil type emulsion by continuously adding approximately stoichiometrical proportions of a concentrated, aqueous, caustic alkali solution and of lower alkyl esters of higher fatty acids to an agitated body of such an already formed emulsion maintained at a temperature of about 35° to 65° C. and containing from 10% to 25% of soap, passing this emulsion at the rate it is formed through an enclosed space in which it is maintained at

a temperature of from about 100° C. to below 140° C. under autogenously developed pressure, until nearly complete saponification of the fatty acids has taken place, and then reducing the pressure on the reaction mixture as it emerges from said enclosed space sufficiently to evaporate off the major part of the lower alcohol and a substantial part of the water present therein, whereby said reaction mixture is cooled and a solid, soap of excellent commercial purity is obtained.

2. A process as claimed in claim 1 wherein the reaction mixture, as it emerges from the enclosed space, is subjected to spray drying under subatmospheric pressure.

3. A process as claimed in claim 1 wherein there are added to the reaction mixture shortly before it emerges from the enclosed space a few per cent of an easily saponified ester of a fatty acid of the group consisting of palmitic and stearic acid.

4. A process as claimed in claim 1, wherein methyl esters of higher fatty acids and a caustic soda solution of about 50% concentration are employed.

GEORGE B. BRADSHAW.

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