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R. B. COLGATE ET AL

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TREATING ORGANIC MATERIAL

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Fig. 1.

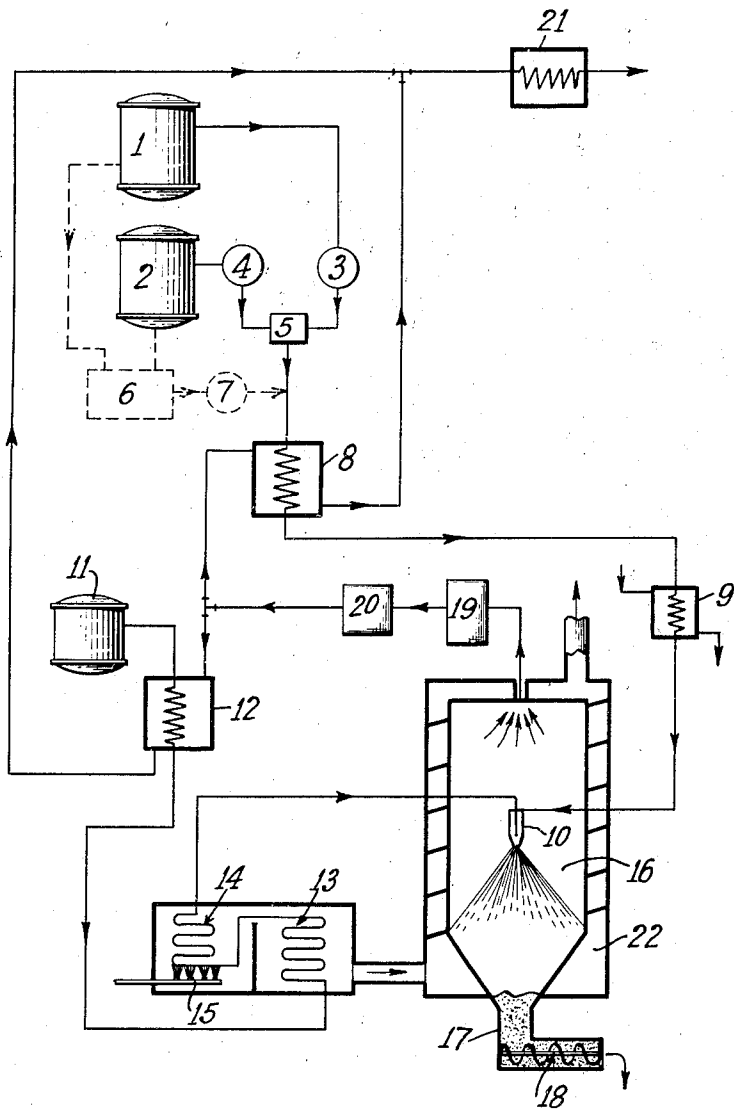
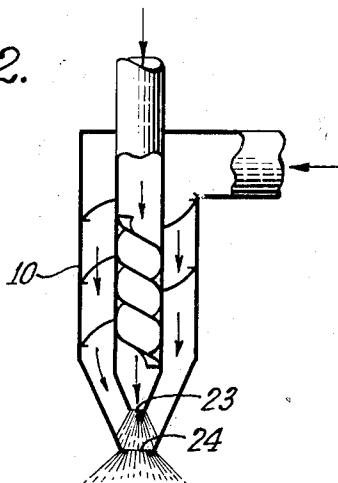


Fig. 2.



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## UNITED STATES PATENT OFFICE

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## TREATING ORGANIC MATERIALS

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8 Claims. (Cl. 260—418)

This invention is directed to a process of handling soap, and more particularly it is directed to a process of preparing dry soap substantially free from unsaponified constituents.

Over a period of many years, numerous methods of continuously preparing and drying soaps have been described and patented. As early as 1855, Tilghman described in U. S. Patent No. 12,142 a process for accomplishing this result. None of these processes has been entirely satisfactory for the production of high grade soaps substantially free from high boiling unsaponified organic material. In most of these prior art processes, before any satisfactory results are obtained, the soap is heated to elevated temperatures for substantial periods without adequate agitation to prevent local overheating and degradation of the product.

It has now been found that soap can be prepared substantially free from glycerine, sterols, fatty alcohols, and other unsaponifiable and unsaponified organic materials, which soaps have good color, odor, hardness and detergent efficiency.

The present invention, in general, comprises heating a solution of soaps and flashing the soap solution while contacting it with highly superheated steam and/or other inert gases such as kerosene vapors, carbon dioxide, flue gases, etc., at the moment of injecting the solution into the flash chamber. This new procedure is superior to those methods not employing superheated steam in the above manner, in that the solution is not subjected for any substantial time to an exceptionally high temperature which is required to volatilize the unsaponifiable material with the water under normally desirable or economical dilutions, nor is the solution excessively diluted as is necessary in order to provide sufficient steam to volatilize substantially all of the unsaponifiable matter at desirable flashing temperatures. The superheated steam should be at an appreciably higher temperature than that of the solution and the contact with the solution should be intimate and at an extremely high velocity, but only for a very short time period before introduction into the flash chamber. The contacting of superheated steam and soap solution may advantageously be accomplished in a specially designed nozzle that permits thorough but only brief direct contact and as little indirect contact as possible before ejection into the flash zone. In this manner, it is possible to supply to the soap solution at the critical point sufficient heat to volatilize the unsaponifiable organic ma-

terial and water without subjecting the solution to decomposition temperatures and without use of uneconomically large quantities of steam or water. Plugging of the pipes and nozzles and decomposition of the products are avoided, since the solution itself is not heated to an operating temperature until just prior to its discharge into the flash chamber. At this time it receives its high velocity and adequate heat momentarily to remove the unsaponifiable material and then it is cooled to the flash chamber temperature.

A detailed description of the operation of one embodiment of the present process with reference to the attached drawings permits a better understanding of the principles of the present invention.

The proportioning pumps 3 and 4 force the molten fat, fatty oil, wax, rosin, fatty acid and/or other saponifiable material from tank 1 and the saponifying reagent, e. g., a 37° Bé. caustic soda solution from tank 2, to flow under pressure into the mixer or homogenizer 5. Although the two pumps 3 and 4 are employed in the preferred apparatus shown, the materials could be mixed in proper proportion in the tank 6 by installing a mechanical mixer therein and the mixture pumped by the pump 7. The pumps 3 and 4 and the homogenizer or mixer 5 could then be omitted.

The homogenizer or mixer 5 brings together a stream of the saponifiable material and a stream of reagent, thereby dispersing the reagent in the fatty material, either by mechanical or jet mixers.

If desired, the mixed solution with or without addition agents, solvents and the like may then be heated and the resulting soap washed with a caustic alkaline brine to remove glycerine, lignin-like, phenolic, colored and potentially colored bodies.

The fatty oil-reagent mixture is then pumped through the solution heater 8. This heater may be a tubular type or coil externally heated, either by combustion products from the boiler and steam superheater, by immersion in steam or hot oil, by electrical means, or by the vapors from the flash chamber, the latter procedure being employed in the process shown diagrammatically in Figure 1. This heating and flow are preferably automatically controlled. The solution may be further raised in temperature by any suitable means, such as a steam heated tubular type apparatus 9. The soap solution will be raised to a temperature between about 25° and 200° C., e. g., at 121° C. (250° F.) at about 30 lbs. per square

inch absolute, the temperature of saturated steam at the pressure under which it is held. The proportion of steam generated can vary from a trace to a quantity corresponding to almost all of the water in the solution. By control of the rate of feed, temperature, and pressure, the quantity of steam formed from the solution may be held at a constant value, preferably about 50% to 90%. The steam generated causes an increase in velocity of flow of the solution from the nozzle. Too great a proportion of water of solution evaporated at this point causes very uneven operation with plugging of the tubes, decomposition of the product and/or generally unsatisfactory results.

The aqueous soap solution is then introduced into the spray nozzle 10. At the same time, water from tank 11 is continuously pumped in regulated quantities through pre-heater 12 and boiler 13 and from this point led into steam superheater 14. The steam is superheated to any desired temperature, preferably between 260° and 700° C., e. g., at 593° C. (1100° F.), in the superheater 14 by means of gas burner 15 or any other suitable means. It is then led into spray nozzle 10 in which it is momentarily but intimately contacted with the heated soap solution. The mixture is sprayed from nozzle 10 at an exceptionally high velocity and at the required pressure drop into flash chamber 16 maintained at a temperature between about 150° C. and 400° C., e. g., about 205° C. (401° F.), and at atmospheric pressure. At this point substantially all of the water and unsaponified material is volatilized. The soap or carboxylate salt, usually as small dry solid or fused particles, drops to the bottom of the spray chamber 16 from which it may be continuously withdrawn, either as a fused or solid product, through the opening 17 by suitable means, such as a continuous screw 18, vibrating device, or the like. The dried product should be kept out of contact with oxidizing conditions until cooled to say about 130° C., depending on the material under treatment. The flash chamber may be operated at atmospheric, elevated or reduced pressure and, if desired, steam may be blown through the chamber (or molten soap if operating at the higher temperature), but, as a matter of convenience and economy, it is usually better to operate at substantially atmospheric pressure. In the event it is desired to operate chamber 16 under sub-atmospheric pressure, the removing means at 17 should have a suitable sealing device.

In the device illustrated, the volatilized unsaponified organic matter and steam pass out of the upper portion of the flash chamber 16 and through dust separator 19 in which any fine particles of suspended soap carried by the vapors are removed. However, a concurrent apparatus may be employed with a suitable arrangement for separating the solids from the vapors, such as cyclone, etc. The dust-free vapors may be compressed in a thermal compressor 20 and are then led through pre-heaters 8 and 12 into the cooler or total condenser 21. The unsaponifiable material may be recovered from this condensate by fractionation or alternatively the unsaponifiable material, such as glycerine, may be fractionally condensed from the vapors.

By inserting the thermal compressor 20, such as a steam injector or a mechanical blower or compressor, the greater part of the heat supplied to the system is salvaged; the sensible heat and the latent heat of condensation of the commingled vapors give up their heat energy to the incoming soap solution and/or water at the desired energy

level. The entire flash chamber is kept at the proper temperature (radiation losses prevented) by means of jacket 22 which completely encloses flash chamber 16. The hot flue gases or a portion thereof issuing from steam superheater 14 and/or boiler 13 are passed into this jacket and are discharged at some point near the top of the apparatus. Should local conditions warrant, an economizer may be added at this point to salvage more heat. The nozzle 10 in conjunction with the pumps 3 and 4 and the quantity of heat added control, to a great extent, the pressure and rate of flow of the soap solution. The quantity of steam preferably should be greater than about 100 parts by weight of total steam to 1 part by weight of unsaponifiable organic material, or about 4 parts by weight of superheated steam to about 1 part by weight of soap solution, although higher or lower ratios may be employed depending on the quantity, volatility and boiling range of the unsaponifiable material. The drop in pressure in the nozzle 10 depends upon the rate of flow of the soap solution and the steam there-through. This rate of flow in turn depends upon the pressure and rate of flow of steam and of soap solution supplied by the pumps as well as the pressure generated by the various heating elements. The nozzle 10 is detachable from the steam and soap solution pipes so that nozzles of various sizes may be employed. It is essential that the construction of the spray nozzle and its functions be properly understood. The object of the system is to contact the soap solution with highly superheated steam for as short a time interval as is consistent with virtually complete equilibrium contact of the steam with the non-saponified material. This is accomplished by means of the nozzle diagrammatically shown. Note that the steam issues from the constricted orifice 23, impinges upon the orifice 24 of the spray nozzle at extremely high velocity just before entering the spray chamber proper. The steam is given a whirling motion inside the jet by a spiral. The solution is led through the annular passage where it attains an enormous velocity. This will result in an almost complete atomization of the solution, thus rendering maximum contact between steam and unsaponified material. At the same time, the solution absorbs the required heat in an extremely short time interval and is rapidly flashed, thus preventing decomposition. The short path of the flow and high velocity prevents any possibility of clogging of orifices 23 and 24. It is also very important that practically no transfer of heat between the steam and the solution occurs before actual physical contact of the two. That is, the pipe or jet conducting the steam should have as little contact as is possible with the soap solution. If the area of contact is not reduced to a minimum, this very high temperature steam (in the neighborhood of 1000° F.) will heat the solution causing a film of solids to deposit on the walls of the pipe and so lead to eventual plugging and at the same time decomposition of the soap product.

In practice the proportion of superheated steam introduced into the nozzle 10 can be regulated so that a solid, dry product; a fused, dry product; a hydrated product; or a solution thereof, is obtained. The product is preferably in the form of a liquid or solid, dry product which can be reduced to flake form by passing it over a cooling roll, or it can be extruded into bars, with or without water or other addition agents. The

cooling step is preferably accomplished very rapidly and/or in an inert atmosphere.

If it is desired to add other agents to the soap product, they can be uniformly mixed with the solution thereof before, during, or after its preparation, and they will be uniformly distributed in the final product. It is also possible to arrange the apparatus so that one or more nozzles are employed to spray the same or different solutions, thereby forming particles of uniform composition, heterogeneous mixtures and/or coated particles. In the case of coated particles, the products may be controlled as to solubility, color, odor, density, stability and/or the like by suitable selection of the coating solution.

The organic salt products may be employed directly in this form, for example, as soaps or they may be converted to the corresponding acids and, with or without fractionations, be used for various other purposes including preparation of glyceride food products, plasticizers, varnishes, paints, solvents and the like.

The acids may be distilled, bleached with chlorine or hypochlorite, clay-treated, elaidinized, extracted, hydrogenated and/or fractionated by any suitable method at an appropriate point in the processing before and/or after the flash treatment of the soaps thereof in order to improve the final products.

The fractionation of organic carboxylic acids is preferably accomplished by fractional distillation before and/or after the flash treatment of the soaps to recover relatively pure acid fractions. The acids, washed and dried, may advantageously be distilled by first heating them in a pipe still. The temperature of this heater is preferably controlled so as to raise the temperature of the acids as they pass therethrough to substantially 250° to 300° C. as rapidly as possible within several minutes. The temperatures and pressures are dependent, to a large extent, upon the nature of organic carboxylic acids being treated. Steam, preferably superheated, may be added to the acids during the heating process in order to assist in the subsequent vaporization.

The partially vaporized acids issuing from the heater pass into a flash chamber preferably at a reduced pressure of about 5-10 mm. In this apparatus the unvolatilized portion, mainly tarry material, is separated from the volatilized portion and drops to the bottom of the flash chamber. Steam superheated to the heater outlet temperature or higher is passed into the bottom of the flash chamber for stripping purposes. If desired, a number of plates may be included below the heater vapor outlet so as to more effectively strip the bottoms of valuable volatile materials. The tarry materials may be withdrawn from the bottom of the flash chamber. Baffles are placed at the top of the flash chamber to remove entrained unvaporized materials from the desired organic acid vapors before introduction into the fractionating zone.

A number of fractionating systems are possible but a series of individual fractionating columns is preferred to the use of only one tower containing many bubble plates.

In the preferred procedure the vapors issuing from the flash chamber are passed into a bubble-plate column supplied with superheated bottom stripping steam. In this column high boiling acid bottoms are removed and an overhead cut is taken. Reflux may be supplied either by means of a partial condenser located at the top of the column or by returning to the top of the column

a portion of the liquefied overhead condensate therefrom. The cooling medium for the partial or total condenser or both may be charging stock already raised in temperature by passage through the partial condensers connected to the succeeding columns that are operated at successively lower temperatures. In this manner the over-all thermal efficiency may be greatly increased. The stripped bottoms discharged from this column are valuable high boiling acids, such as resin acids, and are substantially free from the mixture of lower boiling acids, such as fatty acids, comprising the overhead from this column. In the succeeding columns the now resin-free mixture of lower boiling acids is separated. In general, the number of columns is equal to one less than the number of fractions or cuts desired. By proper control of the individual reflux ratios and bottom steam ratios, taking also into consideration the effectiveness of the columns, it is possible to cut the mixture of acids, such as fatty acids and resin acids, into very narrow boiling fractions. These acids may be fractionated again by the same or by other suitable methods.

An alternate procedure is to separate the mixture by passing the vapors issuing from the flash chamber into a bubble plate fractionating tower. The mixed acid vapors, entering the fractionating tower which maintains a suitable reflux, may be separated by reason of their different boiling points into relatively pure fractions of acids such as resin acids and fatty acids. The hot liquid acids may be drawn from various plates in the tower which contains the largest percentage of individual acids and are passed into individual reboilers. Steam superheated to the proper temperature is passed into the bottom of the reboiler where the feed is stripped of the more volatile portions, which vapors are returned to the column. For a more complete separation, the liquid withdrawn from the stripper may be further fractionated. The liquid drawn from the bottom of this fractionating column consists primarily of a relatively pure high boiling acid depending on the raw material or mixture of raw materials. In order to facilitate fractionation, a current of superheated steam at the proper temperature is passed into the column from an open steam coil positioned in the bottom of the fractionating column.

From the upper bubble plate of the single or the last fractionating column the vapors, consisting principally of steam and a low boiling organic acid, pass through a reflux condenser which furnishes sufficient reflux for the desired fractionation. The non-condensed vapors pass through a line into a vapor condenser wherein the temperature is so regulated that practically all of the remaining acid vapors are liquefied and the steam is left in the vapor state. The acid liquefied in the condenser is substantially pure. Any acids suspended in the steam are removed by passing the steam around suitable baffles whereby the particles of acid are removed. The steam freed from its suspended acids is preferably passed directly to a barometric condenser to which are connected suitable vacuum pumps or steam jets which serve to maintain the entire system under suitable reduced pressure. In either procedure, portions of certain of the acid fractions may be returned to the feed to raise the vapor pressure of the original mixture. It should also be noted that although it is preferred to flash into the flash chamber, in some instances it may be desirable to flash

the acids directly into the fractionating tower. The process may be conducted in a continuous manner or it may be carried out in a batch procedure.

The distillation may be performed with or without additional materials such as aliphatic, alicyclic, terpene and aromatic hydrocarbons, fatty acids, and the like.

Other methods of separation including solvent extraction, fractional crystallization and the like may be used.

#### Example I

About 300 kilograms of an aqueous solution of 10% crude animal grease soap brought to a pH of about 9 to 11 is pumped through a steam heated tubular heater of about 30 feet of steel tubes having an internal diameter of about 0.36 inch wherein the temperature of the solution is raised to about 130° C. (265° F.) at a gage pressure of about 10 lbs. per square inch. Approximately 80% to 85% of the water in the soap solution is vaporized in the tubes during this heating. In a separately fired furnace, steam is superheated to about 510° C. (950° F.) at a pressure of about 150 lbs. per square inch absolute. The partially vaporized solution and highly superheated steam in the proportion of about 100 kilograms of solution to about 1,000 kilograms of superheated steam are separately piped into the flash chamber where they meet in a nozzle such as is depicted in Figure 2. The superheated steam is momentarily, intimately commingled with the solution, thereby sweeping the solution from the nozzle into the flash chamber at an extremely high velocity and supplying enough heat at an optimum temperature to vaporize substantially all the water and substantially all the non-saponifiable as well as any liquid phenolic, organic material held in the soap solution. The flash chamber is held at atmospheric pressure and at a temperature of about 205° C. (400° F.). The cooled product is substantially odorless, dry, granular, unsaponifiable-free soap of good color. The vapors of water, unsaponifiable and other non-soap organic materials are removed from the top of the chamber and condensed to recover about 95% of the unsaponifiable organic material in the original solution.

Among the bases which may be employed for neutralizing the fat, fatty oil, wax, fatty acid resin and/or naphthenic acid, with or without the presence of other saponifiable material, are soda ash, caustic soda, potash, caustic potash, ammonia, lime, limestone, dolomite, methyl amines, ethyl amines, butyl amine, mono-, di-, or tri-ethanol amines, mono-, di-, or tri-glycerol amines, pyridine, aniline, piperidine and the like. Other salts which may be formed include those of magnesium, aluminum, lithium, copper and various mixtures of any of the foregoing organic and inorganic salts. When water-insoluble salts are formed such as calcium soaps, it is of course necessary to prepare solutions of the soaps in other media, such as petroleum oils, gasoline, ethyl alcohol, butyl alcohol, aromatic hydrocarbons and various mixtures of such solvents.

The materials that may be neutralized alone or along with other neutralizable materials are fatty oils, fatty acids, waxes, resin acids, cyclo aliphatic acids and other organic and inorganic acids. Among the specific neutralizable materials which may be used are tallow, olive oil,

palm oil, coconut oil, linseed oil, China-wood oil, castor oil, garbage grease, wool fat, cottonseed oil, cottonseed foots, babassu oil, whale oil, fish oils, peanut oil, tall oil, oxidized petroleum, spermaceti, and the various individual fatty acids in these materials; crude naphthenic acids, rosin, and various mixtures of any of these acids, waxes, oils, and resins. Various other saponifiable materials may be neutralized and treated by the present process, including organic sulphonic acids, sulphuric acid, phenols, alkylated phenols, inorganic acids and the like.

Among the materials that may be admixed with the soaps by mixing with the soap solution before flashing, by simultaneously flashing a second solution thereof and/or by mixing the final products therewith, in addition to the fatty acid soaps, resin acid soaps, naphthenic acid soaps, and/or alkylated naphthenic acid soaps, are salts of organic sulphonic acids; alkaline soap builders, water-soluble water-softening phosphorus acid compounds, and other salts including sodium carbonate, sodium silicates, trisodium phosphate, borax, sodium sesquicarbonate, sodium hexametaphosphate, sodium pyrophosphate, sodium tetraphosphate, sodium biphosphate, sodium sulphate, sodium chloride, sodium acetate, sodium hypochlorite, sodium thiosulphate, sodium perborate, sodium tartrate, sodium citrate and sodium oxalate and the corresponding ammonium, substituted ammonium and potassium salts thereof; solvents including hexalin, naphtha, ethyl alcohol, butyl alcohol and water; insecticidal, germicidal, styptic and medicinal agents including aluminum chloride, mercuric chloride and various copper and lead salts; coloring agents, abrasives and fillers including dyes, lakes, pigments, silica, kieselguhr, silica gel, feldspar, precipitated chalk, pumice, infusorial earth, bentonite, talc, starch and the like. The type of addition agent will depend on the ultimate use of the new composition.

As many widely different embodiments of this invention may be made without departing from the spirit or scope thereof, it is to be understood that the application is not limited to the specific proportions or embodiments thereof except as defined in the following claims.

#### We claim:

1. The process of treating fatty acid soaps which comprises heating an aqueous solution of a fatty acid soap to partially vaporize the water therein, admixing therewith superheated steam of a temperature above that of the solution, and then substantially immediately rapidly reducing the pressure on the solution sufficient to volatilize substantially all the water and unsaponified organic material therein.

2. The process of treating fatty acid soaps which comprises heating a solution of a fatty acid soap to partially vaporize the solvent therein, admixing therewith steam of a temperature above that of the solution, and then immediately rapidly reducing the pressure on the solution to volatilize solvent and non-saponified material therefrom.

3. The process of treating soaps which comprises heating in a confined space an aqueous solution of a fatty acid soap containing volatile non-saponified material so that between 50 and 90% of the water is vaporized, contacting directly the partially vaporized solution with steam at a temperature of at least 260° C., and then substantially immediately rapidly reducing the

pressure so that substantially all the water and non-saponified material are volatilized.

4. The process of continuously making soap which comprises continuously flowing a stream of saponifiable fatty acid material into contact with a stream of saponifying material, continuously heating the mixture to form a partially vaporized soap solution containing unsaponified material, continuously admixing the partially vaporized soap solution with superheated steam at a considerably higher temperature than that of the soap solution to rapidly raise its temperature, and then substantially immediately continuously flashing the soap solution into a lower pressure chamber maintained at an elevated temperature whereby substantially all volatile non-saponified material is separated as a vapor.

5. The process of treating fatty acid soaps which comprises directly contacting a partially vaporized solution containing a fatty acid soap with a substantial quantity of superheated steam of a temperature above that of the solution, and then substantially immediately rapidly reducing the pressure on the solution to a considerably lower pressure whereby solvent and volatile non-saponified organic material in the solution are volatilized.

6. The process of treating fatty acid soaps which comprises directly contacting a partially vaporized aqueous solution containing a fatty acid soap with a substantial quantity of superheated steam of a temperature above that of the solution, and then substantially immediately rapidly reducing the pressure on the solution below the vapor pressure thereof at the operat-

ing conditions whereby substantially all the water and unsaponified organic material in the solution are volatilized.

7. The process of treating fatty acid soaps which comprises directly contacting a partially vaporized solution containing a fatty acid soap with a substantial quantity of a superheated inert gas at a temperature higher than that of the solution, and then substantially immediately rapidly reducing the pressure on the solution below the vapor pressure of the solution at the operating conditions whereby solvent and non-saponified organic material in the solution are volatilized.

8. A continuous process for preparing soap which comprises directly contacting a saponifiable fatty acid material with an aqueous solution of a neutralizing agent, heating the resulting mixture in a restricted space whereby a portion thereof is volatilized directly, contacting the solution with superheated steam of a temperature above that of the partially volatilized solution, rapidly reducing the pressure of the solution to a considerably lower pressure immediately after contacting it with the superheated steam while maintaining the temperature above the boiling point of water at the operating conditions whereby substantially all the water and unsaponified organic material in the solution are volatilized, and condensing the separated vapors.

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