July 27, 1943. S. J. HOLUBA 2,325,320

NEUTRALIZATION

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Fig. 1.

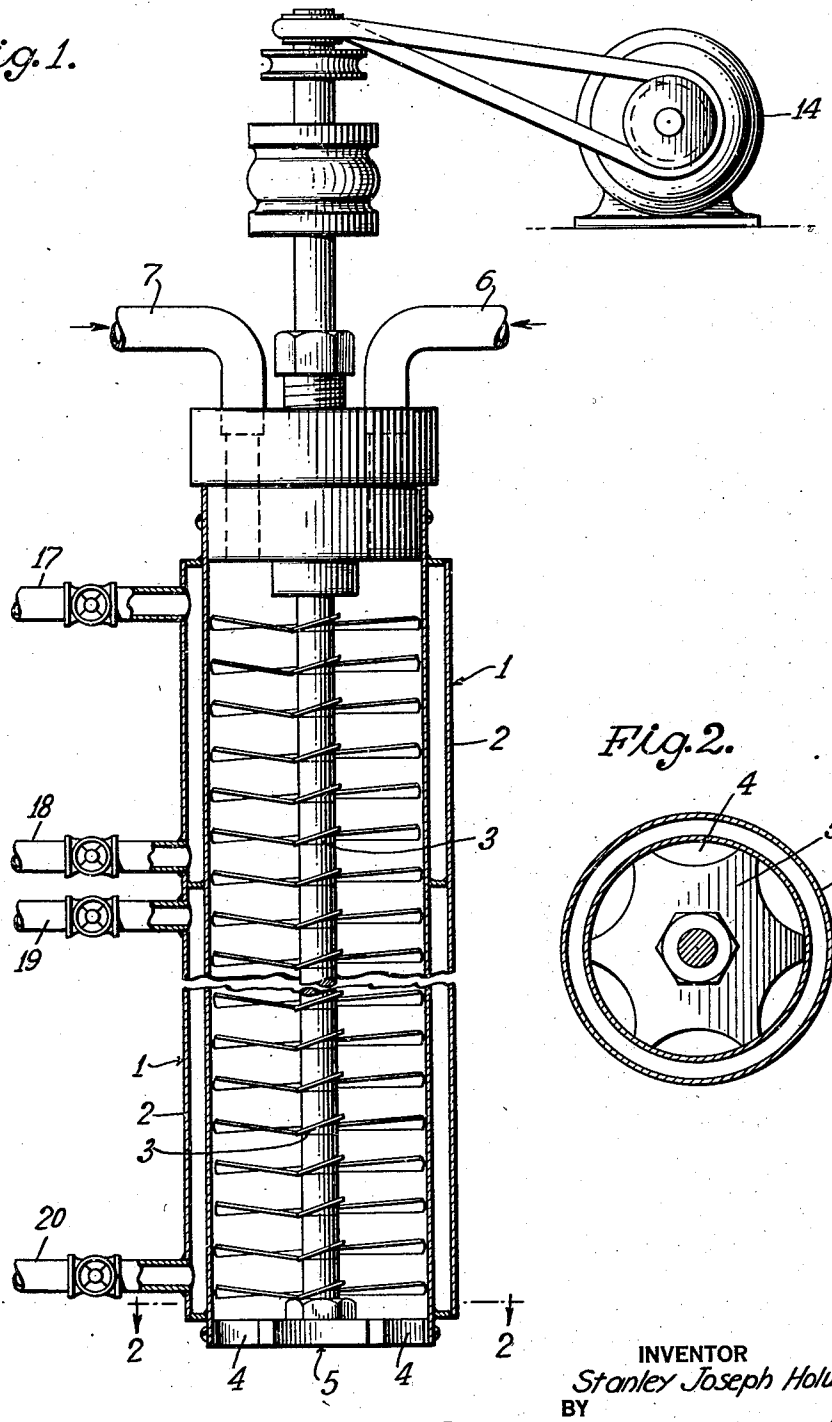


Fig. 2.

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Fig. 3.

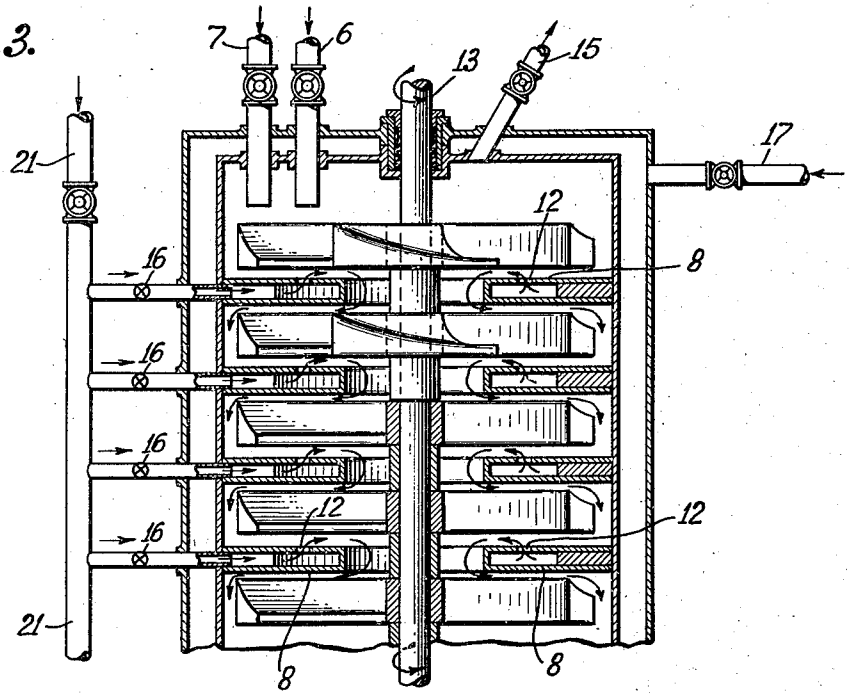
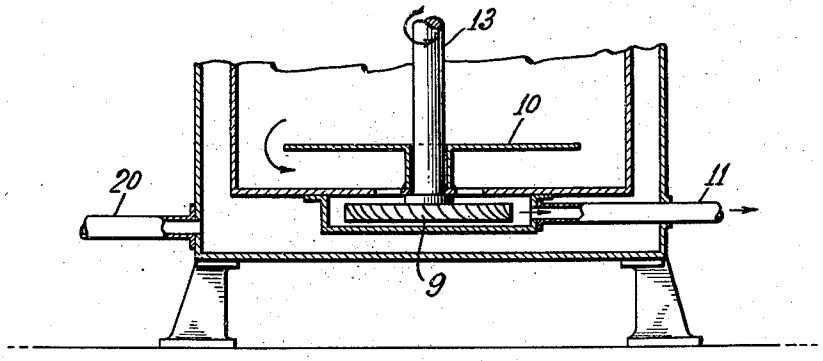


Fig. 4.



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2,325,320

NEUTRALIZATION

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Application August 3, 1940, Serial No. 350,920

7 Claims. (Cl. 260—503)

The present invention is directed to the improved method of neutralizing organic acids with basic salts under conditions which generate a foaming material and a gas.

The use of sodium carbonate as a neutralizing agent has long been desired in the preparation of detergent salts of organic acids such as carboxylic acids including fatty acids, rosin acids, naphthenic acids; organic sulphonic acids, organic phosphoric acids, organic sulphuric acids, and the like. This alkaline material possesses the advantage of lower cost and of generating less heat during the neutralization reaction. Its use has been seriously hampered, however, by the fact that copious and uncontrolled foaming takes place during the neutralization step with overflowing of the container and loss of material. Furthermore, because of the porous or spongy nature of the neutralizing mass due to the gas bubbles dispersed therethrough, it has been found almost impossible to obtain satisfactory uniform heating or cooling of the mixture. Finally the excess of carbon dioxide gas has heretofore prevented complete neutralization but has instead caused the formation of salts, bicarbonates and unreacted material.

It has now been found possible to neutralize organic acids which form normally foaming salts, with salts of strong bases and weak acids which generate gases when reacted with the organic acids. It has also been found possible to prepare a soap of desired water content in a continuous manner. The process of the present invention in general comprises the introduction of the organic acid and the neutralizing salt into a large chamber under pressure in which an agitating means revolves at a high velocity. The flow is usually arranged so that only a small quantity of material is present in the chamber at any one time. Orifices are placed at the bottom, preferably near the periphery from which the materially degassed organic acid salt is removed. Any gas retained in the organic acid salt removed from the chamber is in the form of large bubbles which readily rise to the surface and escape.

It is believed that the foam in the chamber is vigorously agitated and sheared and that the liquid is thrown to the wall by centrifugal action, whereby the bubbles of gas are broken and agglomerated. The liquid freed of a substantial quantity of the gas falls to the bottom of the chamber and may be forced out of the holes in the periphery of the bottom of the chamber by the pressure therein. The applicant is not to be limited by the above theory which is given for a better understanding of the principles and operation of the present invention.

The material usually comes out as a stream or paste, depending on the viscosity, with intermittent large bubbles of gas which can be collected if desired. The discharge of the chamber is at a lower pressure than the chamber interior. It may be atmospheric, super-atmospheric or sub-atmospheric. For economy of operation, atmospheric pressure is usually employed.

The materials may be mixed in the chamber, at the moment of introduction into the chamber or outside the chamber (under pressure) and then be introduced into the chamber. The proportions may be adjusted so that a neutralized product, a superfatted product, or a product containing excess soda ash or other alkalies is formed. Addition agents including alkali soap builders, caustic alkali, solvents, pigments, alkali pyrophosphates, alkali hexametaphosphates, inorganic salts, monoglycerides, and germicides may be added with the reactants or at other points in the mixing and degassing chamber.

The chamber is preferably jacketed in order more exactly to control the reaction. The reactants may be preheated to intiate the reaction and cooling or heating water may surround at least the top of the chamber. With the more highly reactive materials pre-heating is not necessary. In fact, in such cases cooling may be required at the initial reaction point and even pre-cooling of the reactants. Some heating may be required at the lower part of the treating chamber to obtain the maximum fluidity of solution with minimum detrimental effects on the products. It is often advantageous to hold the discharge products at the higher temperatures in order to permit removal of residual gas bubbles, if any.

In order to assist in giving a full understanding of the present invention, the application of the principles thereof to the production of soap from fatty acids with reference to the attached drawings is given.

Figure 1 is the reaction vessel or degassing chamber in front elevation.

Figure 2 is a plan (bottom) view of the mixer illustrated in Figure 1.

Figure 3 is a front elevation of a modification of the top or reaction and agitating section of the degassing chamber.

Figure 4 is a front elevation of a modification of the bottom or removing section of the de-

gassing chamber which may be employed when separate gas removing means are available.

Fatty acid material, such as the fatty acids obtained from the fat hydrolysis process described in Martin H. Ittner's U. S. Patent No. 2,139,589, is flowed under pressure from a storage tank through a preheater and inlet port 6 of the chamber 1. A concentrated aqueous solution or slurry of sodium carbonate is simultaneously flowed under pressure from a storage tank through a preheater and inlet port 7 to chamber 1 where it is contacted with the fatty acid material in the proportion of two mols of fatty acid to a slight excess over one mol of sodium carbonate. The pressure may be applied by pumps, by pressure on the materials in the storage tank, or by elevating the storage tanks to obtain sufficient head.

The reaction takes place at the point of introduction into the chamber 1 and generates considerable heat and carbon dioxide. The material is then converted into a mass of foam. The chamber has a jacket 2 through which steam or hot water is flowed to hold the temperature in the chamber at about 185° F. In the chamber are mechanical agitating means 3 mounted on shaft 13 driven by motor 14 operated at a high speed, which means vigorously mix, beat and centrifuge the foaming material and agglomerate the gas. Completely reacted materials, freed of the major proportion of the gas, tend to accumulate at the wall and bottom 5 of the chamber. The pressure in the chamber forces the molten hydrated soap accumulated at the bottom 5 out the orifices 4 in the bottom 5. Gas bubbles issue from the orifices 4 until additional substantially degassed soap builds up in the bottom 5 and is ejected. Any gas remaining in the soap is in the form of large bubbles and separates readily from the hot molten hydrated soap. If desired, the orifices 4 may be very small, e. g. the size of pinholes, in order to assist in the removal of residual gas.

The procedure may be somewhat modified by operating as illustrated in Figure 3. The acid material is introduced in the inlet port 6. The neutralizing solution is introduced in the inlet port 7 and/or inlet port 21. By using the inlet port 21, it is possible to neutralize in a stepwise manner. If desired, hydrogen ion (pH) control means for controlling flow of reactants through valve 16 may be employed at or near one or more of the inlet ports 12 on the individual plates 8 in order to more exactly control the neutralization. The reaction mass passes over the plates 8 to the center of the vessel. It is then violently sheared and thrown to the sides of the vessel by the blades 3. It again flows to the center and the procedure is repeated several times. Alternatively the neutralizing solution may be introduced through inlet port 7 and the organic acid through inlet port 6 and/or inlet port 21. The separated gas tends to be displaced toward the center of the mixer. If desired, it may be removed at the top through outlet port 15 which may be connected to an evacuating means to maintain a vacuum on the chamber. In such cases, however, the reacting materials should be introduced below one or more of the rapidly rotating blades, and the degassed material should be removed by positive means as illustrated in Figure 4. This positive means may be a centrifugal pump 9 on the bottom of the chamber below a stationary plate 10 which prevents vortex at the outlet, but other pumping means may be attached at outlet port 11. However, the vessel is usually operated at higher pressure than the outlet, hence the degassed material may be removed at the bottom by extrusion from the orifices at the periphery with or without the assistance of positive removal means. The agitating blades in any type apparatus may be rough or corrugated in order to improve the agitating or shearing action of the blades. These blades may be of different slopes to obtain better mixing by some working up and others down, preferably the latter. The intermediate plates may be of different shapes and slopes with or without feeding means, and may even be adjusted to rotate counter to the blades.

The neutralization of organic sulphonic acids or acid halides with or without free sulphonating agent is similarly conducted with the modifications that the reactants usually are not preheated before introduction into the chamber, and that the jacket at the top of the reaction has very cold water or other refrigerant passing through it to absorb the heat of reaction and maintain the temperature below about 130° F., while the bottom jacket of the reaction chamber has cooling water at somewhat higher temperature which maintains the reaction chamber bottom at about 110° F.

The following examples are given for the purpose of illustrating the principles of the present invention but are not intended to be limiting on the scope thereof.

Example I

9,450 grams of a mixture of 2 parts of tallow acids and 1 part of coconut oil acids heated to 140° F., and 7,300 grams of an aqueous solution containing 31% sodium carbonate also heated to 140° F. are uniformly pumped by proportioning pumps into confluence in the top of a stainless steel mixing chamber 14" long and 2" in diameter (Figure 1) at a rate of about 84 grams of mixture per minute. The temperature is maintained at 185° F. in the mixing chamber by means of a steam jacket. The mixing chamber has a vertical ⅝" shaft equipped with 24 propeller blades reaching almost to the walls of the chamber. These blades are set about ½" apart and are twisted to force the material outward and downward. The blades are rotated at a speed of about 1,000 to 1,500 revolutions per minute. The mixer is closed except for the inlet ports for fatty acid and alkali solution in the top, and the five ¼" holes in the periphery of the bottom for removing the soap and gas. The chamber contains a foam of soap solution at a slightly higher pressure than the external pressure. The hot soap (185° F.) practically free of gas, comes out at the bottom intermittently with large gas bubbles.

The product is substantially free of fatty acids, contains only a trace of excess sodium carbonates and about 31% moisture. It may be formed into a cake directly by cooling; it may be crutched with various builders, perfumes and the like and framed; or it may be milled, plodded and extruded into bars.

Example II

4,250 parts by weight of an aqueous mixture containing about equal parts of coconut oil monoglyceride acid monosulphate, and sulphuric acid in water at 60° F., and about 9,350 parts by weight of an aqueous solution containing 31% of sodium carbonate at 60° F. are continuously pumped at a uniform rate of about 227 parts of total mix-

ture per minute in proportions adjusted to obtain a product pH of about 6 by means of proportioning pumps into the neutralizing chamber described in Example I. An aqueous product is obtained substantially free of sodium carbonate and bicarbonate, and containing about 40% water, 36% sodium sulphate and 24% of the sodium salt of coconut oil monoglyceride monosulphates. Some gas remains in the aqueous mixture but this may be removed by standing for a short time. However, the product generally is completely degassed by spraying the solution under pressure at a temperature of about 150° F. into a vacuum chamber against a splash plate. The solution continuously removed from the vacuum chamber is cooled, somewhat concentrated and substantially free of dissolved and dispersed air or other gases. It is then spray dried to obtain a light colored, dense bead.

Example III

2,000 parts by weight of a mixture of about equal parts of a sulphonated mineral oil extract (sulphonated in liquid sulphur dioxide) and sulphuric acid in water at 60° F., and an aqueous solution containing 31% of sodium carbonate at 60° F. are pumped at a uniform rate by means of proportioning pumps adjusted to maintain a product pH of about 7 into the neutralizing chamber described in Example I. The product is an aqueous solution of 30% sodium sulphonate, 60% of sodium sulphate and 40% of water. The product may be completely degassed as in Example II. It is dried on heated rolls to obtain a light colored chip.

Example IV

1,000 parts by weight of a chlorine substituted gas oil sulphonyl chloride prepared by the treatment of gas oil with sulphur dioxide and chlorine gas at about 50° C. in the presence of light is neutralized as follows. The sulphonyl halide is warmed to about 80° C. and pumped into the top of the reaction chamber of Figure 3 where it contacts a stream of a concentrated aqueous sodium carbonate solution warmed to about the same temperature. Reaction immediately sets in and the frothy mixture is violently agitated by the blades, returned to the center by the individual plates at which point or points additional aqueous sodium carbonate solution may be added to more exactly neutralize the resulting aqueous solution. The accumulated solution is ejected from a number of fine or pin holes at the bottom of the vessel. The product is light colored and substantially free of gas.

It is possible to add bleaching agents such as sodium hypochlorite, sodium perborate, sodium peroxide, hydrogen peroxide and other treating agents to the reactants or alone at any point in the chamber.

The process may be similarly applied to other carboxylic acids including rosin, tall oil and other fatty oil acids; oxidized petroleum acids; carboxylic acid halides; aliphatic sulphates such as lauryl acid sulphate; aliphatic phosphates; aliphatic sulphonic acids and acid halides; aliphatic hydroxy sulphonic acids and acid halides; aliphatic sulphoacetates; aromatic sulphonic acids and acid halides, acylated and alkylated aromatic sulphonic acids and acid halides such as lauryl benzene sulphonic acid; other petroleum sulphonic acids; and any other organic derivative which produces normally-foaming salts. These materials may be treated alone or in admixture with other acids such as sulphuric acid, hydrochloric acid, phosphoric acid or the like. The term "aliphatic" includes those compounds which have other groups in the radical such as chlorinated aliphatic radicals, mono- and di-glyceride esters and/or ethers and other partial carboxylic acid and alcohol derivatives of aliphatic polyhydric substances, fatty acids, polyaliphatic ethers, and similar groups.

The base can be any water-soluble salt of a volatile acid weaker than the acid treated. Among the suitable compounds are sodium carbonate, ammonium carbonate, methyl ammonium carbonate, diethyl ammonium sulphite, sodium sulphite, potassium carbonate, pyridinium bisulphate, sodium acetate (particularly for the stable sulphonic acids), sodium bicarbonate, and the other corresponding alkali metal and ammonium and amine salts. Other bases may be employed with these compounds including triethanolamine, sodium hydroxide, caustic potash, tetraethyl ammonium hydroxide, ammonium hydroxide, organic ammonium hydroxides, organic pyridonium hydroxides, organic sulphonium hydroxides, organic phosphonium hydroxides or the corresponding carbonates, sulphites and the like.

It is also advantageous to neutralize the solution in the presence of solvents such as butyl alcohol, ethyl alcohol, dioxane, monoglycerides, ethyl ether, isopropyl alcohol and the like. When employing solvents for the organic products, it is sometimes desirable to employ large quantities of these materials to cause separation of associated inorganic salts such as sodium sulphates and the like.

As many widely different embodiments of the present invention are possible without departing from the spirit and scope thereof, it is to be understood that the application is not to be limited in any way except as defined in the following claims.

I claim:

1. The process of neutralizing organic acids which comprises contacting, in the presence of a liquid solvent and in the upper part of an enclosed, substantially vertically-disposed reaction space, an organic acid which forms normally-foaming salts, with a soluble salt of a strong base and a weak volatile acid, whereby a foamy mass containing a liquid salt product and a generated gas is produced; causing the separation of said liquid product and substantial quantities of said gas by agitation, centrifuging and shearing of the foamy mass; and removing said liquid product from the lower part of the reaction space.

2. The process of neutralizing organic acids which comprises flowing a stream of an organic acid which forms normally-foaming salts and a stream of a solution of a salt of a strong base and a weak volatile acid into contact with each other in the upper part of an enclosed, substantially vertically-disposed reaction space, said streams being under pressure, to form a foamy mass containing a liquid salt product and a generated gas; vigorously agitating, shearing and centrifuging the foamy mass within said enclosed space, thereby causing the separation of said liquid salt product freed from substantial quantities of generated gas; and removing said liquid product from the lower part of said enclosed space.

3. The process of neutralizing organic acids which comprises contacting, in the presence of a liquid solvent and in the upper part of an enclosed, substantially vertically-disposed reaction

space, an organic acid which forms normally-foaming salts, with an alkali carbonate to form a foamy mass containing a liquid salt product and generated carbon dioxide gas; vigorously agitating, shearing and centrifuging the foamy mass within said enclosed reaction space, thereby causing the separation of said liquid salt product freed from substantial quantities of carbon dioxide; and removing said liquid product from the lower part of said enclosed space.

4. The process of neutralizing organic acids which comprises contacting under pressure, in the presence of water and in the upper part of an enclosed, substantially vertically-disposed reaction space, an organic acid which forms normally-foaming salts, with sodium carbonate to form a foamy mass containing a liquid salt product and generated carbon dioxide gas; causing the separation of said liquid product and substantial quantities of said gas by agitation, centrifuging and shearing of the foamy mass; and removing said liquid product from the lower part of the reaction space.

5. The process of neutralizing organic acids which comprises flowing a stream of a fatty acid which forms normally-foaming salts and a stream of an aqueous solution of sodium carbonate into contact with each other in the upper part of an enclosed, substantially vertical cylindrical reaction space, said streams being under pressure, to form a foamy mass containing a liquid salt product and generated carbon dioxide gas; vigorously agitating, shearing and centrifuging the foamy mass within said enclosed reaction space, thereby causing the separation of a liquid salt product freed from substantial quantities of generated gas; and removing said liquid product from the lower end of said enclosed reaction space.

6. The process of neutralizing organic acids which comprises flowing a stream of an organic sulphonic acid which forms normally-foaming salts and a stream of an aqueous solution of sodium carbonate into contact with each other in the upper part of an enclosed, substantially vertical cylindrical reaction space, said streams being under pressure, to form a foamy mass containing a liquid salt product and generated carbon dioxide gas; vigorously agitating, shearing and centrifuging the foamy mass within said enclosed reaction space, thereby causing the separation of a liquid salt product freed from substantial quantities of generated gas; and removing said liquid product from the lower end of said enclosed reaction space.

7. The process of neutralizing organic acids which comprises flowing a stream of an organic sulphonyl halide which forms normally-foaming salts and a stream of an aqueous solution of sodium carbonate into contact with each other in the upper part of an enclosed, substantially vertical cylindrical reaction space, said streams being under pressure, to form a foamy mass containing a liquid salt product and generated carbon dioxide gas; vigorously agitating, shearing and centrifuging the foamy mass within said enclosed reaction space, thereby causing the separation of a liquid salt product freed from substantial quantities of generated gas; and removing said liquid product from the lower end of said enclosed reaction space.

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