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PREPARATION OF GLYCEROL SULFURIC ACIDS

Frederick William Gray, Belleville, N.J., assignor to Colgate-Palmolive Company, Jersey City, N.J., a corporation of Delaware

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7 Claims. (Cl. 260—458)

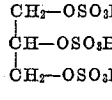
The present invention relates to processes for the production of glycerol sulfuric acids.

Included in the invention are methods of producing the glycerol trisulfuric acid and glycerol sulfuric acid intermediate useful in the production of the trisulfuric acid. These materials are of particular suitability for the production of monoglyceride sulfate detergents and detergent intermediates from fatty triglycerides.

In subsequent descriptions, the words fatty triglyceride, glycerol trisulfuric acid and sulfuric acid monohydrate, as used in the specification and claims have the following meaning.

Fatty triglycerides are those whose acyl groups average from 12 to 18 carbon atoms and are of a degree of unsaturation insufficient to substantially interfere with the manufacture of the detergent compositions described in this application. Only a relatively small part of the acyl groups present in such triglycerides may be of a chain length outside the 12 to 18 carbon atom range. Such triglycerides are usually employed in the forms of coconut or palm kernel oils. However, tallows, greases, lard, cottonseed oil, soybean oil, palm oil and corn oil, or fractions or mixtures of any thereof, may be used if they are first hydrogenated to remove undesirable unsaturated linkages. It is desirable that saturated triglycerides be employed, and since even coconut and palm kernel oils contain some unsaturated triglycerides, it is sometimes preferable to hydrogenate these oils too before reacting them according to the invented process. In this specification, except for the examples given the term "coconut oil" is inclusive of hydrogenated, as well as non-hydrogenated coconut oil.

Glycerol trisulfuric acid,



is produced when glycerol is sulfated under proper conditions. The degrees of sulfation of glycerol sulfated by various methods have been determined by titration with cold sodium hydroxide, and it appears that to secure a satisfactory detergent product from glycerol, fat and sulfation agent, one should first react the glycerol and sulfation agent to produce glycerol trisulfuric acid free of glycerol mono- and di-sulfuric acids. The aforementioned titration result indicates that the intermediate necessary for the production of a satisfactory fatty acid monoester of glycerol monosulfuric acid by the above method is glycerol trisulfuric acid and it is referred to as such. However it must be borne in mind that this term is used to identify the product of processes described in this specification. Therefore, should it be found that any of the products, made by the invented processes, in reality is not glycerol trisulfuric acid, the term nevertheless includes it. It also includes such product when glycerol trisulfuric acid is called for as a reactant in one of the described processes.

Sulfuric acid monohydrate is H_2SO_4 or $SO_3.H_2O$. The term "sulfuric acid monohydrate" identifies H_2SO_4 and excludes water in excess of the one mole combined with the one mole of SO_3 to form H_2SO_4.

It is necessary at this point to define a few more terms used in the specification and claims.

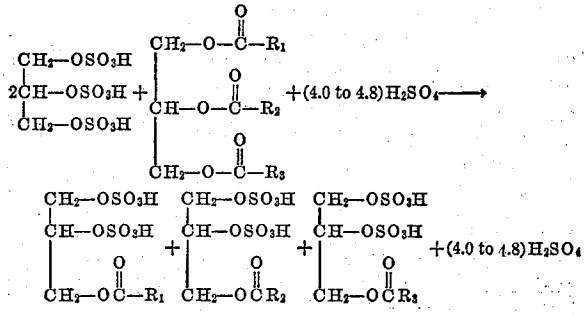
The term "glycerol sulfuric acid" describes any of the glycerol mono-, di- and tri-sulfuric acids, and mixtures thereof. The degree of sulfation of such acids and mixtures is indicated by a number between 0 and 3. Thus, a degree of sulfation of 2.1 might indicate a mixture composed of glycerol di- and tri-sulfuric acids, or more likely one of glycerol disulfuric acid with small amounts of the mono- and tri-sulfuric acids.

"Non-gaseous sulfur trioxide" is the sulfur trioxide in oleum or fuming sulfuric acid, which, if removed, would leave sulfuric acid monohydrate. It is also liquid sulfur trioxide. The term does not include solid sulfur trioxide.

In manufacturing a monoglyceride sulfate detergent of higher content of active detersive ingredient than that generally produced one molecular proportion fatty triglyceride, usually coconut oil, hydrogenated tallow or hydrogenated soya oil, and preferably coconut oil, is reacted with a mixture of two molecular proportions of glycerol trisulfuric acid and from 4.0 to 4.8, preferably from 4.2 to 4.6, molecular proportions, of sulfuric acid monohydrate, at a temperature between 30° C. and 65° C., preferably with the final portion of the reaction being conducted at a temperature between 50° C. and 65° C., to produce a detergent composition intermediate.

In a preferred process the fatty triglyceride, preferably coconut oil, is added, with agitation, within about ten to fifteen minutes to a mixture or solution of glycerol trisulfuric acid and/in sulfuric acid monohydrate at a temperature between 30° C. and 45° C. (higher if the triglyceride is solid at those temperatures) after which the reaction mixture is aged with agitation at from 50° C. to 65° C., desirably 50° C. to 60° C., for ½ to 2 hours, preferably 1 to 1½ hours. If the reaction mixture is one that becomes excessively viscous a non-interfering non-aqueous solvent, e.g., ethylene chloride, may be added to thin it and so enable the reaction to proceed more readily. The speed of reaction may be increased by increasing the degree of contact of the reactants, e.g., by improving mixing techniques, and consequently the mixing times may be correspondingly decreased.

Upon reacting the specified amounts of glycerol trisulfuric acid, fatty triglyceride and sulfuric acid monohydrate the following reaction is believed to occur.



where R_1, R_2, R_3 are the same or different fatty radicals of from 9 to 19 carbon atoms. The products of the above process, excluding the "monohydrate," are hereafter referred to as "disulfated monoacylated glycerol."

It is thought that the sulfuric acid is needed to split the fat and so aid the metathetic reaction, but this explanation of the reaction mechanism is advanced only as a theory.

On reaction with water, the —SO_3H group linked

through oxygen to the carbon of the disulfated monoacylated glycerol is believed to be hydrolyzed off presumably, due to its proximity to the acyl group.

The resulting compound, monoacylated monosulfated glycerol (probably with the substituent groups joined to the glycerol terminal carbon atoms) is hereafter referred to as "detergent acid." The mixture of disulfated monoacylated glycerol and sulfuric acid monohydrate in the proportions resulting from the processes of this invention, is called "detergent composition intermediate." These terms are used to promote simplicity of expression. Since the identity of the various intermediate compounds has not been irrefutably ascertained, and since this invention is of processes for making detergents and intermediates, the terms used describe the products obtained from the invented processes. It is believed that such products are of the formulas given but the designations used in this specification are not limited thereto.

The hydrolysis referred to in a preceding paragraph may take place when the detergent composition intermediate is added to water or a water-ice mixture or when it is treated with a base in the presence of water. Treatment with a base will also result in a substitution of the base cation for the hydrogen of the remaining $-SO_3H$ group, and will render the detergent water soluble. The splitting off of the β-SO_3H group and neutralization may also be conducted by adding the detergent composition intermediate and base to a circulating stream of already neutralized detergent composition, thereby reducing local concentrations of reactants and permitting the "hydrolysis" and neutralization to be conducted at a higher temperature with a consequent lower viscosity and higher practicable detergent composition solids concentration limit, while still avoiding undesirable side reactions which occur at high reactant concentrations and high temperatures.

Among the bases with which the detergent composition intermediate and/or detergent acid and accompanying sulfuric acid, may be reacted to form a detergent salt are sodium, potassium, lithium, calcium, magnesium and ammonium hydroxides and weakly basic salts of the named cations, e.g., carbonates and bicarbonates, and primary, secondary and tertiary amines, e.g., monoethanolamine, diethanolamine and triethanolamine. The detergent salt itself may often be referred to as detergent active ingredient while mixtures of such salts with inorganic sulfates, produced during the course of detergent acid neutralization may be called detergent compositions or detergent salt compositions.

The neutralization reaction which may accompany or follow the "hydrolysis" reaction, is conducted in an aqueous medium at a temperature between 0° C. and 50° C., the higher temperatures being practicable when the reactions are carried out in a circulating medium containing a buffer of already neutralized detergent.

Since the sodium and ammonium salts of monosulfated "monococated" (monoacylated with coconut oil fatty acids) glycerol are at the present time the most important commercial detergents derived from glycerol, it was only natural that most of the work done to verify this invention was conducted with such products. They are the preferred detergent salts and processes leading to their production and the production of compositions containing them by the methods described above for the manufacture of salts of fatty acid esters of monosulfated glycerol are preferred ways to utilize the glycerol sulfuric acids made by the processes of this invention.

It has been found that, when the base, e.g., aqueous sodium hydroxide is reacted rapidly with the detergent composition intermediate, or mixture of detergent acid and sulfuric monohydrate, a detergent salt composition is produced which is of higher quality (lower content of ether soluble material) than a composition formed by slow neutralization. A rapid, uniformly conducted neutralization minimizes hydrolysis of the finished active detergent ingredient (which hydrolysis is known to occur in acidic or basic aqueous media). However, when the neutralization process is conducted in a circulating body of already neutralized material, which acts as a buffer, there is less need for rapid neutralization.

In laboratory experiments detergent composition intermediates, especially those derived from coconut oil, have been "hydrolyzed" and neutralized by first plunging said detergent composition intermediate, made from one molecular proportion of glycerol, into from about 200 to 400 molecular proportions of water at a temperature between 0° C. and 50° C., and then neutralizing rapidly with a solution of a base, usually sodium hydroxide at an operative weight concentration, between 20 and 60 percent in the case of sodium hydroxide. Since the heat of dilution of the detergent composition intermediate is very great, steps must be taken to prevent an undue temperature rise when it is diluted. While in actual production it is the practice to dilute and neutralize in a circulating medium of already neutralized material, in the laboratory or under certain production conditions such methods are impracticable. Hence it is found necessary either to provide refrigerated jackets on the processing vessel or, as is preferable in the laboratory, to use a mixture of ice and liquid water, usually 2 parts ice and one part liquid water as the diluting medium, allowing the temperature thereof to rise from 0° C. to approximately room temperature as the detergent composition intermediate is added.

The preceding descriptions of processes for the manufacture of detergent composition intermediates and detergent compositions include the use of glycerol trisulfuric acid containing minor amounts of sulfur trioxide (not more than 12 parts per 100 parts by weight glycerol trisulfuric acid). Such sulfur trioxide is usually unreacted excess used to force the reaction which results in production of the glycerol trisulfuric acid. While good detergent compositions, high in active ingredient content and low in ether solubles, may be prepared from glycerol trisulfuric acid containing sulfur trioxide, such products are dark in color. Although they may be useful in various applications often it is highly desirable that light products be obtained capable of yielding clear solutions and emulsions. It has been discovered that if there is no sulfur trioxide in the glycerol trisulfuric acid, and therefore none present when the detergent composition intermediate is made, detergent salt compositions made therefrom will be of high quality and light color.

For that reason a preferred embodiment of this invention is in making a glycerol trisulfuric acid free of sulfur trioxide but also included within the invention are the disclosed processes for the production of glycerol trisulfuric acid containing less than 12 parts sulfur trioxide per 100 parts by weight of glycerol trisulfuric acid.

Glycerol trisulfuric acid free of sulfur trioxide may be made by reacting one molecular proportion of substantially anhydrous glycerol (approximately 99.5% by weight) with between 2.5 and 3.0, preferably between 2.7 and 3.0 molecular proportions of non-gaseous sulfur trioxide in a sulfuric acid medium which contains between 2.1 and 3.5, preferably between 2.2 and 2.8 molecular proportions of sulfuric acid monohydrate. It has been discovered that the amount of monohydrate that must be employed to enable one to produce high quality detergent salt, is directly dependent upon the quantity of non-gaseous sulfur trioxide used, according to the equation:

$$X=2.2+2(3-Y)$$

where X is the number of molecular proportions of sulfuric acid monohydrate, and Y is the number of molecular proportions of sulfur trioxide. The reaction should take place at a temperature or temperatures between 15° C. and 45° C., because at lower temperatures the reaction is slow and at higher temperatures side reactions are possible. To secure completely trisulfated glycerol and to improve the overall reaction speed at least part of the

reaction, the final part, must be conducted at a temperature between 35° C. and 45° C.

In the reaction of the type described usually an oleum relatively weak in sulfur trioxide, such as 20% oleum, will first be added to the glycerine, often at about 20 to 25° C. and within about five minutes or so. This mix may then be aged, for approximately ten minutes, after which an oleum stronger in sulfur trioxide, such as 65% oleum, may be added, generally at a temperature higher than that of the original sulfation mix, e.g., 30–35° C. It should be noted that oleums added act as sources of both non-gaseous sulfur trioxide and sulfuric acid monohydrate. The second addition of oleum may take about 15 minutes and is ordinarily followed by aging for about an hour, although lesser aging periods are often satisfactory, at a temperature between 35° C. and 45° C., preferably between 35° C. and 40° C. In place of 20 percent oleum, oleums of other strengths may be employed for the initial sulfation if they are "weak" enough so as not to char the glycerine or promote harmful side reactions. Correspondingly, instead of 65 percent oleum, other oleums may be used to provide, in combination with the "weak" oleum, the proper amounts of sulfuric acid monohydrate and sulfur trioxide. It is also possible to employ liquid sulfur trioxide as a source of sulfur trioxide, sometimes, but not necessarily, added in mixture with an oleum. Two-stage or multi-stage addition of oleum to the glycerol is preferred because, as previously stated the addition of strong oleum to glycerol might char the organic compound or lead to the development of adverse side reactions. It is also desirable because oleums of about 50 percent weight concentration of sulfur trioxide, the approximate concentration yielding 3 parts sulfur trioxide per 2.2 parts sulfuric acid monohydrate, are rather viscous and their lack of mobility impedes the progress of the sulfation reaction.

However it is not necessary to utilize a two- or multi-stage addition of sulfating agents. The reactants, sulfating agents and glycerol, may be mixed in almost any order so long as they are mixed continuously with very good agitation or are reacted in a heel of reaction product, glycerol trisulfuric acid, provided that in both cases, the process is so regulated as to prevent the harmful reactions described above.

Although the detergent composition made from the glycerol trisulfuric acid produced by the above method is light in color, an even lighter product of lower ether solubles content may be made when lower sulfation temperatures are used and air blowing of the resulting product is undertaken. Thus when one molecular proportion of substantially anhydrous glycerol is sulfated with between 3.0 and 3.5, preferably between 3.1 and 3.3, molecular proportions of non-gaseous sulfur trioxide, and approximately 2.2 molecular proportions of sulfuric acid monohydrate, at a temperature between 15° C. and 35° C., preferably between 20° C. and 30° C., according to the methods described above, and when the sulfur trioxide, unreacted after complete sulfation of the glycerol, is removed by blowing the reaction mix with a non-reactive gas, e.g., nitrogen, air, the reaction mix detergent compositions made therefrom are of superior color and quality. Solutions thereof are also clearer than are solutions of detergent compositions made by alternative methods.

For best results blowing should be continued until all sulfur trioxide is removed but less blowing will improve a glycerol trisulfuric acid containing free sulfur trioxide to some extent, by removing some of the trioxide. Times of blowing may vary depending on the amount of free sulfur trioxide present in the glycerol trisulfuric acid, the blowing gas rate and blowing method and the temperatures of the gas and glycerol trisulfuric acid. The determination of blowing conditions, now that the process is revealed, is within the ability of one of ordinary skill in the chemical engineering art.

Glycerol trisulfuric acid can also be made from glycerol disulfuric acid, or rather, glycerol sulfuric acid free of sulfur trioxide and of a degree of sulfation between 2.0 and 2.3, by further sulfating one "molecular proportion" of said glycerol sulfuric acid reactant at a temperature between 15° C. and 65° C. preferably between 20° C. and 60° C., with from 0.5 to 1.0, preferably from 0.7 to 1.0, molecular proportion, but no more than (3—Z) molecular proportions, of non-gaseous sulfur trioxide. The non-gaseous sulfur trioxide is employed in a sulfuric acid medium of from 2 to 3 molecular proportions of sulfuric acid monohydrate, the amount of monohydrate being determined by the equation:

$$X=2.2+2(3-Z-Y)$$

wherein X is the number of molecular proportions of sulfuric acid monohydrate, Y is the number of molecular proportions of non-gaseous sulfur trioxide and Z is the degree of sulfation of the glycerol sulfuric acid reactant.

Since the total amount of sulfur trioxide present when the glycerol sulfuric acid is sulfated, is less than or equal to that needed for sulfation there is no need to remove excess sulfur trioxide to enable one to secure light colored detergent compositions from the glycerol trisulfuric acid.

The glycerol sulfuric acid reactant, non-gaseous sulfur trioxide and monohydrate may be reacted in any order so long as care is taken to prevent side reactions by providing sufficient agitation to remove immediately local concentrations of reactants, or by mixing the reactants in a heel of glycerol trisulfuric acid product. To insure against side reactions it is sometimes advisable, as in the earlier described direct production of glycerol trisulfuric acid from glycerol, to react the glycerol sulfuric acid with a "weak" oleum first, and follow with a "stronger" sulfating agent although, because the glycerol is partially sulfated when first exposed to the sulfating agent, the need for such a process is not as great. As in the earlier description, and as holds true throughout this specification, liquid sulfur trioxide may be used as a source of non-gaseous sulfur trioxide.

In a one-stage process one may, for instance, add the required amount of sulfating agent, as approximately 20 percent oleum at as low a temperature as desired to inhibit side reactions, while yet being high enough to cause the process to proceed at an economic rate. Generally it will be found advisable to initiate the reaction at a temperature in the lower portion of the 15° C. to 65° C. range specified (or the preferred 20° C. to 60° C. range) and then allow the temperature to rise higher to speed the reaction. Below 15° C. the trisulfation occurs too slowly and above 65° C. side reactions take place.

The addition of oleum may take about 15 minutes and the mix may be stirred for another 20 minutes after completion of addition, in cases of sulfation at 15–30° C. If higher temperatures are used a glycerol trisulfuric acid may be obtained that will produce a slightly darker, but still light colored detergent composition and reaction times may be decreased.

To speed the trisulfation reaction and still secure a glycerol trisulfuric acid capable of having produced from it a very light detergent composition, which composition will yield clear water solutions, one may sulfate a "molar proportion" of a glycerol sulfuric acid free of sulfur trioxide, of between 2.0 and 2.3 degrees of sulfation, with from 1.0 to 1.3 molecular proportions of non-gaseous sulfur trioxide in a sulfuric acid medium containing approximately 2.2 molecular proportions of sulfuric acid monohydrate. The excess of sulfur trioxide promotes the completion of the sulfation reaction, and when the glycerol trisulfuric acid prepared in this manner is treated with fatty triglyceride a lighter colored product, lower in ether solubles content, is obtained. Of course the unreacted sulfur trioxide must be removed, before addition of triglyceride, preferably by blowing with a non-reactive gas, or else the detergent composition made therefrom will be dark.

While the trisulfation of this process may be conducted

at temperatures above 30° C. at such temperatures the color of the detergent compositions made from the resulting glycerol trisulfuric acid is somewhat darker than that of detergent compositions made from glycerol trisulfuric acid produced at temperatures from 15° C. to 30° C. Since the higher temperatures will promote trisulfation reactions even in processes in which no excess non-gaseous sulfur trioxide participates, the latter processes will usually be employed, where it is not of utmost importance to secure a very light colored detergent composition solution, because they permit savings of sulfur trioxide, and are reasonably rapid.

In the above descriptions, in all four interrelated methods of producing glycerol trisulfuric acid, it will be noted that generally speaking, it is desirable that there be three moles non-gaseous sulfur trioxide and 2.2 moles sulfuric acid monohydrate present in order to trisulfate one mole of glycerol. In the particular case of trisulfation of disulfated glycerol one may, in the foregoing sentence, include in the "non-gaseous" sulfur trioxide that already combined in the glycerol sulfuric acid reactants cited. An excess of sulfating agents, above the amounts shown, will aid the reaction but will also result in detergent compositions higher in inorganic salt content and therefore is usually to be avoided wherever possible. As a rule higher temperatures will decrease the time necessary for completion of reaction but they will often increase the amount of side-reaction products made.

As is obvious from the formulas given for the determination of the amounts of non-gaseous sulfur trioxide and sulfuric acid monohydrate to be used in sulfating glycerol (or glycerol sulfuric acid), within prescribed limits a deficiency of sulfur trioxide may be compensated for by an increase in the amount of sulfuric acid monohydrate.

In the invented methods of manufacture of glycerol trisulfuric acid wherein excess non-gaseous sulfur trioxide was used, a process for removal of the trioxide by blowing the reaction mixture with a non-reactive gas has been described. It is also possible to remove the excess trioxide by adding water to the mix, thereby forming sulfuric acid.

In the formulas and descriptions given above it is said that approximately 2.2 moles of sulfuric acid monohydrate plus the number of moles needed to overcome the deficiency of sulfur trioxide should be used per mole glycerol involved. The word approximately is used advisedly because slight changes in the amount of monohydrate reactant, while they may hinder reaction if negative or may increase inorganic salt content of the resulting detergent composition if positive, may still nevertheless enable one to make an acceptable detergent composition therefrom. Therefore the word approximately, as used should be construed to broaden the permissible number of molecular proportions of sulfuric acid monohydrate, X, to $X \pm 0.1$. To write the equations in a form that will include this range would be unnecessarily complicating them.

In addition the expressions of amounts of glycerol and fatty triglyceride, e.g., coconut oil, to be used, as fixed whole numbers of molecular proportions is deemed necessary but minor variations from such amounts, so long as they do not interfere with the invented processes, are included within the scope of this invention.

All the four general processes for making glycerol trisulfuric acid, disclosed in this specification, are designed to produce the trisulfuric acid to be used for making detergent compositions according to the methods previously described. It is considered at present, that, of the sources of fatty triglycerides, coconut oil is the most promising; consequently most of the experimental work has been done with that oil.

It has been discovered that glycerol sulfuric acid of a degree of sulfation between 2.0 and 2.3, and thus suitable for used in the invented processes for the production of glycerol trisulfuric acid, can be made by treating glycerol with gaseous sulfur trioxide at a temperature between 35° C. and 65° C. and halting the reaction when the desired degree of sulfation, between 2.0 and 2.3 is attained. It is desirable to use substantially anhydrous glycerol (about 99.5% by weight). Sulfur trioxide alone may not be bubbled through the glycerol to effect two degrees of sulfation, but must be diluted with a non-reactive gas, such as air or nitrogen, to decrease its tendency to form undesirable side reaction products. Since the sulfur trioxide is mixed with air or nitrogen, the invented processes are particularly advantageous because they permit one to utilize directly, without purification, sulfur trioxide made by the catalytic oxidation of sulfur dioxide. This is so because that product normally contains nitrogen and oxygen unreacted in the burning of the sulfur or pyrite used as a source of sulfur dioxide. The molar ratio of sulfur trioxide to inert gas, e.g., air, is preferably from .01 to 0.10, but may be higher so long as the sulfur trioxide is diluted enough to prevent side reactions with the glycerol.

In sulfating glycerol it was found experimentally that approximately 4-moles of sulfur trioxide, mixed with non-reactive gas must be bubbled through or otherwise distributed in the glycerol to effect "absorption" of two moles by the glycerol if the sulfation is conducted at about 35° C., and the use of more sulfur trioxide gas mixture at that temperature will not lead to increased absorption. An increase in temperature will increase the degree of absorption of sulfur trioxide and, at 65° C., 3 moles sulfur trioxide charged will cause 2 moles to be absorbed, while 3½ moles charged will result in 2.3 moles absorbed. Temperatures above 65° C. are avoided to insure the production of a glycerol sulfuric acid free of side-reaction products.

The sulfur trioxide absorbed by glycerol may have been chemically reacted with the glycerol to form a glycerol sulfuric acid or it may have been physically absorbed or otherwise present as sulfur trioxide. To determine whether it is present as glycerol sulfuric acid one may titrate with cold sodium hydroxide and from the weight of SO_3 absorbed and the number of equivalents of alkali required for neutralization one may calculate the percentage of glycerol sulfuric acid present.

It has been discovered that glycerol which has "absorbed" from 2.0 to 2.3 moles of gaseous sulfur trioxide per mole of glycerol, by treatment with sulfur trioxide diluted with non-reactive gas at temperatures from 35° C. to 65° C., contains all the absorbed trioxide as glycerol sulfuric acid and is ideally suited for manufacture into glycerol trisulfuric acid by the previously mentioned invented processes. Glycerols of over 2.3 degrees of sulfation can be made by bubbling more than 3½ moles sulfur trioxide in non-reactive gas through a mole of glycerol at 65° C. but above 2.3 degrees of sulfation the sulfation rate decreases and the reaction mixture darkens in color, indicating the presence of side-reaction products.

It was stated above that at the comparatively low sulfation temperature of 35° C., for every four moles of gaseous sulfur trioxide charged two moles are not absorbed by the glycerol. Corresponding figures were given for sulfation at 65° C. The employment of better reaction techniques such as those including improved agitation or distribution methods, which will increase the degree of contact of the reactants, will undoubtedly minimize the amount of unreacted sulfur trioxide, as will decreases in the rate of sulfur trioxide addition or recycling of the sulfur trioxide not absorbed. However, even if methods are employed which result in the accumulation of unreacted sulfur trioxide admixed with air, such mixtures may be used over again as sulfation agents after fortification with sufficient gaseous sulfur trioxide to replace that reacted with the glycerol.

Methods of sulfating glycerol are old but until this

invention it was not known that glycerol could be sulfated with gaseous sulfur trioxide to a degree of esterification between 2.0 and 2.3 without unwanted side reactions. Previously it had been disclosed that only 1.2 degrees of sulfation could be obtained by sulfation with gaseous sulfur trioxide without excessive side reactions and that necessitated low temperature reaction.

Sulfation with sulfur trioxide to a degree of sulfation between 2.0 and 2.3 results in a glycerol sulfuric acid containing no sulfuric acid or unreacted sulfur trioxide. Where glycerol disulfuric acid is used in the production of various amines and amides of glycerol it can, by the invented process, be made in a state of purity which obviates the necessity for chemical, extractive or other physical purification processes. Thus, reaction of the glycerol disulfuric acid with ammonia, caustic and water, under pressure, results in the production of amino glycerol free of inorganic sulfating agents, which may be converted to amides by acylation with acid chlorides. Such amines and amides may find use as detergent foam stabilizers, and in the manufacture of alkyd resins.

While glycerol trisulfuric acid is known, prior art methods for its manufacture, so far as applicant is aware, do not disclose how it may be made by a process not requiring subsequent purifications, without containing objectionable sulfur trioxide or excessive amounts of sulfuric acid.

The advantage of the invented processes for the production of detergent composition intermediate, resides principally in the characteristics of the final detergent composition resulting from further treatment of the intermediate by methods of this invention. The same thing may be said with reference to the invented processes of making glycerol trisulfuric acid.

The described methods of producing a detergent composition by neutralizing a special sulfated glycerol ester result in products containing 45 percent or more of detergent active ingredient (as a salt) and less than 11 parts of ether soluble material per 100 parts detergent active ingredient, when the detergent active ingredient made is the sodium salt of a monococated glycerol monosulfate. It is plain that the detergent active ingredient content of a detergent composition made by the described processes will depend on the molecular weight of the fatty acid radical which esterifies the glycerol and also on the molecular weight of the cation of the base which forms the detergent salt. While, because of the numberous combinations of fatty acid radical, glycerol sulfate and base cation, it is not possible to disclose the minimum active ingredient content of these products, in all cases products made as described from glycerol trisulfuric acid produced according to the invented processes will have higher detergent active ingredient contents than obtainable by hitherto known processes which resulted in products as low in ether solubles as those made by the invented methods.

Similarly it is not feasible to disclose the ether solubles contents of all possible detergent compositions made according to the described processes. It suffices that such compositions will have low ether solubles/detergent active ingredient and ether solubles/detergent composition solids ratios, and that such ratios are generally desirable.

Because of the desirability of showing quantitatively as well as qualitatively the advantages of the invention, in the following pages (up to the examples) the detergent active ingredient referred to is the sodium salt of monococated glycerol monosulfate and the accompanying inorganic material present in detergent compositions is sodium sulfate. The general terms detergent active ingredient, salt of monoacylated glycerol monosulfuric acid, and detergent composition are used to indicate that the improved properties of the detergent compositions, made in the manner described, are not necessarily peculiar to those made from coconut oil and caustic, but on the contrary are generally typical of the salts of monosulfated monoacylated glycerol, where the average acyl group is a fatty acid radical of from 12 to 18 carbon atoms.

The ether soluble content, which includes unreacted and partially reacted triglycerides and organic products of detergent salt decomposition (by hydrolysis), should, in the case of most cosmetic and washing products, be held to 11 parts or less per 100 parts active ingredient. Thus, in the manufacture of liquid shampoos, if more than the allowable amount of ether solubles is present, it has been found that the shampoos are cloudy and tend to separate, on shelf storage, into two layers. In formulating dental creams if the detergent contains more than the allowable amount of ether soluble material the flavor and stability are adversely affected and cream viscosity is altered. In the manufacture of soap-detergent combination bars the presence of ether soluble material makes even more troublesome, and sometimes impossible, the already difficult operation of producing a relatively dry soap-detergent chip. In both synthetic detergent and soap-detergent toilet bars the presence of ether soluble material, especially if it is high in fatty acid content, promotes odor and color degradation on storage.

Light duty household detergents may often more easily tolerate a high ether solubles content than the other products named above, because odor and color are not as important as in the cases of cosmetics, although they are potent sales factors. However, since the ether solubles content of a detergent is of the same nature as fatty soil, in all products containing excess ether solubles it is only logical to expect the detergency of the active ingredient to be decreased somewhat.

A detergent composition containing at least 45 percent active detergent ingredient and less than 11 parts ether solubles per 100 parts active ingredient can be used directly in many formulas in which a composition lower in active ingredient would be unsuitable. Among these are liquid, paste and cream shampoos, detergent toilet bars, and some light duty household detergents. Even in the cases of formulas where a detergent composition of more than 50 percent inorganic salt content is allowable a composition lower in content of inorganic salt reaction by-products permits the formulator to add various other agents, e.g., sequestering agents, builders, anti-soil redeposition compounds, perfumes, without necessitating a reduction below established minimums of the detergent active ingredient content of the product.

In some finished products the inorganic salt content must be held to such a low level that detergent compositions containing even as much as 45 percent active ingredient may not be utilized in compounding. Usually the active ingredient content of such compositions is increased, and the inorganic salt content correspondingly decreased by alcoholic extraction. Such extraction will permit the ultimate use of detergent compositions low in active ingredient, but, because the ether solubles will accompany the active ingredient (in the alcohol layer), alcoholic extraction will not change the ether solubles/active ingredient ratio and so will not upgrade detergent compositions high in ether solubles.

Despite the fact that extraction treatment may be used to raise the active ingredient content of detergent compositions, because such treatment involves an additional expense, solvent losses, and often production bottlenecks, it is to be avoided or minimized when possible. Thus it is advantageous, even where detergent compositions much higher than 45 percent in detergent active ingredient are needed, to initially make a composition as high in active ingredient as possible.

An increase in the active ingredient content of a detergent composition can also be effected by neutralization of the monoacylated glycerol sulfuric acid and accompanying sulfuric acid with a mixture of bases if the cation

of one of the bases forms an insoluble sulfate while the other forms a soluble sulfate. By proper adjustment of base proportions one can make the insoluble sulfate, e.g., calcium sulfate, and remove it by filtration from a solution of a soluble salt of the detergent, e.g., the sodium salt. The co-neutralization reaction mentioned goes much more readily when the detergent acid is 45 percent active ingredient than when it is 32 percent active. In one experiment the product made by co-neutralizing the detergent acid, made by the described processes, with slaked lime and caustic, was 77.5 percent active ingredient, 13.8 percent alcohol insolubles, and 8.7 percent ether soluble material, no alcoholic extraction step being necessary.

Because this invention aids in lessening inorganic salt content of the detergent composition by decreasing the overall amount of sulfating agent necessary to secure a high quality product, it consequently lowers the number of ions accompanying the resulting detergent active ingredient. On neutralization of monoacylated glycerol monosulfuric acid, accompanying sulfuric acid and sulfur trioxide are also of necessity neutralized. Thus the invention permits a saving in amounts of sulfating and neutralizing agents employed. In plants where the rate of detergent production is determined by the size of either the sulfation or neutralization reaction vessels that limitation can be removed and plant capacity can be increased approximately 50 percent without any major changes in the regular 20% oleum sulfation process.

The following examples of the invented processes (I–VII) and process utilizing glycerol sulfuric acid made by the invented methods (VIII–XI) are given for the purpose of illustration only and are not to be regarded as limiting the scope of this invention. All parts are by weight unless otherwise indicated.

SULFATION OF GLYCEROL BY GASEOUS SO_3

Example I

Sixty-nine parts of 99.5 percent glycerol are placed in a jacketed reaction vessel containing an inlet tube extending below the glycerol surface and an outlet, and provided with means for determining the reaction mix temperature. The combined weight of the reaction vessel, auxiliary equipment and glycerol is determined after which a mixture of sulfur trioxide gas and dry nonreactive gas, in this case air, of a molecular ratio of approximately 1:20 and at a temperature of 25° C., is bubbled through the glycerol at a fairly uniform rate. Periodically the reaction vessel and contents are weighed and an aliquot of the reaction product is poured on ice and titrated rapidly in the cold by sodium hydroxide. The number of moles of sulfur trioxide absorbed per mole of glycerol is determined by gross vessel weight differences while the number of moles of sulfur trioxide used for esterification of the glycerol is calculated from the aliquot equivalents of alkali required for neutralization. The reaction mix temperature is held at 40° C.±3° C. until 2.1 degrees of sulfation results. Since at 40° C. it is not possible, under the conditions given, to further sulfate glycerol, at that point the mix temperature is increased to 55° C. to 60° C. As illustrated by Table 1 below, it is not possible to secure 3 degrees of sulfation by the method given. It should also be noted that the reaction mix darkens between 2.1 and 2.6 degrees sulfation and it becomes difficult to remove, by air blowing, the unreacted absorbed sulfur trioxide.

TABLE I.—SULFATION OF 69 PARTS BY WEIGHT (0.75 MOLAR PROPORTION) OF GLYCEROL AT 40-65° C

Time (min. from start)	SO_3 Charged (t.m.p.) [1]	Air Added (t.m.p.)	Mix Temp. (° C.)	SO_3 Absorbed (t.m.p.)	SO_3 Absorbed (moles SO_3/ Glycerol)	SO_3 used in Esterifying Glycerol (moles SO_3/ Glycerol)	Remarks
0	0	0		0	0	0	
26	0.88	15.9	40±3	0.65	0.87	0.86	Esterification was quantitative based on SO_3 absorbed. Product was white.
49	1.75	30.2	40±3	1.22	1.62	1.63	Esterification was quantitative based on SO_3 absorbed. Product was cream colored, whitish yellow.
81	2.62	49.7	40±3	1.48	1.96	1.96	Esterification was quantitative based on SO_3 absorbed. Product was of a light cream color.
112	3.5	68.7	40±2	1.59	2.12	2.06	After 2 degrees esterification the sulfation is very slow. Product is light yellow and viscous.
137	4.38	84.0	55 to 60	2.06	2.74	2.61	Reaction mix becomes fluid at about 55° C., turns reddish and then brown.
167	5.25	102.4	55 to 60	2.25	3.04	2.77	This product is at "92%" trisulfation. It is dark brown and excess unreacted sulfur trioxide is difficulty removable.

[1] Total molar proportions.

Example II

The same general procedure is followed, as in Example I, except that the reaction mix is held at 65° C.±2° C. throughout the sulfation. As will be seen from Table II, after 2.3 degrees of sulfation the reaction mix turns dark.

TABLE II.—SULFATION OF 69 PARTS BY WEIGHT (0.75 MOLAR PROPORTIONS) OF GLYCEROL AT 65° C.±2° C.

Time (min. from start)	SO_3 Charged (t.m.p.) [1]	Air Added (t.m.p.)	SO_3 Absorbed (t.m.p.)	SO_3 Absorbed (moles SO_3/ Glycerol)	SO_3 used in Esterifying Glycerol (moles) SO_3/ Glycerol	Mix Color
0	0	0	0	0.0	0.0	
28	0.88	17.2	0.70	0.93	0.97	White.
66	1.75	40.4	1.22	1.62	1.58	Whitish cream.
98	2.62	60.0	1.75	2.34	2.26	Changing from cream to yellow to reddish brown.
128	3.36	78.0	2.25	3.04	2.68	Dark brown. Mix is fluid.

[1] Total molar proportions.

PREPARATION OF GLYCEROL TRISULFURIC ACID

Example III

252 parts of a glycerol sulfuric acid of 2.0 degrees sulfation, in this case made by the method of Example I, are placed in a jacketed reaction vessel equipped with means for stirring the contents thereof. Maintaining the

temperature of the mix at approximately 20° C., to the glycerol sulfuric acid is added a mixture of 270 parts of 20 percent oleum and 50 parts liquid sulfur trioxide over a 10 minute period after which the mix is allowed to age under gentle agitation for an additional 10 minutes, also at 20° C.

The excess sulfur trioxide is removed by bubbling nitrogen at 20° C. through the reaction mix at the rate of approximately 3 moles per minute per "mole" glycerol sulfuric acid reacted, until no more sulfur trioxide was evolved. The glycerol sulfuric acid product made is all glycerol trisulfuric acid and contains no sulfur trioxide, either gaseous or non-gaseous.

Example IV

51 parts of a glycerol sulfuric acid of two degrees sulfation, in this case prepared according to the method of Example II, are placed in a jacketed reaction vessel equipped with a stirrer. Keeping the reaction mix at 15° C., to the glycerol sulfuric acid is added with stirring over a period of 15 minutes, 65 parts of 20 percent oleum, after which the mix is aged for 20 minutes at a temperature between 15° and 25° C., being stirred constantly.

By reacting glycerol disulfuric acid with the same amount of 20 percent oleum at higher temperatures, e.g., 60° C., instead of 15° C., 25° C., a comparable glycerol trisulfuric acid product is obtained. However, this product, when made into a detergent salt, yields a composition higher in ether solubles and giving a darker aqueous solution than that obtained by similar reactions from the glycerol trisulfuric acid made at 15° C. to 25° C.

Example V

92.5 parts of 99.5 percent glycerol are placed in a reaction vessel and to the glycerol are added 100 parts of 20 percent oleum, followed by 400 parts of 65 percent oleum. The mix temperature is held at 20° to 30° C. and the additions take ½ hour, after which time the mix is aged for another ½ hour. Dry air is blown through the product until there is no trace of sulfur trioxide in the exit air. The product contains no sulfur trioxide and the glycerol is completely trisulfated.

By following substantially the same procedure, except for omission of the air blowing operation, the glycerol is completely trisulfated but the product obtained contains sulfur trioxide. Detergent compositions made therefrom, while of approximately the same ether solubles content, are darker in color than those made from glycerol trisulfuric acid free of excess sulfur trioxide.

Example VI

Glycerol trisulfuric acid free of sulfur trioxide is made according to the method which follows. 92.5 parts of 99.5 percent glycerol are placed in a reaction vessel and to them at 20° to 25° C., 125 parts of 20 percent oleum are added over a period of about 5 minutes. After aging for 10 minutes 325 parts of 65 percent oleum are also added within about 15 minutes, the mix temperature during said addition being held between 30° and 35° C. Stirring is continued while the mix ages at 37° to 40° C. for an additional hour.

Example VII

The method of Example VI is followed except that the sulfating agents used are 260 parts of 20 percent oleum and 190 parts liquid sulfur trioxide respectively. The finished product contains no sulfur trioxide, and according to neutral equivalent determination all the glycerol is completely sulfated.

PREPARATION OF DETERGENT COMPOSITIONS

Example VIII

To the reaction mix product of Example IV, heated to about 40° C., 65 parts of bleached and refined coconut oil are added with stirring over a period of 15 minutes. After aging under agitation for 75 minutes at 55° to 60° C. the reaction mix is poured into a vessel containing a stirred mixture of 800 parts ice and 400 parts water. The water solution of detergent acid and sulfuric acid is then quickly sub-surface neutralized rapidly by a 50 percent solution of caustic soda. The amounts of ice and water used to dilute the detergent composition intermediate are such that the heats of dilution, hydrolysis, and solution of the organic acid and sulfuric acid, coupled with the heats of neutralization of such compounds, raise the solution to approximately room temperature.

The resulting detergent composition solution is clear and of light color. When roll dried it contains, on a solids basis, 45.2 percent detergent active ingredient, 50.8 percent alcohol insoluble material (principally sodium sulfate) and 4.0 percent ether solubles. The ether solubles content is 8.9 parts per 100 parts detergent salt.

If potassium hydroxide, magnesium hydroxide, ammonium hydroxide, monoethanolamine or triethanolamine solution is substituted for the caustic soda, or if hydrogenated tallow or coconut oil is substituted for the coconut oil, similar high quality light colored products, high in detergent salt content, are obtained.

Example IX

To the white acid mix of Example V are added, within ten minutes, 325 parts of coconut oil, the mixture being at a temperature between 30° and 45° C. during the addition. The mix is then aged at 58° to 60° C. for 1¼ hours after which it is neutralized according to the method of Example VIII. The solution of detergent composition resulting is a clear light yellow. When drum dried, it analyzes 47.0 percent detergent active ingredient, 49.9 percent alcohol insoluble and 3.0 percent ether solubles (6.4 parts per 100 parts active ingredient).

Example X

To the mixture of glycerol trisulfuric acid and sulfuric acid monohydrate produced by the method of Example VI are added, within ten minutes, 325 parts of coconut oil, the reaction mixture temperature being maintained between 35° C. and 45° C. until the completion of the oil addition when it is increased to 58° to 60° C. where it is held during a 75 minute aging period. Subsequently the detergent acid and sulfuric acid are neutralized according to the method of Example VIII and roll dried.

The detergent composition made is, on a dry basis, 49.3 percent active detergent ingredient, 46.4 percent alcohol insoluble material and 4.3 percent ether solubles (8.7 parts ether solubles per 100 parts active ingredient).

When dissolved in water the detergent composition makes a clear light yellow solution.

Example XI

The reaction product mixture of Example VII is treated by the process of Example X except that the drum drying is omitted. The solution resulting is a clear light yellow. It contains on a dry basis, 47.1 percent active ingredient, 48.0 percent alcohol insolubles and 4.9 percent ether soluble material (10.4 parts ether solubles per 100 parts active ingredient).

The above invention has been described in conjunction with various illustrative examples of the invented processes and processes utilizing glycerol trisulfuric acid made according to the invention. It will be obvious to those skilled in the art that other variations and modifications of the invention can be made, and various equivalents substituted therein without departing from the principles revealed or going outside the scope of the specification or purview of the claims.

This application is a division of application Serial Number 487,209, filed February 9, 1955, and now United States Patent 2,868,812.

Having thus described the invention, what is claimed is:

1. A process for the production of glycerol trisulfuric acid free of sulfur trioxide which comprises reacting, at a temperature between 15° C. and 45° C., one molecular proportion of substantially anhydrous glycerol with between 2.5 and 3.5 molecular proportions of non-gaseous sulfur trioxide, in a sulfuric acid medium, which medium contains between 2.2 and 3.5 molecular proportions of sulfuric acid monohydrate, the number of molecular proportions of sulfuric acid monohydrate being approximately determined by the equation $X=2.2+2(3-Y)$, where X is the number of molecular proportions of sulfuric acid monohydrate, and Y is the number of molecular proportions of sulfur trioxide, the term $2(3-Y)$ being considered no less than zero in determining X, and, when Y is over 3.0, blowing the resulting product with an unreactive gas until all unreacted sulfur trioxide is removed.

2. A process for the production of glycerol trisulfuric acid free of sulfur trioxide which comprises reacting one molecular proportion of substantially anhydrous glycerol with between 2.5 and 3.0 molecular proportions of non-gaseous sulfur trioxide, in a sulfuric acid medium, which medium contains between 2.2 and 3.5 molecular proportions of sulfuric acid monohydrate, the number of molecular proportions of sulfuric acid monohydrate being approximately determined by the equation $X=2.2+2(3-Y)$, where X is the number of molecular proportions of sulfuric acid monohydrate, and Y is the number of molecular proportions of sulfur trioxide, at a temperature between 15° C. and 45° C., at least part of which sulfation is conducted at a temperature of between 35° C. and 45° C.

3. A process for the production of glycerol trisulfuric acid free of sulfur trioxide which comprises reacting one molecular proportion of substantially anhydrous glycerol with between 3.0 and 3.5 molecular proportions of non-gaseous sulfur trioxide, in a sulfuric acid medium, which medium contains approximately 2.2 molecular proportions of sulfuric acid monohydrate, at a temperature between 15° C. and 35° C., and removing sulfur trioxide not combined as glycerol sulfuric acid, by blowing the resulting product with a gas which is inert to the reaction mixture.

4. A process for the production of glycerol trisulfuric acid free of sulfur trioxide which comprises reacting one molecular proportion of substantially anhydrous glycerol with gaseous sulfur trioxide at a temperature between 35° C. and 65° C., to produce a glycerol sulfuric acid of between 2.0 and 2.3 degrees of sulfation, and then further sulfating the one molecular proportion of said glycerol sulfuric acid at a temperature between 15° C. and 65° C. with from 0.5 to 1.0 molecular proportion but no more than $(3-Z)$ molecular proportions of non-gaseous sulfur trioxide in a sulfuric acid medium, which medium contains from 2 to 3 molecular proportions of sulfuric acid monohydrate, the number of molecular proportions of sulfuric acid monohydrate, X, being approximately determined by the equation $X=2.2+2(3-Z-Y)$ where Y is the number of molecular proportions of non-gaseous sulfur trioxide and Z is the degree of sulfation of the glycerol sulfuric acid reactant.

5. A process for the production of glycerol trisulfuric acid free of sulfur trioxide which comprises reacting one molecular proportion of substantially anhydrous glycerol with gaseous sulfur trioxide, at a temperature between 35° C. and 65° C. to produce a glycerol sulfuric acid of between 2.0 and 2.3 degrees of sulfation, and then further sulfating the one molecular proportion of glycerol sulfuric acid made with between 1.0 and 1.3 molecular proportions of non-gaseous sulfur trioxide in a sulfuric acid medium which medium contains approximately 2.2 molecular proportions of sulfuric acid monohydrate, at a temperature between 15° C. and 30° C. and removing the sulfur trioxide not combined as glycerol sulfuric acid by blowing the resulting product with a gas which is inert to the reaction mixture.

6. A process for the production of glycerol sulfuric acid which comprises reacting glycerol with a mixture of gaseous sulfur trioxide and gas which is inert to the reactants and reaction mixture, at a temperature between 35° C. and 65° C., and halting such reaction at a degree of sulfation between 2.0 and 2.3.

7. A process for the production of glycerol sulfuric acid which comprises bubbling a mixture of gaseous sulfur trioxide and air through glycerol, at a temperature between 35° C. and 65° C., the molar ratio of sulfur trioxide to air being approximately from .01 to 0.10, and halting such bubbling when the glycerol is at a degree of sulfation, between 2.0 and 2.3.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,979,521 April 11, 1961

Frederick William Gray

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 75, for "used" read -- use --; columns 11 and 12, first table, under the heading "Mix Temp. (° C.)" opposite "112", for "40±2" read -- 40±3 --, same table, column 8, last line, for "difficulty" read -- difficultly --.

Signed and sealed this 10th day of July 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents