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PROCESS FOR THE PRODUCTION OF SULPHONATED FATTY ACIDS

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The present invention relates to a method for the production of sulphonation products, and particularly to a method for the production of sulphonated fatty acids which are valuable as detergent, wetting, and the like agents.

It has long been recognized that ordinary soaps are deficient in many respects when employed in the field of detergent and wetting agents. For example, while soaps act efficiently as detergents in weakly alkaline solutions, they are of no value for this purpose in acid solutions since in such solutions the free fatty acid, insoluble in water, is liberated. On the other hand, in strongly alkaline solutions, ordinary soaps become insoluble and are salted out of solution. Further, in the presence of solutions containing calcium or magnesium salts, such as ordinary hard water, the fatty acid present in a soap is precipitated as a calcium or magnesium soap, such soaps being insoluble, sticky curds which, rather than having any detergent action, are regarded as undesirable impurities in solutions employed in the textile and related industries.

In an attempt to supply products free from the undesirable properties of ordinary soaps, there have been developed as detergent and wetting agents products obtained by the sulphonation of certain fatty acids occurring in oils and fats. These fatty acids are characterized by containing unsaturated linkages and/or hydroxyl groups in the molecule. On sulphonating such acids, products are obtained which contain sulphuric acid ester groups in the molecule and, of course, carboxylic acid groups attached to an end carbon atom. These products, however, in general possess weaker wetting and detergent properties than soap. Such products are also relatively unstable and are capable of being decomposed by hydrolysis.

With the belief that the weaknesses inherent in ordinary soaps and the sulphonation products of unsaturated or hydroxy fatty acids were due to the presence of a carboxyl group in the molecules of these compounds, as a further and more recent development, there have been provided sulphonated products of various types in which the carboxyl group of a fatty acid molecule has been eliminated or has been blocked by esterification or amidation. As examples of such products, there may be mentioned lauryl sulphate and the beta-sulpho-ethyl-ester or amide of oleic acid. These products, however, have the disadvantages that they are not completely stable to hydrolysis and they must be prepared by methods including the elimination of the carboxyl group or esterification or amidation of this group.

As indicated, it has generally been considered that to produce an effective detergent, first consideration should be given to the elimination or blocking of this group. Researches leading to the development of the present invention, however, have shown that the generally accepted theory in this regard is not entirely accurate. Thus, it has been found that the mere fact that a sulphonated fatty acid product contains a carboxyl group is not conclusive as to whether that product is a good detergent since the relative orientation of the sulphuric acid ester or sulphonic acid group and carboxyl group in the fatty acid molecule has a determining effect on the detergent properties of the compound. For example, while in the case of the sulfonated oils, the presence of the carboxyl group has a deleterious effect on the properties of the products, this effect appears to be due in considerable measure to the fact that in such products the sulphuric acid ester group and the carboxyl group are attached to widely separated carbon atoms of the fatty acid molecule.

While sulphonated fatty acid products in which the sulphonic acid and carboxyl groups are properly oriented in the fatty acid molecule have been prepared, their value as detergents seems not to have been generally recognized by the industry. This failure on the part of the industry to recognize the value of such products as detergents is probably based in large measure on the fact that a commercially feasible method for their manufacture has not been devised. Thus, if a saturated higher fatty acid is sulphonated in the usual manner with chlor-sulphonic acid, sulphuric acid, or oleum, it appears that a product containing a considerable proportion of sulphonated fatty acid in which the sulphonic acid and carboxyl groups are properly oriented should be produced. As a practical matter, however, the product of this process is highly colored, and is contaminated with undesirable by-products. For many purposes, therefore, the practical value of this product as a detergent is small.

Accordingly, it is an object of the present invention to provide a method for the preparation of sulphonation products of saturated higher fatty acids which products are characterized by their excellent detergent properties.

A further object of the invention is to provide a complete process by which, from naturally occurring oils and fats, sulphonated fatty

acid products may be prepared in a simple and economical manner.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has been discovered in accordance with the present invention that products possessing excellent detergent properties, and hence of considerable value in the textile and related industries, may be efficiently prepared by sulphonating a saturated higher fatty acid (i .e., a saturated fatty acid which contains at least eight carbon atoms) or an anhydride of such acid with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

In carrying out this sulphonation, it has been found to be essential, if commercially valuable products are to be produced, that the saturated higher fatty acid or anhydride or mixture of such acids or anhydrides should be substantially free from unsaturated fatty acids or anhydrides. Thus, if a saturated higher fatty acid or a mixture of such acids containing substantially more than about five per cent by weight of unsaturated fatty acids is subjected to sulphonation in the above manner, the resulting product has inferior properties apparently due to the presence therein of compounds formed by reaction of the sulphur dioxide and sulphur trioxide with the unsaturated fatty acids. Where products of especially good color are desired, they may be obtained by employing as starting materials saturated higher fatty acids containing two per cent or less of unsaturated fatty acids.

Further, it has been found to be important to carry out the sulphonation reaction under substantially anhydrous conditions. For example, it has been found that the sulphonation reaction mixture should contain not more than about one per cent by weight of water based on the amount of sulphur trioxide used in the reaction. If a materially greater proportion of water is present in the reaction mixture, the extent of sulphonation is substantially reduced and detergents of less value are obtained.

By sulphonating a saturated higher fatty acid or a mixture of such acids containing not substantially more than about five per cent of unsaturated fatty acids with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions, it has been found that sulphonation products may be obtained which are of good color and which are substantially free from undesirable by-products produced by carbonization or oxidation. The products prepared by the process of the present invention will ordinarily be employed as detergents in the form of their partially or fully neutralized salts, and, consequently, at the completion of the sulphonation, the sulphonation mass is preferably treated with a suitable alkaline material such as, for example, a caustic alkali, alkali metal carbonate or ammonia, and the neutralized mass is dried, or the salt of the sulphonated fatty acid formed by this treatment may be recovered from the mass.

The sulphonation mass at the completion of the sulphonation contains a mixture of sulphonation derivatives of the saturated higher fatty acids. Although it is desired that the invention should not be limited to any theoretical explanation, and the exact chemical composition of all of the various compounds making up this mixture has not been accurately determined, it has been found that the mixture contains a large proportion of monosulphonic acid derivatives of the saturated higher fatty acids. It is believed that the mixture also contains a small proportion of disulphonic acid derivatives of the saturated higher fatty acids, and/or sulphonic acid products in which the carboxyl group has been entirely eliminated and/or ketonic sulphonic acid derivatives of the fatty acids. The major portion of the monosulphonic acid derivatives present in the mixture are alpha sulphonic acid derivatives of saturated higher fatty acids. Thus, the products prepared by the process of the present invention are predominantly composed of sulphonation derivatives which contain a sulphonic acid group and a free carboxyl group. Nevertheless, the products have valuable detergent properties which appear to be due, in part, to the orientation of the sulphonic acid group of the fatty acid molecule in relation to the carboxyl group and, in part, to the fact that by sulphonating the saturated higher fatty acids in the manner described above products relatively free from difficultly removable impurities such as are formed in ordinary sulphonation methods are produced. The products, with respect to their detergent properties, are markedly superior to the sulphonated oils. Thus, they are resistant to the action of hard water; the mono-sodium salt being as resistant in this medium as other detergents which are considered to be capable of being used in hard water. While solutions of the di-sodium salts of the sulphonated saturated higher fatty acids become slightly turbid in the presence of extremely high concentrations of calcium salts, whatever precipitate is formed is in a finely dispersed form rather than in the form of sticky curds. In acid solutions, the products prepared by the process of the present invention are completely soluble and have been found to exhibit detergent properties in a marked degree. As contrasted with many available sulphonated products, the products, being derivatives of saturated acids, have little tendency to become rancid. The products possess the advantage over sulphonated products of the type in which the carboxyl group has been eliminated or blocked in that they are considerably more resistant to the hydrolyzing action of strongly acid or alkaline solutions.

The process of the present invention represents a material advance in the present art both with respect to the products obtained and simplicity of operation. For example, by employing saturated higher fatty acids containing not substantially more than about five per cent of unsaturated fatty acids as starting materials in the process, the formation of the relatively undesirable sulphonation products obtained by the sulphonation of oils is avoided. Further, by sulphonating saturated higher fatty acids with sulphur trioxide dissolved in liquid sulphur dioxide under substantially anhydrous conditions, numerous deleterious side reactions which ordinarily accompany the sulphonation of aliphatic substances with the usual sulphonating agents, such as sulphuric acid, chlorsulphonic acid, or oleum, are minimized or completely inhibited. Such reactions include carbonization, dehydration, oxidation, condensation, etc., which lead to wastage of raw material and production of colored compounds difficult to remove from the desired product. It has been found that liquid sulphur dioxide is uniquely valuable as a solvent in the process of the present invention because of its pronounced solvent action on all of the com-

ponents, including the fatty acids, the sulphonated products, and sulphur trioxide. Further, sulphur dioxide is stable, is easily volatilized and condensed, and is inert to the action of sulphur trioxide under all of the conditions encountered in the process of the present invention. Furthermore, it has been found that in the preparation of the sulphonating medium employed in the process of the present invention combinations of processing steps leading to important savings are possible. The methods for the preparation of the sulphonating medium involving these combinations are feasible because of the close chemical relationship between sulphur dioxide and sulphur trioxide, the latter being the product of the catalytic oxidation of the former.

As previously stated, the saturated acids which are sulphonated in accordance with the process of the present invention are those which contain at least eight carbon atoms. Saturated higher fatty acids which contain from 8 to 24 carbon atoms, and especially those containing from 14 to 18 carbon atoms, are of particular value. Among such acids may be mentioned the following: myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, and lignoceric acid. Sulphonation products prepared by sulphonating an acid or a mixture of acids of this type by the sulphonation procedure of the present invention exhibit marked detergent properties in neutral, acid, or alkaline solutions.

As a feature of the present invention, it has been found that sulphonation products of saturated higher fatty acids may advantageously be prepared by employing as starting materials naturally occurring fats and oils. The fats and oils preferably employed are those which are substantially free from glycerides of hydroxy fatty acids, since if an oil or fat containing such glycerides is used, it is advisable to remove the hydroxy fatty acid; sulphonation products of hydroxy fatty acids being undesirable in the final product. As examples of fats and oils which are preferably employed, there may be mentioned tallow, babassu oil, palm oil, cocoanut oil, and fish oils, e. g., menhaden fish oil. These materials contain glycerides of saturated and unsaturated higher fatty acids. Tallow, for example, is composed of glycerides of the saturated fatty acids, stearic acid, palmitic acid and myristic acid and the glycerides of the unsaturated fatty acids, oleic acid and linoleic acid.

In using a naturally occurring fat or oil of this type in the preparation of sulphonated products of saturated higher fatty acids in accordance with the present invention, it is generally preferable first to purify the crude fat or oil, for example, by treating it with suitable absorbents. Of course, where the fat or oil is sufficiently free from impurities that it may be employed in the subsequent steps without purification, this may be dispensed with. The purified fat or oil is then subjected to a hydrogenation treatment which preferably includes contacting the fat or oil with hydrogen at an elevated temperature and under superatmospheric pressure in the presence of a hydrogenation catalyst. This treatment is conducted so as to convert the glycerides of unsaturated fatty acids present in the fat or oil to glycerides of saturated fatty acids. To obtain free saturated fatty acids from the hydrogenated fat or oil, this product is then hydrolyzed as by the action of an inorganic acid, e. g., sulphuric acid, in the presence of a fat-splitting catalyst. The hydrolysis is preferably effected in two stages as described more fully below, and the glycerine liberated in the reaction may be recovered and treated so as to obtain it as a valuable by-product of the process. The free saturated fatty acids recovered from the hydrolysis reaction may be sulphonated without other treatment, but are preferably purified as by subjecting them to a vacuum distillation procedure using steam if desired. Since the saturated fatty acids should be sulphonated under substantially anhydrous conditions, where steam is used in the purification treatment, supplementary drying of the acids may be required so that in the sulphonation there is present not substantially more than one per cent by weight of water based on the sulphur trioxide used. The thus prepared saturated fatty acids are then sulphonated by subjecting them to the action of sulphur trioxide while suspended and/or dissolved in liquid sulphur dioxide, whereby sulphonated products containing a sulphonic acid group and a carboxyl group are obtained. The sulphur dioxide is then distilled off and condensed for use in a succeeding run of the process.

As already indicated, the sulphonated products prepared by the process of the present invention are preferably employed in the form of their partially or wholly neutralized salts. To prepare the salts, the sulphonation mass is preferably dissolved in a minimum of water whereby a mixture containing a small amount of free sulphuric acid and a proportion of impurities in addition to the sulphonated fatty acids is obtained, and this mixture is reacted with an alkaline material, such as a caustic alkali or an alkali metal carbonate, to neutralize the free sulphuric acid and form salts of the free acid sulphonation products. This neutralized mixture may then be dried to obtain a mixture of products containing partially or wholly neutralized salts of the sulphonated fatty acids and a proportion of the salt formed by the neutralization of the sulphuric acid. Since it has been found that for many purposes detergent compositions containing sulphates, for example, sodium sulphate or ammonium sulphate, in addition to the salts of the sulphonated fatty acids, are superior to the sulphonated fatty acids alone, the composition prepared by drying the neutralized sulphonation mixture is a valuable product.

Where a greater quantity of sulphates is desired in the finished compositions than would be present by the neutralization of the ordinary sulphonation mass occurring in the process of the present invention, in some cases an excess of sulphur trioxide may be used in the sulphonation to produce a sulphonation mass which on being dissolved in water will be converted to a mixture containing increased quantities of sulphuric acid. By neutralizing and drying this mixture, a detergent composition containing a relatively high proportion of sulphates is obtained.

On the other hand, where a specially refined product is desired, it has been found as a feature of the present invention that an efficient recovery of the sulphonated fatty acid products from the sulphonation mass may be made by adding to the solution of the sulphonation mass in water only enough alkaline material to neutralize the free sulphuric acid present and form a salt of one acid group leaving the other acid group free. The resulting partially neutralized salt separates as a precipitate and can be recovered by filtration or centrifugation free from other materials, such as disulphonic acids. This manner of proceeding is particularly advantageous in the preparation of the ammonium salt

of the sulphonated saturated fatty acids where it has been found that neutralization of an aqueous solution of the sulphonation mass followed by drying results in a product containing large amounts of impurities. The partially neutralized salt may then be dried in any suitable manner as, for example, by the use of rotary drying drums or the like. If desired, the partially neutralized salt may be fully neutralized before or after drying by adding to a solution of the salt an additional alkaline material which may be the same or different from that employed in the original neutralization.

In order that the invention may be more fully understood, there is described in some detail below a process for the preparation of sulphonation products of saturated higher fatty acids in accordance with the present invention using tallow as a starting material. It will be understood that this description is for illustrative purposes only, and that the conditions may be varied widely within the scope of the invention. The parts are by weight.

100 parts of tallow containing impurities which might interfere with the hydrogenation reaction are subjected to a purification treatment which is advantageously carried out by agitating the tallow with three parts or less of an animal charcoal at a temperature of about 150° C. for a period of about one hour. At the end of this period, the purified fat is cooled preferably to about 70° C. and is separated from the absorbent material containing the impurities by passing the mass through a filter press. About 99.5 parts of a clear, purified fat are obtained.

The purified fat obtained in this manner is then subjected to a hydrogenation treatment to convert the unsaturated glycerides contained therein to the saturated condition. Although the particular method of carrying out the hydrogenation forms no part of the present invention and this step may be conducted in any suitable or well-known manner, in accordance with preferred procedure the purified fat is treated with hydrogen under about five atmospheres pressure at about 180° C. in the presence of a nickel catalyst for a period of time sufficient to convert the unsaturated glycerides to the corresponding saturated compounds. About 100 parts of hydrogenated tallow are obtained as a result of this treatment.

To obtain from the hydrogenated tallow the saturated higher fatty acids contained therein in the form of glycerides, the tallow is hydrolyzed. The hydrolysis is preferably effected in two stages. In the first stage, the hydrogenated tallow obtained in the above manner is treated with a small amount of sulphuric acid, for example, about one-half part of 60° Bé. sulphuric acid, in the presence of about one-half part of a suitable fat-splitting catalyst, such as, for example, a Twitchell reagent prepared by heating together a mixture of concentrated sulphuric acid, oleic acid, and naphthalene. In carrying out the hydrolysis, about 13 parts of water are added to the mixture containing the hydrogenated fat and sulphuric acid, together with about 28 parts of the "sweet waters" recovered from the second stage described below. The resulting mixture is then boiled and agitated by introducing steam for a period of time sufficient to complete the percentage of hydrolysis attained in this step of the process. The water introduced into the mixture by the condensation of steam will be about 27 parts. Ordinarily, the reaction is completed in about 16 hours, and the mixture is then allowed to stand until separation into a water layer and an oil layer occurs. The water layer, which contains the glycerine liberated by hydrolysis of the fat, is removed, and to recover the glycerine contained in this solution, the solution is preferably neutralized with lime, and, after settling and filtration of the precipitated calcium sulphate, is treated in any desirable or suitable manner for the recovery of its glycerine content.

The remainder of the reaction mixture which contains mixed fatty acids, unhydrolyzed tallow, and a proportion of the catalyst for the hydrolysis reaction, is then subjected to the second stage of hydrolysis wherein an additional amount of sulphuric acid, e. g., .1 part of 60° Bé. sulphuric acid, and about 12.5 parts of water are added, and steam is injected to boil and agitate the mixture. The steam treatment is continued for a period of time sufficient to cause maximum hydrolysis of the unhydrolyzed tallow in the reaction mixture. This period, under the conditions specified, has been found to be about 10 hours. About 15 parts of steam are condensed to water in the mixture in this time. After completion of the reaction, the water layer ("sweet water"), which consists of a dilute solution of glycerine, is removed and is recycled to the first stage for the hydrolysis of a succeeding batch of hydrogenated fat. The mixture of higher fatty acids prepared by proceeding in the above manner will contain a small proportion of glycerine and other impurities, and accordingly, to sulphonate this mixture efficiently, it is generally desirable to separate the saturated higher fatty acids from the impurities. It has been found that this may be effectively accomplished by steam-distilling the crude mixture, in which the free sulphuric acid has been neutralized, under a vacuum, preferably, by steam-distilling under a pressure of about 100 mm. of mercury while maintaining the temperature from about 250° C. to about 300° C. It is generally desirable after the distillation to dry the fatty acids to reduce their water content. The saturated higher fatty acids purified by this procedure contain not substantially more than about two per cent of unsaturated fatty acids and are in a satisfactory condition for sulphonation.

A sulphonating mixture is prepared by distilling sulphur trioxide from oleum containing at least 20 per cent sulphur trioxide, and dissolving the sulphur trioxide in liquid sulphur dioxide which may advantageously be that recovered from the sulphonating step described below. The sulphonating mixture is prepared so as to contain from about 50 to about 70 mols of anhydrous liquid sulphur dioxide for each mol of sulphur trioxide dissolved therein. The sulphonating mixture may be prepared, if desired, so as to contain from about 10 to about 125 mols of sulphur dioxide for each mol of sulphur trioxide, although the foregoing proportions are preferable.

The sulphonation of the mixture of saturated higher fatty acids is preferably carried out by dissolving and/or suspending this mixture in substantially anhydrous liquid sulphur dioxide in a suitable vessel capable of withstanding moderate pressures. To this solution or suspension, the sulphonating mixture prepared as described above is added continuously with vigorous stirring over a period of about two hours; the rate of introduction of the solution of sulphur trioxide in liquid sulphur dioxide being such that about three mols of sulphur trioxide are introduced for each mol of saturated higher fatty acids con-

tained in the mixture. The temperature of the reaction mixture is controlled during this sulphonation so as to lie within the range of about 30° C. to about 40° C. and the reaction is allowed to continue for an additional two hours. In order to avoid loss of sulphur dioxide and to assure the satisfactory progress of the reaction, the pressure is preferably maintained at about the vapor pressure of sulphur dioxide at the existing temperature. At the completion of the sulphonation, which will require about four hours under these conditions, substantially all of the sulphur dioxide is vaporized from the reaction mass and condensed in a receiver and stored for use in the preparation of the succeeding batches of sulphonated fatty acids.

The sulphonation mass remaining after the removal of the majority of the sulphur dioxide is dissolved in a minimum quantity of water. To remove residual sulphur dioxide the aqueous solution is preferably heated, although if desired the sulphur dioxide may be removed by passing air or steam through the solution. The solution from which the sulphur dioxide has been removed is neutralized with a saturated solution of soda ash in such amount as to add about 68 parts of soda ash. During the neutralization, about four atmospheres of carbon dioxide is preferably maintained in order to minimize frothing. The reaction mixture after neutralization is in the form of a slurry containing the disodium salts of the sulphonated fatty acids. A dry product may be recovered from this slurry by means of a spray or rotary drum drier. The dry product contains in addition to the salt of the sulphonated fatty acid a proportion of sodium sulphate formed by neutralizing the excess sulphuric acid in the sulphonation mass with the soda ash, and is a valuable detergent composition.

By proceeding in an analogous manner to that described above, there may be prepared sulphonation products of other fatty acid compounds and particularly sulphonation products of other fatty acids occurring in other fats and oils, such as, for example, those previously mentioned. It will be understood, moreover, that the present invention is not limited to the particular details of the above described process since these may be varied within wide limits. For example, where the process of the present invention is carried out employing a naturally occurring fat or oil as the starting material, it is not necessary that the unsaturated glycerides present therein be converted to saturated bodies since, if desired, the fat or oil may be hydrolyzed without hydrogenation and the unsaturated acids liberated by this hydrolysis may be employed for other purposes or the free unsaturated acids may be hydrogenated and used in the present process. The step of hydrogenating the fat or oil prior to hydrolysis is of particular advantage, however, since this offers a simple means of obtaining substantially all of the fatty acids contained in such material in a form available for use in the sulphonation procedure. Further, while for the reasons already mentioned, it is of advantage to employ naturally occurring fats or oils as starting materials in the process of the present invention, products having similar properties may be prepared by using as starting materials saturated higher fatty acids containing not substantially more than five per cent of unsaturated fatty acids without consideration as to their source.

With respect to the purification step described in the above process, it will be obvious that the amount of absorbent used will depend largely upon the particular material selected for this purpose and the amount of impurities in the crude fat or oil. Thus, where a highly activated material, such as an activated charcoal, is used, no more than about 1 per cent of the activated material bsed on the weight of the fat or oil is required, while if less active absorbent materials are used such as an ordinary wood or animal charcoal or fuller's earth, 3 per cent up to about 5 per cent may be required in extreme cases for achieving maximum results.

Although the method outlined above is an advantageous way of preparing a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide, it has been found that this sulphonation mixture may be prepared in other ways. For example, it has been found that sulphonation mixtures may be prepared by preparing solid sulphur trioxide obtained by distillation of oleum and dissolving the solid sulphur trioxide in liquid sulphur dioxide; the latter preferably being obtained by distillation of the sulphonation mass from a preceding run of the process followed by liquefaction. In this method and in the method outlined in the example, the sulphur trioxide gas need not be that obtained by distillation of oleum, but it may be that obtained from a contact plant, for example. Further, it has been found that sulphonation mixtures may be efficiently prepared by stripping sulphur trioxide from oleum by passing gaseous sulphur dioxide therethrough and condensing the mixed gases to produce the sulphonation mixtures. Sulphonation mixtures may also be prepared by partially oxidizing sulphur dioxide, as for example, in a contact process using air or preferably pure oxygen, and then condensing the resulting mixture containing sulphur dioxide and sulphur trioxide.

In carrying out the sulphonation of a saturated higher fatty acid or a mixture of such acids with anhydrous sulphur trioxide in the presence of liquid sulphur dioxide, the temperature maintained may vary but should lie within the range of about 20° to about 60° C. and preferably within the range of about 30° to about 40° C. specified above. The time employed for the sulphonation under the conditions specified is about 2 to about 16 hours, and preferably, for economical operation about 4 to about 8 hours.

In carrying out the sulphonation of saturated fatty acids, it has been found that the sulphonated mixture comprising substantially anhydrous sulphur trioxide dissolved in anhydrous liquid sulphur dioxide should be employed in such proportions that at least two mols of sulphur trioxide are available for reaction with each mol of the saturated fatty acids. In this reaction, apparently there is formed a compound between the fatty acid and the sulphur trioxide other than the sulphonation product which prevents a portion of the sulphur trioxide from being available for true sulphonation, and, hence, with less than two mols of sulphur trioxide, the extent of sulphonation is materially reduced. While two mols of sulphur trioxide is the lower limit of this reagent which should be used, it has been found to be preferable to employ an excess of this reagent which excess seems to catalyze the reaction. Thus, in accordance with the present invention, it is preferred to use from two and one-half to about three and one-half mols of SO_3 to each mol of the saturated higher fatty acids. However, a greater quantity of sulphur trioxide than this

may be used, e. g., up to about five mols of sulphur trioxide may be used if desired.

The foregoing discussion has been mainly concerned with the sulphonation of saturated fatty acids but it is to be understood that the general processes outlined are also applicable for the sulphonation of the anhydrides of the saturated higher fatty acids. For example, stearic acid anhydride can be sulphonated by means of sulphur trioxide in sulphur dioxide solution as easily as stearic acid. Furthermore, the use of saturated higher fatty acid anhydrides as starting materials has the advantage that a smaller excess of sulphur trioxide can be used and the sulphonated products are somewhat lighter in color. The reaction product using stearic acid anhydride as the starting material appears to be composed principally of alpha-alpha'-disulpho-stearic anhydride. This product upon treatment with water and neutralization hydrolyzes to produce the sulphonated fatty acid such as is produced by the direct sulphonation of the free acid.

In general, the conditions required for the sulphonation of the anhydrides are the same as those specified above for the sulphonation of the fatty acids. Thus, the starting material should contain not substantially more than about five per cent of anhydrides of unsaturated higher fatty acids. Of course, since the anhydride is present, the mass will be substantially anhydrous. In sulphonating the fatty acid anhydrides, the preferable molecular ratio of sulphur trioxide to anhydride is from four to one to six to one, i. e., from two to three mols of sulphur trioxide per acid radical of the anhydride.

Although the solvent medium for carrying out the process of the present invention preferably consists only of liquid sulphur dioxide, some carbon dioxide is formed in the reaction and as the sulphur dioxide is reused in the process a small quantity of carbon dioxide builds up in the solvent. It has been found that this has substantially no deleterious effect on the course of the reaction and can be tolerated. In this connection it will be understood that other non-aqueous diluents or additions which do not adversely affect the reaction may be present in the sulphonation mass.

For purposes of illustration, there has been specifically described a procedure in which soda ash has been used to neutralize the water solution of the sulphonation mass to prepare the disodium salts of the sulphonation products of saturated higher fatty acids. The invention, however, is not limited to the use of soda ash, since, as already indicated, the process of the present invention may be carried out with equal facility for the preparation of analogous products by using for this neutralization any suitable alkaline material, such as, for example, caustic soda, caustic potash, potassium carbonate, ammonia, organic amines, among which may be mentioned the following: mono-, di-, and triethanolamine, diethylamine, dimethylamine, pyridine, etc. A particular advantage realized in the use of organic amines for neutralizing the sulphonated fatty acids is the fact that the amine salts are more soluble than the metal salts. Hence, the solubility of a long-chain sulphonated fatty acid may be increased by neutralizing it with a selected organic amine.

Also, while for many purposes it is desirable to employ sufficient alkaline material in this step to neutralize the free sulphuric acid and completely neutralize the sulphonated higher fatty acids, by employing only enough alkaline material to neutralize the free sulphuric acid and partially to neutralize the sulphonated higher fatty acids, upon drying the resulting mixture, a detergent of somewhat different properties may be prepared. Further, as above pointed out, this procedure may be varied so as to produce a specially refined product.

In connection with the neutralization of the sulphonated products prepared by the process of the present invention, it has been found that the step may be carried out so as to prepare a series of detergents whose aqueous solutions have pH values extending over a wide range. This is possible because the products contain two acid groups, one or both of which may be neutralized, and an alkaline material may be used to neutralize one acid group different from the alkaline material used to neutralize the other acid group. For example, by preparing a sulphonated higher fatty acid product in which only one of the acid groups has been neutralized by a relatively weak alkaline material, such as ammonia, a detergent whose aqueous solutions have a low pH value may be prepared. On the other hand, by completely neutralizing a sulphonated fatty acid product with a strong alkali, there results a detergent whose aqueous solutions are alkaline in character. Between these two extremes, by partially neutralizing a sulphonated fatty acid product with a strong alkali or by neutralizing one acidic group with a strong alkali and the other with a weak alkali, detergents whose aqueous solutions have intermediate pH values may be produced. A further valuable property of the sulphonated products is the fact that aqueous solutions of their partially neutralized salts which have pH values included within the neutral and slightly acid range possess the ability of changing but slightly in pH value with the addition of small amounts of acid or alkali. Thus, it is possible to make use of the products in neutral and slightly acid solutions with the assurance that the pH value of the solution will remain relatively constant with small changes in the amount of acid or alkali present.

For many purposes it has been found that the sulphonated fatty acid products are of increased value when combined with other salts. Neutral and acid salts are particularly valuable for this purpose. Thus, compositions containing the sulphonated fatty acid products and up to 50 per cent by weight of such salts as sulphates, chlorides, acid phosphates, and acid phthalates, have been found to be excellent detergents. As specific examples of the salts of this type there may be mentioned sodium sulphate, ammonium sulphate, sodium chloride, monosodium phosphate, and potassium phthalate.

While as previously stated the sulphonated fatty acid products may contain eight or more carbon atoms, it has been found that the products containing from 14 to 18 carbon atoms are especially valuable. Furthermore, the mixtures of products of this type possess superior properties in most detergent actions over the single products.

As already indicated, the sulphonated fatty acid products made by the process hereinbefore described have many valuable uses. They are excellent cleansing, wetting, dispersing, peptizing and emulsifying agents and find applications in all fields requiring the use of capillary active substances, especially in the textile, leather, paper, and ore-refining flotation industries.

They can be used in place of soap in commercial and household laundries and are particularly valuable for washing dishes and glassware. Amine salts of the sulphonated fatty acids are soluble in organic solvents and these types are especially useful for dry-cleaning of fabrics. Miscellaneous uses of the products include fruit washing, preparation of oil-in-water emulsions, dispersing agents for insecticide solutions, spreaders in paints, etc.

The sulphonated fatty acid products have an outstanding advantage over soap and many newer types of detergents in that the maximum cleansing action is manifested in acid solutions. Furthermore the cleansing ability is not decreased by the presence of calcium and magnesium salts such as are responsible for hardness in natural water. These properties make the products extremely useful in many textile processing operations, particularly for treating wool and silk which are affected deleteriously by alkali. The use of the sulphonated fatty acid products in processing raw stock and finished fabrics of both animal and vegetable fibers avoids dinginess due to free alkali, fatty acids, alkali metal and heavy metal soaps such as frequently occurs when soap is used. Adsorbed detergent on the fiber acts as a penetrant and leveling agent in dyeing operations, thus permitting uniform, clean dyeing without streaking or blotching.

The products are of value for scouring, backwashing, fulling, bleaching, sulphuric acid carbonizing and dyeing of wool. The sulphonated fatty acids are not hydrolyzed to ineffective substances in strong acid solutions such as are employed for carbonizing wool and in this respect have an advantage over many other types of sulphonated products. In silk goods manufacture, the products are useful for degumming, washing and dyeing. Cotton, rayon and acetate silks and linen fabrics and raw stock can be advantageously scoured, bleached, dyed and finished by use of the products. They are also effective stripping agents for rags and fabrics to be redyed.

From the foregoing description it will be apparent that the present invention provides a process for the preparation of detergent materials usable in acid, neutral, or alkaline solutions characterized in that a saturated higher fatty acid or anhydride or a mixture of such acids or anhydrides containing not substantially more than about five per cent of unsaturated fatty acids or anhydrides is subjected to sulphonation by sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

The present invention also provides a complete process by which, employing as starting material a naturally occurring fat or oil, detergent compounds and compositions may be obtained in a relatively simple manner.

As above indicated, the saturated higher fatty acids or anhydrides subjected to sulphonation in accordance with the process of the present invention should be free from any substantial amount of hydroxyl-containing higher fatty acids. In the appended claims where a saturated higher fatty acid or anhydride is referred to it will be understood that such acids or anhydrides are intended which are free from an amount of hydroxyl-containing higher fatty acids or anhydrides sufficient to cause the final products to be materially contaminated with reaction products of hydroxyl-containing higher fatty acids or anhydride with sulphur trioxide and/or sulphur dioxide.

Since certain changes may be made in the processes above described without departing from the scope of the present invention, it is intended that the description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. The process for the preparation of sulphonated products which comprises sulphonating a compound selected from the group consisting of the saturated higher fatty acids and anhydrides of such acids containing not more than five per cent of unsaturated higher fatty acids or anhydrides with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

2. The process for the preparation of sulphonated products which comprises sulphonating a saturated higher fatty acid containing not more than five per cent of unsaturated higher fatty acids with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

3. The process for the preparation of sulphonated products which comprises sulphonating a compound selected from the group consisting of the saturated higher fatty acids containing from 14 to 18 carbon atoms and anhydrides of such acids and containing not more than five per cent of unsaturated higher fatty acids or anhydrides with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

4. The process for the preparation of sulphonated products which comprises reacting a compound selected from the group consisting of the saturated higher fatty acids containing from 8 to 24 carbon atoms and anhydrides of such acids and containing not more than two per cent of unsaturated higher fatty acids or anhydrides with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions while maintaining the temperature at about 20° to about 60° C.

5. The process for the preparation of sulphonated products which comprises reacting a saturated higher fatty acid containing from 14 to 18 carbon atoms and not more than five per cent of unsaturated higher fatty acids with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions while maintaining the temperature at about 30° to about 40° C.

6. The process for the preparation of sulphonated products which comprises sulphonating a saturated higher fatty acid compound containing not more than five per cent unsaturated higher fatty acid compounds with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions, and neutralizing the resulting sulphonation product.

7. The process for the preparation of sulphonated products which comprises reacting a saturated higher fatty acid containing not more than five per cent of unsaturated higher fatty acids with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions, the sulphur trioxide being used in such amounts that at least two mols are available for reaction with each mol of the saturated fatty acid, and neutralizing the resulting sulphonated acids.

8. The process for the preparation of sulphonated products which comprises reacting a

compound selected from the group consisting of the saturated higher fatty acids and anhydrides of such acids and containing not more than five per cent of unsaturated higher fatty acids or anhydrides with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions, removing sulphur dioxide from the resulting sulphonation mass, mixing the mass from which the sulphur dioxide has been removed with water whereby an aqueous mixture containing free sulphuric acid and a free sulphonated fatty acid is produced, and neutralizing the free sulphuric acid and the free sulphonated fatty acid.

9. The process for the preparation of sulphonated products which comprises reacting a compound selected from the group consisting of the saturated high fatty acids and anhydrides of such acids and containing not more than five per cent of unsaturated higher fatty acids or anhydrides with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions, removing sulphur dioxide from the resulting sulphonation mass, mixing the mass from which the sulphur dioxide has been removed with water whereby an aqueous mixture containing free sulphuric acid and a free sulphonated fatty acid is produced, adding to said mixture sufficient alkaline material to neutralize the free sulphuric acid and the free sulphonated fatty acid, and drying the resulting aqueous mixture.

10. The process for the preparation of sulphonated products which comprises reacting a compound selected from the group consisting of the saturated higher fatty acids containing from 8 to 24 carbon atoms and anhydrides of such acids and containing not more than five per cent of unsaturated high fatty acids or anhydrides with sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions, mixing the resulting sulphonation mass with water whereby an aqueous mixture containing free sulphuric acid and free sulphonated fatty acids is produced, adding to said mixture alkaline material in such amount as to neutralize the free sulphuric acid and to form a partially neutralized salt of the sulphonated fatty acid contained therein, and recovering said partially neutralized salt.

11. The process for the preparation of sulphonated products which comprises sulphonating a mixture of saturated higher fatty acids obtained by the hydrolysis of a naturally occurring fat or oil, said saturated higher fatty acids containing not more than five per cent of unsaturated higher fatty acids, by subjecting said mixture to the action of sulphur trioxide in a medium consisting of liquid sulphur dioxide under substantially anhydrous conditions while maintaining the temperature at about 20° C. to about 60° C., and neutralizing the resulting sulphonated product.

12. The process for the preparation of sulphonated products which comprises sulphonating a mixture of saturated higher fatty acids obtained by the hydrolysis of a naturally occurring fat or oil, said mixture containing not more than five per cent of unsaturated higher fatty acids, by subjecting said mixture to the action of sulphur trioxide in a medium consisting of liquid sulphur dioxide, the sulphonation being controlled so that no more than one per cent by weight of water based on the amount of sulphur trioxide used is present and the sulphur trioxide being employed in such amount that about two to about five mols of sulphur trioxide are available for reaction with each mol of the saturated fatty acids, and neutralizing the resulting sulphonation products.

13. The process for the preparation of sulphonated products which comprises dissolving a saturated higher fatty acid containing not more than five per cent of unsaturated higher fatty acids in anhydrous liquid sulphur dioxide, introducing into said solution a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide in such proportions that about 2.5 to about 3.5 mols of sulphur trioxide are available for reaction with each mol of saturated higher fatty acid, whereby a sulphonated higher fatty acid is produced.

14. The process for the preparation of sulphonated products which comprises dissolving in anhydrous liquid sulphur dioxide, a mixture of saturated higher fatty acids obtained by the hydrolysis of a hydrogenated naturally occurring fat or oil and containing not more than five per cent of unsaturated higher fatty acids, sulphonating said mixture of fatty acids by introducing into said solution a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide in such proportions that about 2.5 to about 3.5 mols of sulphur trioxide are available for reaction with each mol of saturated higher fatty acid, maintaining the temperature at about 20° C. to about 60° C. during said reaction, mixing the resulting sulphonation mass with water whereby an aqueous mixture containing free sulphuric acid and a mixture of sulphonated higher fatty acids is produced, neutralizing the free sulphuric acid and mixture of sulphonated fatty acids in said aqueous mixture, and drying the neutralized mixture.

15. The process for the preparation of sulphonated products from a material selected from the group consisting of the naturally occurring fats and oils which comprises hydrogenating said material to convert the unsaturated glycerides contained therein to saturated bodies, hydrolyzing the thus hydrogenated material whereby a mixture containing saturated higher fatty acids is formed, recovering said saturated higher fatty acids free from more than five per cent of unsaturated higher fatty acids, and sulphonating said saturated higher fatty acids with sulphur trioxide in the presence of liquid sulphur dioxide under substantially anhydrous conditions.

16. The process for the preparation of sulphonated products from a material selected from the group consisting of the naturally occurring fats and oils which comprises hydrogenating said material to convert the unsaturated glycerides contained therein to saturated bodies, hydrolyzing the thus hydrogenated material whereby a mixture containing saturated higher fatty acids is formed, recovering said saturated higher fatty acids free from more than five per cent of unsaturated high fatty acids, dissolving said saturated higher fatty acids in anhydrous liquid sulphur dioxide, sulphonating said saturated higher fatty acids by introducing into the resulting solution a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide while maintaining the temperature at about 20° to about 60° C., mixing the resulting sulphonation mass with water to form an aqueous mixture containing free sulphuric acid and sulphonated higher fatty acids, and neutralizing the aqueous mixture.

17. The process for the preparation of sulphonated products from a material selected from the group consisting of the naturally occurring fats and oils which comprises hydrogenating said material to convert the unsaturated glycerides contained therein to saturated bodies, hydrolyzing the thus hydrogenated material whereby a mixture containing saturated higher fatty acids is formed, recovering said saturated higher fatty acids free from more than five per cent of unsaturated higher fatty acids, dissolving said saturated higher fatty acids in anhydrous liquid sulphur dioxide, sulphonating said saturated higher fatty acids by introducing into the resulting solution a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide in such proportions that about three mols of sulphur trioxide are available for reaction with each mol of saturated higher fatty acid while maintaining the temperature at about 30° to about 40° C., mixing the resulting sulphonation mass with water to form an aqueous mixture containing free sulphuric acid and sulphonated higher fatty acids, introducing into the aqueous mixture sufficient sodium carbonate to neutralize the free sulphuric acid and to form sodium salts of the sulphonated fatty acids, and drying the neutralized mixture.

18. The process for the preparation of sulphonated products from a material selected from the group consisting of the naturally occurring fats and oils which comprises hydrogenating said material to convert the unsaturated glycerides contained therein to saturated bodies, hydrolyzing the thus hydrogenated material whereby a mixture containing saturated higher fatty acids is formed, recovering said saturated higher fatty acids free from more than five per cent of unsaturated fatty acids, dissolving said saturated higher fatty acids in anhydrous liquid sulphur dioxide, sulphonating said saturated higher fatty acids by introducing into the resulting solution a solution of substantially anhydrous sulphur trioxide in anhydrous liquid sulphur dioxide, mixing the resulting sulphonation mass with water to form an aqueous mixture containing free sulphuric acid and sulphonated higher fatty acids, introducing into the aqueous mixture an alkaline material in such amount as to neutralize the free sulphuric acid and convert the sulphonated higher fatty acids to partially neutralized salts, and recovering said partially neutralized salts.

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