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SULPHONATED FATTY OILS AND METHOD OF MAKING SAME

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The present invention relates to the process of preparing sulphonated oils and it particularly relates to improved sulphonated fatty oils which are produced thereby.

The commercial sulphonated oils are ordinarily produced by reaction between sulphuric acid or a similar sulphonating agent and a saponifiable oil or fat, or their fatty acids, or mixtures thereof. These sulphonated oils usually contain a substantial amount of undesirable impurities which apparently are produced in the course of the sulphonation reaction.

These impurities cause gradually forming sludges or precipitates which may in part settle out after standing or storage or remain suspended for long periods of time as a cloud or haze.

It is among the objects of the present invention to provide a process of producing improved sulphonated compounds of the character described in which the final product will be a clear bright liquid, substantially devoid of precipitate or sludge forming constituents, and which will have a high SO_3 content, all without the need of carrying special sulphonation processes or employing special catalysts or special reagents.

Other objects will be obvious or will appear during the course of the following specification.

These sludge or precipitate forming compounds appear to be generally unsulphonated oily, fatty or fatty acid materials, which have not entered into or do not readily enter into the sulphonation reaction and which not only render resulting sulphonated oil hazy and cloudy and of low quality, but in addition result in a decreased SO_3 content.

It has been found that these unsulphonated fatty or oily materials generally consist of the saturated fatty acids or glycerides, such as palmitin, stearin, or laurin, or the corresponding fatty acids, palmitic, stearic and lauric, which are not readily sulphonated and also include some of unsaturated acids or glycerides, such as olein, oleic acid, and so forth, the major portion of which unsaturated compounds has been sulphonated.

It has now been discovered that these unsulphonated components may be readily removed from the sulphonated product to produce a finished oil having a permanently clear and pleasing appearance and of high quality.

This purification may be most readily accomplished by the addition of an alkaline agent and preferably a strong alkali, such as sodium hydroxide, to the sulphonated oil immediately after sulphonating so that the oil will have a pH of 10 to 12 or higher.

The sodium hydroxide or other alkali so added should be used in quantity over and above that normally utilized in finishing the sulphonated oils. This over alkalization will result in a precipitation and throwing out of the objectionable unsulphonated materials including unchanged unsaturated compounds, as well as the not readily sulphonated saturated compounds.

Apparently the equilibrium of the colloidal suspension of the unsulphonated materials is broken up by the excess quantity of alkali with resultant precipitation.

The alkali should be added gradually to the sulphonated oil to secure the precipitation and removal of these undesirable constituents followed by vigorous agitation after each addition.

When a clouding effect is observed, which gradually assumes a definite emulsion, the addition and agitation may be discontinued.

The mass may then be permitted to pass through a settling or ageing period, at normal or elevated temperatures, during which period a sludge like mass often containing an oily surface layer will gradually rise to the top of the oil.

After this oily sludge has formed on the surface the main body of oil thereunder will assume a clear appearance.

The upper sludge layer may then be removed eliminating the undesirable unsulphonated impurities and the lower layer of clear oil may then be treated to reduce its alkali content, which is somewhat in excess of that suitable for ordinary usage.

To reduce the amount of alkali, the lower layer may be neutralized with a mineral or organic acid, such as sulphuric or acetic, so that a definite alkalinity will result dependent upon purposes for which the oil is to be utilized.

For textile finishing, for example, the sulphonated finished and purified oil should have a pH of about 8; for degumming a pH of about 10; or for use in cosmetics a pH of about 7.

The oil may also be slightly acidified with a mineral or organic acid followed by treatment and agitation with an aqueous salt solution, such as a solution of sodium chloride or sodium sulphate. After the mass has separated, the aqueous solution is drawn off and the excess acid remaining in the oil is neutralized with alkali. The addition of alkali continued until the desired combined alkali content is obtained.

The purified and refined oil so resulting will

remain clear at normal temperatures, will be stabilized so that it may be kept over an indefinite period without separation of unsulphonated fatty compounds or sludge and will possess a very high SO_3 content.

By way of example, to which the invention is not to be limited, the following may be given:

Example

A sulphonated olive oil is prepared by adding 1600 parts of strong sulphuric acid (say 66° Bé. or 98%) slowly to 4000 parts of olive oil.

Other sulphonating agents such as chlorsulphonic acid or fuming sulphonic acid may also be employed.

The mixture during the addition is well stirred and the temperature is controlled either by the rate of addition of the acid or by artificial refrigeration or by both so that the temperature does not exceed 35° C. at any time. The mixture is agitated for 8 to 12 hours after the addition. Then the mixture is treated with an aqueous salt solution for example containing sodium chloride or sodium sulphate.

The oil is then allowed to settle, the aqueous acid-salt layer is removed and the residual acid in the oil is then neutralized with alkali.

This neutralization process is continued beyond the point at which the mixture begins to cloud or to show free alkali, as indicated by reddening upon addition to an alcoholic solution of phenol phthalein.

At this point, the oil being treated assumes an emulsion like appearance which may be enhanced by the addition of a small quantity of water if the oil is too concentrated. The addition of alkali should always be continued until the mass becomes cloudy or forms an emulsion.

After this alkalization, the mixture is agitated and permitted to stand for two or three days to permit a layer of sludge to form at the top of the mass.

Although elevated temperatures accelerate and produce a more complete separation, a temperature of 75° C. should not be exceeded during the ageing period.

The lower portion of the aged mixture containing the refined and purified sulphonated oil may be treated with a mineral or organic acid to reduce the alkali content to neutrality or to acidity. Acidification should be followed by washing with a salt solution and then neutralization with alkali to the proper alkali content.

Instead of the proportions above, it is also possible to add 1500 parts of the 60° Bé. sulphuric acid to 4000 parts of olive oil.

With castor oil, from 1200 to 1300 parts of 66° Bé. sulphuric acid may be employed for every 4000 parts of castor oil.

With corn oil, from 1500 to 1600 parts of 66° Bé. sulphuric acid may be used for each 4000 parts of corn oil.

Among the other oils which may be utilized are menhaden oil, palm oil, mustard seed oil, pea seed oil, linseed oil, cottonseed oil, rape seed oil, castor oil, Neat's foot oil, peanut oil, lard oil, tallow oil, elaine oil, corn oil, sperm oil, and/or fish oil or their fatty acids or mixtures thereof.

The oils should contain substantial or large quantities of unsaturated aliphatic acids, and particularly oleic acid or its glyceride, olein, but linseed oil or other oils containing glycerides of linoleic acid, linolenic acid, ricinoleic acid, and eleostearic acid may also be used. Preferably the saturated glycerides, such a stearin, palmitin, laurin and so forth or their fatty acids should be present in only minor quantities, since they cannot be sulphonated by the above procedures, but only by fuming sulphuric acid at elevated temperatures and pressures.

The proportions given above may be considerably varied but generally about 20 to 50 lbs. of 66° Bé. H_2SO_4 should be used for every 100 lbs. of the oil, with an optimum of about 30 lbs.

In the alkalized oil there should be quantities of free alkali present, but in the finished oil the alkali present, should only be sufficient to neutralize substantially all of the sulphonic acid groups.

However, there should be insufficient alkali present in the alkalized oil to saponify the unsulphonated oil and fatty materials which are removed in the sludge layer.

The invention, however, is not intended to be restricted to any particular example, composition or proportions, or to any particular application, or to any specific manner of use, or to any of various details thereof, herein described, as the same may be modified in various particulars or be applied in many varied relations without departing from the spirit and scope of the claimed invention, the practical embodiments herein described merely showing some of the various features entering into the application of the invention.

What is claimed is:

1. A process of making a sulphonated oil which comprises reacting a fatty oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product, said alkalizing being accomplished by the gradual addition of an alkali with agitation until an actual definite clouding is accomplished, the addition of alkali being stopped substantially before sufficient alkali is added to saponify the unsulphonated oils, permitting the mixture to stand until the sludge containing the unsulphonated oils and fatty acids separates as an upper layer, separating the sludge and then adjusting the alkalinity of the refined oil, said mixture being permitted to stand at a temperature not exceeding 75° C. during the separation of the sludge as an upper layer.

2. A process of making a sulphonated oil which comprises reacting a fatty oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product only until the sulphonated product becomes cloudy, said alkalizing being accomplished by gradually adding caustic soda with agitation followed by standing of the material until the sludge containing unsulphonated oils and fatty acids separates an upper layer separating the sludge and then adjusting the alkalinity of the refined oil.

3. A process of making a sulphonated oil which comprises reacting a fatty oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product only until an emulsion is formed, said alkalizing being accomplished by adding a caustic alkali, followed by vigorius agitation after each addi-

tion and then permitting the mass to settle or age until an upper layer of sludge containing the unsulphonated oils and fatty acids forms, separating the sludge and then adjusting the alkalinity of the refined oil.

4. A process of making a sulphonated oil which comprises reacting olive oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product, said alkalizing being accomplished by the gradual addition of an alkali with agitation until an actual definite clouding is accomplished, the addition of alkali being stopped substantially before sufficient alkali is added to saponify the unsulphonated oils, permitting the mixture to stand until the sludge containing the unsulphonated oils and fatty acids separates as an upper layer, separating the upper sludge layer and then adjusting the alkalinity of the refined oil, said mixture being permitted to stand at a temperature not exceeding 75° C. during the separation of the sludge as an upper layer.

5. A process of making a sulphonated oil which comprises reacting castor oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product, said alkalizing being accomplished by the gradual addition of an alkali with agitation until an actual definite clouding is accomplished, the addition of alkali being stopped substantially before sufficient alkali is added to saponify the unsulphonated oils, permitting the mixture to stand until the sludge containing the unsulphonated oils and fatty acids separates as an upper layer, separating the upper sludge layer and then adjusting the alkalinity of the refined oil, said mixture being permitted to stand at a temperature not exceeding 75° C. during the separation of the sludge as an upper layer.

6. A process of making a sulphonated oil which comprises reacting a corn oil with sulphuric acid to produce the sulphonated oil, treating the reaction mixture with an aqueous salt solution, settling to permit formation of an aqueous layer, separating the aqueous layer from the sulphonated product, alkalizing the sulphonated product, said alkalizing being accomplished by the gradual addition of an alkali with agitation until an actual definite clouding is accomplished, the addition of alkali being stopped substantially before sufficient alkali is added to saponify the unsulphonated oils, permitting the mixture to stand until the sludge containing the unsulphonated oils and fatty acids separates as an upper layer, separating the upper sludge layer which forms and then adjusting the alkalinity of the refined oil, said mixture being permitted to stand at a temperature not exceeding 75° C. during the separation of the sludge as an upper layer.

7. A process of purifying a sulphonated fatty oil and thereby removing unsulphonated oily, fatty or fatty acid materials, which comprises adding an alkali thereto until the mixture is definitely alkaline and becomes cloudy, agitating the alkalized mixture after each addition of alkali, permitting it to stand for several days and then removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top.

8. A process of purifying sulphonated olive oil and thereby removing unsulphonated oily, fatty or fatty acid materials, which comprises adding caustic soda thereto until the mixture becomes cloudy but stopping the addition before there is sufficient caustic soda added to saponify the unsulphonated oil, the mixture being vigorously agitated after each addition, permitting it to stand at a temperature between 35° to 85° C. for between 12 to 96 hours and then separating the layer of sludge containng the unsulphonated oil, fatty or fatty acid materials which forms at the top of the sulphonated mass.

9. A process of purifying a sulphonated oil and thereby removing unsulphonated oily, fatty or fatty acid materials, which comprises alkalyizing the sulphonated oil with caustic soda, said caustic soda being added gradually until an actual definite clouding is accomplished, but the addition being stopped before there is sufficient alkali to saponify the unsulphonated oil and fatty materials, agitating the mixture, permitting it to stand, removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top thereof and then adjusting the alkalinity of the product.

10. A process of purifying a sulphonated oil and thereby removing unsulphonated oily, fatty or fatty acid materials, which comprises alkalizing the sulphonated oil with caustic soda, said caustic soda being added gradually until an actual definite clouding is accomplished, but the addition being stopped before there is sufficient alkali to saponify the unsulphonated oil and fatty materials, agitating the mixture, permitting it to stand, removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top thereof and then adding an acid to reduce the alkali content.

11. A process of purifying a sulphonated oil and thereby removing unsulphonated oily, fatty or fatty acid materials which comprises alkalizing the sulphonated oil with caustic soda, said caustic soda being added gradually until an actual definite clouding is accomplished, but the addition being stopped before there is sufficient alkali to saponify the unsulphonated oil and fatty materials, agitating the mixture, permitting it to stand, removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top thereof and then acidifying and washing with an aqueous salt solution and finally neutralizing with an alkali.

12. A process of purifying a sulphonated oil and thereby removing unsulphonated oily, fatty or fatty acid materials, which comprises alkalizing the sulphonated oil with caustic soda, said caustic soda being added gradually until an actual definite clouding is accomplished, but the addition being stopped before there is sufficient alkali to saponify the unsulphonated oil and fatty materials, agitating the mixture, permitting it to stand, removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top thereof, then acidifying the oil, treating the oil with a sodium salt solution, removing the solution after separation and then neutralizing the excess acid with alkali.

13. The process of preparing a sulphonated olive oil which comprises adding 1600 parts of strong sulphuric acid slowly to 4000 parts of olive oil with stirring, controlling the temperature

so that it does not exceed 35° C., agitating the mass from 8 to 12 hours, mixing with an aqueous salt solution, settling and then drawing off the aqueous acidic salt layer, neutralizing the residual acid in the oil with an alkali, continuing the addition of the alkali until the mixture begins to cloud, and then stopping the addition of the alkali so that there will be insufficient alkali present to saponify the unsaturated oil and fatty materials, again agitating, permitting the mixture to stand for two or three days, removing the layer of sludge containing the unsulphonated oil, fatty or fatty acid materials which forms at the top of the mass and then adding an acid to reduce the alkalinity of the resultant oil.

14. The process of preparing a sulphonated olive oil which comprises adding strong sulphuric acid slowly to olive oil with stirring, agitating the mass, mixing with an aqueous salt solution, settling and then drawing off the aqueous acidic salt layer, neutralizing the residual acid in the oil with an alkali, continuing the addition of the alkali until the mixture begins to cloud, and then immediately stopping the addition of alkali so that there will be insufficient alkali present to saponify the unsulphonated fatty oil or fatty acid materials, again agitating, permitting the mixture to stand, removing the layer of sludge which forms at the top of the mass and then adding an acid to reduce the alkalinity of the resultant oil.

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