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STABILIZING FATTY MATERIAL

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This invention relates to a method for stabilizing and improving the color of fatty acids, esters and oils, and particularly materials of this nature that are intended for use in the manufacture of soap. The invention more particularly relates to the treatment of materials of the aforementioned nature in such manner as to remove from them, and/or to render inactive in them, substances which are capable of imparting undesirable color and/or rancidity to soaps or other products made up from the higher molecular weight fatty acids, esters and oils to which the treatment of the invention is particularly applicable, and which substances may therefore be sometimes referred to hereinafter for convenience and brevity as "latent color bodies." The invention also relates to improved fatty acids, esters and oils that have been treated in the manner and for the purposes indicated more particularly hereinafter.

Relatively high molecular weight fatty acids, esters and oils, the last mentioned generally comprising triglyceride esters of high molecular weight fatty acids, frequently contain small amounts of polyolefinic compounds such as linoleic and linolenic acids and possibly other compounds containing two or more double bonds per molecule. These polyolefinic compounds are particularly undesirable where the high molecular weight fatty acids, esters and oils contaminated therewith are to be exposed under conditions of use to oxidizing conditions, since these polyolefinic contaminants are converted to undesirable peroxides comparatively readily. In certain instances undesirable mono-olefinic contaminants may also be present, and these too are substantially completely removed by the process of the present invention. When the high molecular weight fatty acids, esters and/or oils containing undesirable unsaturated contaminants of the nature indicated are thereafter employed for the manufacture of soap, for instance, the resulting products frequently possess or acquire an undesirable yellow color due to the formation of alkali derivatives of keto hydroxy acids.

It has been proposed to eliminate insofar as possible difficulties of this nature by pretreating the higher molecular weight fatty acids, esters and oils by various methods prior to converting same into the final soap or other products. For instance, it has been proposed to stabilize fatty acids, esters and oils by subjecting them to selective hydrogenation, by subjecting them to bleaching treatment with a suitable contact material such as activated clay in particle form, and by various other methods known in the tech-

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nical literature. However, while such methods may be to some degree satisfactory for the intended purpose, each one possesses one or more serious disadvantages, such as inordinately high cost, the necessity for using hydrogenation catalysts or other contact materials in subdivided form which requires a costly separate filtering operation, a failure to effect anything like complete and permanent removal of the undesired latent color bodies, and perhaps others which would show up during any attempt to practice on a commercial scale any of the previously proposed methods.

It is accordingly an object of the present invention to provide a simple process for treating high molecular weight fatty acids, esters and oils for the purpose of stabilizing them against the formation of rancidity and/or for improving their color, as well as similarly stabilizing and/or improving the color of soaps or other products for which they are used as intermediates.

It is a further object of the invention to provide a process for treating high molecular weight fatty acids, esters and oils in such manner as substantially to inactivate any relatively small proportion of latent rancidity- and/or color-forming bodies that may be present therein, and either with or without subsequent removal of the inactivated contaminants, prior to employing said high molecular weight fatty acids, esters and oils for the manufacture of soaps or other products.

In accordance with the present invention it has been discovered that a high molecular weight fatty acid, ester or oil, such for example as those intended for use in manufacturing soap, is very greatly improved with respect to freeing it from contaminants which give rise to undesired rancidity and/or color, either directly in the high molecular weight fatty acid, ester or oil itself or subsequently in the soap or other products made therefrom, by pretreating at an elevated temperature the high molecular weight fatty acid, ester or oil with a small amount of an aliphatic acid anhydride having an alpha-beta-enal group, preferably maleic anhydride. It has been discovered that under these conditions the acid anhydride preferentially reacts with the olefinic contaminants normally present in small proportions even in what are ordinarily regarded as rather refined grades of high molecular weight fatty acids, esters and oils to form high molecular weight resinous or condensation products which are inert and/or relatively more stable and which, if desired, can be readily removed from

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the high molecular weight fatty acid, ester or oil by methods such as filtration or, in the case of the fatty acids or their simple esters, by distillation. It has also been found that it is not necessary invariably to remove the high molecular weight resins or condensation products formed in this manner and that, on the contrary, the high molecular weight fatty acids, esters and oils which contain such resins or condensation products as a result of pretreatment of the nature indicated may be made up directly into soap or other products, the final products being quite satisfactory for commercial use despite the presence therein of small proportions of resins or condensation products of the character mentioned.

The treatment with maleic anhydride is conducted at elevated temperatures of the order of 150° to 300° C., with temperatures in the range of approximately 160° to 225° C. representing preferred temperature conditions. Especially desirable results have been obtained with temperatures in the range of about 180° to 200° C.

The quantity of maleic anhydride to be employed in the treatment according to the present invention may be varied from scarcely more than a trace up to approximately 7% by weight of the fatty material undergoing treatment, depending upon the degree of contamination thereof and the purpose of the treatment. Generally speaking, from about 1 to about 5% will be found to be very satisfactory. It will be appreciated that a slight excess of maleic anhydride is preferably employed, such slight excess doing no harm if permitted to remain permanently in the fatty material undergoing treatment. The optimum quantity necessary for any particular batch of material undergoing treatment may be readily determined by one or a few trial treatments of small aliquots in order to obtain a quantitative idea of the degree of contamination encountered, and hence the quantity of maleic anhydride required. In those cases where the difference between the iodine and thiocyanogen values of the fatty material to be treated is a measure of polyunsaturated constituents present, these values may be used to compute the minimum amount of maleic anhydride required.

On the other hand, where the purpose of the maleic anhydride treatment is more than that of mere stabilization and color improvement, and has for its object the production of a highly purified product without regard to yield, then it is frequently desirable to employ maleic anhydride in an amount considerably higher than the 7% value mentioned in the preceding paragraph.

The reaction time may vary over wide limits, it being only necessary to afford sufficient time to insure substantially complete reaction between the maleic anhydride and the contaminants present in the fatty material undergoing treatment. Reaction times varying from about 30 minutes to about 3 hours have been found to be satisfactory. Particularly satisfactory results have been obtained in actual practice with reaction times of approximately one hour.

The process may be carried out batchwise or in a continuous manner, the latter being particularly desirable when processing large quantities of high molecular weight fatty acids, esters and oils according to the present invention.

If the resins or condensation products formed by reaction between the maleic anhydride and the olefinic or polyolefinic contaminants are to be removed, this may be done by filtration or,

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in the case of the acids and simple esters which boil fairly readily, by distillation, the purified acids and simple esters being taken overhead in vapor phase leaving the resins or condensation products behind as non-volatile residues.

In order to assist in the better understanding of this invention, but without thereby intending to limit its scope, the following examples are set forth by way of illustration. Unless otherwise specified, all parts represent parts by weight.

Example I

A quantity of fatty acids derived from tallow, and consisting chiefly of stearic, palmitic and oleic with some linoleic, linolenic and other polyunsaturated acids, was heated with 3.0% of maleic anhydride at 160°-190° C. for a period of one hour, followed by distillation, resulting in a mixture of fatty acids of which the color stability had been increased several times over that of the corresponding untreated fatty acids. The maleic anhydride treatment increased by several per cent the amount of still residue left from the distillation operation, as compared with the untreated material.

By way of explanation of the general manner in which the degree of improvement in this and most of the succeeding examples was determined, it may be stated that the procedure was as follows: A sample of overhead, obtained by distillation of the treated material, was placed in an oven and held at 70° C., portions being removed at suitable intervals of time. The portions so removed were dissolved in methanol, 50° Baumé sodium hydroxide was added, the mixture was heated and the color observed visually. Aging of the overhead product obtained from the treated material was continued until a slightly yellow color was obtained upon adding the caustic. The time of aging under these conditions, as compared with the time of aging of the overhead product obtained from an otherwise similar material that was not treated with maleic anhydride, was taken as a measure of the degree of stabilization obtained by the maleic anhydride treatment.

Example II

In order to provide a control, a portion of tallow fatty acids identical with that employed in Example I was treated exactly in the manner there indicated, but without the addition of maleic anhydride. This control showed discoloration in two hours.

Example III

This was a duplicate of Example I, the treated material showing discoloration in four hours.

Example IV

This was a duplicate of Example I except that 1% of maleic anhydride was employed in treating a different batch of tallow fatty acids. The treated material showed discoloration in 43 hours.

Example V

In this example the procedure was applied to the methyl esters of tallow fatty acids. The procedure followed was the same as that set forth above under Example I, except that temperatures of 160°-185° C. were employed. The methyl tallow esters thus treated showed discoloration in 23 hours.

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Example VI

In order to provide a control, the procedure of Example V was repeated, except that the maleic anhydride was omitted. The treated material in this case showed discoloration in 4 hours.

Example VII

In like manner the procedure may be applied to high molecular weight triglycerides, such as vegetable or animal oils. For example, by heating tallow with about 3% maleic anhydride at 160°-190° C. for a period of about one hour, the color stability of the tallow so treated may be improved by a factor of 2 to 3 over that of the untreated tallow.

Example VIII

The procedure of the present invention is also especially applicable to the treatment of red oil (commercial oleic acid which may contain for example about 20% linoleic acid). For example, three portions of red oil (white olein-Gross) were treated by the procedure set forth above in Example I except that one portion was admixed with 3% of maleic anhydride, the second was admixed with 7% of maleic anhydride and the third was not admixed with maleic anhydride, the last thereby serving as a control. The treated materials showed discoloration after 48 hours, whereas the control (untreated) showed discoloration in four hours.

Example IX

As indicated earlier in the present specification, the process of the present invention may be applied to the treatment of fatty acids, esters and oils under circumstances where the production of a highly purified material is the primary desideratum rather than a high yield of product. In such cases it is generally desirable to employ the maleic anhydride in amounts somewhat higher than the 7% maximum indicated hereinbefore. For example, 5600 grams of red oil was treated with 950 grams of maleic anhydride by heating the two in a CO₂ atmosphere for three hours at 200° C. The thus-treated material was thereafter converted to the methyl esters and then subjected to distillation. The methyl esters distilled up to 193° C. at 2 mm., giving a crude yield of 4 kg. which, after refractionation, yielded 2822 grams of highly purified methyl oleate, boiling at 161.2° to 161.8° C. at 1.1 mm. The iodine value was 87.9 and the thiocyanogen value was 83.3, thus indicating that the final product was 93% methyl oleate and only 5% methyl linoleate.

Example X

Methyl oleate may be treated in a manner similar to that set forth in the previous example. Thus, 152 grams of crystallized methyl oleate was treated with 50 grams of maleic anhydride by heating in a nitrogen atmosphere for two hours at 195° to 205° C., and then subjected to distillation. The methyl esters distilled at 152° to 158° C. at 1 mm. and 125 grams of highly purified methyl oleate were recovered having an iodine value of 85.4 and a thiocyanogen value of 85.38 as contrasted with 85.4 for the iodine value and 84.5 for the thiocyanogen value of the original product.

It will be noted that in the two preceding examples a highly purified product was obtained, but with a considerable sacrifice in yield.

It will be apparent from the foregoing that the

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present invention contemplates a process for the pretreatment of high molecular weight fatty acids, esters and oils that is particularly well adapted for stabilizing and/or improving the color properties of such materials when contaminated with small proportions of color- and/or rancidity-imparting bodies such as olefinic or polyolefinic compounds normally present as contaminants even in what would otherwise be regarded as highly refined materials of this nature. After pretreatment in the manner indicated herein, the high molecular weight fatty acids, esters and oils are found to be greatly improved in the respects noted, the improvement being of a permanent nature and carrying over even into the final soap or other products that are manufactured from the high molecular weight fatty acids, esters or oils so treated.

While maleic anhydride has been used to describe and illustrate the invention, other aliphatic acid anhydrides having an alpha-beta-enal group may be substituted with comparable results. Such anhydrides preferably have up to about 7 carbon atoms per molecule, and include fumaric, acrylic, crotonic, itaconic, citraconic, etc., and their homologs and analogs. The corresponding acids, and esters thereof, may be employed as full equivalents of the anhydrides, and therefore the use of the acid or ester form is regarded as falling within the scope of the claims.

Where reference is made in the present specification and claims to the treatment of high molecular weight fatty acids, esters and oils, it is to be understood that this is in reference to materials of these classes containing one or more fatty acid residues having from 8 to 24, and particularly from 12 to 18, carbon atoms. Accordingly, the expression "esters" is employed with reference to simple esters of these high molecular weight fatty acids wherein the alcohol residue contains up to about 4 carbon atoms, while the expression "oils" is employed with reference to esters of these high molecular weight fatty acids having polyhydric alcohol residues such as that of glycerine.

I am aware that numerous variations in the procedures described above may be made without departing from the spirit of the invention as set forth in the following claims, and it should be understood that the methods and compositions specifically referred to herein are intended to be illustrative only and are not intended to limit the scope of the invention.

What is claimed is:

1. The process of stabilizing fatty material which comprises treating a fatty material from the class consisting of high molecular weight fatty acids, fatty acid monoesters and fatty oils containing minor amounts of polyolefinic compounds at an elevated temperature under substantially anhydrous conditions with sufficient acid anhydride having an alpha-beta-enal group to react with said polyolefinic compounds until said polyolefinic compounds have reacted with said anhydride, and discontinuing said treatment before said anhydride reacts with a substantial amount of mono-olefinic constituents of said fatty material.

2. The process as set forth in claim 1 in which said elevated temperature is within the range of 150° to 300° C.

3. The process as set forth in claim 1 in which the said acid anhydride is used in minor proportion relative to said fatty material.

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4. The process as set forth in claim 2 in which the said acid anhydride is used in an effective amount up to about 7% by weight of said fatty material.

5. The process as set forth in claim 4 in which the time of treatment is within the range of 30 minutes to 3 hours.

6. The process of stabilizing impure oleic acid which comprises treating oleic acid containing polyunsaturated fatty acids with maleic anhydride in an effective amount up to about 7% by weight of said oleic acid at an elevated temperature within the range of about 150° to 300° C. under substantially anhydrous conditions for a time sufficient to effect substantially complete reaction of said polyunsaturated acids with said maleic anhydride, and terminating said treatment before said oleic acid has reacted in substantial amount with said maleic anhydride.

7. The process of preparing stabilized oleic acid which comprises heating impure oleic acid with about 1% to 7% by weight of maleic anhydride at a temperature of about 150° to 300° C. for about 30 minutes to 3 hours under substantially anhydrous conditions, and recovering stable oleic acid from the reaction mixture by distillation.

8. The process of stabilizing higher fatty acids containing minor amounts of polyolefinic compounds which comprises treating said higher fatty acids at an elevated temperature under substantially anhydrous conditions with sufficient acid anhydride to react with said polyolefinic compounds until said polyolefinic com-

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pounds have reacted with said anhydride, thereafter discontinuing said treatment, and recovering said stabilized higher fatty acids.

9. The process as set forth in claim 8 wherein the higher fatty acids are separated from the resulting reaction product of said acid anhydride and polyolefinic compounds.

10. The process of stabilizing higher fatty acid monoesters containing minor amounts of polyolefinic compounds, said monoesters having an alcohol residue containing up to about four carbon atoms which comprises treating said higher fatty acids at an elevated temperature under substantially anhydrous conditions with sufficient acid anhydride to react with said polyolefinic compounds until said polyolefinic compounds have reacted with said anhydride, thereafter discontinuing said treatment, and recovering said stabilized higher fatty acids.

11. The process as set forth in claim 10 wherein the higher fatty acid monoesters are separated from the resulting reaction product of said acid anhydride and polyolefinic compounds.

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