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PROCESS FOR THE METHYLATION OF VEGETABLE OIL SOAPSTOCKS

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This invention relates to the methylation of vegetable oil "soapstocks." More particularly, the invention provides a commercially feasible process for the methylation of acidulated vegetable oil soapstocks to improve their properties, value, and utility.

Vegetable oil "soapstocks" or "foots" are the mixtures of soap, entrained vegetable oil and aqueous liquid which are removed from crude vegetable oils in the course of an alkaline refining of the oil. "Raw" foots are the semi-solid untreated mixtures, in the form in which they are produced. Raw foots usually contain about 35 to 50% by weight of vegetable oil fatty acids, in the form of their alkali metal salts and as neutral oil, and about 50% by weight of water. "Acidulated" foots are the black oily liquids produced by treating raw foots with a mineral acid, to release the fatty acids, then isolating the resulting organic phase consisting predominantly of fatty acids and neutral oil. Acidulated foots usually contain from about 85 to 95% fatty acids. "Hydrolyzed" foots is a type of acidulated foots produced by treating the acidulated foots according to the well-known Twitchell process or other processes which convert the neutral oil present to free fatty acids. Vegetable oil soapstocks are normally in surplus supply and of low cost. They are relatively unstable materials unless they receive special treatment, and are difficult to dispose of.

A primary object of the present invention is to provide a process of methylating the acidulated vegetable oil soapstocks to convert them to a stable and more valuable and useful product. A further object of the present invention is to provide an efficient methylation process whereby the major portion of the total fatty acids of the soapstocks are converted to methyl esters, and the resulting methylated soapstock product possesses more desirable physical and chemical characteristics.

The generally practiced method in the prior art for preparing methyl esters from free fatty acids or fatty materials containing free fatty acids consists of boiling under total reflux for from about 3 to 4 hours a mixture comprising approximately 1 part by weight of the fatty material, 4 parts by weight of methyl alcohol, and 3 to 5% by weight of a mineral acid catalyst based on weight of fatty material. Under these reaction conditions, a maximum of only approximately 80% of the fatty acids present can usually be converted to the methyl esters. Using the process of the present invention, it has been found possible to shorten the reaction time to as little as 10 minutes, to reduce the proportion of methyl alcohol required in the reaction mixture, and to increase the percent conversion of the fatty acids to methyl esters to about 90% or greater.

In general, in accordance with the present invention, acidulated vegetable oil soapstocks or "hydrolyzed" vegetable oil soapstocks are methylated by heating said soapstocks at elevated temperatures under pressure with an

excess of methyl alcohol in the presence of an acidic catalyst. Substantially any acidulated or hydrolyzed edible vegetable oil soapstock produced by the conventional alkali or soda ash refining processes can be employed in the process of this invention. Suitable soapstocks include those from cottonseed oil, soybean oil, peanut oil, corn oil and the like.

The methylation treatment is preferably carried out at a temperature and pressure high enough to maintain the methyl alcohol in the liquid state and to make possible an efficient methylation in a short reaction time. For example, at temperatures of 100° and 120° C. pressures of about 40 and 80 p.s.i.g., respectively, are theoretically required to maintain the methyl alcohol in the liquid state. In practice, a safety factor is usually provided for. Accordingly, it is generally preferred in the process of the invention to employ a temperature of from about 100° C. to about 130° C. and a pressure of from about 120 to 180° p.s.i.g. A temperature of 120° C. and a pressure of 150 p.s.i.g. are particularly preferred. Under these conditions, only a short reaction time, usually about 10 to 15 minutes, is required for maximum conversion of the fatty acids to methyl esters. The reaction time is critical in that if it is too brief the maximum conversion of total fatty acids to methyl esters is not achieved, and if it is too long there is danger of degradation of the fatty acids. In the preferred practice, the reaction is generally carried out for from about 10 to 15 minutes. Reaction times in excess of about 20 minutes are not usually necessary or desirable.

Acidic catalysts are preferred for use in the process of the invention because of their tolerance for small amounts of water such as are found in most acidulated soapstocks. Mineral acid catalysts such as hydrogen chloride or sulfuric acid can be employed. However, the preferred catalyst is a Twitchell-type catalyst in an excess of sulfuric acid. This catalyst is prepared by reacting one mole of naphthalene, benzene, or similar cyclic hydrocarbon with one mole of mixed, long chain (predominantly C_{16} or greater) fatty acids and six moles of 100% sulfuric acid. When naphthalene is employed, the product of the said reaction is essentially an anhydrous mixture of fatty acid naphthalenesulfonic acids and excess sulfuric acid which is used as the catalyst without further purification. The sulfuric acid is probably the major catalytic agent present with its activity enhanced by the emulsifying action of the fatty acid naphthalenesulfonic acids. From about 1 to 5% by weight of the catalyst, based on the weight of total fatty acids in the soapstocks, is generally preferred for the methylation reaction of the process of this invention. A particularly suitable amount of catalyst to use is 3%. It is usually convenient to dissolve the catalyst in methyl alcohol prior to adding it to the reaction mixture.

It is preferred to employ a homogeneous reaction mixture for the methylation. Therefore, a sufficient excess of methanol to give complete solution of the soapstocks being methylated is desirable. It has been found that this can be achieved by using approximately 5 moles of methyl alcohol for each mole of total fatty acids in the soapstocks. This preferred ratio of reactants is equivalent to approximately 35% methyl alcohol and 65% soapstocks by weight which is a considerably lower proportion of methyl alcohol than used in conventional processes for the methylation of fatty materials. It provides an adequate amount of the alcohol for the complete methylation of the soapstocks and at the same time is the lowest amount of alcohol giving essentially complete solution of the soapstocks. It is inefficient and uneconomical to use a much larger excess of methyl alcohol than this. It is generally preferred to employ ab-

solute methyl alcohol, but up to approximately 2% by weight of water in the alcohol can be tolerated.

The methylation of the soapstocks is preferably carried out by a continuous procedure employing any apparatus capable of withstanding the operating temperatures and pressures. A continuous reactor of the packed column type, provided with an integral flash evaporator, is particularly preferred. This type of reactor enables the operator to achieve precise control of reaction time, temperature, and pressure and makes possible the use of short reaction times at elevated pressures and temperatures. The operator can use either a single stage reactor or a multiple number of stages, with a single or multiple pass reaction in any stage. The desired extent of methylation can usually be achieved in a single pass or double pass reaction. In view of the high pressures and short reaction times employed for the methylation reaction, it is not generally desirable to use a batchwise procedure.

When employing a continuous reactor according to the preferred operating procedure in the process of the invention, certain conventional auxiliary equipment is used. This auxiliary equipment comprises a feed supply tank or other means for holding the proportioned mixture of soapstock, methanol, and catalyst; a high pressure variable rate positive displacement pump or other suitable device for pumping the reactants through the packed column reactor; a pressure gauge and a variable pressure discharge valve or other means for indicating and maintaining the desired operating pressure; a flash evaporator and condenser, or other means for rapidly removing methanol and water at the end of the reaction period; and suitable receiving vessels for the distilled solvent and for the methylated soapstock product.

In operation of the continuous reactor, the reaction temperature can be conveniently controlled by regulating the pressure of steam introduced into a jacket surrounding the packed column reactor. The pressure in the reactor is controlled by means of the variable pressure discharge valve, and the time of retention of the material in the reactor by the rate of feed input to the reactor.

The preferred type of flash evaporator comprises a flash chamber supplemented by a falling film tube, both being heated by external steam coils or other suitable means and operated under reduced pressure. The hot material is discharged from the packed column reactor via the variable pressure discharge valve into the evacuated flash chamber where the major portion of the excess methanol and the water formed by the reaction are removed by flash evaporation. The remainder, if any, is evaporated from the material as it trickles down the falling film tube attached to the flash chamber.

Flash evaporation serves two important purposes in the process of the present invention. The first of these is to terminate the methylation reaction by almost instantaneous removal of unreacted methanol and of water. The second is that the methylated soapstock product, being free of methanol and water, is satisfactory for distillation or other subsequent treatments or it can be used without further treatment. For example, it is possible to add fresh methanol to the product and repass the mixture through the reactor to increase the yield of esters. The percentage of fatty acids esterified can usually be increased by about 5% or more as the result of a single repass operation under the preferred conditions. After the removal of unreacted methanol and water from the reaction mixture, the catalyst precipitates from the methylated product and can be removed by mechanical means if the operator desires. However, the catalyst is not generally objectionable and can be left in the methylated product.

The process of the present invention provides a convenient means of producing valuable methyl esters of fatty acids from a low cost fatty material, namely vegetable oil soapstocks. When this is the primary aim, it is preferred to employ hydrolyzed soapstocks as the starting material, since essentially all the fatty acids therein are present as free fatty acids, and carry out the methylation in a multiple stage reaction. Under these preferred conditions, about 96% or more of the fatty acids are converted to methyl esters which can be recovered by the conventional distillation procedures.

The methylated soapstocks produced according to the process of the invention do not have the undesirable characteristics of the acidulated or hydrolyzed soapstocks. In contrast to the latter which are solid at room temperature and must be heated to render them liquid before they can be pumped or sprayed, the methylated soapstocks remain liquid at room temperature even in cold weather and can be handled easily. They are low in free fatty acid content, highly resistant to oxidation, noncorrosive to iron and steel vessels and equipment, and do not tend to become rancid like the unmethylated soapstocks which contain a higher percentage of free fatty acids.

Fatty materials are conventionally added to certain animal feeds in up to about 10% concentration by weight of the feed as a high caloric nutrient and anti-dusting component. The methylated soapstocks of the present invention are particularly suitable for this purpose as they possess the previously described desirable chemical and physical properties in addition to being of high caloric value and having anti-dusting properties. When added to a dry material, such as a feed, the methylated product is easily dispersed uniformly throughout the material without forming lumps or balls and reduces the dustiness of the material. The stability and keeping qualities of the resulting mixture are much superior than when unmethylated soapstocks are employed as the additive.

The following examples are given by way of illustration of the details of at least one method of practicing the invention, and are not by way of limitation of the invention.

Example 1

A sample of commercial grade acidulated cottonseed oil soapstocks was used in these experiments. The acidulated soapstocks contained 91.3% total fatty acids and 16% neutral oil.

Representative portions of the sample of acidulated soapstocks were methylated for various periods of time in a continuous, packed column type reactor as previously described using a single pass reaction and the following reaction conditions: temperature, 120° C.; pressure, 150 p.s.i.g.; Twitchell-type catalyst (prepared from naphthalene, mixed cottonseed oil fatty acids, and 100% sulfuric acid as described earlier), 3% by weight based on weight of total fatty acids (TFA) in the acidulated soapstocks; mole ratio of methyl alcohol to total fatty acids, 5 to 1.

The effect of length of reaction time on the conversion of total fatty acids in the acidulated soapstocks to methyl esters is summarized in the following table:

Reaction time, minutes	Percentage of input TFA recovered as methyl esters by distillation
5.1	78.4
10.0	81.4
15.3	82.4
19.7	83.1
25.1	81.9

Example 2

The same lot of commercial grade acidulated cottonseed oil soapstocks used in Example 1 was employed in these experiments.

Representative portions of the soapstock sample were methylated for 10 minutes in the same apparatus and

in exactly the same manner as described in Example 1, except that varying amounts of the Twitchell-type catalyst were used. Experiments were also conducted in which the same methylated product was passed through the reactor twice (10 minutes' reaction time for each pass), the initial 5 to 1 mole ratio of methyl alcohol to TFA being restored by adding the required quantity of fresh methyl alcohol to the alcohol- and water-free methylated product from the first pass. No additional catalyst was used for the second pass.

The effects of catalyst concentration and number of passes on the conversion of TFA in the acidulated soapstocks to methyl esters are summarized in the following table:

Catalyst concentration, percent by weight based on weight of TFA	Percentage of input TFA recovered as methyl esters by distillation	
	Single pass reaction	Double pass reaction
0	8.4	11.8
1	67.5	81.5
1.4	78.1	87.2
3	84.1	90.1
5	87.4	92.7

Example 3

A sample of commercial grade hydrolyzed cottonseed oil soapstocks was used in these experiments. The sample had been prepared by hydrolyzing acidulated soapstocks by the Twitchell process. The hydrolyzed soapstocks contained 94.3% total fatty acids (TFA), 94.1% free fatty acids, and 0.2% neutral oil.

Representative portions of the soapstock sample were methylated in exactly the same manner as described in Example 2, using varying amounts of the Twitchell-type catalyst.

The effects of catalyst concentration and number of passes on the conversion of TFA in the hydrolyzed soapstocks to methyl esters are summarized in the following table:

Catalyst concentration, percent by weight based on weight of TFA	Percentage of input TFA recovered as methyl esters by distillation	
	Single pass reaction	Double pass reaction
0	34.2	50.5
1	86.7	91.9
3	90.9	96.2
5	91.4	96.9

Example 4

A different lot of commercial grade acidulated cottonseed oil soapstocks than that used in Examples 1 and 2 was employed in this experiment. The acidulated soapstocks contained 96.0% total fatty acids and 28.1% neutral oil.

The acidulated soapstocks were methylated for 10 minutes in the same manner and under the same conditions as described in Example 1, except that the reaction temperature varied between 114° C. and 123° C., being 119°–121° C. for approximately 95% of the reaction period.

Following removal of excess methanol and water by the usual flash evaporation procedure, the methylated product was filtered through filter paper. Material removed by filtration represented only 2.1% of the methylated product. The filtered methylated product contained 93.0% total fatty acids, and 87.7% methyl esters plus neutral oil. It was a dark brown to black oily liquid having a somewhat pleasant fruity odor. When incorporated into a standard poultry feed ration at the 5% and 10% fat levels and fed to poultry over a 10 week period, it gave results equivalent to those obtained using a conventional fat additive (stabilized white grease) at comparable fat levels. It was non-toxic to chicks and had an LD_{50} value in excess of 40 cc./kilogram.

We claim:

A process for producing methylated vegetable oil soapstocks from acidulated vegetable oil soapstocks comprising the following steps: heating a homogeneous reacting mixture of vegetable oil soapstocks in methyl alcohol solution for from about 10 to about 20 minutes at a temperature of from about 115° C. to about 125° C. and at a pressure at least sufficient to maintain the methyl alcohol in the liquid state, in the presence of about from 1 to 5% by weight of a Twitchell-type catalyst based on the weight of total fatty acids in said acidulated soapstocks, at least about 5 moles of methyl alcohol being used for each mole of total fatty acids present in said acidulated soapstocks; and flash-evaporating the unreacted methanol and the water from the reaction mixture.

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