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PROCESS FOR NEUTRALIZING VEGETABLE OR ANIMAL OILS OR FATS IN A WATER-SOLUBLE SOLVENT

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This invention relates generally to an improved process for neutralizing oils or fats.

The conventional industrial process for neutralizing oils or fats during the refining thereof consists in treating the oils or fats with caustic soda either in the hot or cold state, with such treatment being followed by various operations, such as washing, salting out, etc. It is a disadvantage of this existing process that a considerable amount of neutral oil is carried along with the saponifying paste and with the soap of the fatty acids, thereby reducing the yield of refined oil.

In order to diminish those losses various measures have been proposed, such as centrifugation of the pastes, neutralization with a continuous process using special centrifuges and so on. However, none of these more or less complicated processes succeed in eliminating or reducing this disadvantage to a substantial extent. Accordingly, it is an object of the present invention to provide a process which reduces such loss of neutral oil to a very low value; and which, moreover, in many cases produces an oil of improved and lighter color as compared with that obtained with traditional methods. The basic principle of the new process is to neutralize the oils or fats with caustic soda or with other alkalis after the oils or fats have been dissolved in a solvent which is miscible in all proportions with both water and the oils or fats at room temperature or at a temperature a little higher than room temperature. Solvents having that characteristic are e.g.: acetone, dioxane and isopropyl alcohol. However, at present the most interesting of these solvents for the purposes of industrial application is acetone owing to both its low cost and the fact that it does not form with water any azeotropic mixtures and, therefore, it is possible to recycle it following concentration in a rectifying column. There are existing publications and patents disclosing the neutralization of oil dissolved in solvents with alkalis. However, in these disclosed processes, principles have been followed which distinguish totally from the principle of the present process.

For example, there have been proposed processes for neutralizing oil dissolved in hexane, which is a solvent wherein oil is soluble but not so the solution of alkalis nor the soap that is formed. With that process the solvent has only the function of diluting the oil and of facilitating contact with the alkalis, while the soap separates in the form of insoluble lumps. In practice, that process has not met with success owing to the difficulty of separating the soap from the oily phase. Only the Solexol-process, which uses liquid propane under pressure, has proved practical in avoiding this difficulty.

In other proposed processes, neutralization is carried out in the presence of ethyl alcohol or of other alcohols. In such cases, the solvent (which only partially dissolves the oil) has the function of dissolving the soap, yielding a solution which has no colloidal characteristics and which therefore, does not tend to form any emulsions.

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However, those processes also have not been practically applied.

The process according to the present invention, on the contrary employs solvents in which both the water and the oils or fats are completely soluble. With such solvents it is possible to carry out complete neutralization of the free acidity of oils or fats, by using alkalis in aqueous solution in cold state and, therefore, without attacking the neutral oil to any appreciable extent, even when using alkalis in strong concentration. This phenomenon is probably explained by the fact that since the solvent is completely miscible with both the oil or fat and the water, the neutralizing reaction takes place in a homogeneous phase.

If the operation is carried out with highly diluted alkalis, the soap which is formed remains dissolved in the water contained in the alkalis. On the contrary, if alkalis in concentrated solution are used for neutralization, the soap separates partly in the solid state but can easily be dissolved completely by subsequently adding more water to the mixture. In any case, upon completion of the neutralization, a large volume of warm water is added for the purpose of diluting the solvent so as to render the neutral oil insoluble therein. In that way two layers or immiscible liquid phases are formed; with one layer or phase containing all of the neutral oil and a small amount of solvent, and the other layer or phase containing all of the water with the dissolved soap, together with all the water-soluble impurities and the greater part of the solvent. Since the neutral oil containing layer or phase does not contain a substantial amount of water, it is free from soap, while the layer, a phase containing the water with soap completely dissolved therein, is free from neutral oil. It is clear that if the operation is carried out in the above described manner, the following objects of extreme importance are attained:

(a) Neutralization is carried out in the cold state and in a total manner, without causing any attack on the neutral oil.

(b) The possibility is afforded of separating the soap formed, in the form of a clear aqueous solution, while avoiding the loss of neutral oil which is inevitably carried along if the soap is separated in the form of a paste.

(c) Since the water containing phase is also rich in solvent, the soap solution does not have any appreciable colloidal characteristics; and hence it does not tend to form emulsions or to foam.

(d) In case there are present water-soluble impurities such as tannin, or gossypol in the form of an alkaline salt, such impurities are dissolved in the water containing phase, thus yielding an oil of increased purity and fine color.

In order to reduce the time of contact between the solution of the fat or oil in the solvent and the alkali, neutralization may be effected in a continuous way, by simultaneously introducing the two liquid reactants into a mixer or other suitable equipment effecting thorough mixing and intimate contact thereof.

In order to facilitate the separation of the two layers or phases obtained by neutralization of the oils or fats, whether in a continuous or discontinuous manner, it may also be convenient to introduce the mixture of the two liquids, after diluting with water if needed, into a centrifuge which may be closed so as to be adapted for use with volatile solvents. With such a centrifuge, the neutralized oil containing little solvent issues from one side, and the soapy solution issues from the other side. In particular cases, in order to encourage the separation of the two layers or phases, the addition of an excess of alkali or salts may be useful, such as, for example, the addition of sodium chloride or sulfate in an amount of

2 to 5% by weight calculated on the basis of the oil or fat being treated.

In order to avoid oxidation, reducing substances, such as sulfites, hyposulfites or the like, may be added.

The two separate phases are distilled separately to recover the solvent. In that way one obtains on the one hand the oil which is perfectly neutralized and of fine color, that can be used in food preparation after undergoing the ordinary processes of decolorizing, demargarizing, deodorizing and the like and, on the other hand, there is obtained a solution of soap dissolved in water, containing the impurities, if any, as well as water-soluble coloring substances. The fatty acids can be recovered from such solution by a conventional acidifying process.

The present process is particularly well suited for the neutralizing of cottonseed oil which contains a considerable quantity of a dyestuff called gossypol which with caustic soda, forms a compound soluble in water. If cottonseed oil is treated in the manner set forth above, all of the gossypol, in addition to the soap, passes into the aqueous phase and the neutral oil obtained in the other phase is recovered in a condition of high purity and with a color that cannot be obtained with ordinary methods. The process also avoids refining losses, which are particularly heavy if cottonseed oil is treated by the conventional process of neutralization in a kettle.

The present process can be favourably used in connection with the extraction of oil from seeds or oily fruits by means of a solvent soluble in water. In fact such oil extraction may make use of solvents which are lipophilic and hydrophilic at the same time, and of a kind similar to those employed in the instant neutralizing process. As a consequence, the treatment with caustic soda can be applied directly to the mixture of oil in solvent as obtained from the extractor and which may be partly concentrated if needed. This results in considerable economy and in a considerable simplification of the process, since the neutralized oil is recovered directly from the oily seeds or fruits, and may, after a few simple filtering, decolorizing and deodorizing treatments, be employed as an edible oil.

If the above mentioned process of simultaneous extraction and neutralization is applied to cotton seed, a particularly interesting result is achieved because the lipophilic and hydrophilic solvents described cause not only the extracting of the oil but also, to a more or less great extent, of the gossypol and of the other objectionable substances contained in the cotton seed. Thus, an exhausted cotton meal is obtained that is practically free from gossypol and is particularly well suited as fodder for any kind of cattle. The mixture of cotton oil in solvents is, in turn, neutralized directly in the manner described, possibly after partial concentration in order to reduce the quantities of solvents to be handled, and cotton oil of high grade color and quality is thus provided.

This process of simultaneous extraction and neutralization can be applied either by directly extracting the cotton meal with the solvent described, or by subjecting said meal to a preliminary pressing in continuous presses and thereafter treating the pressed-flakes with solvent. In the latter case, the oil obtained from pressing may be added to the mixture in the solvent to be neutralized together with the oil recovered by extraction. The following specific examples are presented for the purpose of explanation, but without the intention of limiting the process of the present invention thereto.

Example 1

20 quintals of olive oil having 6% acidity, and extracted by pressure, are dissolved in 60 quintals of acetone having 95% concentration. The solution is passed into a closed neutralizing apparatus equipped with an agitator, and a solution of caustic soda 15° Bé. is introduced therein in a quantity equal to one and one-half times the theoretical amount necessary to neutralize

the acidity of the oil. The time of contact in the neutralizer is 10 minutes. Having carried out neutralization, 100 quintals of hot water at 70° C. are introduced into the apparatus and the whole is stirred. The mixture thus obtained separates into two phases and is sent to a closed type centrifugal separator adapted for volatile solvents, and which separates the two phases, one of such phases being constituted by a soapy solution in water containing the acetone, the excess of soda and the impurities, while the other phase contains the neutralized oil with about 8% of acetone. The two solutions are heated separately up to a temperature of 110° C. to completely evaporate the solvent. Thus 1,850 kg. of neutralized oil are obtained (loss factor 1.25), and such oil is decolorized with 0.8% of fuller's earth. After evaporation of the acetone contained in the soapy solution, the soapy pastes remain dissolved in water and are re-treated with sulfuric acid to recover the fatty acids according to conventional methods.

Example 2

1,000 quintals of cotton seeds having an average content of 18% of oil with 3% acidity, are deprived of linters, hulled and ground by normal methods to obtain 600 quintals of ground cotton pulp containing 178 quintals of oil and 400 quintals of hulls and linters containing 2 quintals of oil. The ground pulp is introduced into an extracting plant of the conventional rotary type, but operated with acetone as a solvent. The acetone employed has a water content of 4.5%. The extraction yields 424 quintals of exhausted cotton meal of very pale color and containing about 2 quintals of oil, about 0.03% of gossypol, and 150,000 liters of a mixture of acetone containing 176 quintals of oil and all of the gossypol and water that was contained in the pulp treated. Such mixture is concentrated in a continuous concentrator to reduce its volume to about 50,000 litres, then it is cooled down and passed on to a continuous mixer in which a solution of caustic soda (containing 40% of NaOH) is added in an amount exceeding 200% of that required to neutralize the acidity. The neutralized mixture leaving the mixer has added thereto approximately an equal volume of water at the temperature of 50° C. and then it is passed to a closed type centrifugal separator suitable for use with volatile solvents, and wherein the mixture is separated into two phases, one constituted by neutralized oil containing about 10% of acetone and the other constituted by water containing the excess of caustic soda, dissolved soap and gossypol in the form of a soluble sodium salt. The oily phase is sent to a continuous vacuum distillation column wherein any trace of acetone is eliminated and 169 quintals of neutralized oil (containing 0.25% acidity) are obtained. That product has a fine color, and may be sent to the subsequent stages of refining. The aqueous phase is also sent to a distillation column operating at atmospheric pressure and wherein the liquid is brought to a temperature of 100° C. so as to recover all of the acetone contained therein. The condensed acetone vapours pass to a tank for diluted acetone, and the latter is recycled from such tank after rectifying in a special rectifying column.

Example 3

500 quintals of cotton seeds having an average content of 18.5% of oil, with 2.5% acidity, are deprived of linters, hulled and ground by normal methods, to obtain 290 quintals of cotton meal. Such meal is subjected to a first pressing in continuous presses (expellers) to obtain 62 quintals of pressing oil and about 225 quintals of cotton flakes containing about 29.5 quintals of oil. The flakes are treated in a continuous Olier system column extracting installation wherein acetone is used as a solvent. The acetonic mixture thus obtained is concentrated and the 62 quintals of oil obtained in the pressing operation are added thereto. The total

volume of the mixture thus obtained is about 28,000 litres. That mixture, subdivided into 4 parts, is neutralized by using a total of 180 kg. of a 40% caustic soda solution. The neutralizing treatment is carried out in a vessel having a capacity of about 20,000 litres and equipped with stirrer, into which there are introduced 7,000 litres of mixture at a time. Having effected neutralization, the mass is diluted with 10,000 litres of water at a temperature of 50° C. so as to form two phases, with all of the soap and the sodium salt of gossypol being contained in the lower phase, while the neutralized oil of pale color is separated in the upper phase. After 10 minutes' decanting, about 12,000 litres of clear solution are tapped from the bottom phase, which contains the greatest part of the acetone. The remainder is centrifuged in a centrifugal separator of closed type, which continuously separates the neutralized oil (containing about 8% of acetone) from the remainder of the aqueous solution. The oil is deprived of the acetone by heating the solution up to 115° C. in a stream of superheated steam while the aqueous phase is distilled in an apparatus equipped at the top with a rectifying column so as to remove the concentrated acetone only from the top, whereupon the concentrated acetone is recycled.

Example 4

20 quintals of oil of grape-stones with 2.5% acidity, obtained by extraction with hexane, are dissolved in 40 quintals of dioxane. The solution is neutralized by adding 15 kg. of caustic potash dissolved in 50 kg. of water. After neutralizing, 80 quintals of water are added at 80° C. to dissolve completely the soapy pastes and to separate the mixture into two phases. The whole mixture is centrifuged and on one side there is obtained the oil containing a small proportion of the dioxane while, on the other side, there is obtained a diluted dioxane solution containing all of the soap. After removing the solvent from the oil by evaporation in a steam current, 1,930 kg. of neutralized oil of fine color are obtained.

We claim:

1. A process for neutralizing vegetable and animal oils and fats, comprising the steps of dissolving said oils and fats in a solvent miscible in all proportions with both water and said oils and fats, treating the solution thus obtained with at least one substance selected from the group consisting of the hydroxides and carbonates of an alkali metal of the group consisting of sodium and potassium until neutralization of said oils and fats has been obtained, intimately contacting said substance with said solution in order to accelerate the neutralization of said oils and fats, adding substantial quantities of hot water following said neutralization to strongly dilute the neutralized miscella thus obtained, whereupon two immiscible liquid phases are obtained having different specific gravities, separating said liquid phases from each other, distilling off the solvent from said liquid phases individually, collecting the solvent-free neutralized oils and fats, and discarding the solvent-free aqueous phase which is a solution of soap and water-soluble impurities.

2. A process according to claim 1, wherein said solvent miscible in all proportions with both water and said oils and fats in acetone.

3. A process according to claim 1, wherein the liquid phases are separated by decantation which removes the lower clear aqueous phase containing the soap, and, thereafter, centrifuging the upper phase together with an intermediate portion of the phase system which contains the neutralized oil, water, solvent and impurities.

4. A process according to claim 1, wherein said sol-

vent miscible in all proportions with both water and said oils and fats is dioxane.

5. A process according to claim 1, wherein the liquid phases are separated by centrifugation.

6. A process according to claim 1, wherein said treatment of said solution of oils and fats in said solvent with said substance is performed in a continuous mixer.

7. A process for neutralizing vegetable and animal oils and fats, comprising the steps of extracting said oils and fats from a source material with a solvent miscible in all proportions with both water and said oils and fats, treating the solution thus obtained with at least one substance selected from the group consisting of the hydroxides and carbonates of an alkali metal of the group consisting of sodium and potassium until neutralization of said oils and fats has been obtained, intimately contacting said substance with said solution in order to accelerate the neutralization of said oils and fats, adding substantial quantities of hot water following said neutralization to strongly dilute the neutralized miscella thus obtained, whereupon two immiscible liquid phases are obtained having different specific gravities, separating said liquid phases from each other, distilling off the solvent from said liquid phases individually, collecting the solvent-free neutralized oils and fats, and discarding the solvent-free aqueous phase which is a solution of soap and water-soluble impurities.

8. A process for neutralizing vegetable and animal oils and fats, comprising the steps of extracting said oils and fats from a source material with a solvent miscible in all proportions with both water and said oils and fats, concentrating the solution thus obtained, treating the concentrated solution with at least one substance selected from the group consisting of the hydroxides and carbonates of an alkali metal of the group consisting of sodium and potassium until neutralization of said oils and fats has been obtained, intimately contacting said substance with said solution in order to accelerate the neutralization of said oils and fats, adding substantial quantities of hot water following said neutralization to strongly dilute the neutralized miscella thus obtained, whereupon two immiscible liquid phases are obtained having different specific gravities, separating said liquid phases from each other, distilling off the solvent from said liquid phases individually, collecting the solvent-free neutralized oils and fats, and discarding the solvent-free aqueous phase which is a solution of soap and water-soluble impurities.

9. A process according to claim 8, wherein the solution obtained from said extraction is concentrated to a solvent-oil volumetric ratio of about 1.5 to 1 before being treated with said substance.

10. A process according to claim 8, wherein an oil selected from the group consisting of vegetable and animal oils is added to said solution obtained from the extraction in order to concentrate the same.

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