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PROCESS FOR STABILIZING ESTER TYPE
OILS AGAINST COLD

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This invention relates to the selective removal of higher melting components from fatty oils of the ester type and the like. It deals particularly, altho not exclusively, with the so-called "wintering" of ester type oils whereby they may be rendered stable against cold. By "stability against cold" as used in the vegetable oil art, for example, is understood the property of an ester type oil of remaining clear and not throwing down a deposit when cooled to a certain temperature, for example to -10°C. , for a certain time, for example one hour. Ester type fatty oils satisfy such conditions only when the higher melting, so-called stearin-like, components, which easily precipitate have been removed. Our invention provides a process whereby such separations may be more efficiently and simply effected with minimum loss of valuable oil.

Originally ester type oils were stabilized against cold by simple cooling until the undesirable precipitable components were solidified and then filtering off the resulting solids. This involved long cooling periods, much filtering difficulty and considerable contamination of the precipitate by valuable oil with resulting poor yields of cold-stable oil. Some of the operating difficulties such as long cooling time were obviated in part by carrying out the cooling by partial evaporation of liquefied gases added directly to the fatty oil being treated. Such procedure does not improve either the yield or stability to cold of the resulting product but on the contrary, usually gives poorer results in one or both of these respects. We have found that this is due to the fact that the compounds used by the prior art workers are solvents for the materials which it is desired to eliminate. We have discovered that instead of or in addition to, such prior art addition agents, there should be used a liquid which preferentially dissolves those components of the ester type oil which it is desired to preserve (e. g. those components which are stable, i. e. liquid, under the cold test) to produce a liquid phase in which the higher melting undesired components are insoluble or only slightly soluble. These agents will for the sake of simplicity be referred to hereinafter as "selective stabilizing diluents." One of their functions appears to be that of creating a condition under which the undesired components have a reduced solubility in the phase containing the remaining desirable components of the ester type oil. They also reduce the viscosity of the chilled fatty ester oil so that not only a more complete but also a quicker separation of undesirable components may be effected thru their use. The selective

stabilizing diluents of the process of our invention are thus primarily characterized by the fact that they contain a liquid in which the higher melting components of ester type oils, which are responsible for instability under cold, are only slightly, or not at all, soluble. The selective stabilizing diluents as used in the process of the present invention may consist of only a single substance or of a mixture of substances. Thus, for example, where the chosen diluent is not sufficiently miscible with the valuable components of the ester type oil being treated, to be present in the oil phase in sufficient quantity to create the desired conditions of minimum solubility of instability producing compounds and of minimum viscosity, a solubility enhancing agent may be used with the selective stabilizing diluent. Such solubility enhancing agents are solvents for both the selective stabilizing diluent used and for the ester type oil being treated. They may themselves possess selective stabilizing diluent properties to a certain extent.

A wide variety of different compounds may be used as selective stabilizing diluents in the process of our invention. These selective stabilizing diluents are characterized by their selective dissolving power for aromatic hydrocarbons. That is, they are polar compounds which are selective solvents for aromatic hydrocarbons in the presence of paraffinic hydrocarbons. We have found that by mixing fatty oils of the ester type with such selective solvents before or during cooling, the yield of cold stable oil may be materially increased, the time and degree of cooling required may be reduced and filtration may be greatly improved.

Typical selective stabilizing diluents which may be used in the process of our invention are for example, polar cyclic compounds, such as benzene or like carbocyclic rings or heterocyclic rings, such as furone, thiophene, pyridine or like rings containing one or more substituents such as $-\text{OH}$, $=\text{CO}$, $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$ (where R is an alkyl, aryl or aralkyl radical), $-\text{NO}_2$, $-\text{NH}_2$, $-\text{ONO}$, $-\text{SH}$, $=\text{CS}$, $-\text{CONH}_2$, $-\text{SCN}$ or $-\text{CN}$ groups or halogen atoms, or aliphatic compounds of the class consisting of aliphatic acids, acid anhydrides, ketones, alcohols and esters containing not more than four carbon atoms per molecule and substituted aliphatic alcohols, aldehydes, ketones, ethers, acids, acid anhydrides and sulfur analogues thereof containing at least one halogen, $-\text{CN}$, $-\text{SH}$, $=\text{CS}$, $-\text{CONH}_2$, $-\text{SCN}$ or $-\text{NH}_2$ group or liquid inorganic compounds of S, Se, Sn, Sb and the like such as SO_2 , SnCl_4 , etc.,

which are substantially unreactive with ester type oils.

Specific examples of suitable selective stabilizing diluents which may be used in the process of our invention are: benzene nitrile, benzene nitrite, nitrobenzene, nitrotoluene, aniline, diphenylamine, phenol, cresol, cresylic acid, quinoline, pyridine, furfural, thiophene, thiophenol, lutidine, picoline, thionaphthol, "acid oils" (i. e. the products of an apparently hydroxy-aromatic nature obtainable by treating petroleum oil, such as cracked distillate oil, with a concentrated sulfuric acid, removing the sludge, neutralizing the remaining oil, separating a second sludge and acidifying the separated sludge) diacetone alcohol, acetic acid, butyric acid, lactic acid, acetic anhydride, acetone, methyl-ethyl ketone, isopropyl alcohol, butyl alcohol, ethyl formate, ethyl acetate, methyl carbonate, thio-acetic acid, $\beta\beta'$ dichlorethyl ether, dichlorobutyl ether, dibromomethyl ether, chloroacetic acid, ethanalamine triethanolamine, nitro methane, acetonitrile, and the like. Of these methyl-ethyl ketone and acetates such as butyl acetate, etc., for examples, are representative of those selective stabilizing diluents which possess sufficient dissolving power for fatty ester type oils so that they can be used alone.

Suitable solubility enhancing agents which may be used with selective stabilizing diluents such as furfural, dichlorethylether and the like which are not sufficiently miscible with many ester type oils so that maximum advantage, particularly in decreasing the solubility of the higher melting components which it is desired to remove, may be obtained thru their use alone, are, for example, carbon bisulfide, hydrocarbons, including both aliphatic and aromatic hydrocarbons, i. e. straight and/or branched, open and/or closed chain hydrocarbons, such for example, as propane, isobutylene, isopentane, gasoline or kerosene fractions, benzene, toluene, tetraline, aromatic mineral oil extracts and the like, halogen derivatives of such hydrocarbons, e. g. carbon-tetrachloride, chloroform, ethyl chloride and the like, aliphatic ethers such as dimethyl ether, methyl-isopropyl ether, di-isopropyl ether etc., aliphatic compounds containing more than four and preferably less than thirteen carbon atoms per molecule of the following types: aliphatic alcohols, aldehydes, acids, ketones, amines and sulfur analogues thereof, typical of which are, for example, primary, secondary and/or tertiary amyl alcohols, hexyl aldehyde, diethyl ketone, dipropyl thioether, and the like.

The selective stabilizing diluent and solubility enhancing agents chosen may be used in widely varying proportions. The optimum in any particular case will depend upon the nature of the ester type oil being treated and the degree of cold-stability which it is desired to impart and can usually be quickly determined by a few preliminary tests in which the proportions are varied until a ratio is found at which as little oil as possible is carried down with the solid stearin-like constituents on cooling to a predetermined temperature. For example, to stabilize neat's-foot oil against -10° C. a mixture of acetone and benzol in the proportion of about four volumes of acetone to one volume of benzol, is very effective. It will in general be more advantageous to use the minimum quantity of solubility enhancing agent which is required to cause the chosen selective stabilizing diluent and the fatty oil to form a homogeneous liquid phase at the temperature at which the separation is to be made. But greater

or smaller amounts may also be used as conditions in any particular case warrant.

The volume of treating agent, i. e. selective stabilizing diluent alone or mixture of selective stabilizing diluent and solubility enhancing agent, used to dilute a given volume of ester type oil will be determined by the viscosity needed at the filtration or settling temperature and will vary with the character of the ester type oil, and of the treating agent involved, but can readily be determined by empirical methods in any particular case. Volume ratios within the range of about $\frac{1}{4}$ to about 4 volumes of treating agent per volume of fatty ester type oil are usually effective.

The process may be carried out continuously or intermittently or by batch methods. Diatomaceous earth or other suitable filter aids or the like may be used in the process. The chilling of the mixture may be effected by means of brine coils or other suitable refrigerating means but is preferably effected thru the evaporation of a part of one or more of the treating agents added. Thus where a low boiling selective stabilizing diluent such as methyl alcohol, for example, is used, vacuum evaporation of a part thereof may be effective in producing the desired low temperature with or without supplementary cooling. It is generally more advantageous to utilize the self refrigeration obtainable with compounds of the solubility enhancing agent type as many such compounds are readily available which are normally gaseous and hence not only may be used without resort to vacuum evaporation but also are more effective cooling agents.

Our process of destearinizing vegetable oils and the like may suitably be combined with processes for extracting these oils from their source materials such as seeds, plant fibers, animal tissues, etc. Thus, for example, the chosen selective stabilizing diluent may be used as extracting agent or more preferably the solubility enhancing agent may be so used and the selective stabilizing diluent added to the extract which may, if necessary, be first suitably concentrated, before chilling to effect separation of higher melting components.

Our process is applicable to the stabilization of any ester type fatty oil whether of animal, vegetable or fish origin. It may also be applied to the removal of higher melting components from normally solid ester type fatty mixtures, i. e. fats and waxes. Thus not only may our process be used to prepare low cold test vegetable salad oils, e. g. by destearination of corn oil, cotton-seed oils and the like but also it may be used to separate spermaceti from sperm oil, stearin and palmitin from lard oil, soy bean oil, etc. In fact, the yield and purity of free fatty acids from fatty oils may be greatly improved by applying our process to the oil prior to saponification.

The following example showing the application of the process of our invention to the stabilization of neat's-foot oil, illustrates the advantages of our method over prior procedures.

One part of neat's-foot oil was dissolved in one part of a mixture made up of $\frac{1}{3}$ part of benzol and $\frac{2}{3}$ part of acetone. The mixture was cooled, while stirring, to about -10° C. and maintained at that temperature until a small sample showed stability against cold of -10° C. after filtration. The mixture was then filtered in a refrigerated filter press. After freeing the filtrate of solvent, a yield of 77% of neat's-foot oil stable at -10° C. was obtained. This compares with a yield of 45% obtained from the same oil by the usual method in which no selective

stabilizing diluent was used. The product had furthermore a lower iodine number, i. e. 75 as against 82 for ordinary cold-stable neat's-foot oil. The stearin-like constituents recovered after evaporation of the solvent from the precipitate were solid at ordinary temperature which is further evidence of the sharpness of the separation effected by our process.

It will be apparent that the cold stabilization process of our invention offers many advantages, particularly in efficiency and ease of separation of high melting constituents, over prior methods of removing such materials from ester type oils. It is especially notable that by the use of a compound which is a selective solvent for aromatic type hydrocarbons, we are enabled to bring about a more complete separation of undesirable higher melting components of ester type oils, fats and waxes, in a more rapid manner and with material heat economy since higher temperatures of precipitation may be used. The products thus obtained are much superior to those formerly secured because of their greater purity.

Our invention is not only capable of wide variation with respect to the ester type oils, fats and waxes which may be treated thereby and to the selective stabilizing diluents and solubility enhancing agents which may be used, but also the operating details, described by way of illustration, may be greatly varied. Thus, for example, in addition to the ester type oils, etc., already given as examples, it will be evident that mutton or beef tallow, coconut butter, cod liver oil, palm oil, olive oil and the like, may be similarly treated if proper allowance is made for the differences in melting points involved. Furthermore, it will be clear that while saturated compounds have in general been emphasized in describing the suitable selective stabilizing diluents, unsaturated compounds such as allyl alcohol, crotonaldehyde, etc., are also effective in the process of our invention.

We claim as our invention:

1. The process of refining neat's-foot oil to produce low cold test oil which comprises diluting said oil with $\frac{1}{4}$ to 4 volumes of a mixture one part benzol to four parts acetone by volume, lowering the temperature to at least about -10° C. and separating the material solidified thereby.

2. The process of stabilizing fatty oils of the ester type against cold which comprises adding thereto liquid sulfur dioxide and a liquefied normally gaseous hydrocarbon and then lowering the temperature of the mixture sufficiently to cause separation of the higher melting substances present in the oil.

3. The process of stabilizing fatty oils of the ester type against cold which comprises adding thereto a solvent which has a selective dissolving power for aromatic hydrocarbons and a liquefied normally gaseous hydrocarbon, subsequently reducing the pressure on the mixture to permit evaporation of sufficient of said hydrocarbon to lower the temperature of the remaining mixture to a point at which separation of higher melting glycerides from lower melting glyceride present in the oil takes place.

4. In a process of stabilizing against cold a fatty oil of the glyceride type containing a normally solid fatty glyceride by cooling said oil to a temperature at which said solid fatty glyceride is precipitated and separating precipitate from remaining liquid fatty glyceride, the method of increasing the yield and stability of the stabilized oil which comprises adding to the oil sufficient

acetone to render said solid fatty glyceride substantially insoluble in the mixture at the operating temperature and sufficient of a liquefied normally gaseous hydrocarbon to maintain said quantity of acetone substantially miscible with said liquid fatty glyceride after evaporation of sufficient of said hydrocarbon to lower the temperature of the remaining mixture to a point at which separation of said solid fatty glyceride takes place and subsequently reducing the pressure on the mixture to permit said evaporation to take place.

5. In a process of stabilizing a fatty oil of the ester type against cold by cooling said oil to a temperature at which higher melting esters present therein are precipitated and separating precipitate from remaining liquid fatty ester, the method of increasing the yield and stability of the stabilized oil which comprises adding to the oil a polar aliphatic solvent having a selective dissolving power for aromatic hydrocarbons which solvent has a limited miscibility with said liquid fatty ester in an amount in excess of said miscibility and sufficient of a mutual solvent for said polar solvent and said fatty oil to maintain said excess of the polar solvent miscible with said liquid fatty ester under the operating conditions whereby the concentration of said polar aliphatic solvent may be increased beyond its normal saturation point and lowering the temperature of the mixture sufficiently to cause separation of higher melting ester.

6. In a process of removing higher melting components of oils, fats and waxes of the ester type by cooling said ester type material to a temperature at which said higher melting components are precipitated and separating precipitate from remaining lower melting components, the method of increasing the sharpness of said separation and the yield of said lower melting components which comprises adding to said ester type material sufficient of a polar substituted hydrocarbon having a selective dissolving power for aromatic hydrocarbons to substantially reduce the solubility of said higher melting components in the mixture and sufficient of a mutual solvent for said polar compound and said ester type materials to maintain said quantity of said polar compound miscible with the lower melting components of the ester type material under the operating conditions whereby the concentration of the polar substituted hydrocarbon may be increased beyond its normal saturation point, cooling the resulting mixture to a temperature at which said higher melting components separate and removing the thus separated components.

7. In a process of stabilizing a fatty oil of the ester type against cold by cooling said oil to a temperature at which higher melting substances present therein are separated in solid form and removing such solids from remaining liquid fatty esters, the method of increasing the yield and stability of the stabilized oil which comprises adding to the oil a polar aliphatic solvent of less than five carbon atoms per molecule which has a selective dissolving power for aromatic hydrocarbons and an amount of a mutual solvent for said polar compound and said fatty oil not substantially greater than that required to form a homogeneous liquid phase under the operating conditions whereby the concentration of said polar aliphatic solvent may be increased beyond its normal saturation point and then lowering the temperature of the mixture sufficiently to cause separation of higher melting ester.

8. In a process of stabilizing a fatty oil of the

glycerine ester type against cold by cooling said oil to a temperature at which higher melting glycerides present therein are separated in solid form and removing such solids from remaining liquid fatty glycerides, the method of increasing the yield and stability of the stabilized oil which comprises adding to the oil a polar aliphatic carbonylic compound of less than five carbon atoms per molecule and a mutual solvent for said carbonylic compound and said liquid fatty glycerides whereby the concentration of the polar aliphatic carbonylic compound may be increased beyond its normal saturation point and then lowering the temperature of the mixture sufficiently to cause separation of higher melting glycerides.

9. In a process of stabilizing a fatty oil of the glycerine ester type against cold by cooling said oil to a temperature at which higher melting glycerides present therein are separated in solid form and removing such solids from remaining liquid fatty glycerides, the method of increasing the yield and stability of the stabilized oil which comprises adding to the oil a ketone of not more

than four carbon atoms per molecule and a mutual solvent therefor and for said fatty oil whereby the concentration of said ketone may be increased beyond its normal saturation point and then lowering the temperature of the mixture sufficiently to cause separation of higher melting glycerides.

10. In a process of stabilizing a glyceride type vegetable oil against cold by cooling said oil to a temperature at which a crystallizable stearin present therein crystallizes and removing the crystallized material, the method of increasing the yield and stability of the treated oil which comprises adding to the oil an organic hydroxy compound which has a selective dissolving power for aromatic hydrocarbons and a hydrocarbon in the liquid phase, cooling the resulting substantially anhydrous mixture to a temperature at which said stearin crystallizes and separating liquid glyceride from said organic hydroxy compound and hydrocarbon.

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