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UNITED STATES PATENT OFFICE

2,610,915

WINTERIZED GLYCERIDE OIL AND PROCESS OF PRODUCING THE SAME

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11 Claims. (Cl. 99—118)

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This invention relates to treating fatty glyceride material, and it has to do more particularly with the manufacture of an improved glyceride oil.

In the processing of glyceride fatty material an important problem is the removal of the high melting point glycerides which are normally solid at room temperatures and which tend to separate from the oil at relatively high temperatures. The conditioning of a glyceride fatty material to effectuate separation of the liquid fats from the undesirable solid fats must be carefully controlled in order to obtain the solid fat in a crystalline form suitable for filtration. Under the best conditions, filtration is inefficient, for the solid fats often separate as extremely small particles and remain suspended in the oil as colloidal dispersions, thus making the straining operation very difficult.

I have now discovered that certain compositions hereinafter to be described and referred to as crystal inhibiting and modifying agents are extremely useful in prolonging the cold test of glyceride oils and in facilitating the "winterizing" process.

In "winterizing" a glyceride oil or processing a fatty material such as sperm oil or white grease to obtain "lard oil," the conditioning of the oil or fatty material to effectuate separation of the liquid fats from the solid fats must be carefully controlled in order to obtain the solid fat in a crystalline form suitable for filtration. Under the best present-day conditions filtration is inefficient, for the solid fats often separate as extremely small particles and remain suspended in the oil as colloidal dispersions, thus making the straining operation very difficult. The difficulties attending the process of winterizing as hitherto practiced may be overcome by incorporating into the glyceride oil or glyceride fatty material, such as sperm oil or white grease, a small amount of the crystal inhibitors and modifiers, hereinafter described. I have found that the addition of such substance profoundly affects crystallization whereby the crystals of the solid fats are rendered firmer and better defined. The form of the crystals is so improved that a more facile and complete separation of the undesirable solids from the liquid constituents of the oil is effected. In addition to improving winterization, these substances are usually present in sufficient amounts to lengthen substantially the cold test of the oil, although this effect is not so pronounced as that which results when the crystal inhibitor is added after the oil has been winterized.

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An important object of the present invention is, therefore, to provide an improved method for separating the solidified fat crystals from the liquid fats in glyceride fatty material.

Another object of the present invention is to provide a method of improving the "winterizing" of glyceride oils.

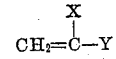
Still another object of the invention is to provide a glyceride oil having an improved cold test.

A still further object of the present invention is to provide an improved glyceride oil which will remain clear and homogeneous for long periods of time at relatively low temperatures.

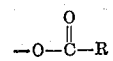
Another object of the invention is to provide an improved glyceride oil which will exhibit good stability at relatively low temperatures when incorporated in an emulsion.

Additional objects of the invention will be apparent from the description and claims to follow.

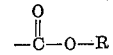
Broadly, the invention contemplates the addition to a glyceride oil or glyceride fatty material, either before or after winterization, of a small amount of an oil-soluble polymerization product of esters having vinyl or substituted vinyl group, according to the following general formula; namely, esters of the formula



wherein X is a hydrogen atom and alkyl or aromatic hydrocarbon group, and Y is



or



in which R is a monovalent hydrocarbon radical containing more than 4 carbon atoms or an ether derivative of said hydrocarbon radical.

Compounds of the above type are the esters of acrylic acid or of its alpha-alkyl or alpha-aryl substitution products and monohydric alcohols containing more than 4 carbon atoms, such as octyl, decyl, lauryl, or cetyl esters of acrylic acid, alpha-methacrylic acid, and other alpha-substituted homogenous or acrylic acid, as more fully described in U. S. Patent 2,091,627.

The most effective polymers for the present purpose are the oil-soluble polymerized esters of acrylic acid or alpha-methacrylic acid and monohydric, saturated, primary aliphatic alcohols containing from 12 to 18 carbon atoms or molecules, such as lauryl, cetyl, or octadecyl esters.

These esters need not be pure but may be mixtures of one or more of the higher aliphatic alcohols and the acrylic or methacrylic acid polymerization products. A mixture of two or more of the foregoing polymers may also be used.

These polymers are preferably prepared by heating the monomeric esters or mixtures thereof at 70–100° C. in the presence of small amounts of polymerization-inducing catalysts, such as peroxides or ozonides, as more fully disclosed in U. S. Patents 2,100,993 and 2,114,233.

Preferably the amount of the foregoing crystal modifiers used ranges from .005 to 1.0 per cent. Where it is desired to add the crystal modifier prior to the winterizing operation to facilitate filtration, it is often advantageous to add additional amounts to replace that which may be removed with the solid matter during filtration. Larger amounts of the crystallization inhibitor may be used but generally is not commercially advisable.

The following examples illustrate how the invention may be practiced, and are not intended to limit the scope of the invention:

Example I

To 100 grams of winterized cottonseed salad oil having a cold test of about 9 hours was added 1.0 per cent of the oil-soluble polymerization product of an ester of alpha-methacrylic acid and lauryl alcohol. After the said polymerization product is uniformly distributed throughout the oil, a cold test of the treated oil gave a value of 45 hours.

Example II

To 100 grams of winterized cottonseed salad oil having a cold test of about 9 hours was added 0.10 per cent of the oil-soluble polymerization product of an ester of alpha-methacrylic acid and lauryl alcohol. The cold test of the treated salad oil gave a value of 35 hours.

Example III

To a sample of winterized cottonseed oil having a cold test of 15 hours, 0.02 per cent of cetyl-alpha-methacrylate soluble in oil was added and uniformly distributed therethrough. The oil containing the above crystal-inhibiting agent exhibited a cold test of 60 hours.

Example IV

Mayonnaise made with a winterized cottonseed salad oil containing 0.02 per cent n-cetyl-acrylate soluble in oil was placed in a cooler maintained at a temperature of 28° F., and the mayonnaise emulsion did not break until after being held seven days at the said temperature. A similar sample of mayonnaise stood up for two days when placed in a cooler maintained at a temperature of 24° F. The control sample of mayonnaise consisting of a winterized cottonseed oil having the same initial cold test but which was not treated with a crystal-inhibiting agent broke in less than one day at 24° F. and less than three days at 28° F.

Example V

A sample of refined and bleached cottonseed oil containing 0.20 per cent lauryl-alpha-methacrylate soluble in oil was placed in a cooler maintained at 45° F. for three days. Upon filtering the sample by gravity through a standard filter cloth, the yield of oil from the sample containing the above crystal-inhibiting agent was 82 per cent. The yield of the control sample of the refined and bleached cottonseed oil was 71 per cent.

Example VI

To a sample of white grease was added 0.10 per cent of an ester of alpha-methacrylic acid and octadecyl alcohol soluble in oil and the sample seeded for five days at 55° F. The yield of oil upon pressing the white grease treated in the foregoing manner was 65 per cent. The yield from the control chamber of the white grease containing no crystal-inhibiting agent was 55 per cent.

Example VII

A sample of crude sperm oil containing 0.05 per cent n-lauryl acrylate soluble in oil was seeded in 45° F. for six days and then pressed. The yield of winterized sperm oil treated in the foregoing manner was 82 per cent. The yield of the control sample of the sperm oil was 75 per cent.

As hereinbefore mentioned, the above-described crystal inhibitors and modifiers may be added to the glyceride materials before or after winterization. The addition of the crystal modifier before winterization serves primarily to facilitate and improve the winterizing operation. Although crystal formation is retarded in the presence of the additive, once the crystals are formed they are of such form as to settle quickly, and because of the nature of the crystals a sharp separation of the undesired solids from the liquid constituents of the oil is possible. An advantage of the improved filtering operation is that the yields of oils are greatly increased over the winterizing process as hitherto practiced. Often it is desirable to add an additional small amount of the additive after the winterization operation so as to replace that which was filtered out along with the high melting glyceride crystals.

In case it is desired to have a glyceride oil of very long cold test, the materials described above are added to the oil after it has been winterized, the extent of lengthening the cold test depending on the quality of oil chosen, the additive being more effective in an oil having an original longer cold test than in an oil of shorter cold test.

Another important advantage of the invention flows from the use of oil treated with the described agents in emulsions. An emulsion, such as mayonnaise, containing a vegetable oil treated in the foregoing manner will remain stable for much longer periods of time than has been hitherto possible to maintain such emulsions.

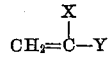
While the invention described herein has particular application to the manufacture of salad oils, the invention is not limited to such an operation. It should be understood that the invention is useful in treating various fatty glyceride materials wherein a solid or crystalline fraction is separated from a liquid fraction as in the separation of a crystalline fraction from animal oils such as lard oil, oleo oil, sperm oil, and animal fats and greases used in the preparation of lard oil and the like. In treating various vegetable and animal oils it is often desirable to separate a solid fraction such as stearin, palmitin, spermaceti and other high melting point fractions by crystallizing such fraction with or without the presence of a solvent and then separating the crystallized fraction by cold settling, pressing, centrifuging of filtration. The crystal modifying agents herein described may also be used to modify the crystal structure of the solid phase

whereby it may be more readily separated from the liquid phase when extracted with a suitable solvent.

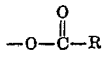
Obviously many modifications and variations of the invention hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

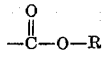
1. A glyceride oil composition of improved cold test, comprising a glyceride oil having incorporated therein a small amount of an oil-soluble product to improve the cold test thereof, said product being the polymerization product of esters containing a radical selected from the group consisting of vinyl and substituted vinyl compounds according to the general formula



wherein X is selected from the group consisting of hydrogen and alkyl and aromatic hydrocarbon radicals and Y is selected from the group having the formula

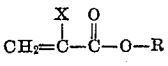


and



wherein R is selected from the group consisting of a monovalent hydrocarbon radical containing more than 4 carbon atoms and oxy derivatives thereof.

2. A glyceride oil composition of improved cold test comprising a glyceride oil having incorporated therein a small amount of an oil-soluble product to improve the cold test thereof, said product being a polymerization product of a substituted vinyl compound according to the general formula



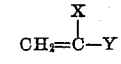
wherein X is an alkyl radical and R is an aliphatic monohydric saturated alcohol radical having more than 12 carbon atoms.

3. A glyceride oil composition of improved cold test comprising a glyceride oil containing relatively high melting point constituents having incorporated therein a small amount of an oil-soluble product to improve the cold test thereof, said product being the polymerization product of an ester of acrylic acid and a monohydric saturated alcohol containing more than 12 carbon atoms per molecule.

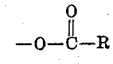
4. A glyceride oil composition of improved cold test comprising a glyceride oil containing relatively high melting point constituents having incorporated therein a small amount of an oil-soluble product to improve the cold test thereof, said product being the polymerization product of an alpha-alkyl substituted acrylic acid and a monohydric saturated alcohol containing more than 12 carbon atoms per molecule.

5. A glyceride oil composition of improved cold test comprising a glyceride oil containing relatively high melting point constituents having incorporated therein a small amount of an oil-soluble polymerization product in an amount between .005 and 1.0 per cent by weight to improve the cold test thereof, said product being a member of a group consisting of lauryl, cetyl, and octadecyl esters of alpha-methacrylic acid.

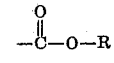
6. In a method of separating a glyceride fatty material into higher and lower melting point constituents by fractionating the liquefied fatty material, the improvement which comprises dispersing throughout the said fatty material a small amount of an oil soluble crystal modifying product to increase the rate at which the relatively high melting point crystals settle, said product being the polymerization product of esters containing a radical selected from the group consisting of vinyl and substituted vinyl radicals according to the general formula



wherein X is selected from the group consisting of hydrogen and alkyl and aromatic hydrocarbon radicals and Y is selected from the group having the formula

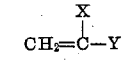


and

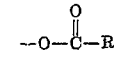


wherein R is selected from the group consisting of a monovalent hydrocarbon radical containing more than 4 carbon atoms and oxy derivatives thereof.

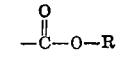
7. An improved method of separating a glyceride fatty material into higher and lower melting point constituents, which comprises dispersing throughout a liquefied glyceride fatty material a small amount of an oil-soluble polymerization product of esters containing a radical selected from the group consisting of vinyl and substituted vinyl radicals according to the general formula



wherein X is selected from the group consisting of hydrogen and alkyl and aromatic hydrocarbon radicals and Y is selected from the group having the formula



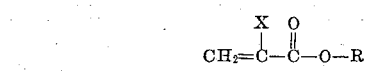
and



wherein R is selected from the group consisting of a monovalent hydrocarbon radical containing more than 4 carbon atoms and oxy derivatives thereof, cooling the said fatty material containing the added polymerization product to crystallize the higher melting point constituents, and separating the said constituents from the lower melting point constituents remaining in the liquid glyceride fatty material, the crystals of said higher melting point constituents formed on cooling being firmer and better defined to facilitate separation from the said lower melting point constituents.

8. An improved method of separating a glyceride fatty material into higher and lower melting point constituents, which comprises dispersing throughout a liquefied glyceride fatty material a small amount of an oil-soluble polymerization

product of a substituted vinyl compound having the general formula



wherein X is an alkyl radical and R is an aliphatic monohydric saturated alcohol radical having more than 12 carbon atoms, cooling the said fatty material containing the added polymerization product to crystallize the higher melting point constituents, and separating the said constituents from the lower melting point constituents remaining in the liquid glyceride fatty material, the crystals of said higher melting point constituents formed on cooling being similar and better defined to facilitate separation from the said lower melting point constituents.

9. An improved method of separating a glyceride fatty material into higher and lower melting point constituents, which comprises dispersing throughout a liquefied glyceride fatty material a small amount of an oil-soluble polymerization product of an ester of acrylic acid and monohydric saturated alcohol containing more than 12 carbon atoms per molecule, cooling the said fatty material containing the added polymerization product to crystallize the higher melting point constituents, and separating the said constituents from the lower melting point constituents remaining in the liquid glyceride fatty material, the crystals of said higher melting point constituents formed on cooling being similar and better defined to facilitate separation from the said lower melting point constituents.

10. An improved method of separating a glyceride fatty material into higher and lower melting point constituents, which comprises dispersing throughout a liquefied glyceride fatty material a small amount of an oil-soluble polymerization product of an alpha-alkyl aryl substituted acrylic acid and monohydric saturated alcohol containing more than 12 carbon atoms per molecule, cooling the said fatty material containing the added polymerization product to crystallize the higher melting point constituents, and separating the said constituents from the lower melting point constituents remaining in the liquid glyceride fatty material, the crystals of said higher melting point constituents formed on cooling being similar and better defined to facilitate separation from the said lower melting point constituents.

11. An improved method of separating a glyceride fatty material into higher and lower melting point constituents, which comprises dispersing throughout a liquefied glyceride fatty material a small amount of an oil-soluble polymerization product selected from the group consisting of polymerized lauryl esters of alpha-methacrylic acid, cetyl esters of alpha-methacrylic acid, and octadecyl esters of alpha-methacrylic acid, cooling the said fatty material containing the added polymerization product to crystallize the higher melting point constituents, and separating the said constituents from the lower melting point constituents remaining in the liquid glyceride fatty material, the crystals of said higher melting point constituents formed on cooling being similar and better defined to facilitate separation from the said lower melting point constituents.

KARL F. MATTIL.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,079,336	Ralston et al.	May 4, 1937
2,266,591	Eckey	Dec. 16, 1941
2,418,668	Royce	Apr. 8, 1947
2,518,917	Mattil	Aug. 15, 1950