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WINTERIZING OILS

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This invention relates to the separation of normally solid crystals from liquids in which they are dissolved and more particularly to the production of vegetable oils that are highly resistant to freezing and that are suitable for use as salad oils.

In the preparation of salad oils, for example, from cottonseed oil, it has been the practice to separate the normally solid glycerides from oils intended for use in salad dressings and particularly for use in mayonnaise and dressings of the liquid type, such as French dressing. This is necessary in order to improve the emulsion stability under ice-box and refrigerator temperature conditions as well as under normal winter temperatures. The tendency for a mayonnaise to "break" upon chilling is believed to be due to the spontaneous crystallization of certain fractions of triglycerides normally occurring in cottonseed oil, corn oil and other oils used for this purpose. This condition is normally minimized by a process commonly known as winterization, which is simply a process of cooling the salad oil to such a temperature that normally solid triglycerides become insoluble in the main body of the oil and thereupon separate in crystalline form. The crystallized fraction is then separated and is known in commerce as stearine. The stearine cake is not actually tristearin, but is largely a mixture of triglycerides, including ones composed of two palmityl or two stearyl or one palmityl and one stearyl acid group, with oleyl or linoleyl as the third acid group. Stearine contains, in addition to the fractions which crystallize on cooling, considerable portions of entrained oil of approximately the same concentration as the filtrate.

The yields of filtrate are variable, depending upon the quality of the starting oil. Usually, with commercial pressure filtering, the filtrate constitutes from 80 to 88% of the starting oil. Another factor governing the yield is the degree to which the oil temperature is lowered. A lower temperature of winterization gives a filtrate which is more resistant to subsequent freezing.

However, there is a practical limitation to the degree to which an oil may be cooled in the winterization process and, therefore, a limitation upon the quality of oil which may be manufactured. The lowest temperature to which an oil may be chilled for this purpose is that temperature at which it still exists as a mixture of crystallized and liquid fat and, therefore, may still be separated. At lower temperatures the whole oil becomes solid and does not flow. No

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useful result is obtained by subjecting a normal winter oil or filtrate from a normal winterizing operation to a second winterization, since the factors causing complete solidification or gelling are still present and the winter oil will also solidify upon the second winterization.

It is an object of the present invention to provide an improved procedure for separating from vegetable oils or other liquids, crystals of substances dissolved in the liquid. Another object is to provide an improved procedure for increasing the freeze resistance of vegetable oils. It is also an object to provide an improved vegetable oil resulting from such a procedure. Other objects will become apparent.

We have discovered that an additional fraction of triglycerides may be separated from a normally winterized oil by adding to such oil a suitable crystallization modifying agent and subjecting the mixture to further cooling. Although it is not intended to limit the invention to any particular theory of operation, the action of the crystallization modifier appears to be that of lowering the freeze point of the main body of the oil and supplying a limited number of nuclei for crystallization of the triglycerides, whereby relatively large crystals are obtained. Without the crystal modifier the separate triglycerides form such small crystals that they entrap the remaining oil and thus form a non-flowing mass.

A crystal modifier we have found to be very effective is vegetable lecithin. The quantity of lecithin required to effect the further fractional crystallization of a normal winterized vegetable oil will vary with the quality of the oil resulting from the first winterization. For example, with a starting winterized cottonseed oil having a cold test as low as 7 hours at 32° F. (i. e., one that will cloud when subjected for that length of time to the cold test, described at page 440 of the Official and Tentative Methods of Analysis of Official Agricultural Chemists (5th edition, 1940)), we have found that 0.1% of soya bean lecthin is sufficient to cause the separation of additional crystals from the oil fraction upon further winterization and provide a filtrate that will give a much higher cold test at 32° F. With a better winter oil, such as a 24 hour cold test cottonseed oil, only 0.01% lecithin will be required to achieve a similar result.

As a specific example of the use of the invention 40 pounds of single-bleached soya bean lecithin was dissolved in 40,000 pounds of cottonseed winter oil prepared in the usual manner of winterizing at 45° F. and having an iodin value

of 112.7 and cold test (32° F.) of 12 hours. The solution was cooled to 32° to 35° F. and allowed to stand for 48 hours. At the end of the crystallization period, the mixture was filtered under pressure in a filter press. The yield of liquid oil was 86.8% of the winter oil treated. The filtrate had an iodin value of 114.7 and a cold test at 32° F. of more than 72 hours.

The filtrate was tested for its lecithin content, by means of an aqueous acid extraction by which it is easily possible to demonstrate the presence of less than 0.01% of lecithin by the usual phosphomolybdate procedure in the standard method of analysis for phosphates, and gave a completely negative result. Therefore, the lecithin added was entirely or at least largely removed in the filtering operation.

Most natural seed oils contain some vegetable lecithin. However, this is removed during the alkaline refining to which the oil is normally subjected before winterizing. Also, that which is not removed in that way, will be removed during the 45° F. winterization and, if the cottonseed oil is further cooled to 32° F., the whole mass becomes solid and cannot be filtered.

It has previously been suggested to add small quantities of lecithin and other substances to salad oil to improve its keeping qualities or to improve the resistance to cold test of the salad oil containing the lecithin. However, an important feature of the present method is the fact that the subsequent winterizing removes the solid crystals that are retained in such other oil, thus avoiding the necessity of having the lecithin, etc., present and providing a salad oil having a high cold test value while containing no licithin or at most only traces of lecithin. In the preferred operations, the lecithin is removed with the crystals.

Improvement may also be effected with a smaller proportion of the vegetable lecithin and the following table illustrates the effect of varying concentration of soya lecithin upon quality and quantity of filtrate:

	Yield by gravity filtration after 5 days at 27–29° F.	Iodin # Filtrate	Cold test of Filtrate	
			Clear	Cloud
Control (cottonseed oil-cold test 19 hrs.)	*Per cent* 34	114.3	*Hrs.* 56	*Hrs.* 72
Control+0.01% soya lecithin	44	114.4	56	72
Control+0.05% soya lecithin	57	114.3	72	112
Control+0.1% soya lecithin	68	114.0	72	112

Because the starting oil used in the above series was a relatively good salad oil, it was necessary to allow five days for precipitation at a temperature of 27 to 29° F. The exact time of the cold test was not determined in these tests, but would be between the times specified for "clear" and "cloud."

Samples of the same 19 hour salad oil containing corn oil lecithin in the same range of concentration in place of the soya bean oil lecithin required a much longer time to precipitate under the same conditions. In general, this has been found to be the case and in order to obtain satisfactory precipitation in a reasonable period of time when using corn lecithin, anywhere from about one-tenth to one-half the quantity of soya lecithin otherwise required has been found to be sufficient.

For example, with a cottonseed winter oil (that clouded at 12 hours under the cold test and, upon standing five days at 30° F. before filtering, gave very little free oil, such oil showing a cold test of over 139 hours), the addition of 0.1% soya lechithin gave about 80% of free oil, showing a cold test of over 139 hours, on standing five days at 30° F. and then filtering by gravity, while 0.1% corn lecithin gave about 95% of a similar filtrate under the same conditions. With .05% corn lecithin less solid crystals were obtained than with .1% soya lecithin, and with .01% corn lecithin about the same amount of solid, and filtrate having a cold test of over 139 hours, were obtained as with .1% soya lecithin. Some improvement over the control was obtained with .005% corn lecithin. The corn lecithin used in this test was a commercial grade containing about 58% lecithin, calculated from the per cent of phosphorus found therein. The soya lecithin was also a commercial grade containing about 62% lecithin.

The corn lecithin acts somewhat differently from the soya lecithin in that it remains in solution when added to a previously treated clear oil which is again chilled, whereas the soya bean lecithin will separate from the clear oil upon chilling, even though there is no separation of fat crystals. When added before the removal of fat crystals, however, both the corn lecithin and the soya lecithin are coprecipitated during the crystallization of the solid fractions of the oil. The invention is not limited to the removal of lecithin simultaneously with the crystalline fraction and, although it may aid in the practice of the invention, particularly when soya lecithin is used, it is not an essential factor. An alkaline refining procedure, such as the addition of sodium hydroxide or other alkaline substance, may be used if it is desired to remove the last traces of phosphatides after removal of the crystals.

The separation of the crystals and lecithin from the oil may be accomplished in the usual way, for example, by gravity filtration, decantation, centrifuging or filtering under low pressure, that is, under pressure insufficient to force the soft crystals through the press cloth or papers, and is preferably conducted at the same temperature as the winterization.

If desired, the separated crystals may be remelted and subjected to recrystallization at higher temperatures, for example, at 70° to 75° C., and the vegetable lecithin present will aid in this crystallization and separation.

As indicated in the above examples, the quantity of crystalline solids separated varies with the type of vegetable lecithin used and the proportion in relation to the amount of solid dissolved in the oil. A very small amount of the lecithin causes the solids to separate in relatively large crystals that may be readily separated and that carry with them the added lecithin. As the proportion of lecithin is increased in relation to the dissolved solids, the amounts of crystals become smaller, are less easily separated, and carry less of the lecithin with them. Therefore, in utilizing the invention, variations may be made in the proportions used, depending upon the material treated and the results desired.

The cottonseed oil treated as described above may be used in the usual way in the preparation of mayonnaise or other salad dressings, such, for example, as French dressings, to provide a prod-

uct of good freeze resistance. It may also be used as a substitute or diluent for more expensive oils or for oils having other less desirable properties. For example, it may be used as a substitute for olive, corn, soya bean and peanut oil in their many applications, including use as cooking oils. Or it may be used as a diluent for such oils or for cod liver oil, cod liver oil concentrates, etc., without imparting lowered freeze resistance to such oil. For instance, cottonseed oil, when treated as described herein, has the advantage of a freeze resistance equal to or better than oils such as corn oil, sesame oil or soya bean oil when winterized by the usual procedure, and has a more acceptable flavor than those oils.

In describing the invention, particular reference has been made to the application of the process to cottonseed oil. The invention is not limited, however, to such use and may be used to advantage with other oils in which it is desirable to remove higher melting point fractions. It may be used, for instance, in connection with the separation of pressed oils, where the cake is the desired component of the starting oil, as in the preparation of cacao butter substitutes, or in the pressing of stearic acid or in the dewaxing of mineral oils. In such instances, it may be desirable to use a crystallization modifying agent that remains dissolved in the oil. Oxidized or blown cacao butter provides such an agent.

The invention may also be used to advantage in the initial separation of crystals from vegetable oils that have had their natural lecithin removed by the alkaline or other treatments that usually precede the winterizing step. By the addiition of vegetable lecithin as described herein to such an oil before the normal winterizing step, a greater percentage of the normally solid glycerides may be removed in a single winterizing step. It may also be used in the fractional crystallization of vegetable oils at higher temperatures than those referred to above. For example, stearin separated during the normal winterization may be remelted and subjected to recrystallization at higher temperatures, for instance, at 70° to 75° C., after addition of a vegetable lecithin, as described herein.

The invention may also be used in the fractional crystallization of esters of other polyhydric alcohols or of esters of monohydric alcohols, such as in the separation of methyl, ethyl, etc., esters of fatty acids from each other or from other esters in which they are dissolved.

Although particular reference has been made to the use of vegetable lecithins such as soya bean oil lecithin or corn oil lecithin, as the crystallization modifying agent, other substances may also be used for this purpose. Such substances should have the ability to serve as nuclei for the crystals of triglycerides or fats normally solid at the cold test temperatures and, for use in the preparation of salad oils free from lecithin, they preferably are removable with such crystals in the filtering or other separating operation used. They should also be substances that will reduce the solidification point of the bulk of the oil being treated. Of course, they should be substances that would not have a detrimental effect upon the oil being treated.

Many modifications may, of course, be made in utilizing the invention and it is not intended to limit it to the particular details given as illustrative. For example, the chilling temperatures and times may be varied, depending upon the oils treated and the results desired. The terms used

in describing the invention have been used as terms of description and not as terms of limitation and it is intended that all equivalents of the terms used be included within the scope of the appended claims.

We claim:

1. A method for separating solid crystals from a glyceridic oil in which they are in solution, comprising adding to the glyceridic oil a crystallization modifying agent comprising lecithin which is soluble in the glyceridic oil and which reduces the solidification point of the glyceridic oil, chilling the glyceridic oil sufficiently to crystallize the solid crystals, and separating the glyceridic oil therefrom.

2. A method for separating solid crystals from a glyceridic oil in which they are in solution, comprising adding to the glyceridic oil a crystallization modifying agent comprising lecithin which is soluble in the glyceridic oil and which reduces the solidification point of the glyceridic oil, chilling the glyceridic oil sufficiently to crystallize the solid crystals and simultaneously precipitate the crystallization modifying agent, separating the glyceridic oil therefrom, and subsequently melting the mixture of crystals and crystallization modifying agent and recrystallizing solid crystals at higher temperatures.

3. A method for separating fractions of mixed glyceridic oils, comprising chilling the oil to crystallize a fraction of the mixed glycerides, separating the liquid fraction, adding a crystallization modifying agent comprising lecithin to the liquid fraction, chilling the liquid fraction to separate further crystals and separating a liquid fraction therefrom.

4. A method for improving the resistance of a winterized vegetable oil to freezing, comprising adding a crystallization modifying agent comprising lecithin to it, chilling the oil fraction to separate further crystals and separating liquid oil therefrom.

5. A method for improving the resistance of a vegetable oil to freezing, comprising chilling the oil to crystallize a fraction thereof, separating the oil fraction and adding vegetable lecithin to it, chilling the oil fraction to separate further crystals and separating liquid oil therefrom.

6. A method for improving the resistance of a vegetable oil to freezing, comprising chilling the oil to crystallize a fraction thereof, separating the crystals from the oil fraction, adding to the oil fraction corn lecithin, chilling the oil fraction to separate further crystals, and separating liquid oil therefrom.

7. A method of improving the resistance of a vegetable oil to freezing, comprising chilling the vegetable oil to crystallize a fraction of the oil, separating the crystals, chilling the oil fraction below 45° F. in the presence of 0.005 to 1% of vegetable lecithin and separating liquid oil.

8. A method of improving the resistance of a vegetable oil to freezing, comprising chilling the vegetable oil sufficiently to crystallize a fraction of it, separating the resulting crystals, adding about .01 to .1% of vegetable lecithin to the oil fraction, chilling it to 20° to 45° F. to effect further crystallization of a fraction of the oil, and separating the liquid oil from the resulting crystals.

9. A method for improving the resistance of cottonseed oil to freezing, comprising chilling the cottonseed oil to crystallize a fraction thereof, separating the resulting crystals, adding a vegetable lecithin to the oil fraction and further

chilling it to crystallize a further fraction thereof, and separating the liquid oil from the resulting crystals.

10. A method for improving the resistance of cottonseed oil to freezing, comprising chilling the cottonseed oil to crystallize a fraction thereof, separating the resulting crystals, adding corn lecithin, to the oil fraction and further chilling it to crystallize a further fraction thereof, and separating the liquid oil from the resulting crystals.

11. A method for improving the resistance of cottonseed oil to freezing, comprising chilling the cottonseed oil to crystallize a fraction thereof, separating crystals therefrom, adding about .005 to .05% of corn lecithin to the oil fraction, further chilling the oil fraction to crystallize another portion thereof, and separating liquid oil from the crystals.

12. A method for improving the resistance of cottonseed oil to freezing, comprising chilling the cottonseed oil to crystallize a fraction thereof, separating crystals therefrom, adding about .01 to .1% of soya bean lecithin to the oil fraction, further chilling the oil fraction to crystallize another portion thereof, and separating liquid oil from the crystals.

13. A method for improving the resistance of cottonseed oil to freezing, comprising chilling a winterized cottonseed oil to 20° to 45° F. in the presence of 0.01 to 0.1% soya bean lecithin and separating the liquid oil.

14. A method for improving the resistance of cottonseed oil to freezing, comprising chilling a winterized cottonseed oil to 20° to 45° F. in the presence of 0.005 to .05% corn lecithin and separating the liquid oil.

15. A vegetable oil of improved freeze resistance prepared by chilling a vegetable oil to crystallize a fraction thereof, separating the crystals, adding a vegetable lecithin to the oil fraction and chilling it to crystallize a further fraction thereof and separating the oil from the crystals.

16. A cottonseed oil of improved freeze resistance prepared by chilling a cottonseed oil to crystallize a fraction thereof, separating the crystals, adding about .005 to 1% of vegetable lecithin to the oil fraction, further chilling the oil fraction to crystallize more crystals and separating the oil from the resulting crystals.

17. A cottonseed oil of improved freeze resistance prepared by chilling a cottonseed oil to about 45° F. to crystallize a fraction thereof, separating the crystals, adding about .01 to 0.1% of soya bean lecithin to the oil fraction, further chilling

the oil fraction to about 20° to 45° F. to effect a crystallization of a further fraction and separating the liquid oil from the crystals.

18. A cottonseed oil of improved freeze resistance prepared by chilling a cottonseed oil to about 45° F. to crystallize a fraction thereof, separating the crystals, adding about 0.005 to .05% of corn lecithin to the oil fraction, further chilling the oil fraction to about 20°° to 45° F. to effect a crystallization of a further fraction and separating the liquid oil from the crystals.

19. A method for improving the resistance of a vegetable oil to freezing, comprising chilling the oil to crystallize a fraction thereof, separating the crystals from the oil fraction, adding to the oil fraction soya bean lecithin, chilling the oil fraction to separate further crystals, and separating liquid oil therefrom.

20. A method for improving the resistance of cottonseed oil to freezing, comprising chilling the cottonseed oil to crystallize a fraction thereof, separating the resulting crystals, adding soya bean lecithin to the oil fraction and further chilling it to crystallize a further fraction thereof, and separating the liquid oil from the resulting crystals.

21. In the process of winterizing a vegetable oil, including chilling and separating solid material therefrom, the improvement of adding a minor proportion of lecithin to the refined oil prior to chilling.

22. In the process of winterizing a vegetable oil including chilling and separating solid material therefrom, the improvement of adding a minor proportion of soya bean lecithin to the refined oil before chilling.

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