Patented Jan. 25, 1949

2,459,820

UNITED STATES PATENT OFFICE

2,459,820

FRACTIONATION OF UNSATURATED GLYCERIDE OILS

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No Drawing. Application June 23, 1943, Serial No. 491,974

5 Claims. (Cl. 260—428.5)

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This invention relates to the fractionation of glyceride oils into at least two fractions, one having a higher, and the other having a lower degree of unsaturation than that of the unfractionated glyceride oil. More particularly the invention relates to the fractionation of oils of the drying type, such as linseed oil, and oils of the semi-drying type, such as soybean oil.

While the invention relates generically to fractionation of the above-defined glyceride oils, it assumes particular importance in connection with the fractionation of soybean oil because of the large quantity of this oil that is available, because of certain characteristics of soybean oil which suit it for treatment by the process, and because of the superior properties of each of the fractions for certain purposes as compared with the original oil.

It is an object of the invention to fractionate unsaturated glyceride oils into a fraction more saturated than the original oil and suitable more particularily for edible uses, soaps and other purposes for which the more saturated oils and fats are adapted, and into another fraction more unsaturated than the original oil and suitable particularly for paints, varnishes and other similar purposes.

It is a further object of the invention to fractionate unsaturated glyceride oils utilizing but a single solvent, although this may be any one of a wide variety which is readily recovered and reused.

A further object of the invention is the provision of a process in which the oil may be fractionated continuously.

Still an additional object of the invention is to provide a process in which the final separation of the two fractions may be accomplished by means of a centrifuge.

Soybean oil is characterized by a so-called "reversion" factor. This is associated with certain odor and taste characteristics, which become particularly apparent when the oil is subjected repeatedly to higher temperatures.

It is an object of the invention, when it is applied to soybean oil, to separate the oil into a more saturated fraction and a more unsaturated fraction, and in which the so-called reversion factor is substantially contained in the more unsaturated fraction where it is not objectionable in paints, and to leave the more saturated fraction, which is adapted for edible purposes, relatively free from the reversion factor.

It has been proposed heretofore to separate saturated from unsaturated fatty acids by means

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of fractional distillation. This process is based upon the fact that the unsaturated acids have a lower boiling point than the saturated acids of the same molecular weight. This process is expensive and disadvantageous because of the high vacuum necessary and the relatively large amounts of heat required. In addition it requires splitting the glycerides and re-esterifying the acids.

It has also been proposed to separate unsaturated oils in a liquid-from-liquid extraction process utilizing a selective solvent in which either the saturated or unsaturated glycerides are selectively soluble. The fractions to be separated are two liquids. This process requires the use of certain "polar" solvents.

A two-phase solvent system in addition has been suggested. This uses a non-polar solvent and a polar solvent, each of which has a selective solvent action upon the glycerides. This process has the disadvantage of requiring two solvents.

It has also been proposed to chill unsaturated glycerine oils to precipitate saturated glycerides at a low temperature, following which the precipitate is separated by filtration. Such a process is known generally as "winterizing." This process has also been used in connection with a solvent such as acetone, but in such a process the saturated glycerides are precipitated in solid crystalline form so that they can be pressed or separated by filtration.

In accordance with the invention the unsaturated oil to be fractionated is diluted with an organic solvent either polar or non-polar and then subjected to chilling to such a low temperature, at such a rapid rate, and under such appropriate agitation and other conditions, as to result in the precipitation of the saturated glycerides in a solid form, but nevertheless in flowable condition. The precipitate may be amorphous or in a very fine crystalline state. The solid fraction in an amorphous or flowable form is somewhat analogous to a very viscous liquid. The chilled oil containing the saturated glycerides in this solid but flowable condition may be subjected to a continuous centrifugal separation, inasmuch as the solids in this form will flow through the centrifuge.

The process is a solid-from-liquid separation and is to be distinguished from the liquid-from-liquid separations referred to above. It is also to be distinguished from the solid-from-liquid separation in which the solid is in a crystalline form which can be filtered but not centrifuged. In order to filter the solid from the liquid fraction

it is necessary to use a polar solvent such as acetone in order to obtain distinct or large crystals through which the liquid will flow in the filter press. However, such a process results in crystals which pack or interlock in a centrifuge and will not flow through it.

The process of the invention is adapted to a continuous type of operation in which the oil is continuously mixed with the solvent in a preferred ratio, then passed in continuous fashion through a chilling and agitating unit where the oil is chilled at the proper rate to the desired low temperature, following which the chilled mixture is sent to a continuous type centrifuge where the solid more saturated fraction is separated from the liquid more unsaturated fraction; the latter contains most of the solvent, also any objectionable odorous reversion factor that may be present in the original oil. Following this the fractions can be heated to recover the solvent, and this may be used in the treatment of an additional quantity of the oil.

It is an advantage of the process that non-polar solvents, such as petroleum ether, hexane, trichlorethylene, and any other hydrocarbons, or chlorinated hydrocarbon may be used. These solvents result in the solid fraction being precipitated in the preferred form for centrifuging and are also much cheaper. Under these circumstances the non-polar solvents are the preferred species. This is to be distinguished from all of the prior art processes which require a polar solvent. The polar solvents, such as acetone, furfural, etc., can be used in the process, but they have a tendency to result in crystalline precipitates that are more difficult to separate centrifugally. However, under controlled conditions, particularly the rate of chilling and the proper degree of agitation, the crystallization may be minimized to an extent to permit centrifugation. Thus any organic solvent which is a solvent for the glycerides may be used.

The ratio of solvent to oil may be varied over a wide range. This ratio may be varied in accordance with the temperature and rate of chilling and also the extent of the separation desired. In general, the larger the amount of solvent the greater will be the spread in iodine values between the two fractions. For example, if the oil to be treated is soybean oil having an iodine value of 132.2, it may be separated using 7 parts of solvent (acetone) to 3 parts of oil. The solid fraction yields an oil having an iodine value of 129.2, and the liquid fraction yields an oil having an iodine value of 144.7. The larger the amount of solvent used, the lower will be the iodine value of the solid fraction. When a ratio of 10 parts of solvent (petroleum ether) to 1 part of soybean oil is used, the iodine value of the solid fraction will be of the order of 92.0. In general, the range is 1 part of oil to 1 to 20 parts of solvent. Since the solvent is used to give the entire mass of oil a sufficient fluidity at the lower temperature to permit handling, it is apparent that for a given temperature it may be possible to separate the solid fraction with greater facility and with less entrainment of the liquid fraction if more solvent is used. Also, the spread in iodine value is greater. However, the use of larger quantities of solvent increases the cost of chilling and the cost of solvent recovery, and the economical factors must be taken into account in the commercial adaptation of the invention.

The process may be carried out, if desired, in two stages. If the solvent to oil ratio is to be 20 to 1, the oil may be treated with a solvent in a 10 to 1 ratio and separated, and then either of the fractions again treated in a 10 to 1 ratio. As will be seen from Table I, however, the two stage treatment, insofar as retreatment of the more unsaturated fraction is concerned, does not appear to result in an oil of higher unsaturation.

As indicative of the results that may be obtained utilizing acetone as the solvent the following table is set forth:

Table I

[Chilling temperature −40° C.]

Acetone-Oil Ratio	Per cent Oil in Liquid Fraction	Per cent Oil in Solid Fraction	I. V. of Liquid Fraction Oil	I. V. of Solid Fraction Oil
7:3	8.6	91.4	152.7	127.9
5:1	20.0	80.0	150.5	125.8
10:1	36.3	63.7	147.7	120.0
5:1+ 5:1 [1]	32.6	67.4	----------	119.0
20:1	58.0	42.0	145.0	106.1
10:1+10:1 [1]	58.0	42.0	----------	106.8

[1] 2-stage.

As indicative of the effect of different temperatures the following results are set forth:

Table II

[Acetone-Oil Ratio 5:1]

Acetone-Oil Ratio	Per cent Oil in Liquid Fraction	Per cent Oil in Solid Fraction	I. V. of Liquid Fraction Oil	I. V. of Solid Fraction Oil
−24° C.	55.0	45.0	138.6	121.5
−32° C.	25.7	74.3	146.6	124.3
−40° C.	20.0	80.0	150.5	125.8

As indicative of the results that may be obtained using petroleum ether, the following results are given:

Table III

[Chilling Temperature −40° C.]

Petroleum Ether-Oil Ratio	I. V. of Liquid Fraction Oil	I. V. of Solid Fraction Oil
2:1	136.2	117.2
10:1	134.3	92.0

The temperature at which the oil is ultimately chilled, the rate of chilling, and the extent of agitation, are more or less related to each other, to the solvent used, to the oil treated and to the products wanted, and should be adjusted relative to each other.

In general, the temperature used should be not above −20° F. In few instances will it be economically advantageous to employ temperatures of lower than −60° F. In general, the rate of chilling should be as rapid as the facilities will permit; the retention of a relatively small mass of oil in the chilling apparatus at any one time and with rapid passage through the chilling apparatus is preferred. This is generally known as a "shock" chilling. These factors also will vary dependent upon the characteristics of the oil being treated, the state of refinement, etc., as well as the ratio of solvent to oil, and in some instances in the type of centrifuge and the ability to handle amorphous solids of different forms and viscosities. In addition, the factors must be selected and adjusted in view of the economics in-

volved, and the degree of saturation or unsaturation wanted in the final products. It is difficult, if not impossible, to specify any particular details as to the inter-relation of these variables other than the ranges specified heretofore, but it is believed that one skilled in the art, in view of the disclosure herein, will be enabled to select such factors in view of the product wanted and the economic factors to be considered.

In the application of the invention to soybean oil, it has been found that a fractionation to yield a more saturated fraction with an iodine value of about 125 or less is substantially free from the reversion factor. When this fraction is hydrogenated in the usual manner and tested by the deep-fat doughnut frying test it shows substantially none of the odor characteristics of a shortening made by similarly hydrogenating untreated soybean oil. It is admirably suited for edible purposes. Shortening prepared from this fraction also is higher in the naturally occurring saturated glycerides (i. e., glycerides of palmitic acid) than are present in a shortening prepared by hydrogenating the unsaturated oil. Such a shortening has desirable plastic and digestible characteristics.

When the invention is applied to soybean oil the more unsaturated fraction has its drying properties greatly improved. For example, the iodine value may be readily raised from about 130 to at least 150. While this more unsaturated fraction perhaps does not possess as good drying properties as tung or other natural drying oils, the drying properties are such as to permit the use of larger quantities in paints, varnishes, etc.

The invention has been described particularly with reference to soybean oil, but it will be understood that it may be applied to other oils, for example linseed oil, to obtain a more unsaturated fraction having superior drying properties. This is economically advantageous because the more saturated fraction which is separated will be relatively free from the characteristic odor and taste ingredients and may be used in an edible product. Similarly, the invention may be applied to fish oils and the same advantages accrue. Such advantages are particularly important under economic conditions where it is desired to divert the more unpalatable oils, or at least a portion of them into edible uses. The invention may be applied to other oils, such as cottonseed oil, but the advantages would not suggest this particular application because the oil has desirable characteristics in its natural form.

It will be apparent that the invention includes many modifications and variations of the preferred embodiment disclosed as illustrative, and all of these are included in the invention as are within the following claims.

I claim:

1. A process of fractionating soybean oil, which comprises mixing one part of soybean oil with an amount of a non-polar solvent within the range of 1 to 20 parts, rapidly chilling said mixture of oil and solvent to a temperature within the range of −20° to −60° F., the rapidity of chilling, the amount of solvent within the above range and the chilling temperature within the above range being interrelated so as to precipitate a fraction in an amorphous flowable form having a lower iodine value than the iodine value of the soybean oil, and to leave the remainder of the oil as a liquid fraction having a higher iodine value than the soybean oil, and continuously separating the precipitated amorphous flowable fraction from the liquid fraction in a continuous type centrifuge, said precipitated fraction of lower iodine value being suitable for hydrogenation to form an edible shortening, and said liquid fraction of higher iodine value having improved drying properties.

2. The process in accordance with claim 1 in which the non-polar solvent is a hydrocarbon.

3. The process in accordance with claim 1 in which the non-polar solvent is petroleum ether.

4. The process in accordance with claim 1 in which the mixture of the non-polar solvent and soybean oil is continuously chilled while being agitated.

5. The process in accordance with claim 4 in which the non-polar solvent is petroleum ether.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
144,000	Simonin	Oct. 28, 1873
1,974,542	Parkhurst	Sept. 25, 1934
2,113,960	Grote	Apr. 12, 1938
2,193,767	Manley	Mar. 12, 1940
2,228,040	Voogt	Jan. 7, 1941
2,288,441	Ewing	June 30, 1942
2,340,104	Brown	Jan. 25, 1944