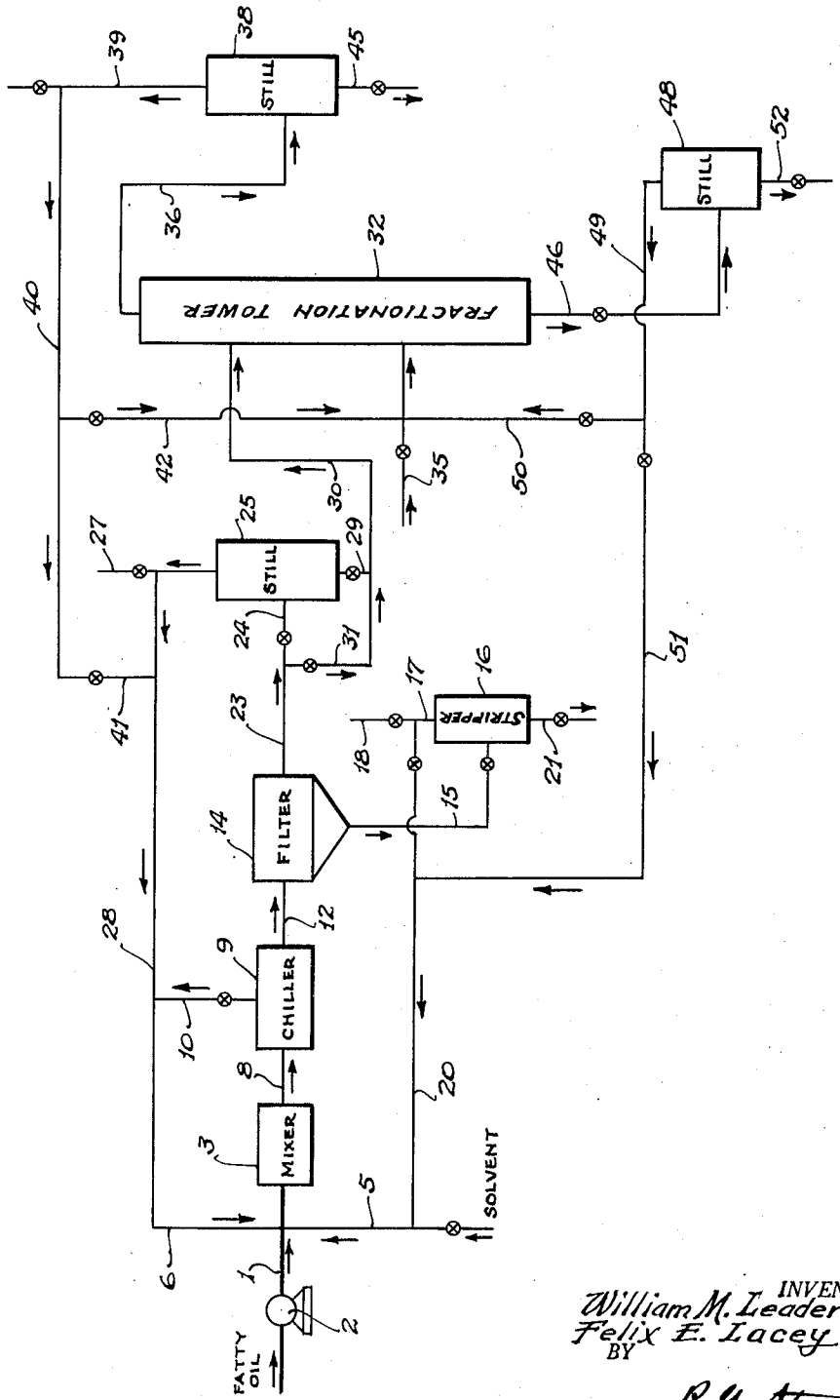
Nov. 27, 1951 W. M. LEADERS ET AL 2,576,841

SOLVENT FRACTIONATION

Filed Jan. 17, 1946



INVENTOR.
William M. Leaders
Felix E. Iacey
BY
R. G. Story
ATTORNEY

Patented Nov. 27, 1951

2,576,841

UNITED STATES PATENT OFFICE

2,576,841

SOLVENT FRACTIONATION

William M. Leaders and Felix E. Lacey, Chicago, Ill., assignors to Swift & Company, Chicago, Ill., a corporation of Illinois

Application January 17, 1946, Serial No. 641,712

3 Claims. (Cl. 260—419)

1

This invention relates to the treatment of fatty materials and has to do particularly with the treatment of fatty materials with solvents to separate valuable constituents therefrom.

The invention is applicable to the treatment of fats and fatty oils, either animal and vegetable, such as greases and tallows, soybean oil, cottonseed oil, linseed oil, fish oils, peanut oil, and sunflower seed oil. Fatty acids derived from the aforesaid oils may also be treated in accordance with the invention.

Commercial fats and fatty acids are generally composed of components of different degrees of saturation. The proportion of the saturated and unsaturated constituents varies with the different products, depending on their origins. For example, fats and fatty oils derived from animal sources contain from about 40% to 60% saturated compounds and the remainder of unsaturated compounds of varying degrees of unsaturation. Fatty oils of vegetable and marine origin usually contain about 1% to 20% of saturated constituents and the remainder of unsaturated materials. The fatty acids from the above oils also contain saturated and unsaturated constituents in about the same proportion as the fats and fatty oils from which hey are derived.

It is often important to separate fatty materials into fractions of different degrees of unsaturation, since there are specific uses for materials composed of compounds having substantially the same degree of saturation. This is particularly true in the manufacture of paint oils and resins, in the compounding of edible products, and in the manufacture of chemical derivatives. For such specific purposes the fatty material becomes more valuable as the degree of purity of the desired components is improved in the product. As applied to commercial fats and fatty acids, the separation is usually on the basis of the number of unsaturated bonds. Accordingly, it is possible to separate a fat and fatty acid into components containing substantially saturated constituents, compounds having one double bond, compounds containing two double bonds and materials of even a higher degree of unsaturation.

An object of the present invention is to provide a more efficient process for the separation of fatty materials into components of different degrees of unsaturation.

Another object of the invention is to provide a process for the fractional separation of fatty materials to produce improved yields of desired products.

A further object of the invention is to provide

2

a process for the fractionation of fatty materials wherein a sharper separation between the materials of different degrees of unsaturation is obtained.

Also an object of the invention is to provide an improved process whereby fatty materials may be separated into products of improved quality.

Heretofore attempts have been made to separate fatty materials into the various constituents by distillation, and while some success has been obtained in the separation of fatty acids into components of varying degrees of unsaturation by distillation, this method has not been entirely satisfactory. The boiling points of certain saturated and unsaturated constituents are so nearly alike, it is often difficult to obtain any substantial degree of separation by fractional distillation.

Attempts have also been made heretofore to separate the constituents of fatty materials by seeding and crystallization of a portion of the material, particularly the more saturated components, and then the separation of the crystals from the oily materials by pressing. Such a process is useful for the separation of the wholly saturated components, but the method has not proved satisfactory for the fractionation of the unsaturated constituents.

It has also been proposed heretofore to fractionate fatty materials with the aid of solvents. For example, fairly good success has been obtained with the separation of saturated compounds, such as stearine from animal fats by the use of a crystallization solvent. Some success has also been obtained in the fractionation of unsaturated compounds by the use of solvents both by crystallization and liquid-liquid phase fractionation. However, in the fractionation of fatty materials, on the basis of unsaturation with the use of solvents, excessive amounts of solvents and extreme temperatures are required, and even under such undesirable operating conditions the separation is not fully satisfactory because the more unsaturated constituents interfere with the proper fractionation of the materials of lesser degrees of unsaturation.

There are certain advantages in the separation between the unsaturated components of fatty materials by liquid-liquid phase solvent fractionation. For example, the fractionation of the unsaturated constituents may be performed under more favorable conditions, particularly of temperature, by liquid-liquid phase operation. However, fatty materials generally contain a substantial amount of saturated constituents which tend to interfere with efficient fractionation of the un-

saturated components. We have found that liquid-liquid phase separation is more efficiently accomplished if the more saturated constituents are first removed, particularly such saturated constituents as can be efficiently separated by solvent crystallization.

It has been proposed heretofore to separate a fatty material into saturated and unsaturated fractions and then fractionally distill the two fractions separately. Thus, the saturated constituents of a fatty acid mixture are separated from the unsaturated constituents by solvent crystallization. The two fractions are then subjected separately to fractional distillation. The process, however, is applicable only to fatty acids since glyceride oils cannot be separated by fractional distillation. Furthermore, high losses occur in the process on account of the high temperatures required; for example, polymerization losses as high as 15% are not uncommon.

The present invention contemplates a two-stage process wherein the fatty material is first subjected to solvent crystallization to separate the more saturated portion, and then the lesser saturated portion is subjected to solvent fractionation in a liquid-liquid phase operation to separate the material into fractions of different degrees of unsaturation. The amount and type of materials separated in the first step of our process will depend on the nature of the materials treated. If the material to be treated contains a substantial amount of saturated constitutents, the fraction separated in the first step will consist mainly of saturated materials. The latter will usually be the case in treating fatty acids derived from tallow, greases, or mixtures of tallow and grease of animal origin.

When treating glyceride oils, the fatty acids are often combined in a glyceride molecule in combination with the unsaturated fatty acid radicals present to give mixed triglycerides. Usually the material separated in the crystallization stage will be substantially di-saturated mono-unsaturated triglycerides, and will contain all of the tri-saturated fat present and a minor portion of di-unsaturated mono-saturated material. In this way, substantially all the saturated fatty acid groups present in the original fatty material will be separated as one or more of these triglycerides. The distribution of the fatty acids in natural occurring fats is such as to practically eliminate the presence of simple triglycerides containing three radicals of the same fatty acids. For this reason, the degree of separation that is possible, even from a theoretical consideration, is less than when treating fatty acids or mono-hydric esters of the fatty acids.

When treating materials containing very little or substantially no saturated constituents in the first step of our process, the fraction separated in the first stage may not be a highly saturated material but contain substantial amounts of the less saturated materials. For example, in treating oils such as soybean oil, cottonseed oil, etc., the fraction initially separated will contain substantially all of the saturated fatty acid groups present along with a considerable amount of the unsaturated groups of the lowest degree of unsaturation. With the oils just mentioned, the glycerides separated would be composed substantially of esters of the fatty acids such as palmitic, oleic, and linoleic, with only minor amounts of the esters of more highly unsaturated fatty acids.

In the second step of our process, we intend to fractionate materials from the first stage of our process into two or more fractions of varying degrees of unsaturation. If the fatty materials treated are fatty acids, the fatty materials will be separated into fractions containing substantially one type of fatty acids. For example, one fraction will contain substantially all of the oleic acid and the allied fatty acids of one double bond. The next fraction will contain substantially all of the linoleic acid and isomers containing two double bonds. And the third fraction will contain linolenic acid and some less highly unsaturated fatty acids.

In treating fats and oils, a fractionation similar to that described in connection with the fatty acids is desirable. However, the mixed composition of the triglycerides makes it impossible to obtain as high a degree of resolution when the individual fatty acids are combined as glycerides. The first fraction will contain a substantial amount of esters of oleic acid with a minor portion of esters of linoleic acids and linolenic acids combined as glycerides. The second fraction will contain glycerides with substantial quantities of linolenic acids with minor quantities of oleic and linoleic. The third fraction will contain substantial quantities of linolenic acid and more highly unsaturated fatty acids, with only minor quantities of oleic and linoleic acids.

The first step of our process is essentially a crystallizing operation wherein the fatty material is mixed with the required amount of solvent and the mixture chilled to cause crystallization of the more saturated constituents. The amount and type of material crystallized will depend upon the type and amount of solvent, the temperature and the nature of the fatty material treated. In carrying out this initial step of the operation one may be guided by the principles set forth above as to the type of materials to be crystallized, and this material may be predetermined by iodine number, titer, melting point, thiocyanogen value, and, in the case of fatty acids, lead salt precipitation.

The amount of material crystallized in the first step may vary from 10% to 60%. For example, in the case of cottonseed oil, the amount will be approximately 10% and in the case of tallow and fatty acids, as much as 60%. Other materials may vary within the above range. The solution containing the crystallized compounds is subjected to appropriate separation operations, preferably filtration in a continuous filter, wherein the crystallized portion is filtered from the solution.

We may use a number of solvents in the crystallization step including both polar and non-polar solvents, such as propane, butane, pentane, hexane and members of the alkane series up to decane; methyl and ethyl alcohol; ethyl ether; carbon disulfide; B-B^1-dichlor ethyl ether; nitro propane; ethylene dichloride; acetone; methyl ethyl ketone; isopropyl acetate; amylacetate; monomethyl ether of ethylene glycol; and monoethyl ether of ethylene glycol.

When using volatile solvents, for example, a normal gaseous solvent, such as propane or butane, we may obtain chilling of the solution by vaporization of a portion of the solvent. When using less volatile solvents, chilling with an extraneous refrigerant is desirable.

In the second step of the process we prefer to further separate the fatty materials treated in the first step into two or more fractions of

varying degrees of unsaturation, as indicated by iodine value. The product from the first stage may be charged to the second stage with or without the addition of more of the same solvent or a different solvent. When using certain solvents, such as the normal gaseous hydrocarbons, for example, propane or butane, the solution from the first stage after the separation of the crystallized fraction may be charged directly to the second stage. In case it is desired to use a different solvent in the second stage than was used in the first stage, then the solvent employed in the initial stage may be removed, all or in part, from the fatty material.

In the case where two solvents are to be used in the second stage, the solvent used in the first stage may be retained with the fatty material and charged directly to the second stage wherein a second solvent charge is introduced. For example, in the separation of fatty acids using normally liquid hydrocarbons as a crystallizing solvent, a combination of hydrocarbon and furfural may be employed to accomplish the separation in the second stage.

Suitable solvents that may be used alone in the second stage include furfural, sulfur dioxide, furfuryl alcohol, phenol, and nitro benzene. When using such solvents, the solvent used in the first stage is usually partially or completely removed. Suitable solvents which may be used in both stages of our process are butane, propane, acetone, hexane, beta-beta-dichlorethyl ether, methyl Cellosolve, and ethyl Cellosolve. When using the latter solvents all or a portion of the solvent used in the first stage may be used in the last stage.

The operating conditions in the second step will vary depending on the type and amounts of solvent and the nature of the oil treated. The operation is usually carried out at above room temperatures and may vary from slightly above room temperature, for example, 100° F. to 110° F. in the case of furfural, up to around 200° F. in the case of propane.

When using a volatile solvent, such as propane, sufficient pressure is maintained to keep the solvent in the liquid phase. Such pressures may be up to 650 pounds to 700 pounds per square inch. The solvent treatment may be conducted in a batch, semi-batch, or continuous system. We prefer to use a continuous countercurrent tower wherein one fraction is drawn from the top of the tower and the other fraction from the bottom of the tower. In most cases the less unsaturated fraction will be withdrawn from the top of the tower and the more unsaturated fraction from the bottom of the tower, but the relative positions for drawing off fractions of different degrees of unsaturation will depend on the density of the solvent. For example, with a high density solvent the more saturated fraction may be withdrawn from the bottom of the tower and the more unsaturated fraction from the top of the tower.

The invention will be more fully understood from the following description read in connection with the accompanying drawing.

Referring to the drawing, the fatty material to be treated is introduced through the line 1 and forced by the pump 2 through the mixer 3, wherein the oil is thoroughly mixed with the solvent which may be introduced through the line 5 or the line 6. The mixer may be any suitable mechanism for thoroughly mixing the solvent and oil, such as a paddle type mixer, a coil for creating turbulent flow or a passageway provided with orifices or baffles or both. The proportions of the solvent and the oil will usually be around four to five parts of solvent to one part of oil by volume. The solution of oil and fatty material is conducted through the line 8 to a chiller 9. In the chiller the solution is cooled to a temperature sufficiently low to crystallize out the desired amount of more saturated compounds. The temperature in the chiller may range from about +30° F. to as low as about —70° F., depending on the solvent and fat used. The chiller may be a double pipe scraped wall type for the use of extraneous refrigerant or a simple enclosed tank fitted with a vapor escape lock for use with normally gaseous hydrocarbon or other low boiling, self-refrigerating solvent. If a self-refrigerating solvent is used, the portion of the solvent vaporized will be removed through the pipe 10 and condensed and recycled to the system through the line 6. The mixture of liquid and crystals from the chiller 9 is conducted through line 12 to the filter 14. The filter is preferably a rotary drum type filter and may be vapor tight for use with volatile solvent and should be equipped to operate under both positive pressure and reduced pressures as low as 10 mm. of mercury absolute. The crystallized portion of the fatty material along with some solvent is discharged from the filter through the line 15 into the stripper 16, wherein the solvent is stripped from the more saturated fraction. The stripper may be operated under reduced pressure and with injected steam, if necessary. The solvent is removed from the upper portion of the stripper through the line 17 and may be discharged from the system through the line 18 or recycled to the system through the line 20. The more saturated fatty constituents are withdrawn from the lower portion of the stripper through the line 21.

The solution of fatty material and solvent separated as a filtrate in the filter 14 is discharged through the line 23 and may be further treated in either of two ways. If it is desired to remove the solvent from the fatty material at this stage, as may be the case when it is preferred to use a different solvent in the second stage, the solution is conducted through the line 24 to a still 25. In the still the solvent may be removed all or in part as vapors. The distilled solvent may be removed from the system through the line 27 or recycled through the line 28. The bottoms in the still containing the fatty material may be drawn off of the lower portion thereof through the line 29 and conducted through the communicating line 30 to fractionation column 32. In some cases, as for instance when it is desired to use the same solvent in the second stage as was used in the first stage, the still 25 may be by-passed and the solution in line 23 conducted through the line 31 and line 30 to the fractionation column 32.

While we have shown the charge line 30 as entering the fractionation tower in the upper section, the position for introduction of the fatty material into the fractionation tower will vary, depending on the type of solvent used. In case the solvent density is greater than the density of the fatty material, as in the case of furfural, the fatty material will be introduced into the lower section of the tower and rise through the falling tower of solvent. When the density of the solvent is less than the fatty material, as in the case of the normally gaseous hydrocar-

bons, such as propane or butane, the fatty material will be introduced into the upper portion of the tower and descend through a rising column of solvent. As an illustration, if the fatty material charged to the fractionation tower is the filtrate directly from the filter 14—say, a solution of fatty material and propane—the solution would be charged into the upper portion of the tower. Additional solvent, which might be propane or butane, would be charged into the lower portion of the tower. If the solvent in the first stage is removed in the still 25 and the straight fatty material is charged to the fractionation column, such charge may be introduced into the lower portion of the tower when it is intended to use a high-density solvent such as furfural or beta-beta-dichlorethylether, which solvent would be introduced into the upper portion of the tower. In the drawing we have shown the solvent introduced into the lower portion of the tower through the line 35. Such position of introducing the solvent is suitable when using a low-density solvent such as propane. When using a solvent which has a higher density than the fatty material, then the relative positions of introducing the solvent and fatty material should be the reverse of those shown in the drawing.

The fractionation tower is operated under temperature and pressure conditions to maintain the solvent in the liquid phase and to cause a separation of phases. The interface is ordinarily between the points of introduction of the solvent and of the fatty material. The materials are drawn off from each phase from the top and bottom of the tower. Again, as shown in the drawing wherein a low density solvent is used, the upper layer or phase containing the major portion of the solvent and relatively rich in fatty material of lower degree of unsaturation is drawn off from the top of the tower through the line 36 and discharged into the still 38. In the still the solvent is vaporized and removed through the line 39 or recycled to the system through the line 40. Line 40 communicates with branch line 41, whereby the solvent may be returned to the first stage, and with the branch line 42, whereby the solvent may be returned to the fractionation tower 32. The fatty material may be withdrawn from the bottom of the still 38 through the line 45. The layer collected in the lower portion of fractionation tower 32 containing a minor proportion of the solvent and fatty material relatively rich in materials of a higher degree of unsaturation is drawn from the bottom of the tower through the line 46 and discharged into the still 48. Solvent removed in still 48 may be returned through the line 49 and branch line 50 to the fractionation tower 32 or through the line 49 and branch line 51 to the first stage of the system. Fatty material removed in the still 48 may be withdrawn through the line 52.

For purposes of illustration, examples will now be given of the operation of the invention. It is to be understood, however, that the invention is not limited to the specific examples.

Example 1

Cottonseed oil fatty acids, having an iodine number of 112.5, were dissolved in three volumes of petroleum ether. The solution was cooled slowly with agitation to 10° F., at which temperature a distinct grain had developed in the solution. The solid material was filtered from the solution of fatty acids, and this solution was charged to a solvent removal tower where a part of the solvent was removed from the filtrate to give a solvent to fatty acid ratio of approximately five to three by volume. This solution was charged directly into the lower section of a packed tower at two-thirds the rate of charge of furfural which was utilized as a fractionating selective solvent and introduced into the upper portion of the tower. The temperature of the tower was about 89° F. in the upper portion and about 88° F. in the lower portion. The interface was maintained approximately one-fourth the distance up from the foot of the column. A raffinate fraction was withdrawn from the top of the tower and an extract was withdrawn from the bottom of the column. The raffinate fraction contained 50% petroleum ether, 13% furfural, and 37% fatty acids. The extract contained 13% petroleum ether, 73% furfural, and 14% fatty acids. The ratio of raffinate to extract was approximately one to three. This ratio of raffinate to extract, as well as the amount of solvents used, was determined experimentally so as to give approximately a 50–50 distribution of the fatty acids in the raffinate and extract. The iodine number of the fatty acids obtained in the raffinate was 82.5. The iodine number of the fatty acids in the extract layer had an iodine number of 142.1. The crystallized fatty acids removed in the filtration step amounted to approximately 15% of the original charge and had an iodine number of 23.2 and a saponification number of 208.0. This fraction consists mainly of palmitic acid in mixture with a small amount of stearic acid and oleic acid.

Example 2

Soybean oil, having an iodine number of 137.6, was dissolved in four volumes of propane at a temperature of approximately 120° F. and 270 pounds pressure. The pressure was slowly reduced to allow a small portion of the solvent to vaporize, thereby cooling the solution. The rate of temperature drop was controlled at approximately 1° F. per minute. The solution was cooled to 0° F. and filtered. The solid fraction obtained in the filter amounted to approximately 10% of the initial oil charged and had an iodine number of 63.0. This fraction contained substantially all the combined saturated fatty acids present in the original soybean oil along with some oleic and a small amount of linoleic acids. The solution from the filtration operation was passed through a heating zone and the temperature raised to about 168° F. This warm solution was introduced, under pressure, into a packed tower flooded with propane. The solution was introduced approximately two-thirds of the way up from the bottom of the tower. Additional solvent, amounting to fifteen volumes on the basis of the oil charged, was introduced into the lower portion of the tower. The fractionating tower was maintained at a temperature of 178° F. at the top of the tower, dropping off gradually to 170° F. at the lower portion of the tower. The interface was maintained in the lower fourth of the tower. Sufficient pressure was maintained in the tower to prevent vaporization of the solvent propane. The raffinate fraction, containing substantially all of the propane and the more saturated oil, was removed from the upper portion of the tower. The extract fraction containing approximately one volume of solvent on the basis of the oil, was removed from the bottom of the tower. These solutions of raffinate and extract were subjected

to a primary stripping operation to remove most of the solvent and to a final step of steam stripping to remove the last traces of the solvent. The raffinate fraction had an iodine number of 91.5. The extract fraction had an iodine number of 165. Approximately 64% of the higher iodine fraction and about 36% of the lower iodine fraction calculated on the basis of the oil charged to the fractionating column were obtained.

Example 3

Cottonseed oil fatty acids, having an iodine number of 114.2 and a saponification value of 190.8, were dissolved in four volumes of propane at 120° F. and 270 pounds pressure. The pressure was slowly reduced and the solution chilled by the evaporation of a portion of this solvent at a rate of 1° F. per minute to a temperature of 11° F. The solution was filtered and the solid material washed with one-half a volume of cold solvent. The filtrate and the wash solution were combined and passed through a heating zone, where the temperature was raised to 195° F. This heated solution was introduced into the middle section of a packed fractionating tower into the lower portion of which was charged an additional quantity of liquid propane, amounting to forty-five volumes on the basis of the fatty acid charged. The upper portion of the tower was maintained at 204° F. and the lower portion of the column at 197° F. Necessary heat to maintain this temperature and the temperature gradient was supplied by a series of electrical heating coils spaced throughout the length of the tower. The overhead fraction, containing substantially all of the propane and the more saturated fatty acids, gave a fatty acid with an iodine number of 87.5 and a saponification value of 188.0. The bottom fraction, containing approximately one volume of solvent to fatty acids, had an iodine number of 134.2 and a saponification value of 196.5. The iodine number of the solid fraction separated in the filter was 11.0.

Example 4

Cottonseed oil was degummed by treating the oil with 2% water at 160° F. and settling the gums. The degummed oil was mixed with four volumes of acetone at a temperature of about 110° F. to insure complete solution. The resulting solution was slowly agitated and passed through a chiller wherein the temperature was gradually decreased by the use of cold brine solution circulating in a coil. The temperature of the solution was lowered at the rate of approximately 1° F. per minute to a temperature of about 30° F. A precipitate began to appear as the temperature reached 40° F. and a slurry developed slowly as the temperature was further reduced. The chilled slurry was passed through a filter operating under reduced pressure to remove the solid portion from the filtrate. The filter cake was washed with one-half volume of cold acetone and the wash solution combined with the filtrate. The filter cake, which amounted to about 10% of the original oil charged, was melted and the solvent removed. The solid product had a free fatty acid content of 1.8% and an iodine number of 63. The combined filtrate and wash was introduced into a still wherein the solvent was removed under vacuum. The last traces of solvent were removed by a five-minute steam stripping operation at a temperature of about 175° F. under reduced pressure. The oil from the solvent removal process was introduced into the upper portion of a continuous countercurrent fractionating tower. Into the lower portion of the tower forty volumes of liquid propane were introduced for every volume of the oil. The tower temperature was maintained at around 190° F. A 5° temperature gradient was maintained throughout the length of the fractionating tower, the higher temperature being maintained at the top of the tower. Two fractions were continuously removed from the tower, one from the top and one from the bottom. The bottom fraction, consisting of approximately 50% of the oil charge and containing a small percentage of solvent, was passed directly to a solvent recovery unit wherein the propane was removed under atmospheric pressure. Final removal of propane was accomplished by steam stripping at approximately 225° F. and atmospheric pressure. The bottom fraction had an iodine number of 131.0. The fraction removed from the top of the tower contained a large proportion of the solvent and the other 50% of the oil. The product was preheated to 200° F. and introduced into a solvent recovery tower, wherein the propane was removed under atmospheric pressure. A steam stripping operation at atmospheric pressure of 225° F. was used as the final step in the solvent removal. The top fraction had an iodine number of 86.5 and a free fatty acid content of approximately 1%.

Example 5

A sample of cottonseed oil was subjected to a crystallization operation similar to that described in Example 4, above. The filtrate from the filter was denuded of solvent in a still. The oil was then introduced into the lower section of a countercurrent fractionating tower. Into the upper portion of the tower two volumes of furfural to one of oil were introduced. The interface between the two liquid phases was maintained at approximately one-third of the distance up from the bottom of the tower. An average temperature of about 100° F. was maintained in the tower, the temperature gradient from the bottom to the top of the tower being about 3° F. An extract fraction containing the majority of the solvent and approximately 50% of the oil was removed from the bottom of the tower. A raffinate containing approximately 20% solvent and the other 50% of the charged oil was drawn from the top of the tower. These solutions were introduced into separate solvent recovery units after pre-heating to a temperature of 250° C. The solvent recovery units were two-stage processes operated under high vacuum, the first stage being a simple fractional distillation, and the second a steam stripping operation at about 200° C. and around ten millimeters absolute pressure. The solvent furfural remaining in the oil was reduced to less than one part in ten million and showed only a faint test by the analine-acetic acid testing procedure, which is the common method of detecting traces of furfural. The overhead raffinate fraction had an iodine number of 91.5 and the extract fraction had an iodine number of 130.2. The extract had a free fatty acid content of approximately 1.3%. It will be noted that in this example the fatty acids are selectively withdrawn with the higher iodine fraction, whereas by the use of propane, as in Example 4, the fatty acids were selectively withdrawn with the lower iodine fraction.

The present invention has the advantage of providing a process wherein a single solvent may be used for separating a saturated portion of a fatty material and then the same solvent used for fractionating the remainder of the fatty material into fractions of different degrees of unsaturation.

Another advantage of the present invention is that an over-all yield of 98% or better can be obtained from the original charge of fatty acids and an over-all yield of 99% and better can be obtained when working with glyceride oils. This advantage is due almost entirely to the low temperature of the operation throughout the various stages. This low temperature of operation also gives a superior quality product, especially in the more unsaturated fractions where excessive temperatures cause polymerization and heat bodying.

A further advantage of the invention is that the saturated material present in the charged stock is removed by a simple method which eliminates one of the interfering elements normally encountered in a liquid-liquid phase extraction. By separating the saturated material first we are not troubled by the common phenomenon of the saturation of our selective solvent with this saturated phase and we are able to obtain in a single countercurrent operation a much greater degree of resolution between the various unsaturated constituents present.

Obviously, many modifications and variations of the invention, as 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.

We claim:

1. A process for the treatment of fatty materials containing relatively saturated and unsaturated constituents to obtain an improved separation of the highly unsaturated constituents, which comprises: first cooling a solution of the fatty material in a liquefied normally gaseous hydrocarbon as a solvent to a temperature of between +30° and −70° F. by evaporation of a portion of the solvent to crystallize between 10 and 60 percent of the more saturated constituents from the solution, and filtering the crystals from the solution; then warming the solution free of the more saturated constituents in the presence of additional normally gaseous hydrocarbon as solvent to an elevated temperature and pressure to form two liquid phases, separating the phases and recovering from the separated phases constituents of the fatty material having a higher and lower iodine value respectively.

2. A process for the treatment of fatty materials containing relatively saturated and unsaturated constituents to obtain an improved separation of the highly unsaturated constituents, which comprises: first cooling a solution of the fatty material in a liquefied normally gaseous hydrocarbon acting as a solvent to a temperature between +30° and −70° F. whereby between 10 and 60 percent of the more saturated constituents crystallize from the solution, and separating the crystals by filtration; then subjecting the resulting solution containing the more unsaturated constituents free of the more saturated constituents to countercurrent extraction in the presence of additional normally gaseous hydrocarbon as solvent at an elevated temperature and pressure whereby the solution separates into two liquid phases, one of said phases comprised substantially of constituents having an iodine value of at least 40 points higher than that of the other phase, and separating said phases.

3. A process substantially as described in claim 2 wherein the step of crystallization is carried out in propane as the solvent and the countercurrent extraction step is carried out at a temperature between about 170° and 200° F. and at an elevated pressure between about 650 and 700 p. s. i.

WILLIAM M. LEADERS.
FELIX E. LACEY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,113,960	Grote et al.	Apr. 12, 1938
2,118,454	Schaafsma	May 24, 1938
2,285,795	Batchelder	June 9, 1942
2,290,609	Goss	July 21, 1942
2,320,238	Jenkins	June 1, 1943
2,352,883	Bolley	July 4, 1944
2,360,860	Morris et al.	Oct. 24, 1944

FOREIGN PATENTS

Number	Country	Date
402,651	Great Britain	Dec. 7, 1933