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FRACTIONATION OF TRIGLYCERIDES

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This invention relates to the fractionation of triglycerides by means of liquefied, normally gaseous hydrocarbons, more particularly to the segregation of the relatively saturated and relatively unsaturated constituents of triglyceride mixtures to produce technologically valuable products. These products comprise improved raw materials for the production of drying oils, soaps, salad oils and the like. This application is a continuation in part of application, Serial No. 393,480, filed May 14, 1941.

This present application is a re-file of application Serial No. 533,410, filed April 29, 1944.

The present invention stems from the discovery that liquefied, normally gaseous hydrocarbons such as propane possess the necessary saturated triglycerides from relatively unsaturated triglycerides of the same molecular ponderability when employed in the manner to be more fully described later.

That the invention is based upon an unexpected and critical action of such solvents is apparent from the prior knowledge of the art, evidenced in the literature, in which the discovered effect was specifically sought and not discovered. Moreover, the discovered effect is contrary to the broad generalizations which have been found prevalent in the solubility field of which it is a part.

Triglycerides are esters formed by the esterification of glycerine with long chain fatty acids. The essential characteristics of a triglyceride are largely established by the type of fatty acids present in the molecular structure. Naturally occurring triglycerides normally contain a variety of esterified fatty acids. With but minor exceptions the composition of the triglycerides is essentially similar to what would be predicted if it were assumed that the fatty acids were portioned among the triglycerides by random distribution. Since unsaturated as well as saturated acyl groups are combined in the same molecule, it is impossible to separate these by a physical method such as selective solvent extraction; however, some of the triglycerides in naturally occurring fatty oils are relatively more unsaturated than other triglyceride molecules. These relatively or preponderantly unsaturated molecules may be separated from the relatively saturated molecules by the method of the present invention. In the further discussion it is clearly to be understood that in referring to saturated and unsaturated compounds a relative or differential unsaturation is comprehended.

The technical value of this discovery will immediately be apparent in that it presents a new tool or technique for segregating different components of triglyceride mixtures. In a technological classification triglycerides may be divided into three general classes, namely; drying oils, such as linseed oil; semi-drying oils such as soybean oil; and non-drying oils such as olive oil. The essential difference between the three classes is a difference in the number of double bonds; olive oil contains a relatively small number of double bonds, soybean oil a larger number and linseed oil a still larger number. These oils are comprised of mixtures of different triglycerides in varying proportions but each contains constituents common to the others. Could these oils be treated to extract the similar molecules, the resulting oils would have the same properties regardless of the source. If, for example, the relatively unsaturated molecules of soybean oil could be separated from the other molecules, the oil thus produced would possess better drying properties than the original oil so that a drying oil comparable to linseed oil could be produced. A similar treatment of cottonseed oil would produce two fractions one of which is more unsaturated than the other. It is common knowledge that the more unsaturated triglycerides possess lower melting points than the more saturated triglycerides. When refined, but otherwise untreated cottonseed oil is marketed as a salad oil, it meets with poor consumer acceptance because a portion of it solidifies in the household refrigerator where it is normally stored in the home. To overcome this condition, fatty oils to be used as salad dressings or for like purposes must be winterized. Oils are winterized by chilling them to a comparatively low temperature for a sufficient period of time to cause the more saturated, higher melting components to solidify. The solid fats are separated from the liquid fats by filtration. It has also been proposed (Parkhurst U. S. Patent No. 1,974,542), to dissolve oils in propane and then reduce the temperature. When the temperature is reduced, the saturated components come out of solution as a solid. The propane solution containing the unsaturated components is separated from the solid triglycerides by any suitable means. We have found that by dissolving the fatty oil in a solvent such as propane and by heating rather than cooling, the more unsaturated, lower melting components come out of solution as a second liquid phase and the more saturated, higher melting point components remain in solution. The winterization of fatty oils

is a well-known art but it is a comparatively expensive operation. The lowering of the cloud point of a fatty oil can be achieved by the present invention as well as can be accomplished by winterizing and at a smaller cost.

To those skilled in the art it was obvious that it would be advantageous to be able to segregate the unsaturated constituents of a naturally occurring fatty oil from the saturated constituents by an inexpensive process. Aside from the winterizing procedure, no method of accomplishing this separation was available until the process described by Freeman, U. S. Patent Nos. 2,200,390 and 2,200,391 was developed. In U. S. Patent No. 2,200,391 Freeman discloses the use of polar solvents to separate components from the unsaturated components of a naturally occurring fatty oil. He points out that hydrocarbons possess no selectivity with regard to unsaturation. Moreover, he shows that while certain polar or active solvents cannot be employed by themselves because of undue miscibility with both saturated and unsaturated triglycerides, they can be used effectively when the active solvent is mixed with an aliphatic hydrocarbon such as hexane, butane, propane, dodecane or the like, which is relatively immiscible with the polar solvent. It will be shown that liquefied, normally gaseous hydrocarbons such as propane when employed in the manner to be described below possess selectivity and can separate the unsaturated components of a naturally occurring fatty oil from the saturated components without the simultaneous use of a polar solvent.

Fatty oils possess many diverse uses. As this process is used to treat naturally occurring fatty oils, its employment will affect the production of raw materials that go into a variety of fields. One of the important fields, and it is emphasized, one out of a number of important fields, is the production of improved drying oils. To properly comprehend the application of this invention in the drying oil field it is necessary to recall that the more unsaturated fatty oils such as linseed oil usually are the better raw material for the production of varnishes and paints. Another important attribute of a raw material for the varnish and paint field is that the non-drying or saturated components be absent or constitute but a small percentage of the whole. Thus, it is well-known that fish oils are not superior drying oils although they possess high iodine values, which is a measure of unsaturation, because they contain a considerable fraction of triglycerides which are not reactive. These non-reactive triglycerides do not oxidize or polymerize but remain in the ultimate film as diluents which, of course, decreases the hardness of the film and keeps it tacky for a long time. Practically all naturally occurring fatty oils possess some non-reactive components. Anything which can remove these components completely or partially will improve the drying quality of the components left behind. It has been pointed out that prior to Freeman's process no method of fractionating naturally occurring fatty oils had been developed. Methods have, however, been developed to remove these non-reactive components from bodied oils. As bodied oils are used in the production of varnishes and to a small extent in paints, these processes resulted in the production of improved raw materials for these industries.

The prior processes, other than Freeman's, were feasible as pointed out above, because the varnish industry employs bodied oils. Oils are bodied by subjecting them to elevated temperatures for protracted periods of time. The temperature and time vary with the oil being processed and the product desired. The result of this heat treatment is to cause polymerization reactions to occur. The mean molecular weight of the oil increases and the body or viscosity of the oil increases tremendously. It is known that when bodied oils are used in oleoresinous varnishes, the films dry more quickly, are tougher and have better water, alkali, and chemical resistance than films made from raw oil. Bodied oils are used in varnishes to reduce the cooking time, and to impart the inherent qualities of bodied oils. The increased molecular weight and increased density caused by bodying cause the resulting dry films to possess less permeability, greater gloss and more durability from the standpoint of resistance to weathering by the elements. Bodied oils possess better wetting qualities, promote more flow, and have better drying qualities as well as better color retention than unbodied oils. However, bodied oils have decidedly poorer brushing qualities than the unbodied oils, the adverse effect being directly proportional to the degree of polymerization. As a result of the poorer brushing characteristic imparted by bodied oils, the binder commonly used in house paints is composed of about 92% refined linseed oil and 8% of bodied linseed oil (about Q on the Gardner-Holdt scale in viscosity).

Bodied linseed oil is popularly called stand oil. The unpolymerized portions of stand oil comprise glycerides with molecular weights not greater than about 900 and the usual products of decomposition found in and produced in bodied oils. As pointed out previously, these low molecular weight substances tend to make the film soft and tacky. In addition they make the film non-resistant to water. The advantages of being able to remove these low molecular weight substances from the oils going into the varnishes and paints becomes obvious. Three different methods of accomplishing this have been suggested to date. In each case the oil is subjected to a bodying process first and then the lower molecular weight substances separated from the higher molecular weight substances.

One method separates the low molecular weight substances from the higher molecular material by vaporizing the low molecular weight material under conditions which prevent the polymers from becoming volatile. The low molecular weight substances in this case are so difficult to vaporize that exceedingly low pressure must be maintained to effect the distillation. This process was first described by Oosterhof, van Vlodrip and Waterman, U. S. Patent No. 2,065,728.

An earlier process depended upon the fact that certain oxygenated solvents possess the ability to dissolve ordinary triglycerides but do not dissolve polymerized triglycerides. An example of a process of this type is that described by Behr in U. S. Patent No. 2,239,692. In this process oxygenated compounds such as acetone or butyl alcohol at temperatures a little above room temperature are employed to extract the unpolymerized, low molecular weight triglycerides from a bodied oil. The undissolved oil is composed of polymerized triglycerides and has improved drying characteristics over the original oil and the extracted fraction.

A third process utilizes the selectivity possessed by certain liquefied, normally gaseous materials such as propane, butane or dimethyl ether for

fractionating mixtures on the basis of molecular weight. It is a widely practiced art in the petroleum industry to separate the higher molecular components of crude lubricating oil from the lower molecular constituents by using propane at elevated temperatures to precipitate or reject the higher molecular weight components of the crude lubricating oil. As the higher molecular weight components of crude lubricating oil are asphaltic in nature, this provides an economical method of deasphalting lubricating oil. In the lubricating oil field it is sometimes advantageous to separate the more viscous or high molecular weight components from the lower molecular weight more fluid components. The selective solvent ability of propane at elevated temperatures can be utilized to effect this separation. At temperatures in the neighborhood of its critical temperature, propane dissolves the lower molecular weight, more fluid components of lubricating oil but does not dissolve the more viscous higher molecular weight components. A two phase system is thus formed. The upper phase is composed of propane in which the lower molecular weight components are dissolved. The lower phase contains the higher molecular weight components of the mixture. By separating the phases and removing the propane associated with each, the mixture is fractionated on the basis of molecular weight. Schaafsma (U. S. Patent 2,118,454) has applied this separation method to the high molecular weight, organic, non-hydrocarbon field.

Schaafsma applied this fractionation method to mixtures of polymerized triglycerides. In one case, he fractionated a polymerized triglyceride mixture produced by voltolizing olein. Voltolization is a method of polymerizing oils by subjecting them to a silent electrical discharge. In this operation he used butane as the treating agent and secured three fractions of different molecular weights. In another case, he treated a stand oil, that is a heat polymerized linseed oil with dimethyl ether as the treating agent. He secured two fractions which obviously differed considerably in molecular weight from the large differences in the two fractions in density and in refractive index. The original oil must have been heavily bodied for its original specific gravity was .963 and its original refractive index was 1.492. A naturally occurring linseed oil will possess a specific gravity of about .930 and a refractive index of about 1.482.

The method of polymerizing oil and subsequently separating the unpolymerized fraction from the polymerized fraction is undesirable because the bodying operation causes the degradation of the separated fraction. Furthermore, it is uneconomic in that it involves bodying a large quantity of oil of which but a fraction is desired in the polymerized condition. The process described by Freeman does not suffer from the handicap of necessitating a bodying operation. However, his preferred solvent furfural, is a comparatively expensive solvent. Furthermore, vacuum or steam and high temperatures are required to recover the solvent completely. If the process is not carried out with great care, anti-oxidants are formed which prevent the drying oil fraction from reacting with air and thus prevent rapid film formation. Moreover, furfural is not adapted to the removal of color bodies, fatty acids, and the mucilaginous substances which are termed the "break" material in fatty oil parlance, without using water as an auxiliary solvent. In our copending application, Serial No. 308,221, filed December 8, 1939, we have described how liquefied, normally gaseous hydrocarbons such as propane may be used to separate these substances from crude fatty oils. These same solvents when used in the manner to be described below are capable of separating saturated triglycerides from unsaturated triglycerides. Thus, a single solvent not only can be employed to separate all the different types of materials found in crude fatty oil but can also be used to fractionate the triglycerides on the basis of unsaturation. Moreover, as will be shown below the separations which take place, occur in a most unexpected manner.

This invention is the result of observations made in studying the solubility behavior of fatty acids in liquefied, normally gaseous hydrocarbons. In U. S. Patent No. 2,219,652, the present inventors have described a method of refining fatty acids with liquefied, normally gaseous hydrocarbons. Additional study of this field in equipment especially adapted for visual observation resulted in the discovery that Freeman was in error when he implied that propane could not be employed to fractionate mixtures of fatty acids or triglycerides to separate the more saturated components from the less saturated components. An even more unexpected result was to find that Schaafsma's broad generalizations were incorrect when liquefied, normally gaseous hydrocarbons such as propane were applied to the fractionation of unbodied triglycerides.

The equipment used in the preliminary studies which led to this invention was a Jerguson gauge and an oil bath whose temperature could be varied and accurately controlled at any desired temperature. A Jerguson gauge is essentially a heavy steel oblong vessel fitted with thick glass windows to permit visual observation of what occurs in the interior of the vessel and capable of standing the pressure of liquid propane at its critical temperature. A quantity of pure stearic acid (molecular weight 284) was put into the gauge. Sufficient propane was added to make the ratio of solvent to solute 9 to 1 by volume. A clear solution was formed. The gauge and its contents were placed in the oil bath and the temperature slowly raised. At a temperature of about 93° C., a second phase formed. This, then, is approximately the temperature at which propane and stearic acid are no longer completely miscible. When palmitic acid (molecular weight 256) is used, the phase point is about 96.5. If myristic acid (molecular weight 228) is employed, the phase point is found to be about 103.5° C. If lauric acid (molecular weight 200) is dissolved in propane under the same conditions, a phase point is not reached even at 111° C. These phase points clearly illustrate the effect of additional methylene groups in the saturated fatty acid series. They also disclose the possibility of fractionating mixtures of saturated fatty acids with respect to molecular weight or chain length when the mixtures consist in part of fatty acids greater in molecular weight than lauric acid by using propane as a selective solvent.

If oleic acid (molecular weight 282) is studied in the same way, a phase point is found at 90° C. This is surprising for the molecular weight of oleic acid is lower than the molecular weight of stearic acid and a higher phase point would have been anticipated if there was to be a difference in phase points. When linoleic acid (molecular weight 280) was studied, the phase point was

found to be about 86° C. This was even more unexpected for the molecular weight of linoleic acid is even lower than the molecular weight of oleic acid and the phase point is considerably lower than the phase point of stearic acid. There was no reason to expect that the propane fatty acid system was so sensitive to small changes in molecular weight and it was even more surprising to learn that presence of a double bond in the chain was equivalent to adding about two methylene groups to the length of the chain. In other words, the reduction in molecular weight by the loss of two hydrogen atoms to form a double bond was equivalent to raising the molecular weight by about 28 or in this case about 10%.

Liquefied, normally gaseous hydrocarbons such as propane can thus be used to fractionate a mixture of fatty acids. The fatty acids may be fractionated according to molecular weight or unsaturation. Fatty acids which have about the same molecular weight may be separated on the basis of unsaturation for the unsaturated acids precipitate or come out of solution at a lower temperature than the saturated acids. When a mixture of fatty acids contains acids of varied molecular weight and varied unsaturation and when the higher molecular weight acids are also the more unsaturated, the separation is even simpler. This happens to be the case with fish oil fatty acids. Propane can be employed to separate the longer carbon chain, more unsaturated fatty acids from the shorter chain, more saturated fatty acids. A batch extraction will not permit a clean cut separation but a continuous countercurrent extraction system employing a temperature gradient will permit the separation of the fatty acids containing 20 carbon atoms and above from the fatty acids containing fewer than 20 carbon atoms.

When pure triglycerides were examined by the same technique, similar unexpected results were obtained. A solution of tristearin (molecular weight 891) had a phase point of about 70° C. Under similar conditions tripalmitin (molecular weight 807) had a phase point of about 74° C. The fact that a change in molecular weight of about 10% caused an appreciable change in the phase point was unexpected in view of the fact that the phase point was about 25° C. below the critical temperature of propane. When a sample of triolein (molecular weight 885) was examined it was found that the phase point was about 64.5° C. The slight reduction in molecular weight caused by the removal of 6 hydrogen atoms to form 3 double bonds was equivalent to raising the molecular weight more than 10% and this at a temperature far removed from the critical temperature of the solvent. There is no prior record of studies of this fundamental type. Moreover, there is no record of the study of the solubility characteristics of unbodied triglycerides in liquefied, normally gaseous hydrocarbons with temperature. The broad generalizations hitherto believed valid in this field are obviously incorrect when applied to unbodied, unsaturated triglycerides. The prior art would have suggested that triolein (molecular weight 885) should precipitate at a higher phase point than tristearin (molecular weight 891) because it is lower in molecular weight, assuming that the propane-triglyceride system is sufficiently sensitive to slight changes in molecular weight that there be any difference in phase point at all. Exactly the opposite has been found to be the case.

The value of these discoveries, namely, that liquefied normally gaseous hydrocarbons such as propane are selective solvents with respect to quite small changes in molecular weight and that they are very sensitive with respect to unsaturation and in a direction opposite to what prior generalizations would lead one to expect, will be apparent when it is realized that these discoveries have led to the development of a process for fractionating triglycerides which is eminently simple, inexpensive, efficient, amenable to the treatment of naturally occurring fatty oils and capable of being carried out readily on a large scale.

The scope and utility of the invention can be more readily appreciated by a number of examples of how triglycerides may be fractionated. An unbodied linseed oil was intimately contacted with about 30 volumes of propane to each volume of oil in a packed tower about 20 feet high. The oil was pumped into the tower close to the top. The propane entered the tower close to the bottom. The temperature at the bottom of the tower was maintained at about 195° F., the temperature at the bottom was about 160° F. Under these conditions the propane and oil were not completely miscible and two liquid phases were present throughout the greater length of the tower. The propane phase being lower in density passed up the tower selectively extracting those constituents in the oil of greater molecular weight and rejecting the lower molecular weight, more unsaturated constituents. The propane solution passed out of the top of the tower to a still. In the still the propane was separated from the dissolved oil by distillation. The propane is easily vaporized and the oil is only volatile at conditions which exist in the "molecular still." This permits the simple, easy recovery of the selective solvent at low temperatures. The oil which is not soluble in propane under the conditions existent in the tower is heavier than the propane phase and leaves the tower at its base. It will have dissolved some propane which may be removed and recovered by distillation in a second still. The original oil was split into two fractions; 16.4% of the original oil left the top of the tower dissolved in the propane phase, and 83.6% left the tower at the bottom. The original oil had an iodine number of 186.2; the 16.4% fraction's iodine number was 162; and the iodine number of the 83.6% fraction was 191.4.

To show that the limits had not been reached, the 83.6% fraction was rerun. The ratio of solvent to oil was maintained at 30 to 1 but the top temperature was lowered to 175° F. and the bottom temperature raised to 165° F. These conditions were chosen arbitrarily and although the choice was poor, it was found that the oil was split into two nearly equal fractions. Based on the original oil, 37.8% of the oil went overhead and 45.8% left the tower as the bottom fraction. The more unsaturated fraction was the bottom fraction once more. Its iodine number was 196. The top fraction had an iodine value of 183.9.

The above experiment indicates the results that may be obtained when linseed oil is extracted with propane under conditions adapted to insure a two phase system in a continuous counter-current manner. That similar but not nearly so striking results can be obtained by a simple batch treatment is shown by the results obtained as follows:

A sample of linseed oil with an iodine number of 185.5 was placed in a steel bomb together with

10 volumes of propane. The bomb and its contents were heated to 180° F., agitated vigorously and permitted to rest quietly to permit two well defined liquid layers to form. It was found that this procedure had caused the original oil to be split into two fractions. One fraction, 16.6% by weight of the original oil, had an iodine number of 177.6. The iodine number of the other fraction was 186.8. The low iodine number oil was contained in the lighter liquid, or propane, phase.

When a similar experiment was run with soybean oil of 132.7 iodine number, it was found the oil was divided into two fractions; 21.7% and 78.3% of the charge oil by weight. The 21.7% fraction had an iodine number of 128.5.

When the above soybean oil was extracted with about 29 volumes of propane per volume of oil in a packed tower adapted for continuous counter-current operation while maintaining a temperature of about 180° F. at the top of the tower and a temperature of 160° F. at the bottom of the tower, the oil was split into two nearly equal fractions. The oil obtained from the liquid phase leaving the bottom of the tower had an iodine number of 148.

The above examples exemplify the sort of separation that may be accomplished when all the components of a fatty oil are very similar. Much more striking results can be obtained when oils are treated which contain triglyceride components of widely differing iodine number and where there are a considerable percentage of each component. Fish oils, in particular, contain a substantial percentage of low iodine number components although they consist primarily of high iodine number components.

For example, a quantity of menhaden fish oil was extracted with about 29 volumes of propane per volume of charge oil in a packed tower adapted for continuous counter-current operation. The temperature at the top of the tower was maintained at about 193° F. the bottom of the tower was held at a temperature of 166° F. 14.7% of the over came overhead. Its iodine number was 129. The iodine number of the other fraction was 198. The charge oil had an iodine number of 192.

Even more striking results were obtained with sardine oil which was treated as follows:

A sample of sardine oil with an iodine number of 188.3 was fractionated in the packed tower with 29.5 volumes of propane per volume of oil. The temperature at the top of the tower was 178° F.; at the bottom 170° F. The overhead fraction represented 51% of the charge oil. It had an iodine number of 169.9. The bottom fraction had an iodine number of 213.9. The upper fraction was recharged to the extraction unit under slightly different conditions. The ratio of propane to oil by volume was 50 to 1. The temperature at the top of the tower was 203° F. The temperature at the bottom of the tower was 179° F. The overhead fraction constituted 22% of the oil charged to the operation or 11% of the original oil. Its iodine number was 105.7. The iodine number of the bottom fraction was 186.7 which incidentally, is very close to the iodine number of the original charge oil. It is evident that this fractionation procedure has permitted two fractions to be secured from a sample of sardine oil that differed in iodine number by about 108 units and without any pretreatment of the oil. The fraction having an iodine value of 105.7 was almost solid at room temperature. The fraction with the 213.9 iodine number was practically a winterized oil.

In addition to the iodine numbers, the specific gravity and the viscosity in Saybolt seconds of the initial oil and each fraction was determined. The results are shown in the following table:

RUN I

Fraction	Iodine Number	Specific Gravity	Viscosity in Saybolt Seconds at 210° F.
Charge Oil (Initial Sample)	188.3	.9291	49.6
Overhead	169.9	.9248	48.6
Bottom	213.9	.9309	48.5

RUN II

Charge Oil	169.9	.9248	48.6
Overhead	105.7	.9170	49.7
Bottom	186.7	.9267	48.4

The above results show that the initial oil was a normal, naturally occurring sardine oil for its iodine number and specific gravity are typical of such oils. The two fractions obtained in the first run have widely different iodine numbers but differ only slightly in gravity and practically not at all in viscosity. The more unsaturated triglycerides are more dense than the more saturated triglycerides of about the same molecular weight. The results obtained are in conformity with this generalization. The viscosity of the original oil and the two fractions all practically coincide. Normally, if a sample of oily material is fractionated on the basis of molecular weight, the more viscous material possesses the greater mean molecular weight. It is evident from these results that there is very little difference, if any, in the mean molecular weight of the triglycerides in each sample. Obviously then, the oils have been separated because they differed with respect to unsaturation. This shows the selective solubility power of propane under the conditions described for the more saturated triglyceride components of a naturally occurring fatty oil. The results obtained in the second run are similar to those secured in the first run.

When a sample of soup fin shark liver oil was treated in approximately a similar manner, a fraction was obtained which represented 9.3% of the original oil. It possessed an iodine number of 116. The original oil had an iodine number of 172.

It will be appreciated that this novel method of fractionating triglycerides is particularly adaptable to a continuous counter-current extraction process and especially with a temperature gradient maintained between the extremities of the extraction system. While propane is the preferred solvent, similar results can be obtained with mixtures of other liquefied, normally gaseous hydrocarbons such as ethane and isobutane, propane and ethane, propane and butane, and the like. The availability and inexpensiveness of the solvent is a substantial economic advantage. While the ratio of solvent to solute is higher than in most solvent extraction processes, it must be remembered that propane solutions are very fluid due to their low viscosity thus pumping costs are low although the volumes circulated are large. In addition, the specific gravity of propane at the temperatures employed is about .3. Thus, the weight of propane circulated is not excessive. It will be apparent that the principal item of expense in large installations will be the cost of steam for vaporizing the propane in order to sep-

arate the oil from the solvent. In this connection it must be remembered that the latent heat of vaporization of propane in the temperature range used in this process is about 200 B. t. u. per pound.

The process is of wide utility for it may be applied to all the naturally occurring triglycerides. It can be employed to segregate superior drying oil fractions from an oil such as linseed oil or to produce a superior salad oil from cottonseed oil. While the pressures are somewhat above atmospheric, they are still moderate and no difficulty is found in designing, building and operating large plants. The temperatures employed are low. The great difference in volatility between the solvent and oil make the problem of complete recovery of the solvent simple.

While preferred modifications of the invention have been described it is to be understood that these are given to illustrate the fundamental principles involved and not as limiting the invention to the specific treatments or source materials described.

We claim:

1. A method of treating an unbodied fatty oil containing a mixture of relatively saturated and relatively unsaturated triglycerides, the molecular weights of which all fall within a relatively small range, to obtain an oil fraction enriched in unsaturated triglycerides which comprises contacting said oil with a liquefied, normally gaseous hydrocarbon solvent, the ratio of liquefied, normally gaseous hydrocarbon solvent to oil and the contacting temperature being selected to form two immiscible liquid phases differing in density, said temperature being higher than the highest temperature at which the unbodied fatty oil and the solvent are completely miscible at the selected ratio; the less dense phase containing the bulk of the solvent and a portion of the fatty oil enriched in relatively saturated triglycerides and the more dense phase containing the remainder of the solvent and fatty oil said remaining portion of the fatty oil being enriched in relatively unsaturated triglycerides, separating the less dense phase from the more dense phase and removing the solvent contained in the more dense phase to recover an oil fraction enriched in relatively unsaturated triglycerides.

2. The process of claim 1 in which the unbodied fatty oil is soybean oil.

3. A method of treating an unbodied fatty oil containing a mixture of relatively saturated and relatively unsaturated triglycerides, the molecular weights of which all fall within a relatively small range to obtain an oil fraction enriched in unsaturated triglycerides which comprises contacting said oil with liquid propane, the ratio of liquefied propane to oil and the contacting temperature being selected to form two immiscible liquid phases differing in density, said temperature being higher than the highest temperature at which the unbodied fatty oil and the liquid propane are completely miscible at the selected ratio; the less dense phase containing the bulk of the liquid propane and a portion of the fatty oil enriched in relatively saturated triglycerides and the more dense phase containing the remainder of the solvent and fatty oil said remaining portion of the fatty oil being enriched in relatively unsaturated triglycerides, separating the less dense phase from the more dense phase and removing the solvent contained in the more dense phase to recover an oil fraction enriched in relatively unsaturated triglycerides.

4. The process of claim 3 in which the unbodied fatty oil is soybean oil.

5. The process of treating an unbodied fatty oil containing a mixture of relatively saturated and relatively unsaturated triglycerides, the molecular weights of which all fall within a relatively small range to obtain an oil fraction in unsaturated triglycerides which comprises contacting the unbodied fatty oil in a continuous counter-current extraction system with a liquefied, normally gaseous hydrocarbon solvent, the ratio of liquefied normally gaseous hydrocarbon solvent to unbodied fatty oil and the contacting temperature being selected to form two immiscible liquid phases differing in density, said temperature being higher than the highest temperature at which the unbodied fatty oil and the solvent would be completely miscible at the selected ratio, the less dense phase containing the bulk of the solvent and a portion of the oil enriched in relatively saturated triglycerides and the more dense phase containing the remainder of the solvent and oil said remaining portion of the oil being enriched in relatively unsaturated triglycerides, separating the less dense phase from the more dense phase and removing the solvent contained in the more dense phase to recover an oil fraction enriched in relatively unsaturated triglycerides.

6. The process of claim 5 in which liquid propane is the liquefied, normally gaseous hydrocarbon solvent.

7. A process according to claim 5 in which a temperature gradient is maintained in the extraction system, the highest temperature prevailing at that part of the system at which the less dense phase leaves the system.

8. The process of treating an unbodied fatty oil containing a mixture of relatively higher melting point triglycerides and relatively lower melting point triglycerides, the molecular weights, viscosity and specific gravity of which all fall within a relatively narrow range to obtain an oil fraction enriched in relatively higher melting point triglycerides which comprises, contacting the unbodied fatty oil in a continuous counter-current extraction system with a liquefied, normally gaseous, paraffinic hydrocarbon solvent; the ratio of liquefied, normally gaseous, hydrocarbon solvent to unbodied fatty oil and the contacting temperature being selected to form two immiscible liquid phases of different density, said temperature being higher than the highest temperature at which the unbodied fatty oil and the solvent would be completely miscible at the selected ratio; the more dense phase containing a minor amount of the solvent and a portion of the oil enriched in relatively lower melting point triglycerides and the less dense phase containing the bulk of the solvent and the remainder of the oil said remaining portion of the oil being enriched in relatively higher melting point triglycerides, separating the more dense liquid phase from the less dense liquid phase and removing the solvent contained in the less dense liquid phase to recover an oil fraction enriched in relatively higher melting point triglycerides.

9. The process of claim 8 in which the liquefied, normally gaseous hydrocarbon solvent is liquid propane.

10. The process of claim 8 in which the unbodied fatty oil is a fatty oil of marine origin.

11. The process of claim 8 in which the unbodied fatty oil is cottonseed oil.

12. The process of treating unbodied linseed oil containing a mixture of relatively poorer drying triglycerides and relatively better drying triglycerides the molecular weights of which all fall within a relatively narrow range, to obtain an oil fraction enriched in better drying triglycerides which comprises contacting the unbodied linseed oil in a continuous countercurrent extraction system with a liquefied, normally gaseous hydrocarbon solvent; the ratio of unbodied linseed oil to liquefied, normally gaseous hydrocarbon solvent and the contacting temperature being selected to form two liquid, immiscible, phases of different density, said temperature being higher than the highest temperature at which the unbodied linseed oil and the solvent would be completely miscible at the selected ratio; the less dense phase containing the bulk of the solvent and a portion of the oil enriched in poorer drying triglycerides and the more dense phase containing the remainder of the solvent and oil said remaining oil being enriched in better drying unbodied triglycerides, separating the less dense phase from the more dense phase and removing the solvent contained in the separated more dense phase to recover an oil fraction enriched in relatively better drying triglycerides.

13. The process of treating unbodied linseed oil containing a mixture of triglycerides of relatively high and relatively low iodine values, the molecular weights of which all fall within a relatively narrow range to obtain an oil fraction enriched in relatively high iodine value triglycerides which comprises contacting the unbodied linseed oil with liquid propane in a continuous counter-current extraction system; the ratio of unbodied linseed oil to liquid propane and the contacting temperature being selected to form two immiscible liquid phases of different density, said temperature being higher than the highest temperature at which the unbodied linseed oil and the liquid propane would be completely miscible at the selected ratio, the less dense phase containing the bulk of the propane and a portion of the oil enriched in relatively low iodine value triglycerides and the more dense phase containing the remainder of the solvent and linseed oil, said remainder of the linseed oil being enriched in relatively high iodine value triglycerides, separating the less dense liquid phase from the more dense liquid phase and removing the propane contained in the separated more dense phase to recover an oil fraction enriched in relatively high iodine value triglycerides.

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