

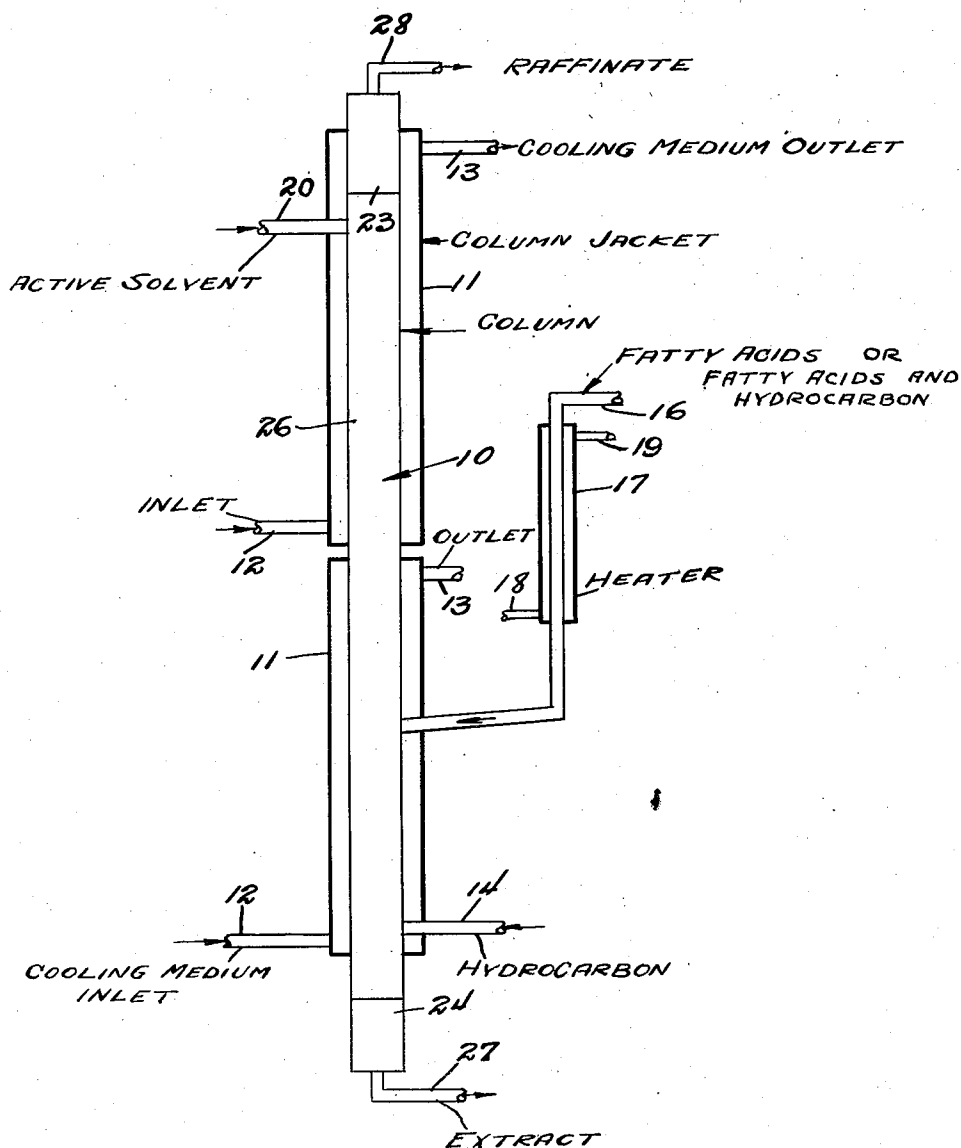
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S. E. FREEMAN

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FRACTIONATION OF FREE FATTY ACIDS

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Inventor
STEPHEN E. FREEMAN

By

Olen E. Bee

Attorney

UNITED STATES PATENT OFFICE

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FRACTIONATION OF FREE FATTY ACIDS

Stephen E. Freeman, Wauwatosa, Wis., assignor
to Pittsburgh Plate Glass Company, Allegheny
County, Pa., a corporation of Pennsylvania

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The present invention relates to a method of separating mixtures of a plurality of free fatty acids into fractions, each of which is relatively enriched in certain components of the mixture and correspondingly impoverished in other components, and it has particular relation to the fractionation of such mixtures by liquid phase extraction with a polar solvent which is a more powerful solvent for certain components of the mixtures of acids than for others.

One object of the invention is to provide a process of solvent extraction for fractionation of mixtures of free fatty acids, by means of which it is possible to fractionate mixtures with polar solvents possessing such degree of miscibility with all components of the acid mixture as to render it difficult to make a liquid phase fractionation by ordinary methods.

This and other objects of the invention will be apparent from consideration of the following specification and the appended claims.

In my copending applications Serial Nos. 144,315 now issued as Patent 2,200,390 and 251,340 issued as Patent 2,200,391, filed respectively May 22, 1937, and January 17, 1939, are disclosed processes of extracting mixtures of glycerides such as occur in natural vegetable and animal oils by selective extraction with a polar solvent to obtain fractions, some of which are enriched in one component and correspondingly impoverished in others.

It has been found that the fractionation of the mixture of free fatty acids derivable by saponification of the glycerides fractionation with many selective solvents disclosed in the foregoing applications or similar solvents is somewhat difficult because all components of the mixture possess such substantial degree of solubility in the solvents at working temperatures as to mask the selectivity due to active polar groups and render it difficult to obtain immiscible phases.

It has now been found that in those cases where the selective solvent is strongly miscible with all components of the oil, it may be combined with a secondary relatively non-polar solvent, which is immiscible in said selective solvent, to obtain separable phases of acids. The more active or polar components of the mixture of acids are more strongly attracted to the polar solvent than are the less active components so that there is considerable degree of separation of the components of the mixture. In particular the process is applicable to the use of petroleum hydrocarbons, as secondary solvents. These are immiscible with many active polar solvents and

are of low gravity so that separation into phases is rapid and relatively complete. Preferably the hydrocarbon is open chain, and liquid at the operating temperatures. Isooctane is a good example of such solvent.

If the petroleum hydrocarbon and a polar solvent immiscible therewith be conjointly contacted by agitation or countercurrent flow or other suitable method with a mixture of free fatty acids, such as are derivable by saponification of various glyceride oils, including linseed oil, tung oil, soya bean oil, cottonseed oil, perilla oil, marine oils, such as menhaden, sardine, whale, cod and the like, lard, tallow, coconut oil, palm oil or to tall oil, it is possible to extract certain components upon the basis of degree or activity, due to differences in degree of unsaturation or differences in chain length. The acids are simply appropriately contacted with the polar and the non-polar solvents at a temperature at which the two solvents are immiscible, but all components remain in liquid state. Perhaps, as a result of the presence of double bonds in the unsaturates or of short chain length, some components of the mix are more polar than the saturated compounds or compounds of greater chain length, and have a greater affinity for the polar solvents. In other words they are more active with respect to the polar solvents.

As a result the system separates into two liquid phases, one consisting of a selective solvent containing a fraction relatively rich in active components of the acid mixture and the other consisting of petroleum hydrocarbon in which is dissolved a fraction relatively rich in less active saturates.

If the process be applied to the fractionation of free fatty acids of varying chain length such as obtained by the saponification of coconut oil or palm oil, it is found that the acids of relatively short chain length are preferentially dissolved in the selective polar solvent while the acids of longer chain length tend to remain in solution in the petroleum hydrocarbon. The liquid phases thus obtained may be separated from each other by simply allowing them to settle for a sufficient period of time and then drawing them off into separate containers. It is also possible to make a separation by centrifugation in conventional apparatus. After the separation of the mixture, the solvents may be eliminated by evaporation, crystallization, or other suitable methods.

It will be apparent that the process is applicable to batch operation in which the free fatty

acid mixture is simply agitated with the selective polar solvent and the immiscible hydrocarbon in a suitable container until a satisfactory degree of equilibrium is reached. The phases may be allowed to settle out and are then separated as above described.

Countercurrent flow extraction as subsequently described may be employed. Various other processes involving modifications and combinations of these two processes may, also, be employed in contacting the free acids and the solvents.

The following constitute specific examples of polar solvents which may be combined in various ratios, for example 1 to 1 ratio with an immiscible petroleum hydrocarbon, such as isooctane or the like and applied to the liquid phase extraction of the free acids herein enumerated or to similar free acids:

Table A

Hydroxyl	Ester—Double Bond—Ether
Methyl alcohol	Methyl furoate
Ethylene glycol	Furfuryl acetate
Propylene glycol	
Glycerine	Ester, Halogen
Hydroxyl, Ester	Methyl chloroacetate
beta-Hydroxy ethyl acetate	beta-Chloroethyl acetate
Methyl lactate	Acetoethylhydrin
Ethyl lactate	
Diacetin	Ester, Cyanide
Hydroxyl, Carbonyl	Methyl cyanoacetate
Methyl butanolone	Amino (or Imino)
Acetyl methyl carbinol	Diethylene triamine
Hydroxyl, Ether	Triethylene tetramine
Methyl Cellosolve (b-methoxy ethanol)	Amino (or Imino), Double Bonds
Diethylene glycol	Aniline
Triethylene glycol	Toluidine
Carbitol	Nitrile
2-Hydroxy methyl-1, 3-dioxolane	Propionitrile
Carboxyl	Sulfate
Formic acid	Dimethyl sulfate
Acetic acid	Aldehyde
Hydroxyl, Double Bonds	Methoxy acetaldehyde
Phenol	Furfural
Benzyl alcohol	Cinnamaldehyde
Hydroxyl, Triple Bonds	Benzaldehyde
Dimethyl ethynyl carbinol	m-Nitrobenzaldehyde
Hydroxyl, Halogen	Carbonyl
Ethylene chlorhydrin	Acetonyl acetone
Propylene chlorhydrin	Carbonyl, Ether, Double Bonds
beta, gamma-dibromo propyl alcohol	Furfural acetone
Hydroxyl, Other	Carbonyl, Double Bonds
beta-Hydroxy propionitrile	Benzal acetone
beta-Ethoxy ethyl lactate	Carbonyl, Amide
beta-Ethoxy ethyl glycolate	Formamide
Furfuryl alcohol	Acetamide
Eugenol	Carbonyl, Chloro
Salicylaldehyde (aldehyde, double bond)	1-chlor butanone-2
2-Nitro-1-butanol	Ether
2-Nitro-2-methyl-3-hexanol	Dimethoxy tetraglycol
Acid Anhydride	Ether, Chloro
Acetic	beta, beta'-Dichloro diethyl ether
Ester	Chloroethoxy chlorethyl ether
Ethylene glycol diformate	Ether, Imino
Triacetin	Morpholine
Glycol diacetate	Ether, Nitro
Ethyl acetyl glycolate	o-Nitro anisole
Ethylidene diacetate	o-Nitro phenotole
Methyl malonate	Ether, carbonate
Ethyl oxalate	beta-Methoxy ethyl carbonate
Methyl oxalate	Nitro
Ester, Carbonyl	Nitromethane
Methyl levullinate	Nitrobenzene
Ethyl levullinate	Thiocyanate
Methyl acetoacetate	Methyl thiocyanate
Ethyl acetoacetate	Phosphate
Ester, Ether	Trimethyl phosphate
Methyl Cellosolve formate	Triethyl phosphate
Methyl Cellosolve adipate	
Dimethyl Cellosolve succinate	
Ester, Imido	
Ethyl n-methyl carbamate	
Ester, double bond	
Ethyl maleate	

The ratio of active or polar solvent to hydrocarbon may vary over a range of from about 4 to 1 up to 10 or more of the latter to one of the former. The immiscible mixtures of selective polar solvent and hydrocarbon may be applied to the free fatty acids in varying ratios. For example, in ratios from 1 to 1 up to a ratio of 10 or 12 parts of the solvent mixture to 1 part of acid. In general it is possible by increasing the temperature to obtain complete miscibility of almost any of the systems herein disclosed. Conversely, they can be cooled to effect splitting into liquid phases, which can be separated from each other. The miscibility temperature for different systems will vary, but can easily be determined for a given system by cooling a miscible system until a cloud appears. The division or removal of the fractions, preferably is effected at a temperature somewhat below that of complete miscibility, but above that which the components tend to separate by crystallization. In general the division should be effected within a range of about 2 to 40° C. below that of complete miscibility of the system. As the system of acids and solvents approach the temperatures of complete miscibility, it will be apparent that the components go more and more into solution in each other, but so long as the phases separate it is possible to effect some degree of fractionation. The degree of fractionation desired in any particular mixture of acids will depend upon the characteristics desired in the fractions. In some cases a small degree of fractionation is sufficient. In other cases relatively marked differences between one or more components and the original acid mixture may be desired. Such separation can be attained by appropriate reduction of the temperature of the system. Such reduction, of course, is attended by corresponding reduction of the yield of the desired component.

In my compending applications above referred to the addition of water to the selective solvent in order to reduce miscibility at low temperatures of the relatively saturated or long chain component of a glyceride oil mixture is referred to. The same principles may be applied to the extraction of the free fatty acids derived from the oil. Manifestly this principle is of particular applicability to the fractionation of glyceride oil acids with a solvent which possesses a substantial degree of solubility with water. Examples of such water soluble polar solvents are furfural and the various alcohols including methyl, ethyl alcohol, ethylene glycol, propylene glycol and glycerin. To these water may be added in varying amounts, for example, of from 1 to 15 per cent. In general the addition of water tends substantially to increase the temperature at which the glyceride oil acids and the polar solvent become completely miscible in each other. In some cases this is of advantage because it permits the operation of the system at a temperature substantially above that of the atmosphere. This is sometimes desirable because it obviates cooling of the system in order to obtain separation of the liquid phases, and also because it is easier to maintain substantially constant working conditions at an elevated temperature than at a low temperature.

It is also possible to admix two or more of the selective polar solvents with each other and to admix non-selective polar solvents at least in limited amounts with the system.

The following constitutes specific examples of

the application of the principles of the invention to acid mixtures:

	Parts by volume
Linseed oil acids.....	200
Petroleum ether B. P. 30-60° C.).....	200
Anhydrous furfural.....	400

These were agitated together at room temperature and allowed to separate into layers. The solvents were then distilled off from the two fractions separately under vacuum

Iodine value of original acid.....	173
Iodine value of acid in hydrocarbon.....	166
Iodine value of acid in furfural.....	193

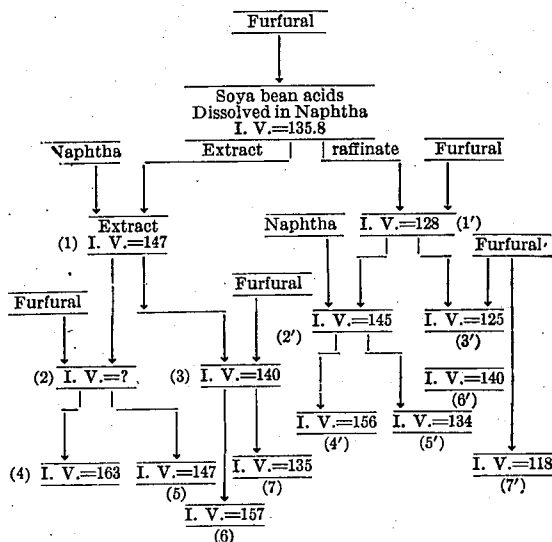
A 30 per cent mixture of linseed oil fatty acids in the same hydrocarbon was agitated with 1 volume of furfuryl alcohol and separated into fractions at room temperature.

Iodine value of original acid.....	173
Iodine value of acid in hydrocarbon.....	162
Iodine value of acid in solvent.....	203

Ethylene glycol diacetate was agitated at room temperature with a 12 per cent by volume mixture of linseed oil fatty acids in petroleum ether, and the mixture was separated into fractions from which the solvents were eliminated.

Iodine value of original acids.....	173
Iodine value of acids in hydrocarbon.....	168
Iodine value of acids in solvent.....	175

Free fatty acids may be subjected to repeated stages of extraction with the hydrocarbon in order to remove additional amounts of the less active constituents therefrom. In the case of mixtures containing unsaturated acids it is possible by application of a relatively few stages of washing the hydrocarbon to obtain the substantially pure acid. The following flow diagram illustrates the treatment of free fatty acids with a mixture of furfural in a series of stages:



water it is possible to increase the temperature of treatment several degrees. The solvents, when left to stand, separated into liquid layers that could be drawn off into separate containers. The solvents were then eliminated by vacuum distillation. The raffinate fraction (that dissolved in the naphtha) had a substantially higher melting point than the original oil or that extracted by the furfural. Conversely the melting point of the extract from the furfural was substantially lower than that of the original oil. Apparently separation had been upon the basis of chain length.

In the case of more highly unsaturated glyceride oils, such as tung oil, linseed oil, fish oil, soya bean oil, cotton-seed and others herein enumerated, the more unsaturated or actively unsaturated components are extracted preferentially by the polar solvents listed, while the more saturated components prefer the hydrocarbon phase.

What I claim is:

1. A process of extracting a relatively active fraction from a mixture of free fatty acids comprising such active fatty acid in admixture with less active fatty acid, which process comprises contacting the mixture with a two phase solvent system comprising a relatively non-polar hydrocarbon solvent and an active polar solvent immiscible therewith, separating the immiscible solvents and eliminating them from the fatty acids dissolved therein.

2. A process of extracting a relatively active fraction from a mixture of free fatty acids comprising such active fatty acid in admixture with less active fatty acid, which process comprises contacting the mixture with a two phase solvent system comprising a relatively non-polar hydrocarbon solvent and an active polar solvent immiscible therewith, the free fatty acids being passed in at an intermediate point in the length of a column, polar solvent being passed in above the inlet for free acids and non-polar solvent being passed in at a point below the inlet for free acids, the immiscible solvents carrying respective components dissolved therein, being withdrawn at opposite ends of the column.

3. A process of extracting a relatively active fraction from a mixture of free fatty acids comprising such active fatty acid in admixture with less active fatty acid, which process comprises contacting the mixture with a two phase solvent system comprising a relatively non-polar hydrocarbon solvent and an active polar solvent immiscible therewith, in which the polar solvent is a compound from Table A, separating the solvents and eliminating them from the free acids contained therein.

4. A process as defined in claim 3 in which the non-polar solvent is a paraffinic hydrocarbon.

5. A process as defined in claim 3 in which the hydrocarbon is isooctane.

6. A process as defined in claim 1 in which the polar solvent is furfural and the non-polar solvent is a paraffinic hydrocarbon.

7. A process as defined in claim 1 in which the non-polar solvent is iso-octane.

8. A process of extracting a relatively active fraction from a mixture of free fatty acids comprising such active fatty acid in admixture with less active fatty acid, which process comprises contacting the mixture with a two phase solvent system comprising a relatively non-polar hydrocarbon solvent and an active polar solvent immiscible therewith, said polar solvent containing a substantial amount of water, separating the solvents and freeing them from the free acids dissolved therein.

9. A process as defined in claim 3 in which the acids are those from oils of a class consisting of marine oil, soya bean oil, linseed oil, perilla oil, tung oil, cottonseed oil, coconut oil, lard, tallow and tall oil.

10. A process as defined in claim 1 in which the polar solvent is wet furfural and the hydrocarbon is isooctane.

11. A process as defined in claim 1 in which the free acids treated are those from an oil of a class consisting of linseed oil, tung oil, coconut oil, soya bean oil, cottonseed oil, perilla oil, lard, tallow and tall oil, the solvent is wet furfural and the hydrocarbon is isooctane.

STEPHEN E. FREEMAN.