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EXTRACTION OF PHOSPHATIDES, FREE FATTY ACIDS, AND THE LIKE FROM GLYCERIDE OILS

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The present invention relates to removal of certain materials, notably such materials as lecithin-like phosphatides, free fatty acids and similar constituents from glyceride oils.

One object of the invention is to provide a process of simultaneously removing gum-forming or "break" forming constituents and free fatty acids from a glyceride oil and notably of vegetable oils, which process is relatively simple and inexpensive in its nature.

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

In my copending Patents 2,200,391 and 2,200,390, having the issue date of May 14, 1940, are disclosed processes of extracting glyceride oils and notably such oils as comprises a mixture of relatively highly unsaturated and more completely saturated glycerides into fractions, upon the basis of the degree of saturation or unsaturation. Such fractionation may be effected by numerous polar solvents of which furfural is a typical example. In these extractions the polar solvent and the oil are simply intimately contacted by batch or countercurrent process, or by a suitable countercurrent batch operation.

The oils in addition to comprising mixtures of relatively saturated and unsaturated glycerides also include in some cases lecithin-like phosphatides, which are of considerable value for various pharmaceutical and industrial purposes. The oils also include certain percentages of free fatty acids which are applicable to numerous purposes, for example as constituents in artificial resins or as stock for the manufacture of soaps.

The phosphatide material in some cases is objectionable in the fractionation of the glyceride oils, because upon contact with a solvent such as furfural it tends to precipitate out to form a sludge which collects at the inter face between the solvent and the oil body. This sludge may tend to clog the extraction apparatus and for that reason it is desirable preliminarily to remove it before the oil is subjected to fractionation. The phosphatides may be removed from the oil by washing with water or with an aqueous solution of water and alkaline salt, such as sodium carbonate. However, such process is not effective to remove the free fatty acids also contained in the oil.

According to provisions of the present invention it is proposed simultaneously to remove free fatty acids and sludge-forming constituents such as lecithin and the like from glyceride oils by subjecting the latter to intimate contact with a solution of or an intimate mixture of a selective polar solvent, such as furfural and an aqueous medium such as water. The oils preferably are of vegetable origin and raw soya bean oil or linseed are particularly good examples of oils which are benefited by such treatment. The selective polar solvent may be simply saturated or partially saturated with the aqueous medium or an excess of the aqueous medium may be employed and in part maintained as a separate liquid phase during the extraction. The oils and the extraction medium may be contacted by countercurrent flow in a suitable column or by simple agitation together, followed by subsequent settling or centrifugation. Various polar solvents may be employed in the operation, but the following are considered to be particularly advantageous because they possess a considerable degree of solubility with respect to water:

Table A

Hydroxyl

Methyl alcohol
Ethyl alcohol
n-Propyl alcohol
Iso-propyl alcohol
Ethylene glycol
Propylene glycol
Glycerine
Tertiary butyl alcohol
Dimethyl ethynyl carbinol

Hydroxyl—Other

Allyl alcohol
Ethylene chlorhydrin
Glycerol monochlorhydrin
Beta,gamma-dibromo propyl alcohol
Beta-hydroxy propionitrile
Beta-ethoxy ethyl lactate
Beta-ethoxy ethyl glycolate
Furfural alcohol
2-nitro-1-butanol
Diethyl ammo ethanol
Propylene chlorhydrin

Hydroxyl—Ester

Methyl glycolate
Ethyl glycolate
Beta-hydroxy ethyl acetate
Ethyl lactate
Mono acetin
Diacetin

Hydroxyl—Carbonyl

Methyl butanolone
Acetyl methyl carbinol
Diacetone alcohol
Methyl acetyl lactate

Hydroxyl ether

Methyl Cellosolve
Cellosolve
Diethylene glycol
Triethylene glycol
Carbitol
2-hydroxy-methyl-1,3-dioxolane
Butyl carbitol
Butyl Cellosolve

Ether

Dioxane
Dioxolane
Dimethyl Cellosolve
Dimethoxy tetraglycol

Acid

Formic acid
Acetic acid
Propionic acid
Isobutyric acid

Ester

Methyl formate
Ethylene glycol diformate
Triacetin
Glycol diacetate
Methyl malonate
Methyl oxalate
Ethyl oxalate

Ester—Other

Methyl Cellosolve formate
Methyl Cellosolve acetate
Methyl Cellosolve adipate
Dimethyl Cellosolve succinate
Ethyl n-methyl carbamate
Methyl chloroacetate
Methyl cyanoacetate

Ester—Carbonyl

Methyl levulinate
Ethyl levulinate
Methyl acetoacetate
Ethyl acetoacetate
Isopropyl acetoacetate

Aldehyde

Acetaldehyde

Aldehyde—Other

Methoxy acetaldehyde
Furfural
m-Nitrobenzaldehyde

Ketone

Acetonyl acetone
Acetone

Amine

Diethylene tetramine
Triethylene tetramine
Pipyridene
Pyridene

Nitrile

Propionitrile

Esters of inorganic acids

Trimethyl phosphate
Triethyl phosphate
Beta-methoxy ethyl carbonate
Dimethyl sulfate

Amides

Formamide
Acetamide
Propionamide
Butyramide

Nitro

Nitromethane
Nitroethane

Various ratios of solvent to oil may be employed in the extraction, but a ratio of about 1 to 1 seems to be satisfactory, but this ratio may be substantially increased or decreased if so desired. The temperature of extraction preferably is substantially below that of miscibility of the glycerides in the oil being extracted. But little difficulty will be encountered in maintaining sufficiently low temperature because in the presencee of water solubility of the oils in the solvents is very limited, except at fairly elevated temperatures. Most of the extractions can be effected quite conveniently at or near normal atmospheric temperatures. Degumming of soya bean oil with aqueous furfural may be effected at 80 or 90° F. The aqueous medium may be water alone or an aqueous solution of an alkaline salt, such as sodium carbonate or a 25% solution of sodium phosphate. Contact of the oil with aqueous solvent results in precipitation of the lecithin sludge in the oil from which it can be removed by centrifugation or filtering. The free fatty acids are carried away by the solvent phase and may be freed of solvent by vacuum distillation.

It will be apparent that the process involves essentially a thorough washing of a body oil with aqueous solvent in contradistinction to separation of dissolved solvent from oil by addition of an aqueous medium. The amount of water may be relatively low, e. g., 2 or 3% by volume of the polar solvent, or it may be equal to or even exceed the total volume of the latter. Where large volumes of water are employed with furfural, only a limited amount will dissolve, the remainder will be maintained as a third phase in the system.

The extracted oil can be employed for various purposes, but it is particularly suitable for further extraction by the processes disclosed in my foregoing patents for purposes of fractionating it upon the basis of unsaturation.

The acids as previously indicated can be used for various purposes including the manufacture of soap and the manufacture of modified resins. Lecithin is useful for addition to food products, as emulsifying agent and for numerous other purposes.

What I claim is:

1. The process of obtaining a fraction rich in phosphatides and a fraction rich in free fatty acids from glyceride oils, which process comprises intimately contacting the oil with furfural approximately saturated with water to obtain a plurality of liquid phases, one consisting of furfural and water containing the free fatty acids and the other consisting primarily of oil with the phosphatides precipitated as a suspension therein, then separating off the phases and separating the phosphatides from the oil.

2. A process as defined in claim 1, in which the glyceride oil undergoing treatment is soya bean oil.

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