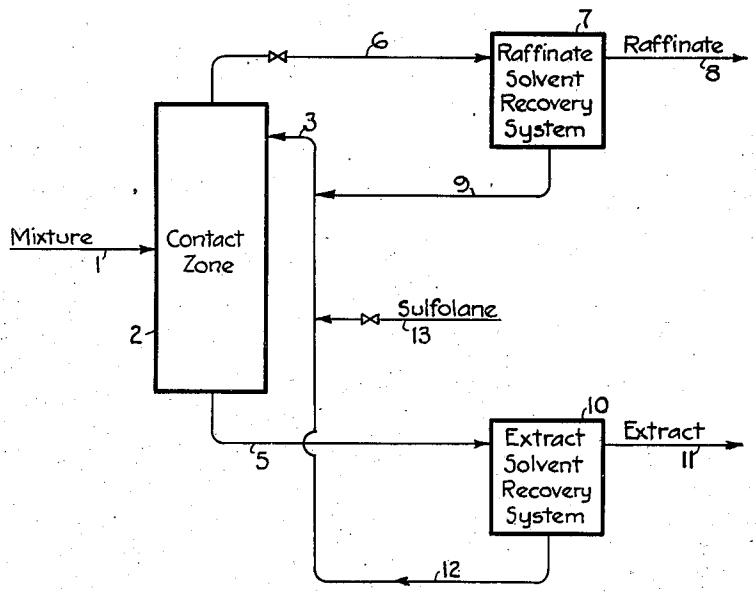
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SOLVENT EXTRACTION PROCESS

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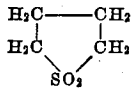
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11 Claims. (Cl. 260—428.5)

This invention relates to a process for separating mixtures of fatty acids or fatty acid esters by extraction with selective solvents comprising a sulfolane.

The compound sulfolane has the formula:



Its derivatives are compounds wherein one or more of the hydrogen atoms is replaced by an organic radical which may contain a polar grouping and more specifically may contain oxygen, nitrogen, sulfur and/or halide atoms. In hydrocarbon-substituted sulfolanes the hydrocarbon radicals are preferably alkyl radicals. Sulfolane derivatives containing oxygen include hydroxy sulfolanes, sulfolanyl ethers, and esters; sulfolane derivatives containing nitrogen include sulfolanyl amines, nitriles and nitro sulfolanes; sulfolane derivatives containing sulfur include sulfolanyl sulfides, sulfoxides and sulfones. Other sulfolane derivatives may contain halide radicals, inorganic ester or mixed radicals of those above mentioned, such as acid amides, halohydrins, sulfonamides, etc. Derivatives may be made by condensing a conjugated diolefin with sulfur dioxide, and then subjecting the resultant product to hydrogenation, alkylation, hydration, amination, chlorination, nitration and/or other substitution or addition reactions.

It is a purpose of this invention to separate mixtures of fatty acids and fatty acid esters into various fractions economically, efficiently and effectively by solvent extraction. Some specific purposes, among others, are to produce various fractions of fatty acids and fatty acid esters, particularly suitable for use in paints, synthetic resins, food products, plastics, soaps, etc.; to produce pure fatty acids and fatty acid esters; to separate mixtures of fatty acids and fatty acid esters of different degrees or types of unsaturation into fractions containing a higher ratio of the more unsaturated or more actively unsaturated components than the original mixture; and to provide a method of extracting fatty oils from pulps or meals containing them and leaving most of the phosphatides in a readily removable form in the meal.

Generally, the process of this invention comprises the steps of (A) contacting the mixture to be separated in the liquid state with a liquid selective solvent to produce a raffinate phase and an extract phase, (B) separating the two phases from each other, and (C) removing the solvent from at least one of said phases to produce a raffinate and/or an extract and, usually, also recovering the solvent removed for further contact with more of said mixture. These steps, common to all solvent extraction processes, may be carried out in any suitable manner known to those skilled in the art.

The accompanying drawing is a general flow diagram of a solvent extraction process.

A mixture to be separated is introduced in the liquid state through feed line 1 into contact zone 2 and admixed with a suitable sulfolane introduced into the same zone through a separate line 3. This is the first step (A) in all solvent extraction processes. Suitable equipment for carrying it out may comprise either an impinging jet mixer, an agitation vessel, a baffle plate column, or a packed tower.

In the contacting zone the mixture and sulolane are caused to produce a raffinate phase and an extract phase which are separately withdrawn respectively through lines 6 and 5. If separation of phases has not occurred under the conditions employed, cooling or injection of a demixing agent, etc., may have to be employed. This is the second step (B) of all solvent extraction processes, namely the separation of two phases produced in the contacting zone, and may be effected by settling, decantation, or centrifuging.

The third step (C) common to all solvent extraction processes comprises the recovery of sulfolane from one or both phases. The raffinate phase is passed through line 6 into the raffinate solvent recovery system 7 to produce a solvent-free raffinate, which is withdrawn through line 8, and recovered sulfolane which is withdrawn through line 9 and is preferably returned through line 3 to contact zone 2. This recovery system may comprise a crystallization chamber, distillation column, or washing column. If the sulfolane is washed from the raffinate phase an additional step for its recovery is necessary, such as distillation, to separate the sulfolane from the wash solvent.

The extract phase is introduced into a solvent recovery system 10, which is similar to recovery system 7. From recovery system 10 a solvent-free extract is withdrawn through line 11 and the recovered sulfolane is withdrawn through line 12 and returned through line 3 to contact zone 2 for recontact with more of the mixture. Fresh sulfolane may be added to the system from time to time through line 13 as required.

The extraction temperature generally may range within wide limits, provided it is above the

melting temperature of the solvent and below the boiling temperature of both the mixture and the solvent. The temperature for contacting the solvent mixture may be such that both the solvent and the mixture are completely miscible with each other and then the temperature may be lowered until phase separation takes place, or the contact may be entirely carried out below the temperature of complete miscibility of the sulfolane and the mixture. The extraction temperature may range between about —50° C. and about +300° C.

The ratio of solvent to the feed mixture must be such that two phases will form. If the ratio is too high, all of the mixture may dissolve in the solvent; if it is too low, the solvent may dissolve in the mixture. Useful solvent-to-feed ratios may range from about ½ to 20 by volume.

Some specific examples of substances which may contain mixtures of fatty acids and/or fatty acid esters include free fatty acids, fats, natural waxes, essential oils, and mixtures thereof. The fatty acids may be derived by hydrolysis of the various fats listed below and may be saturated or unsaturated. Some specific examples of these fatty acids include capric, undecylic, undecylenic, lauric, sabinic, myristic, palmitic, palmitolinic, margaric, stearic, oleic, iso-oleic, linolenic, linoleic, stearoleic, ricinoleic, arachatic, behenic, brassidic, erucic, montanic, mellissic, psyllic, pysllostearic, etc.

The fats may be normally liquid or normally solid, drying, semi-drying, or non-drying, and animal or vegetable. Some specific examples of these fats are candlenut, hempseed, linseed, poppyseed, sunflower, tung, walnut, soya bean, beechnut, corn, cottonseed, pumpkin seed, rapeseed, mustard seed, almond, olive, peanut, hazelnut, and castor oils, palm oils, myristica oils, cocoanut butters, cocoanut oils, fish oils, liver oils, blubber oils, lard oil, sheep's-foot oil, neat's-foot oil, animal fats, beef and mutton tallow, horse and beef marrow, butter, etc.

The waxes may be animal or vegetable in origin and may be normally liquid or normally solid, and saturated or unsaturated. Such waxes include sperm oil, jojoba oil, carnauba wax, montan wax, candelilla wax, cottonseed wax, palm wax, beeswax, insect wax, wool grease, psylla wax, etc.

Some essential oils comprising aliphatic esters are chamomile oil, geranium oil, heracleum oil, rose oil and fruit essences from such fruits as mirabelles, raspberries, peaches, red currants, apples, pears, strawberries, pineapples, bananas, quinces, etc.

The sulfolanes of this invention may be employed as selective solvents by themselves singly or as mixtures of two or more, or as aqueous solutions, or together with auxiliary selective solvents or antisolvents, provided the additives to the sulfolane do not react with it and are stable under the temperature conditions of the process.

The sulfolane should not crystallize out of solution at the highest concentration which may occur at any point in the process and at a temperature above about 150° C. It is desirable that it melt at a temperature not greater than 150° C. and preferably below 100° C., and it is further desirable that it be not more than 50% soluble at room temperature in kerosene having a Watson characterization factor of at least 12 (see Industrial and Engineering Chemistry, vol. 27, page 1460, December 1935, "Characterizations of petroleum fractions," by K. M. Watson, E. F. Nelson, and George B. Murphy). Higher solubility in such a kerosene frequently is an indication of poor selectivity.

Some suitable specific sulfolanes are: sulfolane, hydrocarbon-substituted sulfolanes such as alkyl sulfolanes preferably containing not more than about 14 carbon atoms; hydroxy sulfolanes such as 3-sulfolanol, 2-sufolanol, 3-methyl-4-sulfolanol, 3,4-sulfolanediol, etc.; sulfolanyl ethers such as methyl-3-, propyl-3-, allyl-3-, butyl-3-, crotyl-3-, isobutyl-3-, etc.; methallyl-3-, methyl vinyl carbinyl-3-, amyl-3, hexyl-3-, octyl-3-, nonyl-3-, glycerol alpha-gama-diallyl-beta-3-, tetrahydrofurfuryl-3-, 3,3,5 - tetramethylcyclohexyl-3-, m-cresyl-3-sulfolanyl ethers, corresponding 2-sulfolanyl ethers; disulfolanyl ethers, etc.; sulfolanyl esters such as 3-sulfolanyl acetate, 3-sulfolanyl propionate, -butyrate, -caproate, etc.; N-sulfolanes such as 3-sulfolanylamine, N-methyl, N-ethyl, N-N-dimethyl, N-allyl, N-butyl, N-octyl-3-sulfolanylamines, etc.; sulfolanyl sulfides such as ethyl-3-, tertiary butyl-3-, isobutyl-3-, methallyl-3-sulfolanyl sulfides, di-3-sulfolanyl sulfide, etc.; sulfolanyl sulfones such as methyl-3-, ethyl-3-, propyl-3-, amyl-3-sulfolanyl sulfones; sulfolanyl halides such as 3-chloro-, 3,4-dichloro-, 3-chloro-4-methyl sulfolanes, etc.; and mixed sulfolanes such as 4-chloro-3-sulfolanol, 4-chloro-3-sulfolanol acetate, 3-sulfolanyl amine hydrochloride, N(3-sulfolanyl) acetamide, etc.

Of the sulfolanes useful in this invention, some are more heat-stable than others; thus, in particular, the halogen, amine, acid, some aldehyde, and some ester derivatives are relatively heat-unstable. Some may begin to decompose at temperatures as low as 150° C. Other sulfolanes, on the other hand, are extremely heat-stable even at temperatures as high as 300° C.

Some commonly known solvents, selective solvents, and/or modifying agents which may be employed in conjunction with the sulfolanes include water, various mono- and poly-hydric alcohols such as methanol, ethanol, propanol, furfuryl alcohol, benzyl alcohol, glycols, glycerols, etc.; various ketones such as acetone, methyl ethyl ketone, diethyl ketone, cyclopentanone, benzophenone, phenyl tolyl ketone, diphenylene ketone, etc.; various aldehydes such as crotonaldehyde, acrolein, furfural, etc.; ethers such as ethylene glycol and diethylene glycol mono-alkyl ethers, mono- and diglycerol ethers, glycerol diethers, chlorinated dialkyl ethers (e. g. beta-beta-dichlorethyl ether), dioxane, etc.; lower aliphatic acids such as formic, acetic, propionic acids, acetic anhydride, etc.; esters such as benzoic, phthalic acid esters, etc.; phenol, cresylic acids, alkyl phenol mixtures, naphthols, alkyl naphthols, etc.; liquid ammonia, various organic amines such as lower aliphatic primary amines having one to eight carbon atoms, aniline, alkyl anilines, morpholine, diphenyl amine, ditolylamine, etc.; various nitriles such as acetonitrile, propionitrile, lactonitrile, butyronitrile, benzonitrile, etc.; various nitro hydrocarbons such as nitromethane, nitroethane, nitrobenzene, nitrotoluene, nitroxylenes, etc.; various pyridines and quinolines; liquid sulfur dioxide; various modifying salts such as those disclosed in U. S. Patent 2,246,257 to Kohn; and the like.

The sulfolane or mixture of sulfolane with auxiliary solvent must be at least partially and not more than partially miscible with the feed mixture to be separated under the conditions of the process.

Furthermore, antisolvents may be employed together with the sulfolanes such as are employed

in the DuoSol process for the countercurrent extraction of lubricating oils. Some such antisolvents include propane, butane, pentane, n-hexane, iso-octane, paraffinic gasoline, kerosene, gas oil, lubricating oil, various ethers, trichlorethylene, carbon tetrachloride, etc. Still further, compounds of two or more solvents together with one or more antisolvents may also be employed.

The amount of auxiliary or antisolvents which may be employed in conjunction with the sulfolanes to make up the solvent may range up to 90% by volume, preferably less than 50% by volume, of the solvent.

Example I

A sample of a mixture of fatty acids containing stearic, oleic and linoleic acids obtained from animal fats and having an iodine number of 52.2 (determined by the Wijs method—see "Methods of Analysis of the Association of Official Agricultural Chemistry," 4th ed., 1935, page 412), was contacted with unsubstituted fulfolane in the ratio of one part of the mixture to two parts of sulfolane. The mixture was warmed to approximately 80° C. at which temperature the mixture became one liquid phase. After mixing thoroughly the mixture was allowed to cool to about 75° C., at which temperature two phases were formed, which were separated and the sulfolane was removed by washing each phase with water. 50% of the original acid mixture was contained in each phase. The iodine numbers of the extract and raffinate phases were determined to be 56.9 and 50.8 respectively, resulting in a difference of 6.1. This method of evaluating selective solvents for separating glyceride oils is described in the Freeman U. S. Patent 2,200,391.

Example II

A sample of a mixture of fatty acids containing a mixture of oleic and linoleic acids derived from animal fat and having an iodine number of 131.1 was contacted with unsubstituted sulfolane in a ratio of one part fatty acid to one part sulfolane. The mixture was warmed to produce one liquid phase, thoroughly mixed, and then cooled to about 30° C., at which temperature two phases were formed. These phases were then separated and the sulfolane was removed from each phase by washing with water. 20% of the original fatty acids was present in the extract phase and the extract and raffinate phases were separately tested to have an iodine number of 142.3 and 125.7 respectively, resulting in a difference in iodine number of 16.6.

Example III

A mixture consisting of 22 gms. of fatty acids containing oleic and linoleic acids obtained from animal fats and having an iodine number of 131.2, 50 gms. dimethyl sulfolane and 50 gms. of octanes, was warmed to a temperature of about 80° C. to produce a single liquid phase. The liquid was then allowed to cool to about 25° C. at which temperature two phases were formed. The upper hydrocarbon phase was separated from the lower sulfolane phase and both were washed with hot water to remove the sulfolane, and then vacuum distilled to remove the octanes. About 50% of the original acids was contained in each phase. The extract and raffinate phases were tested to have iodine numbers of 138.4 and 125.4 respectively, resulting in a difference in iodine number of 13.0.

We claim as our invention:

1. In a solvent extraction process for the separation of a liquid mixture of compounds selected from the group consisting of fatty acids and fatty acid esters, the steps comprising contacting said mixture with a sulfolane which is liquid and stable at the temperature of contacting to produce an extract phase and a raffinate phase, and separating said phases.

2. The process of claim 1 wherein the mixture is an essential oil.

3. The process of claim 1 wherein the mixture is a fat.

4. The process of claim 1 wherein the mixture consists essentially of fats of different degrees of saturation.

5. The process of claim 1 wherein the mixture is a natural wax.

6. The process of claim 1 wherein the melting temperature of the sulfolane is below about 150° C.

7. The process of claim 1 wherein the sulfolane at room temperature is less than 50% by weight soluble in kerosene having a Watson characterization factor of at least 12.

8. In a solvent extraction process for separating a mixture of compounds selected from the group consisting of fatty acids and fatty acid esters, the steps comprising contacting said mixture with a sulfolane which is liquid and stable at the temperature of contacting to produce an extract phase and a raffinate phase, separating said phases, recovering said sulfolane and returning the recovered sulfolane for further contact with more of said mixture.

9. In a solvent extraction process for separating a mixture of compounds selected from the group consisting of fatty acids and fatty acid esters, the steps comprising contacting said mixture with a selective solvent to produce two phases, and separating said phases, said selective solvent comprising not less than 10% by volume of a sulfolane which is liquid and stable at the temperature of contacting.

10. The process of claim 9 wherein the solvent comprises more than 50% by volume of said sulfolane.

11. The process of claim 9 wherein the solvent-to-mixture ratio ranges between ½ and 20 by volume.

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