

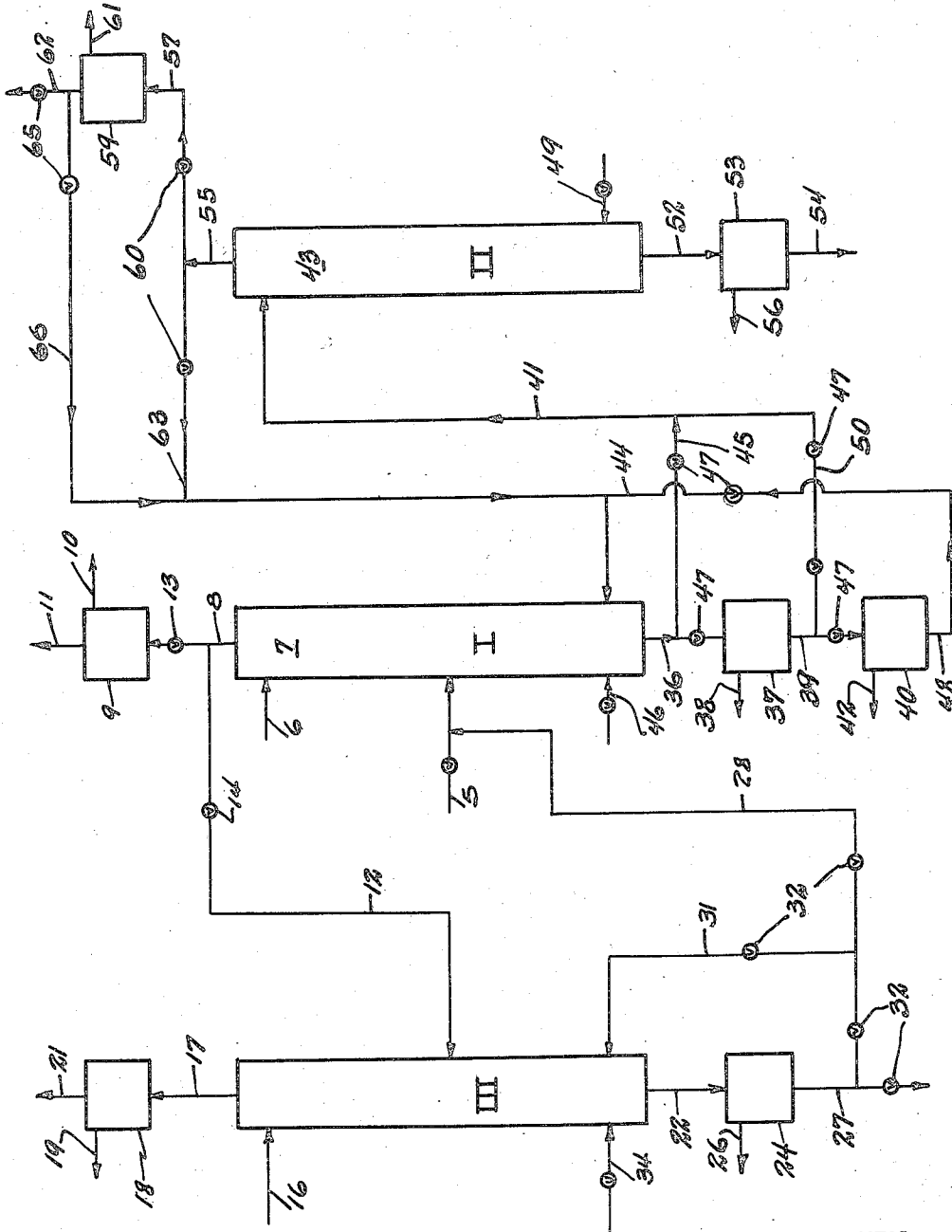
Nov. 6, 1951

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2,573,902

SOLVENT CONCENTRATION OF VITAMINS

Filed July 9, 1949



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UNITED STATES PATENT OFFICE

2,573,902

SOLVENT CONCENTRATION OF VITAMINS

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Application July 9, 1949, Serial No. 103,880

14 Claims. (Cl. 167—81)

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The present invention relates to a process of fractionating natural glyceride oils and it has particular relation to a process of fractionating glyceride oils containing such vitamins as A and D.

One object of the invention is so to treat a glyceride oil containing vitamins A and D as to effect separation of the oil into a plurality of fractions, one of which is greatly enriched in vitamins.

A second object of the invention is to provide a process of the foregoing type, the application of which does not result in a substantial loss of the vitamins in the oil.

A third object is to provide a process of obtaining vitamin concentrates which is simple and relatively inexpensive to operate.

A fourth object is to provide a process of obtaining vitamin concentrates of substantially better odor and taste than the original oil.

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

It has heretofore been proposed to fractionate a natural glyceride oil consisting of a complex mixture of saturated and unsaturated glycerides upon the basis of unsaturation by use of a selective polar solvent such as furfural or ethyl acetate. These solvents are found to have a selective affinity for the more unsaturated glycerides and by selection of an appropriate temperature of operation it is possible by their application to the oil to dissolve out the more unsaturated components as an extract, leaving the saturated components as an undissolved raffinate. The unsaturates are then recovered by evaporating off the solvent. Processes of this type are disclosed in Patents Nos. 2,200,390 and 2,200,391 to Stephen E. Freeman.

Many natural glyceride oils and notably the fish liver oils contain vitamins such as A and D. These oils are usually objectionable in odor and taste so that the modern tendency is to administer them in capsules or pills. However, the concentration of the vitamins in most of the oils is low, making it necessary to resort to certain premium oils of high vitamin content for capsules or tablets or else compelling the user to take excessive quantities of the capsules in order to obtain the necessary vitamins. In order to obviate these objections, it has been proposed to distill off concentrates of vitamins from the vitamin containing oils, by application of high vacuum processes. However, the processes are expensive and it would appear that there is loss of vitamins in these

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operations. For these reasons vitamin pills of high potency have always remained expensive.

In Tischer Patent No. 2,090,738 it is proposed to treat natural glyceride oils such as cod liver oil or the like with furfural in order to dissolve out certain odor or taste constituents without substantially affecting the vitamin content of the oil.

The present invention is based upon the discovery that natural glyceride oils containing such vitamins as A and D and notably fish liver oils can be treated at moderate expense with selective polar solvents such as furfural or others of the type disclosed in Freeman Patent No. 2,200,391 to obtain a relatively small extract fraction which is highly enriched in vitamin A and also vitamin D, if it is present, while leaving a relatively large raffinate fraction which is substantially impoverished in these vitamins.

This extract solution in addition to containing a concentrate of vitamins A and D also contains the more unsaturated glycerides, free fatty acids and certain taste and odor constituents. It has been found that if this extract solution is washed with naphtha, the major portion of the vitamins A and D as well as the glyceride oil is extracted away from the polar solvent by the naphtha, leaving a fraction impoverished in vitamins and comprising the major portion of the free fatty acids and certain taste and odor constituents in the polar solvent. The removal of the free fatty acids from the extract solution, therefore, increases the concentration of vitamins in the naphtha extract fraction. The taste and odor of the naphtha extracted fraction after the removal of the solvent is considerably better than the original oil. Natural antioxidants such as tocopherol and the like are also concentrated in the extract fraction in the primary extraction with polar solvent. It has been found that upon washing this polar solvent extract solution with naphtha, that the natural antioxidants concentrate in the naphtha extract or vitamin concentrate fraction. By application of the invention, it is thus possible to obtain vitamin concentrates suitable for use in capsules and tablets or for other purposes in which a high concentration of vitamins is desirable and at the same time obtain fractions of oil of enhanced value, as well as by-products adapted for use as sources and intermediates of pharmaceuticals.

Various of the solvents disclosed in Freeman Patent No. 2,200,391 which are immiscible with naphtha are suitable for use in the practice of the invention. In all instances, these are em-

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ployed in such ratio and at such temperature as to obtain a relatively small fraction of the total glyceride oil in the extract phase and the major portion in undissolved state in the raffinate phase. In general, the selective polar solvent will be employed in a ratio of 3 to 30 parts per part of original oil feed as determined by volume. Preferably, the temperature of treatment is so selected that the extract yield is not more than about 30 or 40% and preferably 2 to 30%, of the total glyceride content of the feed oil.

The amount of naphtha employed in backwashing the polar solvent extract solution is generally in a ratio of 3 to 30 parts per part of original oil feed as determined by volume.

The following constitutes a partial list of polar solvents which are immiscible with iso-octane at 25° C. and their use or the use of similar solvents in conjunction with naphtha in operating this duo-solvent process is within the purview of the invention:

Table A

Furfuryl alcohol
Formic acid
Ethylene glycol diformate
Glycol diacetate
Methyl malonate
Methyl alcohol
Propylene glycol
Monomethyl ether of ethylene glycol
Monobutyl ether of diethylene glycol
Beta hydroxy propionitrile
Beta ethoxy ethyl glycolate
Ethyl levulinate
Triacetin
Methyl oxalate
Ethylene glycol
Methyl lactate
Monoethyl ether of diethylene glycol
Phenol
Methyl levulinate
Ethyl acetoacetate
Ethyl-N-methyl carbamate
Methyl furoate
Methoxy acetaldehyde
Cinnamaldehyde
Acetonyl acetone
Acetamide
Beta-methoxy ethyl carbonate
Nitrobenzene
Trimethyl phosphate
2-Nitro 1-butanol
Acetic anhydride
Methyl acetoacetate
Formic acid ester of the monomethyl ether of ethylene glycol
Ethyl maleate
Methyl cyanoacetate
Furfural
Formamide
Nitromethane

It is to be understood that the use of iso-octane as the naphtha in the above illustrations is given merely by way of example and that naphtha as hereinafter used in this specification denotes any hydrocarbon or mixture of hydrocarbons which is immiscible with furfural or other polar solvent being used and generally is composed of a mixture of paraffinic hydrocarbons such as hexanes, heptanes, octanes, nonanes and decanes.

Suitable ratios of polar solvent to oil and temperatures of operation for the primary fraction-

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ation of a dogfish liver oil into a raffinate of lower vitamin A potency and extract of higher vitamin A potency with various solvents are given below.

Table B

Solvent	Parts Solvent to One Part Oil	Temperature ° C.
Methyl alcohol	10 parts to 1	39
Methyl lactate	5 parts to 1	57
Monomethyl ether of ethylene glycol	5½ parts to 1	40
Furfuryl alcohol	4 parts to 1	40
Acetic anhydride	6 parts to 1	41½
Glycol diacetate	5 parts to 1	51½
Methyl levulinate	6 parts to 1	14
Methyl acetoacetate	5 parts to 1	22
Furfural	8 parts to 1	17
Acetonyl acetone	6 parts to 1	25½
Beta methoxy ethylcarbonate	2 parts to 1	40
Nitromethane	9 parts to 1	60

It is to be understood that the ratios and temperatures given above are merely by way of example. Higher and lower ratios and temperatures than those given above can be employed. It is to be noted that in extractions made under conditions of constant solvent and constant reflux ratio, the size of the fraction of oil dissolved in the solvent increases as the temperature of the solvent is increased while the concentration of the vitamins therein is found to be correspondingly lowered. (The method of applying reflux as here referred to is described later in the disclosure.) In most instances, it is preferred, as previously stated, so to operate as to take an extract fraction constituting not more than 30 or possibly 40% of the total feed oil. From 2 to 30% of the total feed oil in the extract fraction is to be preferred.

The polar solvent extract solution produced in the primary fractionation is preferably cooled to about 15° C. to 25° C. and then contacted either batchwise or by methods of countercurrent extraction with naphtha in a ratio of about 3 to 20 parts of naphtha per part of original oil feed. The naphtha removed the major portion of the glyceride oil, vitamin A and also vitamin D, if it is present, from the primary extract solution and leaves the free fatty acids, constituents objectional to taste and odor, and only minor amounts of the vitamins in the polar solvent.

A suitable embodiment of apparatus for use in the practice of the invention is illustrated diagrammatically in the single figure of the drawings in which like numerals refer to like parts throughout. In the drawings are shown three columns, I, II, III designed for the countercurrent extraction of the glyceride oils containing the vitamins. A natural glyceride oil containing vitamin A and possibly vitamin D is introduced by line 5 into the column I at about the mid section thereof. A selective polar solvent such as furfural or other of the polar solvents recognized to have a selective affinity for unsaturated glycerides is introduced into the upper part of column I as indicated at 6. Usually the introduction is effected at a short distance below the top of the column in order to provide a quiescent zone in the upper part as indicated at 7 for the separation of the raffinate phase. Raffinate oil containing some dissolved solvent is taken off from the top of the column as indicated at 8 and may be passed to a suitable still 9 for the removal of solvent contained therein. The solvent as removed is drawn off through line 10 for storage and re-use. After distillation of the solvent, the raf-

finiate impoverished in vitamins A and D passes off at 11 to storage or for further treatment as may be desired.

In some instances, it may be desirable further to extract the raffinate fraction from column I in order to obtain additional concentration of vitamins therein. For this purpose, all or a portion of the raffinate phase may be drawn off through line 12. Valves 13 and 14 in the lines 8 and 12 constitute means for regulating and directing the flow of raffinate. Of course, to promote the flow in these lines appropriate pumps may also be employed, but since they are conventional they have not been illustrated. It is to be understood that pumps similarly may be employed in any other portions of the system in order to promote flow of and to proportion oils and solvents as may be required. The raffinate oil containing solvent may be passed to extraction column III to which a solvent such as furfural in a ratio of 3 to 30 parts by volume per part of raffinate feed oil is supplied by means of a line 16. The raffinate as thus extracted passes out at the top of the column III as indicated at 17 to a still 18 for the removal of the solvent contained therein. The solvent as removed is drawn off through line 19 for storage and re-use. The raffinate free of solvent is drawn off through line 21. Extract solution taken from the raffinate obtained in column I is taken off from column III near the bottom thereof as indicated by line 22. This fraction is subjected to distillation in still 24 in order to eliminate solvent which is passed out through line 26 to storage. The extract from column III after distillation of the solvent passes off through line 27. It may pass in its entirety to storage or, if preferred, the column III may be so operated as to obtain vitamin concentration in the extract approximately corresponding to the feed oil passing in at 5 to column I. In this latter case, the extract is passed through line 28 to the feed of column I. It is also permissible to draw off a portion of the extract from column III through line 31 and use it as a reflux near the bottom of the column III. The amount of reflux oil used is about .1 to 2 parts by volume to 1 part of raffinate feed oil to column III. Suitable valves 32 in the lines 27, 28 and 31 provide means for the control of the flow of the extract oil. It will be understood that instead of employing a reflux of oil to the lower portion of the column III a reflux of naphtha may be employed or, if preferred, the two may be employed simultaneously. To this end, a line 34 discharges into column III slightly above the bottom thereof and naphtha in a ratio of about .1 to 1 part by volume to 1 part of feed oil to column III may be introduced.

In order to remove free fatty acids as well as objectionable color, odor and taste from the extract as produced in column I, it is desirable to refractonate the extract solution in column II by means of a naphtha wash, whereby the major portion of the glyceride oil, vitamin A and also vitamin D, if present, is extracted from the polar solvent by means of the naphtha, leaving in the polar solvent the free fatty acids as well as constituents of objectionable taste, color and odor. It is obvious that in the above process the polar solvent and naphtha used should be immiscible in one another at the temperatures of operation, or should become immiscible upon the addition of small amounts of water, say 1 to 15% of the polar solvent con-

tent. Some solvents of this type are disclosed in Table A.

The extract solution from column I is drawn off at the bottom portion of the column through line 36. Various methods of handling this extract solution in order to provide an oil-polar solvent solution feed to column II as well as a reflux medium for column I are possible. Some of the variations possible are listed in methods A through E. Method A is the preferred procedure.

Method A.—All of the extract solution coming from column I may pass directly to column II through lines 45 and 41. This solution is introduced into column II somewhat below the top of the column in order to provide a quiescent zone 43 in the top portion of column II. If this method is used and it is desirable to use extract product oil as reflux to column I, the reflux oil is supplied through line 66 or through a combination of lines 66 and 63. The details of obtaining this reflux oil or oil-naphtha solution is given later in the disclosure.

Method B.—Under some conditions of operation, especially those using high solvent ratios, it may be desirable to remove some of the polar solvent before the extract solution is sent to column II. In this method all the solution from line 36 is passed to still 37 which preferably is of low pressure, flash type for the removal of about 25 to 90% of the solvent present in the original extract solution. The solvent is drawn off from still 37 as indicated, through line 38 and returned to storage. The concentrated oil solution is drawn off from still 37 through line 39 and is then passed to column II through lines 50 and 41. In this method as in Method A, reflux oil is supplied through line 66 or a combination of lines 63 and 66.

Method C.—If it is desired part of the extract solution from line 36 may by-pass still 37 and pass directly to column II, the remainder passing to still 37 for the removal of about 25 to 90% of the solvent present in this solution. This concentrated solution is then passed to column II through lines 39, 50, and 41. By this combination of methods A and B the amount of oil present in the polar solvent feed to column II can be varied. Reflux oil is supplied to column I if it is desired as described in method A and B.

Method D.—In method A it may be desirable to obtain extract product reflux oil without treating the whole extract solution with naphtha in column II. In this case, part of the extract solution is passed to still 37 for the partial removal of solvent and thence to still 40 for the complete removal of solvent. The solvent from still 40 is drawn off as indicated at 42 and is passed to storage. The solvent free extract product oil is then passed to the bottom portion of column I through line 44.

Method E.—In method B and C it likewise may be desirable to obtain extract product reflux oil without treating the whole extract solution with naphtha in column II. In this case part of the concentrated extract solution passing out of still 37 through line 39 is sent to still 40 for the complete removal of solvent. This solvent free extract product oil is then passed to the bottom portion of column I through line 44.

Conventional valves 47 control the flow of extract solution, concentrated extract solution and solvent free extract product in lines 45, 36, 39, 44, and 50. If it is so desired, a reflux of naphtha of about .1 to 1 part by volume per

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part of original feed oil may be introduced into the bottom zone of column I through line 46.

In column II, the extract solution or concentrated extract solution is subjected to further extraction by means of a hydrocarbon solvent such as naphtha in a ratio of about 5 to 20 parts per part of original oil (volume basis) introduced through line 49 near the bottom of the column and flowing upwardly countercurrently to the extract solution from line 41. This hydrocarbon effectively dissolves substantially all the glyceride oil and vitamins from the extract solution from column I leaving in the selective polar solvent about 1-3% based upon the original oil of a by-product which passes out through line 52 at or near the bottom of column II. The by-product solution is subjected to distillation in a still 53 and solvent free by-product is then drawn off through line 54 to storage. The solvent evaporated in the still 53 passes off through line 56 to storage. The hydrocarbon phase carrying in solution nearly all of the glycerides and vitamins A and D extracted from the oil in column I passes out at the top of column II through line 55 and passes through line 57 to still 59 in order to remove the solvent which is drawn off through line 61. Still 59 preferably is of low pressure flash type operating at as low pressure as is practicable to attain in order to avoid overheating the product. The product from the still 59 includes most of the extracted glycerides from column I as well as the vitamins A and D and passes out through line 62 to storage. If it is desired, a portion of this vitamin concentrate oil may be recycled to column I as reflux through line 66 in order to increase the vitamin concentration of the extracted oil from the latter column. The amount of reflux oil used is about .1 to 2 parts by volume to 1 part of feed oil to column I. Conventional valves 65 in lines 62 and 66 control the amount of oil passing through either of these lines.

An optional method of adding reflux to column I may include the addition through line 63 of a part of the hydrocarbon solution from line 55 as a reflux medium to column I. The amount of solution to be used as reflux is about .1 to part 1 by volume per part of feed oil to column I. Conventional valves 65 in lines 57 and 63 control the amount of hydrocarbon solution passing through these lines.

Any of the solvents heretofore described can be employed in the apparatus as shown. However, furfural is particularly satisfactory for the purpose and, as stated, may be employed in a ratio of about 3 to 30 parts by volume per part of oil being treated. Various vitamin containing oils, notably the fish liver oils, may be employed in the process. These oils include dogfish liver oil, soup fin shark liver oil, cod liver oil, sardine body oil, gray fish liver oil, viscera oil and the like.

An example illustrating the invention when furfural is used as the selective solvent, dogfish liver oil as vitamin bearing oil and the extraction is carried out in columns I and II of suitable length is given in Example I.

EXAMPLE I

Furfural that has been saturated with naphtha was pumped to column I through line 6, and dogfish liver oil containing 17,200 units of vitamin A per gram was pumped into column I through line 5. The ratio of solvent feed to oil feed was 20 parts solvent to 1 part feed oil by

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volume. Extract product oil in a ratio of 0.21 part to 1 part of feed oil was fed as reflux through line 66 to the bottom portion of the column. The means of obtaining this extract product oil will be later herein described. Naphtha in a ratio of 0.41 part to 1 part of feed oil was also fed into the bottom portion of column I through line 46. Column I was operated with an 80° F. temperature gradient, the top being maintained at approximately 157° F. and the bottom at approximately 77° F.

The raffinate solution produced in the above fractionation was removed from column I through line 8 and passed to still 9 where all the solvent was removed. The final raffinate product oil passed out of the still through line 11 and was obtained in a yield of 82.2% having a vitamin A potency of 3,440 units per gram. In this example, the raffinate was not re-fractionated, however, if it had been desired it could have been pumped through line 12 to column III and refractionated according to the general descriptions previously given.

The extract solution from column I was drawn off through line 36 and all of its was sent to column II through lines 45 and 41, thereby bypassing still 37. Naphtha in a ratio of 14.3 parts to 1 part of feed oil was pumped into column II through line 49. The naphtha passed countercurrently to the extract solution which entered near the top of the column, and in so doing removed the major portion of the glyceride oil and the vitamin A from the furfural solution. This naphtha solution containing the vitamin concentrate passed from column II through lines 55 and 57 to still 59 in which all of the solvent was removed from the oil. A portion of this solvent free extract product oil was fed to the bottom portion of column I as reflux by means of line 66, the remainder of the extract product was sent to storage through line 62. The yield of extract product amounted to 15.1% of the feed oil and had a vitamin A potency of 92,800 units per gram.

The major portion of the free fatty acids present in the extract solution from column I remain in the furfural when the extract solution is washed with naphtha in column II. Constituents objectionable to odor and taste as well as other minor ingredients, unsaponifiable matter, and lesser amounts of glyceride oil and vitamins remain with the free fatty acids in this by-product, furfural solution.

The by-product solution passed from column II through line 52 to still 53 where all of the solvent was removed. The final solvent free by-product left still 53 through line 54 and passed to storage.

The by-product was obtained in a yield of 2.7%, having an acid value of 102.6 and a vitamin A potency of 6,830 units per gram.

The results obtained in the above example are tabulated below:

Oil used.—Dogfish liver oil containing 17,200 units of vitamin A/gram.

Column I

Solvent ratio, 20:1 based on oil feed rate
Solvent used, naphtha-saturated furfural
Oil reflux, 0.21:1 based on oil feed rate
Naphtha reflux, 0.41:1 based on oil feed rate
Temperature:
Top, 157° F.
Bottom, 77° F.

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Column II

All of the extract solution from Column I was fed directly into the top of column II through lines 45 and 41.

Naphtha, 14.3:1 based on oil feed rate
Temperature, 72° F.

Products	Per Cent Yield	Line	Units Vitamin A/gm.
Extract.....	15.1	62	92,800
Raffinate.....	82.2	11	3,440
By-Product.....	2.7	54	6,830
Original Oil.....			17,200

A number of other examples illustrating the use of column II as a naphtha backwash process or the use of column III as a raffinate re-fractionation process are given in Examples II, III and IV.

EXAMPLE II

Oil used.—Dogfish liver oil containing 10,000 units of vitamin A/gram.

Column I

Solvent ratio, 8:1 based on oil feed rate
Solvent used, anhydrous furfural
Oil reflux, none
Naphtha reflux, none
Temperature, 58–60° F.

Products	Per Cent Yield	Line	Units of Vitamin A/gm.
Extract.....	17.4	48	24,800
Raffinate.....	82.6	12	5,840

The raffinate containing 5,840 units of vitamin A per gram was re-fractionated in column III under the following conditions:

Column III

Solvent ratio, 10:1 based on raffinate oil feed rate
Solvent used, anhydrous furfural
Oil reflux, none
Naphtha reflux, none
Temperature, 96–100° F.

Products	Per Cent Yield	Line	Units of Vitamin A/gm.
Extract.....	40.3	27	12,360
Raffinate.....	59.7	21	2,100

EXAMPLE III

Oil used.—Dogfish liver oil containing 17,300 units vitamin A/gram.

Column I

Solvent ratio, 8:1 based on oil feed rate
Solvent used, naphtha-saturated furfural
Naphtha reflux, 0.23:1 based on the oil feed rate
Oil reflux, none
Temperature:
Top, 150° F.
Bottom, 68° F.

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Column II

All the extract solution from column I was fed directly into the top of column II through lines 45 and 41.

5 Naphtha, 5:1 based on the oil feed rate
Temperature:
Top, 75° F.
Bottom, 68° F.

Products	Per Cent Yield	Line	Units Vitamin A/gram
Extract.....	14.2	62	74,600
Raffinate.....	84.3	11	7,410
By-Product.....	1.5	54	5,760
Original Oil.....			17,300

The following example illustrates the concentration of vitamins in sardine oil (a body oil of low vitamin content):

EXAMPLE IV

Oil used.—Sardine oil containing 450 units vitamin A/gram and 60 U. S. P. units of vitamin D/gram.

Column I

Solvent ratio, 5:1
Solvent used, naphtha-saturated furfural
30 Naphtha reflux, 0.24:1 based on oil feed rate
Oil reflux, none
Temperature, 65° F.

Column II

35 All the extract solution from column I was fed directly into the top of column II through lines 45 and 41.

Naphtha feed, 5.2:1 based on oil feed rate

Products	Per Cent Yield	Line Units	Vit. A/gm.	U. S. P. Units Vit. D
Extract.....	18.4	62	785	150
Raffinate.....	81.1	11	440	30
By-Product.....	0.5	54		
Original Oil.....			450	60

Examples V and VI illustrate the use of other polar solvents than furfural in conjunction with the naphtha backwash process for the removal of free fatty acids and other undesirable constituents from extract solutions in which the vitamin A and also vitamin D, if it is present, has been concentrated.

EXAMPLE V

55 510 parts of dogfish liver oil containing 17,000 units of vitamin A per gram was thoroughly mixed with 3,250 parts of methyl acetoacetate and the mixture held at 60° C. with intermittent stirring for sufficient time to ensure equilibrium at that temperature. The mixture was finally allowed to separate into two layers, the upper raffinate layer being impoverished in vitamins and the lower extract layer being enriched. This lower extract solution layer was withdrawn and mixed thoroughly with naphtha and the mixture allowed to cool to 27° C. The mixture was stirred from time to time until equilibrium had been attained and then the lower methyl acetoacetate layer was withdrawn. The solvent was removed by vacuum distillation from both the lower methyl acetoacetate by-product fraction as well as the upper naphtha extract fraction.

75 The raffinate or top fraction obtained in the initial separation with methyl acetoacetate at

60° C. was also distilled under vacuum for the removal of the solvent.

The products obtained by the above series of fractionations are given below:

Product	Per Cent Yield	Units Vitamin A/gm.	Acid Value
Raffinate.....	86.9	13,150	1.1
Extract.....	10.0	40,200	11.5
By-Product.....	3.1	11,620	124.9

The extract fraction had better odor and taste than the original oil.

EXAMPLE VI

525 parts of dogfish liver oil containing 17,000 units of vitamin A per gram was thoroughly mixed with 2,940 parts of methyl Cellosolve and the mixture held at 40° C., with intermittent stirring, for sufficient time to ensure equilibrium at that temperature. The mixture was finally allowed to separate into two layers, the upper raffinate layer being impoverished in vitamins and the lower extract layer being enriched. This lower extract solution layer was withdrawn and mixed thoroughly with naphtha and the mixture allowed to cool to 27° C. The mixture was stirred from time to time until equilibrium had been attained and then the lower methyl Cellosolve layer was withdrawn. The solvent was removed by vacuum distillation from both the lower methyl Cellosolve by-product fraction as well as the upper naphtha extract fraction.

The raffinate or top fraction obtained in the initial separation with methyl Cellosolve at 40° C. was also distilled under vacuum for the removal of the solvent.

The products obtained in the above series of fractionations are given below:

Products	Per Cent Yield	Units Vitamin A/gm.	Acid Value
Raffinate.....	92.2	14,800	0.7
Extract.....	5.7	38,500	14.2
By-Product.....	2.1	7,610	103.5

The extract fraction had better taste and odor than the original oil.

In further examples, grayfish liver oil of 19,200 units of vitamin A per gram was treated with naphtha saturated furfural, the temperatures of separation being 88° F. and the ratio being 100 parts of grayfish liver oil per 600 parts of naphtha saturated furfural.

Similarly, soup fin shark liver oil of 25,200 units of vitamin A per gram was treated with naphtha saturated furfural at 88° F., the ratio being 100 parts of oil to 400 parts of naphtha saturated furfural.

A viscera oil of 31,400 units of vitamin A per gram was treated with naphtha saturated furfural at 88° F. in a ratio of 100 parts by weight of oil to 500 parts by weight of the naphtha saturated furfural.

Cod liver oil containing 752 units of vitamin A per gram was extracted with naphtha saturated furfural at 70° F., the ratio of oil to solvent being 100 parts per 470 parts of naphtha saturated furfural.

In each instance, a fraction of oil constituting 30% or less of the total oil treated was dissolved in the naphtha saturated furfural and the oil in this extract was found to be greatly enriched in

vitamin A content. Vitamin assays showed that when vitamin D is present in the original oil, the extract fraction is also greatly enriched in this vitamin.

It is to be understood that in the operation of the apparatus described it is preferable to operate the apparatus in such manner as to exclude the oil and solvent from contact with the air. This may be done by blanketing the exposed oil-solvent surfaces with an inert gas such as carbon dioxide or nitrogen.

The forms of the invention herein described are to be considered merely as exemplary. It will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

This application is a continuation-in-part of my copending application Serial No. 625,767, filed October 31, 1945, now abandoned.

The use of columns for effecting counter-current extraction of vitaminiferous oils has been described. However, other modes of counter-current contact are contemplated. The process and apparatus as shown in my copending application, Serial No. 51,026, filed September 24, 1948, are contemplated. In this process, three centrifuges of the Podbielniak type (see Patent 2,286,157) are employed in place of towers. The furfural extract solution from a first centrifuge is passed from the first to a second where a naphtha reflux is applied. The naphtha solution is then returned to the first and the furfural extract is passed to a third for naphtha backwashing to remove glycerides. With fish liver oil, the vitamins would be taken out in the naphtha solution from the latter centrifuge.

I claim:

1. A process of obtaining glyceride oil solutions of high vitamin A concentration from fish liver oils containing said vitamin in low concentration, which process comprises countercurrently extracting the glyceride oil in a first vertically elongated zone with a liquid polar compound which is a partial solvent of the oil and is relatively insoluble in naphtha, in a ratio of about 3 to 30 parts of the solvent per part of oil, introducing a reflux comprising a small amount of naphtha into the zone near the bottom thereof and the zone being maintained at a temperature to obtain solution in said solvent of about 2 to 30 percent of the oil as an extract phase, the extract in said solvent comprising unsaturated glycerides, free fatty acids and vitamin A, and further to obtain a raffinate fraction comprising the rest of the oil, extracting out the glycerides and vitamin A from the solution and leaving the fatty acids in solution in the solvent, by passing the extract solution to a second vertically elongated zone and contacting the extract solution in the second zone with naphtha whereby to obtain a solution of glyceride oil and vitamin A in the naphtha and a by-product impoverished in vitamin A and comprising the fatty acids in solution in the polar solvent and recovering the glyceride oil and vitamin A from the naphtha.

2. A process as defined in claim 1 in which a portion of naphtha extract product oil is returned as a reflux to the bottom portion of the first zone.

3. A process as defined in claim 1 in which a reflux of about 0.1 to 1.0 part by volume of naphtha and about 0.1 to 2 parts by volume of extract product oil to 1 part of feed oil is intro-

duced into the lower portion of the first zone.

4. A process as defined in claim 1 in which a reflux of extract solution containing oil in a ratio of .1 to 2 parts per part of original feed oil is stripped of polar solvent and returned to the lower portion of the first zone.

5. A process as defined in claim 1 in which a portion of naphtha extract product is returned as a reflux to the bottom portion of the first zone, the polar solvent is introduced in the upper portion of the zone and the feed oil is introduced intermediate to the reflux and the solvent feed.

6. A process of obtaining vitamin concentrates from dogfish liver oil containing vitamins, which process comprises countercurrently extracting the oil in a first vertically elongated zone with furfural, the liquids in the top portion of the zone being maintained at a temperature of about 150° F. and the liquids in the bottom portion being maintained at a temperature of about 68° F., the furfural being in a ratio of about 3 to 30 parts by volume to 1 part of oil treated and the zone further being supplied with a reflux to the bottom portion thereof of naphtha extract product oil of a substantially higher vitamin content per gram than the original oil, the oil reflux being in a ratio of about 0.1 to 2 parts per part of original feed oil by volume, the extract solution from said zone being further treated with naphtha in a second vertically elongated zone in a ratio of 5 to 20 parts to 1 part by volume based upon the original oil feed, the liquids in the top portion of the second zone being at a temperature of approximately 75° F. and the liquids in the bottom portion being at a temperature of approximately 68° F., whereby to obtain a naphtha extract of glyceride oil highly enriched in vitamin content from the second zone, then evaporating the naphtha from the extract.

7. A process of obtaining vitamin concentrates from dogfish liver oil containing vitamins, which process comprises countercurrently extracting the oil in a first vertically elongated zone with furfural, the liquids in the top portion of the zone being maintained at a temperature of about 150° F. and the liquids in the bottom portion being maintained at a temperature of about 68° F., the furfural being in a ratio of about 3 to 30 parts by volume to 1 part of oil treated, and the bottom portion of the zone being further supplied with a reflux of naphtha in a ratio of 0.1 to 1.0 part per part of feed oil and a reflux of solvent free extract oil of a substantially higher vitamin content than the original oil, said extract oil being in a ratio of about 0.1 to 2 parts per 1 part by volume of original feed oil, the extract solution from the bottom portion of said zone being further countercurrently extracted with naphtha in a second vertically elongated zone in a ratio of about 5 to 20 parts to 1 part by volume based upon the original feed oil, the liquids at the top portion of the second zone being at a temperature of approximately 75° F. and the liquids at the bottom portion being at approximately 68° F. whereby to obtain a naphtha extract of glyceride oil highly enriched in vitamin content from the second zone, then evaporating the naphtha from the extract.

8. A process as defined in claim 7 in which a portion of naphtha extract product is returned as a reflux to the bottom portion of the first zone, the polar solvent is introduced in the upper portion of the zone and the feed oil is intro-

duced intermediate to the reflux and the solvent feed.

9. A process of obtaining glyceride oil solutions of high vitamin A concentration from fish liver oils containing said vitamin A in low concentration, which process comprises countercurrently extracting the glyceride oil by introducing furfural into an upper portion of a first vertically elongated zone and the oil into an intermediate portion, the furfural being in a ratio of about 3 to 30 parts per part of oil, introducing a reflux comprising naphtha into the lower part of the zone and maintaining the zone at a temperature to obtain solution in the furfural of about 2 to 30% of the oil as an extract phase comprising unsaturated glycerides, free fatty acids and a concentrate of vitamin A, and further to obtain a raffinate fraction comprising the rest of the oil, extracting out the glycerides and vitamin A from solution in furfural by countercurrently extracting the solution in a second vertically elongated zone with naphtha, whereby to obtain a solution of glyceride oil and vitamin A in naphtha and a by-product impoverished in vitamin A and comprising the fatty acids in solution in the furfural, and recovering the glyceride oil and vitamin A from the naphtha.

10. A process of obtaining glyceride oil solutions of high vitamin A concentration from fish liver oils containing said vitamin in low concentration, comprising countercurrently extracting the glyceride oil in a first vertically elongated zone with monoethyl ether of ethylene glycol, in a ratio of about 3 to 30 parts per part of oil, and at a temperature to obtain solution in said monoethyl ether of ethylene glycol of about 2 to 30% of the oil as an extract phase, the extract in the monoethyl ether of ethylene glycol comprising unsaturated glycerides, free fatty acids and vitamin A, and further to obtain a raffinate fraction comprising the rest of the oil, passing the extract solution to a second vertically elongated zone and contacting the extract solution in the second zone with naphtha to extract out the glycerides and vitamin A from the monoethyl ether of ethylene glycol and leave the fatty acids in solution therein, whereby to obtain a solution of glyceride oil and vitamin A in the naphtha and a by-product impoverished in vitamin A and comprising the fatty acids in solution in the monoethyl ether of ethylene glycol, and recovering the glyceride oil and vitamin A from the naphtha.

11. A process of obtaining glyceride oil solutions of high vitamin A concentration from fish liver oils containing said vitamin in low concentration, which process comprises countercurrently extracting the glyceride oil in a first vertically elongated zone with methyl acetoacetate in a ratio of about 3 to 30 parts per part of oil and at a temperature to obtain solution in said methyl acetoacetate comprising unsaturated glycerides, free fatty acids and vitamin A, and further to obtain a raffinate fraction comprising the rest of the oil, passing the extract solution to a second vertically elongated zone and contacting the extract solution in the second zone with naphtha to extract out the glycerides and vitamin A from the methyl acetoacetate and leave the fatty acids in solution therein, whereby to obtain a solution of glyceride oil and vitamin A in the naphtha and a by-product impoverished in vitamin A and comprising the fatty acids in solution in the methyl acetoacetate, and re-

covering the glyceride oil and vitamin A from the naphtha.

12. In a process of obtaining glyceride oil products of high concentration of vitamin A, the steps which comprise introducing a feed of 3 to 30 parts by volume of a polar solvent which is insoluble in naphtha and a partial solvent of fish oil into an extraction system at a first point of inlet thereof, introducing a mixture of .1 to 1 part by volume of naphtha and .1 to 2 parts by volume of fish oil of relatively high vitamin A content at a second point of inlet of the system, flowing the polar solvent and the mixture in countercurrent contact, introducing a continuous feed of 1 part by volume of fish oil of relatively low concentration of vitamin A at a third point of inlet intermediate the first and second points, drawing off a solution, in naphtha, of raffinate oil containing a lower concentration of vitamin A than said feed of fish oil, at a point of outlet near the first mentioned point of inlet and an extract solution of oil enriched in vitamin A in polar solvent at a point of outlet near the second mentioned point of inlet, said system being maintained at such temperature that 2 to 30% of the original oil is retained in said extract solution, passing the extract solution to a second elongated extraction system and countercurrently contacting the extract solution in the second system with naphtha in a proportion of 3 to 30 parts by volume of naphtha per part of original feed oil to obtain a vitamin A concentrate in the naphtha and a solution of fatty acids in the polar solvent and recovering vitamin A concentrate from the naphtha.

13. In a process of obtaining glyceride oil products of high concentration of vitamin A, the steps which comprise introducing a feed of 3 to 30 parts by volume of polar solvent which is insoluble in naphtha and is a partial solvent of fish oil, in continuous flow into an extraction system at a first point of inlet thereof, introducing in continuous flow .1 to 1 part by volume of naphtha at a second point of inlet of the system, flowing the polar solvent and the naphtha in countercurrent contact, introducing a continuous feed of 1 part by volume of fish oil of relatively low concentration of vitamin A at a point of inlet intermediate of the first and second points, drawing off a solution in naphtha of raffinate oil containing a lower concentration of vitamin A than said feed of fish oil at a point of outlet near the first mentioned point of inlet and an extract solution in polar solvent of oil of higher concentration of vitamin A than said feed of fish oil at a point of outlet near the second point of inlet, said system being maintained at such temperature that 2 to 30% of the original oil is retained in said extract solution, pass-

ing the extract solution to a second elongated extraction system and countercurrently contacting the extract solution in the second system with naphtha in a proportion of 3 to 30 parts by volume of naphtha per part of original oil to obtain a vitamin A concentrate in naphtha and a solution of fatty acids in the polar solvent and recovering said product from the naphtha.

14. In a process of obtaining glyceride oil products of high concentration of vitamin A, the steps which comprise introducing a feed of 3 to 30 parts by volume of a polar solvent which is insoluble in naphtha and is a partial solvent of fish oil in continuous flow into an extraction system at a first point of inlet, introducing .1 to 2 parts by volume of fish oil of relatively high vitamin A content at a second point of inlet in the system spaced from the first mentioned point, causing the polar solvent and the fish oil to permeate countercurrently through each other, introducing a continuous feed of 1 part by volume of fish oil of lower concentration of vitamin A at a point of the system intermediate of the first and second points, drawing off raffinate comprising oil containing a lower concentration of vitamin A than said feed of fish oil at a point of outlet near the first mentioned point and an extract solution in polar solvent of oil of higher concentration of vitamin A than said feed of fish oil at a point of outlet near the second mentioned point, said system being maintained at such temperature that 2 to 30% of the original oil is retained in said extract solution, passing the extract solution to a second extraction system and countercurrently contacting the extract solution in the second system with naphtha in a proportion of 3 to 30 parts by volume of naphtha per part of original feed oil to obtain a vitamin A concentrate in naphtha and a solution of fatty acids in the polar solvent and recovering said product from the naphtha.

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