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PROCESS OF REFINING VITAMINIFEROUS OILS

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The invention relates in general to the refining of vegetable and marine oils and in particular to a process for refining vitamin-containing oils.

Heretofore, the free fatty acids in animal, vegetable and marine oils, including the vitamin-containing oils, have been removed by various processes, the most common of which is known as the alkali refining process wherein the free fatty acids are saponified by means of an alkali. In the refining of vitamin and provitamin oils, such as the fish liver oils, palm oil, carrot oil and the like, the process of saponifying the free fatty acids contained therein in the presence of a water-immiscible solvent has proved quite advantageous in that a more efficient separation of the resulting soap and the acid-free oil is afforded. Difficulties have been encountered, however, in the vitamin field as the refined oil has invariably been characterized by having an obnoxious taste and odor and a dark color. In an attempt to rid the refined oil of these undesirable properties, the use of earths, clays and activated carbons was resorted to, but the results were none too encouraging. This factor has worked a hardship on the producers of refined vitamin oils and concentrates thereof as the value of such products depends largely upon the taste, odor, color and clarity thereof.

The general object of the invention is to obviate the foregoing and other disadvantages.

Another object of the invention is to provide an improved process for refining oils containing vitamins A and/or D.

A specific object of the invention is to provide a process which will yield a highly refined vitamin oil possessing a light color with substantially no odor or taste.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has now been found that the foregoing and other objects may be realized by the practice of the process of the invention which comprises removing a portion of the free fatty acids by means of an alkaline agent, subjecting the partially refined vitaminiferous oil to the action of activated carbon and subsequently neutralizing the remaining free fatty acids with an alkaline agent. The whole process is preferably carried out in the presence of a solvent in which water and soap will not dissolve.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the process hereinafter disclosed, and the scope of the invention will be indicated in the claims.

The first step in carrying out the process of the invention comprises removing the major portion of the free fatty acids from a vitaminiferous oil by saponification with an alkaline agent. This step is preferably, though not necessarily, carried out in the presence of a water-immiscible solvent which will not dissolve the soap formed in situ. Such solvents include, inter alia, heptane, ethylene dichloride, trichlorethylene, dichlorethyl ether, ethyl ether, petroleum ether, chloroform, cyclohexane, etc., the first two named being highly preferred. In the event that the oil is solvent-extracted from its original source as from fish livers, for example, the resulting vitaminiferous oil-solvent mixture may be directly processed according to the invention thereby eliminating the usual step of freeing the oil from solvent after the extraction step. Any suitable alkaline agent such as potassium hydroxide, sodium hydroxide, sodium carbonate, etc. may be used to neutralize the free fatty acids. The alkaline agent may be added to the oil-solvent batch in any suitable form, a relatively concentrated aqueous solution being preferred. The concentration of the aqueous alkaline solution should be adjusted according to the specific gravity of the solvent used. If a heavy solvent such as ethylene dichloride is used, a more concentrated alkaline solution may be used which produces a relatively heavy soap, but which will easily float on the heavy solvent. On the other hand, a less concentrated alkaline solution should be used when a lighter solvent such for example as heptane is used to insure the formation of a lighter soap which will also separate and float to the surface of the solvent. An amount of alkaline agent sufficient to neutralize all but about 3% to 15% of the free fatty acids present should be stirred into the oil. Upon completion of saponification, the soap formed may be readily removed from the oil and extracted with solvent to recover the oil occluded therein.

The next step in the process of the invention comprises subjecting the vitaminiferous oil-solvent mixture to the action of an activated carbon. Any suitable activated animal or vegetable carbon may be employed, examples of which include, inter alia, the following well-known products available on the market under the tradenames of "Nuchar XXX," "Nuchar #2," "Nuchar 000," "Nuchar Aqua," "Nuchar C-145," "Nuchar Wa," "Darco 60," "Darco 90," "Darco K," etc. The foregoing and other similar products may

be used alone or in combination with each other as well as in combinations with colloidal clays, earths, etc. Likewise in certain cases a filter-aid may also be used to facilitate filtration of the treated oil, although the use of colloidal clay with the activated carbon renders the use of a filter-aid unnecessary. After selection of the desired carbon or carbon-mixture has been made, it is admixed with a suitable solvent which will dissolve or appropriately serve as a vehicle for the oil-solvent mixture during treatment thereof. Solvents of the aforementioned type are suitable and the same solvent as is already in the oil should be used or one that is at least miscible therewith. The activated carbon-solvent mixture should preferably be completely deaerated before treating the vitamin-containing oil therewith. The deaeration step may be conveniently effected by merely stirring the carbon and solvent in a vessel with or without the aid of heat and/or reduced pressure. It is very important to completely deaerate the carbon-solvent mixture to guard against the subsequent loss of any of the vitamin A which is highly sensitive to oxygen.

After complete deoxygenation of the carbon-solvent mixture has been effected, the vitaminiferous oil-solvent mixture is slowly added or vice versa with constant stirring. This operation may be carried out in either an open or closed vessel. In either case, the solvent will volatilize sufficiently to provide a solvent vapor airfree zone immediately above the surface of the liquid thus inhibiting any possible oxidation by the ambient atmosphere. The carbon treatment may be accelerated by the use of heat if so desired. Upon completion of this operation, the purified oil and solvent may be separated from the carbon and the impurities adsorbed thereon by filtering, decanting, centrifuging or the like, filtering being preferred. The resulting product when freed from solvent displays a marked improvement in taste, odor and color.

The resulting purified oil and solvent which still contains some of the original free fatty acids is then subjected to a final treatment with an alkaline agent. An amount of alkaline agent sufficient to just neutralize (or a slight excess) the remaining free fatty acids present in the oil is added. The soap thus formed separates out from the unsaponified oil and solvent and is removed therefrom. The soap is usually extracted with fresh solvent to ensure recovery of all the vitaminiferous oil. The solvent is then distilled off from the refined oil in the presence of a suitable inert gas. The final step of neutralizing the remaining free fatty acids may be effected after removal of the solvent if desired.

The present process is adapted for use in the refining of any suitable vitaminiferous oils such as crude or partially refined fish liver oils derived from cod, ling cod, jew fish, pollack, shark, swordfish, tuna, herring, halibut, sardine and other fish as well as palm oil and carrot oil (which contain provitamin A) and wheat germ oil or rice bran oil (which contain vitamin E). In those cases where the original crude oil contains only about 25% or less of free fatty acids, the first saponification step may be omitted if desired.

For purpose of abbreviation the expression "F. F. A." is used herein to represent "free fatty acids." The term "units of vitamin A" is to be interpreted as the "U. S. P." units of the given vitamin.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following examples which are given merely to further illustrate the invention and are not to be construed in a limiting sense, all parts given being by weight.

Example I

Weigh into a vessel 20 parts of crude halibut liver oil (F. F. A.—52.5%, potency 25,000 U. S. P. units vitamin A/gm.) and 80 parts ethylene dichloride. While stirring, add sufficient 38% KOH (4.3 parts) to neutralize all but 10 per cent of the F. F. A. Extract the soap four times with 10 part portions of ethylene dichloride. Combine the extracts and treat with a deaerated mixture of 2 parts of "Nuchar XXX" in ethylene dichloride. Agitate for 30 minutes and filter. Extract residue 5 times with 10 part portions of ethylene dichloride. To the filtrate add adequate 38% KOH (1 part) to neutralize the remaining 10% of F. F. A. Remove the soap and re-extract twice with 10 part portions of ethylene dichloride. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil: 9.4 parts.

F. F. A	per cent	0.2
Potency	units A/gm.	53,000

Color is a golden yellow; taste is bland; and the odor is very much improved.

Example II

Weigh into a vessel 20 parts of crude blue tuna fish liver oil (F. F. A.—30%, potency 30,000 units D and 25,000 units A per gram) and 80 parts ethylene dichloride. While stirring, add sufficient 45% KOH (2.1 parts) to neutralize all but 5% of the F. F. A. Extract the soap four times with 10 part portions of ethylene dichloride. Combine extracts and treat with a deaerated mixture of 2 parts of "Nuchar #2" in ethylene dichloride. Agitate for 1 hour at room temperature and filter. Extract residue 5 times with 10 part portions of ethylene dichloride. To the filtrate add adequate 45% KOH (0.45 part) to neutralize the remaining 5% of F. F. A. Remove the soap and re-extract twice with 10 part portions of ethylene dichloride. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil 14 parts.

F. F. A	per cent	0.0
Potency	units A/gram	35,000

Color is a light golden yellow; taste is bland; odorless.

Example III

Weigh into a vessel 40 parts of crude liver oil from tuna (bonita) (F. F. A. 70%, potency 50,000 units D and 60,000 units A per gram) and 60 parts ethylene dichloride. While stirring add sufficient 45% KOH (9.3 parts) to neutralize all but 15% of the F. F. A. Extract the soap six times with 10 part portions of ethylene dichloride. Combine the extracts and treat with a deaerated mixture of 8 parts of "Nuchar XXX" in ethylene dichloride. Agitate for 1 hour and filter. Extract residue 5 times with 10 part portions of ethylene dichloride. To the filtrate add sufficient 45% KOH (2.5 parts) to neutralize the remaining 15% F. F. A. Extract the soap three times with 10 part portions of ethylene dichloride. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil: 12 parts.

F. F. A	per cent	0.5
Potency	A/gm.	195,000

Color is a golden yellow; taste is bland; odorless.

Example IV

Weigh into a vessel 30 parts of crude fish liver oil (F. F. A.—50%, potency 120,000 units A per gram) and 70 parts heptane. While stirring add sufficient 30% KOH (7.6 parts) to neutralize all but 10% of the F. F. A. Extract soap four times with 10 part portions of heptane. Combine the extracts and treat with a deaerated mixture containing 3 parts of "Nuchar XXX" in heptane. Agitate for 30 minutes (temperature 60° C.) and filter. Extract the residue 5 times with 10 part portions of heptane. To the filtrate add adequate 30% KOH (1.9 parts) to neutralize the remaining 10% of F. F. A. Extract the soap three times with 10 part portions of heptane. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil: 14.8 parts.

F. F. A.....per cent..	0.6
Potency.....units A/gm..	235,000

Color is a light golden yellow; taste is bland; odorless.

Example V

Weigh into a vessel 2 parts of "Nuchar XXX" and 80 parts heptane. Stir for 5 minutes to deaerate the carbon and add slowly 20 parts of crude halibut liver oil (F. F. A.—20%, potency 60,000 units A/gm.). Continue stirring for 30 minutes at room temperature and filter. Wash residue 5 times with 10 part portions of heptane. While stirring add sufficient 38% KOH (2 parts in gms.) to the filtrate to completely neutralize the free fatty acids. Remove the soap and re-extract three times with 10 part portions of heptane. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil: 16 parts.

F. F. A.....per cent..	0.2
Potency.....units A/gm..	75,000

Color is light yellow; taste is bland; odorless.

Example VI

Weigh into a container 4 parts of "Nuchar XXX" and 60 parts of ethylene dichloride. Stir for 5 minutes to deaerate the carbon and add slowly 40 parts of crude swordfish liver oil F. F. A.—12%, potency 160,000 units A/gm.). Continue agitation for 30 minutes and filter. Wash residue 5 times with 10 part portions of ethylene dichloride. While agitating add sufficient 30% KOH (3.1 parts in gms.) to the filtrate to completely neutralize the free fatty acids. Remove the soap and re-extract three times with 20 part portions of ethylene dichloride. Remove the solvent by vacuum distillation in the presence of nitrogen gas. Yield oil: 35 parts.

F. F. A.....per cent..	0.3
Potency...U. S. P. units vitamin A/gm..	180,000

Color is a light yellow; tasteless; odorless.

The process of the invention makes possible the production of refined vitamin oils which are far superior in every respect to oils produced by prior known refining methods. The products produced by the novel process are characterized by being greatly improved as to color, taste and odor. The success of the present process is attributed to the order of the steps as executed. This fact is based upon the theory that unrefined vitaminiferous oils contain colloidal and/or suspended impurities which impart the undesirable dark color, taste, and odor thereto. When such an oil is alkali refined at the outset to remove all the free fatty acids, the alkali serves to solubilize the impurities in the oil, thereby fixing the objectionable impurities therein. After these impurities have thus been fixed in the oil, activated carbon appears to have less power to adsorb the same. In the present process only a portion of the free fatty acids are removed before treatment with activated carbon. No fixation of impurities takes place in this step of removing only a portion of the free fatty acids. This result is due to the fact that a major portion of the fatty acids are readily saponified so that the alkali becomes completely spent in a relatively short period of time and thereby it has no time to attack and solubilize the impurities. The fatty acids which do not readily react with the alkali remain in the oil and are not saponified and removed until after the colloidal and/or suspended impurities have been removed by the treatment with activated carbon. It has further been found that activated carbon functions much more efficiently when the oil contains at least a small percentage of free fatty acids which further enhances the value of the present process. Moreover by removing the major portion of the free fatty acids at the outset the efficiency of the process is increased as less activated carbon, which adsorbs some of these acids, is used.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the invention, which as a matter of language might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In a process of refining fat-soluble vitamin-containing oils the step which comprises subjecting the oil to the action of activated carbon before the removal of all of the free fatty acids present therein.

2. In a process of refining vitaminiferous oils the step which comprises subjecting a partially refined fat-soluble vitamin-containing oil to the action of activated carbon before the removal of all of the free fatty acids present therein.

3. A process of refining vitaminiferous oils which comprises removing a portion of the free fatty acids from a fat-soluble vitamin-containing oil, subjecting the partially refined oil to the action of activated carbon and finally removing the remaining free fatty acids.

4. A process of refining vitaminiferous oils which comprises removing a major portion of the free fatty acids from a fat-soluble vitamin-containing oil, subjecting the partially refined oil to the action of a completely deaerated mixture of activated carbon and solvent and finally removing the remaining free fatty acids from the oil.

5. A process of refining a fat-soluble vitamin-containing oil which comprises removing a major portion of the free fatty acids by treating the oil with an alkaline agent, subjecting the partially refined oil to the action of activated carbon and finally removing the remaining free fatty acids by treatment with an alkaline agent.

6. A process of refining a fat-soluble vitamin-containing oil which comprises removing a major portion of the free fatty acids by treating the

oil with an alkaline agent, subjecting the partially refined oil to the action of a completely deaerated mixture of activated carbon and solvent and finally removing the remaining free fatty acids by treatment with an alkaline agent.

7. A process of refining a fat-soluble vitamin-containing oil which comprises removing a major portion of the free fatty acids by treating the oil with an alkali in the presence of a solvent, subjecting the solvent-oil mixture to the action of activated carbon, and finally removing the remaining free fatty acids by treatment with an alkali.

8. A process of refining a fat-soluble vitamin-containing oil which comprises removing a major portion of the free fatty acids from the oil by saponification in the presence of a solvent, treating the partially refined oil with a completely deaerated activated carbon-solvent mixture and finally removing the remaining free fatty acids from the oil by saponification.

9. A process of refining vitaminiferous oils which comprises removing a major portion of the free fatty acids from a fish liver oil by saponification in the presence of a solvent, treating the partially refined oil with activated carbon and finally removing the remaining free fatty acids from the oil by saponification.

10. A process of refining a vitaminiferous oil which comprises removing a major portion of the free fatty acids from a fish liver oil by saponification in the presence of ethylene dichloride, treating the oil-solvent mass was a completely deaerated mixture of activated carbon in ethylene dichloride, separating the oil and solvent from the carbon and impurities adsorbed thereon and finally removing the remaining free fatty acids from the oil by saponification.

11. A process of refining a vitaminiferous oil which comprises removing a major portion of the free fatty acids from a fish liver oil by saponification in the presence of heptane, treating the oil-solvent mass with a completely deaerated mixture of activated carbon in heptane, separating the oil and solvent from the carbon and impurities adsorbed thereon and finally removing the remaining free fatty acids from the oil by saponification.

12. A process of refining a vitaminiferous oil which comprises removing a major portion of the free fatty acids from a fish liver oil by saponification in the presence of trichlorethylene, treating the oil-solvent mass with a completely deaerated mixture of activated carbon in trichlorethylene, separating the oil and solvent from the carbon and impurities adsorbed thereon and finally removing the remaining free fatty acids from the oil by saponification.

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