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REFINING AND CONCENTRATING THE UNSAPONIFIABLE FRACTION OF FATS AND OILS

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This invention relates to the purification and concentration of the unsaponifiable fraction of an oil or fat, and more particularly to the concentration and purification of said materials by removing therefrom the saponifiable fraction thereof. In one of its more specific aspects, the invention is directed to the purification and concentration of vitamins.

Prior to this invention it was the practice to separate the unsaponifiable fraction of a vitamin-rich oil or fat by reacting said fat or oil with KOH or NaOH to saponify the saponifiable fraction thereof. Then, to the entire resultant soapy mass was added a solvent, such as ethylene dichloride, ether, petroleum ether and the like, to dissolve the unsaponifiable fraction of said fat or oil. The solution of that portion of the unsaponifiable fraction dissolved in said solvent was separated from the soap and the solvent was distilled from said solution to obtain the unsaponifiable fraction of said oil or fat. In most cases the quantity of the unsaponifiable fraction in said solution varied between 40% to 60% of the unsaponifiable fraction in the original oil or fat. The undissolved portion of the unsaponifiable fraction was adsorbed, absorbed, entrapped and/or in some other manner locked to or coupled with the soap. The soap was then subjected to about seven or more washings with fresh solvent in an endeavor to remove the unsaponifiable fraction therefrom. But it was found that even with a large number of washings, a considerable percentage, and generally no more than 50% of the unsaponifiable fraction coupled with the soap, could be removed therefrom by said solvent because a portion of said fraction is so locked to the soap that the fresh solvent does not come in contact therewith. This part of the unsaponifiable fraction so locked to the soap that the same could not be removed from the soap without great difficulty, was not recovered because the cost for extracting said part of the unsaponifiable fraction from said soap was so very high as to be prohibitive in commercial practice. Thus, in the prior art practice the total quantity of recovered unsaponifiable fraction was generally between approximately 50% to 70% of the quantity of said fraction in the oil or fat so treated. Besides having this disadvantage of low yield, the old practice was costly due to the large number of washings required, the large quantity of solvent employed and because of other reasons known to those in the art.

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

A specific object of the invention is to provide an improved method for purifying and concentrating the unsaponifiable fraction of fats and oils.

A further object of the invention is to provide a method for refining and concentrating vitaminiferous materials and recovering a large percentage of said refined material at a reasonable cost.

A further object of the invention is to provide a commercially practical method for separating the saponifiable fraction from oils and fats and consistently obtaining a yield of the unsaponifiable fraction thereof, which is at least as great as 85% of the unsaponifiable fraction in said oils and fats.

A further object of the invention is to provide an improved method for separating the saponifiable fraction from the unsaponifiable fraction of a vitamin-rich oil or fat and consistently recovering 90% to 100% of the unsaponifiable fraction at a reasonable, commercially practical cost when practiced in commercial plant production.

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

According to the invention, the oil or fat, and preferably one rich in vitamins, is added to a quantity of solvent, the weight of which is less than that of the oil or fat. This mass is stirred and in the course of stirring there is added thereto a quantity of an alkali such as NaOH or KOH to form the alkali soap of the saponifiable fraction of said oil or fat. An inert gas such as nitrogen may or may not be passed into the oil-solvent mass before and/or during the addition of the alkali. This mass, preferably at room temperature, is continuously stirred until sufficient soap is formed to provide a heavy supersolvented emulsion which does not break when stirring ceases, and is then insulated against heat losses and allowed to stand for 12 to 24 hours to ensure further saponification. The mass is heated and stirred gently and then there is added thereto an additional quantity of solvent. In the course of this treatment the saponification is carried to completion and the soap changes in character from a gelatinous mass to feathery particles which separate from and rise to the top of or sink to the bottom of the solution, depending on the relative specific gravity of the solvent, which is now of a hazy and somewhat cloudy appearance due to soap and water particles suspended in said liquid. After allowing to cool to

room temperature, the entire mass is again stirred, whereupon the soap and water particles suspended in the liquid are adsorbed or absorbed by the feathery soap particles which again rise to the top of or sink to the bottom of the solution leaving the same clear. The soap is removed from the liquid layer and it is subjected to a number of washings with fresh solvent to remove any of the unsaponifiable fraction coupled therewith. This solvent solution containing said unsaponifiable fraction obtained from the soap washings is added to the first solution and the solvent is distilled off leaving behind 90% to 100% of the unsaponifiable fraction present in the original oil or fat treated.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

According to the invention, the substance to be treated may be any oil or fat which contains an unsaponifiable fraction which it is desired to separate from the saponifiable fraction thereof. One of the chief classes of said oils or fats is an animal, vegetable or marine oil or fat rich in vitamin A and/or D, vitamin E or provitamin A, and the invention will be described in conjunction with this particular class of oils and fats, although it may be applied in the same general manner to any oil or fat. Among others of said substances which may be treated are the fish liver oils, such as cod liver oil, pollack liver oil, tuna liver oil, dog fish liver oil, sword fish liver oil and halibut liver oil; the fish oils, such as sardine oil, pilchard oil and whale oil; and vegetable oils, such as palm oil, carrot oil, rice bran oil, soybean oil and wheat germ oil.

To a quantity of said oil or fat rich in vitamin A and/or D, vitamin E or provitamin A, there is added a limited and predetermined quantity of solvent therefor. The solvent should be an organic water-immiscible solvent, such as ethylene dichloride, heptane, trichloroethylene, hexane, CCl_4, cyclohexane, methyl cyclohexane, or an admixture of two or more of these or other solvents, which will not dissolve any appreciable amount of water or alkali soap of the saponifiable fraction of said oil or fat. The quantity of said solvent added to said fat or oil should be within the range of 15 to 99% by weight based upon the weight of the oil or fat, and preferably materially less than, or about 25 to 75% by weight based upon the oil. Said oil or fat, together with said limited and predetermined quantity of solvent, are stirred to obtain a substantially homogeneous mass. In order to promote the saponification in the next step, there may also be added to said mass a small quantity of a saponification promoting catalyst such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc. alcohols or the like, which is uniformly distributed throughout said solvent-oil or fat mass by stirring. Then to said homogeneous mass of catalyst-solvent-oil or fat is added a quantity of a caustic aqueous alkali such KOH or NaOH to saponify the saponifiable fraction of said oil or fat. The quantity of alkali used may vary, and it is preferably greater than the quantity necessary to saponify all the saponifiable fraction of said oil or fat. The concentration of said caustic alkali, which is preferably KOH, is such that the specific gravity of the soap formed by the reaction of the free fatty acid or saponifiable fraction of said oil or fat will be considerably less than that of the liquid in which it is contained so that at a particular stage of this process the soap will rise to the top of the liquid, and this result may be obtained by using an aqueous solution of 40–50% KOH. It has been found that the moisture content of the soap should lie within the range of about 18% to about 28% and preferably between about 22% and 26%. The moisture content of the soap can very readily be adjusted to the proper value by adjusting the concentration of the alkali solution added, or in the event that the moisture in the soap is too low, sufficient water may be added to the mass to provide the aforementioned conditions. The moisture content of the soap is quite significant in that if it is too low the soap tends to dissolve in the solvent, and if the moisture content is too high the soap becomes somewhat gelatinous and is not properly wetted by the solvent. The mass of catalyst-solvent-oil of fat-KOH is continuously and vigorously agitated by stirring preferably at room temperature. In the course of stirring said mass, the potassium soap of the free fatty acid or saponifiable fraction of said oil or fat is formed and becomes emulsified in the liquid part of said mass. The vigorous stirring of said mass is continued until there is sufficient soap formed therein so that the mass becomes a heavy super-solvented emulsion which does not break when stirring ceases. This emulsion simulates a gel and is of a pasty and heavy consistency; it will not run or pour nor will it bleed. The so perpared emulsified mass consists essentially of a large number of soap particles having entrapped therein and/or therebetween, or in some other manner coupled therewith, the liquid which consists essentially of said solvent, said catalyst, the unreacted portion of the KOH and the unreacted portion of the saponifiable fraction coupled with unsaponifiable fraction of said oil or fat. Thus the mass includes a large number of super-solvented soap particles together with the other constituents. The super-solvented soap particles, or soap micelles, consist essentially of the soap which has entrapped therein a solution of said solvent together with a part of the unsaponifiable fraction of said oil or fat. The foregoing saponification step may be carried out in a sealed container or in a reflux apparatus so that none of the solvent will be lost. In order to ensure saponification of the saponifiable fraction, the mass is insulated against heat losses and preferably allowed to stand for a period of 12 to 24 hours. Thereafter, the mass which shows no indication of separation of any liquid therefrom is gently stirred and heated to a temperature approximating the boiling point of the solvent used for approximately one hour which completes the saponification and causes the solvent locked in and between the soap particles to become vaporized and expanded to separate the particles of soap from each other and also to break the individual particles of soap themselves into individual and separate, fluffy, feathery and granular particles which are comparatively small and thin and have large surface areas per unit of weight thereof. Because the soap particles have the foregoing characteristics, substantially all the unsaponifiable fraction locked in or on the soap particles as they were originally produced is now readily accessible for solvent action or extraction from the soap. After the soap of the mass has been converted into feathery, individual, separate and fluffy particles, and while the mass is still at said elevated temperature, the unsaponifiable

fraction, coupled with said individual, separate, feathery and fluffy soap particles, may be extracted from said particles, by adding to said mass a quantity of solvent which may preferably be about 5 to 7 times the quantity of said solvent originally used, while stirring is continued, whereupon the individual and separate soap particles rise to the top of the liquid which is somewhat cloudy and hazy in appearance. The mass is allowed to cool or is artifically cooled to room temperature and is again stirred for a short time and then substantially all the soap particles will rise to the top of the liquid which is now a clear solution of unsaponifiable fraction of said oil or fat dissolved in said solvent. In the course of the last mentioned stirring operation, the individual soap particles adsorb or absorb the traces of water in said liquid and also take out of the liquid those small particles of soap which may have had water coupled therewith to change the liquid from a hazy to a brilliantly clear solution which may be separated from all the soap without the necessity of a filtering operation. The bottom liquid layer is separated from the soap layer and placed in a distillation chamber. To said soap layer is added a batch of fresh solvent and the mixture is vigorously agitated by stirring or the like at room temperature. When stirring ceases, the soap again rises to the top of the solvent which has extracted a portion of the unsaponifiable fraction which was coupled with said soap particles. The bottom liquid layer is again separated from the soap and is also added in said chamber. The soap is again and again treated in the same manner with a number of fresh solvent washes to extract the unsaponifiable fraction therefrom until the lower liquid layers of the last two washings or extractions are substantially devoid of color. Each washing may be carried out with a quantity of solvent which may be approximately the same as that employed in the first extraction. All the bottom liquid layers are combined in said chamber and are devoid of the saponifiable fraction of said fat or oil but contain dissolved in the solvent between 90% to 100% of the unsaponifiable fraction of the original oil or fat so that 90% to 100% of the vitamin A and/or D, vitamin E or provitamin A constituents of said fat or oil are recovered in a medium which is substantially devoid of constituents of the saponifiable fraction. The unsaponifiable fraction may be recovered from said liquid by merely distilling off said solvent therefrom. Reference has been made above to the effect that the soap particles rise to the surface of the solvent after the breaking of the emulsion. Such result is obtained when the solvent employed has a specific gravity greater than that of the soap. In those cases where the specific gravity of the solvent is less than the soap, the latter will settle to the bottom rather than rise to the surface of the solvent solution of the unsaponifiable fraction; the net result in either case is substantially identical as far as the efficiency of the process of the invention is concerned. The expression "vitamin" is used herein to include provitamin as well as vitamin.

The foregoing saponification procedure can be advantageously modified by passing an inert gas into or through the oil-solvent mixture prior to and/or during the addition of the saponifying agent. The inert gas serves a dual purpose in that it protects the vitamin A from oxidative destruction. Secondly, the inert gas is partially dissolved and partially entrapped in the mass in such a manner that when the mass is heated the dissolved and entrapped gas aids the solvent in further expanding or exploding the soap particles which enhances the fluffy and feathery characteristics of the final soap particles. Any suitable inert gas may be used, such as, nitrogen, carbon dioxide, etc., the former being preferred. The inert gas is preferably bubbled through the mass from the bottom of the kettle or other receptacle so that the stirrer will whip the gas into the mass.

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

100 parts of pollack fish liver oil, 50 parts of ethylene-dichloride and 3 parts of isopropanol are placed in a container. The mass in said container is thoroughly agitated by stirring at room temperature until the same is substantially homogeneous throughout. Thereafter, and while the agitation is continued, an aqueous 45% solution of KOH (10% excess) at a temperature of 40° to 60° C. is added thereto and the entire mass, whose temperature is now slightly elevated, is continuously agitated until there is a heavy super-solvented emulsion formed which does not break when the stirring ceases and which will not bleed. At this stage the mass is of a paste-like consistency and will not pour, the individual particles being granular in structure. The mixture is insulated and allowed to stand overnight, after which time the mass should evidence no separation of liquid from the soap thereof. This mass is then heated to a temperature of 60° to 80° C. while gently agitated for a period of about one hour, whereupon the soap changes from a super-solvented, paste-like mass to separate and individual granular, fluffy and feather particles. Then, and while the mass is at said elevated temperature, there is added thereto, while stirring, 250 parts of ethylene dichloride. The mixture is allowed to cool to room temperature. Upon cooling, most of the soap will have risen to the top of the liquid which now is somewhat hazy in appearance. After the mass has cooled, it is subjected to gentle stirring, whereupon the soap particles adsorb those very small soap particles and traces of moisture which caused the solution to exhibit the cloudy or hazy appearance. After the stirring is stopped, all the soap, together with all the water, will rise to the top and float on the liquid layer which now is clear and brilliant. The liquid layer is drawn off and placed in a distillation chamber. Thereafter 300 parts of ethylene dichloride are added to the soap and the mixture is stirred for about 5–10 minutes. When stirring ceases, the soap rises to the top. The clear, brilliant liquid is withdrawn therefrom and transferred to the distillation chamber. The soap is again washed with another batch of fresh ethylene dichloride in the same manner as heretofore described and these washings are continued until the liquid of the last two washings is substantially devoid of color, and in each instance the liquid layer is placed in the distillation chamber. Thereafter the liquid in the distillation chamber is heated under vacuum in order to vaporize off the ethylene dichloride and leave behind the unsaponifiable fraction.

Yield: 100% of the unsaponifiable fraction substantially free from the saponifiable fraction.

Example II

100 parts of virgin cold pressed soybean oil, 50 parts ethylene dichloride and 4 parts of isopropanol are placed in a container. The mass in said container is thoroughly agitated at room temperature until the same is substantially homogeneous throughout. Thereafter and while the agitation is continued, an aqueous 48% solution of KOH (10% excess) at a temperature of 40° to 60° C. is added thereto and the entire mass, whose temperature is now slightly elevated is continuously agitated to saponify the fatty glycerides or the saponifiable fraction thereof, heavy emulsion is formed which does not break when stirring ceases and will not bleed. At this stage the mass is of a somewhat gelatinous or paste-like consistency and paste-like consistency and will not pour. The mixture is insulated and allowed to stand overnight, after which time the mass does not show any separation of liquid from the soap thereof. This mass is then agitated at a temperature of 70° to 80° C. for a period of one hour, whereupon complete saponification is assured and the soap changes from a paste-like mass to individual granular, feathery and fluffy particles. Then, and while the mass is at said elevated temperature, stirring is continued and there is added thereto 250 parts of ethylene dichloride. The mixture is allowed to cool to room temperature and upon cooling most of the soap will have risen to the top of the liquid which is now somewhat hazy in appearance. After the mass has cooled, it is subjected to gentle stirring, whereupon the individual soap particles adsorb or absorb those very small soap particles and traces of moisture which cause the solution to exhibit the hazy appearance. After the stirring is stopped, all the soap, together with all the water, will rise to the top and float on the liquid layer which is now brilliantly clear. The liquid layer is drawn off and placed in a distillation chamber; thereafter 300 parts of ethylene dichloride are added to the soap and the mixture is stirred for about five to ten minutes. When stirring ceases, the soap rises to the top. The clear, brilliant liquid is withdrawn and transferred to the distillation chamber. The soap is again washed with another batch of fresh ethylene dichloride in the same manner as hereinbefore described and these washings are continued until the liquid of the last two washings is substantially devoid of color, and in each instance the liquid layer is placed in a distillation chamber. Thereafter the liquid in the distillation chamber is heated under vacuum in order to vaporize off the ethylene dichloride and leave behind the unsaponifiable fraction.

Yield: 98% of the unsaponifiable fraction substantially free from the saponifiable fraction.

Example III

225 parts of ling cod liver oil, 115 parts of ethylene dichloride and 7 parts of isopropanol are admixed in an insulated kettle. The mass is thoroughly agitated by stirring at room temperature, and at the same time nitrogen gas is bubbled into the mass from a point at the bottom of the kettle. After the mass has been stirred sufficiently to render the same substantially homogeneous throughout, and while agitation is continued, an aqueous 45% solution of KOH (15% excess over the stoichiometrical quantity) at a temperature of 40° to 60° C. is added, and the entire mass, whose temperature is now slightly elevated, is continuously agitated until a heavy super-solvented emulsion is formed which does not break or bleed when the stirring is discontinued. The resulting mass is allowed to stand overnight in the heat insulated kettle. The mass is then heated to a temperature of 60° to 80° C. while gently agitating for a period of about one hour, whereupon the soap changes from a super-solvented, paste-like mass to separate and individual granular, fluffy and feathery particles. 500 parts of ethylene dichloride are added with stirring and the mass allowed to cool to room temperature, whereupon the soap particles rise to the top of the liquid. If the liquid layer remains hazy, the soap particles may be circulated by agitating the mass, whereby the soap absorbs the moisture in the solvent. The liquid layer is now drawn off and the solvent removed by distillation under reduced pressure to yield the unsaponifiable fraction of the original oil. The soap is preferably washed with fresh solvent to remove the adsorbed unsaponifiables thereon. By this process a yield of 97% of the unsaponifiables in the original oil was obtained.

Example IV

By following the process of Example III substituting as the starting material shark liver oil, a yield of 98% of the unsaponifiables was recovered.

Very often the types of oils or fats to be treated according to this invention contain various undesirable odors, tastes and color impurities which are not eliminated during the process and remain along with the unsaponifiable fraction. In order to insure a light-colored, substantially odorless and tasteless unsaponifiable fraction, the original oil or fat may be subjected to a refining step which preferably comprises treating the oil or fat with a deaerated solvent-activated carbon mixture. The latter mixture is preferably prepared by admixing an activated carbon such as "Nuchar" or the like with a suitable solvent and stirring and/or heating the mixture to free the same of air, as the oxygen contained therein destroys readily oxidizable substances present in the oil, including, among others, vitamin A. The solvent and quantity used in the refining step may coincide with that proposed in the saponification step so that the carbon-treated oil and solvent solution are ready for treatment in accordance with the above-described saponification procedure. However, if the solvent content is above the desired value, it may be partially removed to the desired ratio. The unsaponifiable fraction may also be treated with a deaerated activated carbon-solvent mixture. This step may be carried out before all or part of the solvent is removed from the unsaponifiable fraction as removed from the soap.

This application is a continuation-in-part of our application Serial No. 255,046, filed February 7, 1939.

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 separating the unsaponifiable fraction from a fatty material the steps which comprise admixing, in the presence of a saponifying catalyst, a fatty material selected from the class consisting of oils and fats having a lesser quantity of a water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said fatty material, stirring the mass to form a heavy super-solvented emulsion and breaking the emulsion by means of heat to flocculate the soap.

2. A process of separating the unsaponifiable fraction from a fatty material which comprises admixing, in the presence of a saponifying catalyst, a fatty material selected from the class consisting of oils and fats having a lesser quantity of a water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said fatty material, stirring the mass to form a heavy super-solvented emulsion, breaking the emulsion by means of heat to flocculate the soap, adding a further quantity of water-immiscible organic solvent to cause complete separation of the flocculated soap particles and separating the solvent solution of the unsaponifiable fraction from the soap particles.

3. In a process of separating the unsaponifiable fraction from a fatty material the steps which comprise admixing in the presence of a saponifying catalyst, four parts by weight of a fatty material selected from the class consisting of oils and fats having one to three parts by weight of a water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said fatty material, stirring the mass to form a heavy super-solvented emulsion and heating the emulsion to complete saponification and break the emulsion.

4. A process of separating the unsaponifiable fraction from a fatty material which comprises admixing in the presence of a soponifying catalyst, four parts by weight of a fatty material selected from the class consisting of oils and fats having one to three parts by weight of a water-immiscible organic solvent dissolved therein with at least the stoichiometric quantity of alkali required to react completely with the saponifiable portion of said fatty material, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of water-immiscible organic solvent to cause complete separation of flocculated soap particles and separating the solvent solution of the unsaponifiable fraction from the soap particles.

5. In a process of producing a fat-soluble vitamin concentrate the steps which comprise admixing, in the presence of a saponifying catalyst, a fat-soluble vitamin-containing oil having a lesser quantity of water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring and breaking the emulsion by means of heat to flocculate the soap thus formed.

6. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of a saponifying catalyst, a fat-soluble vitamin-containing oil having a lesser quantity of a water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of a solvent of the aforementioned type to cause complete separation of flocculated soap particles and separating the solvent solution of the vitamin-containing fraction from the soap particles.

7. In a process of producing a fat-soluble vitamin concentrate the steps which comprise admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of a hydrocarbon solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring and breaking the emulsion by means of heat to flocculate the soap thus formed.

8. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of a hydrocarbon solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of a solvent of the aforementioned type to cause complete separation of flocculated soap particles and separating the solvent solution of the vitamin-containing fraction from the soap particles.

9. In a process of producing a fat-soluble vitamin concentrate the steps which comprise admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of a halogenated hydrocarbon solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring and breaking the emulsion by means of heat to flocculate the soap thus formed.

10. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of a halogenated hydrocarbon solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of a halogenated hydrocarbon solvent to cause complete separation of flocculated soap particles and separating the solvent solution of the vitamin-containing fraction from the soap particles.

11. In a process of producing a fat-soluble vitamin concentrate the steps which comprise admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of ethylene dichloride dissolved therein

with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring and breaking the emulsion by means of heat to flocculate the soap thus formed.

12. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of an alcoholic saponifying catalyst, a fish liver oil having a lesser quantity of ethylene dichloride dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles and separating the ethylene dichloride solution to the vitamin-containing fraction from the soap particles.

13. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of a small quantity of isopropanol, a fish liver oil having a lesser quantity of ethylene dichloride dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, permitting the emulsion to stand for several hours, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles and separating the ethylene dichloride solution of the vitamin-containing fraction from the soap particles.

14. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of a small quantity of isopropanol, a fish liver oil having in the order of about one-half its weight of ethylene dichloride dissolved therein with at least the stoichiometrical quantity of a 40%–50% aqueous solution of potassium hydroxide, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, permitting the emulsion to stand for several hours, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles and separating the ethylene dichloride solution of the vitamin-containing fraction from the soap particles.

15. A process of producing a fat-soluble vitamin concentrate which comprises admixing, in the presence of a small quantity of isopropanol, a fish liver oil having in the order of about one half its weight of ethylene dichloride dissolved therein with at least the stoichiometrical quantity of a 40%–50% aqueous solution of potassium hydroxide, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, permitting the emulsion to stand for several hours, heating the emulsion to the boiling point of ethylene dichloride to complete saponification and break the emulsion, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles, stirring the mass to allow the soap particles to absorb the moisture in the ethylene dichloride phase, and separating the ethylene dichloride solution of the vitamin-containing fraction from the soap particles.

16. A process of producing a fat-soluble vitamin concentrate which comprises treating a fish liver oil with a deaerated water-immiscible solvent-activated carbon mixture, removing the solvent-oil mixture from the activated carbon, adjusting the ratio of solvent to oil in the solution to one part solvent to more than one part oil, admixing, in the presence of a saponifying catalyst, the oil-solvent solution with at least the stoichiometrical quantity of alkali required to completely react with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion which will not break upon cessation of stirring, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of a solvent of the aforementioned type to cause complete separation of flocculated soap particles, and separating the solvent solution for the vitamin-containing fraction from the soap particles.

17. A process of separating the unsaponifiable fraction from a fatty material which comprises admixing, in the presence of a saponifying catalyst, and in the presence of an inert gas a fatty material selected from the class consisting of oils and fats having a lesser quantity of a water-immiscible organic solvent dissolved therein with at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said fatty material, stirring the mass to form a heavy super-solvented emulsion, breaking the emulsion by means of heat to flocculate the soap, adding a further quantity of water-immiscible organic solvent to cause complete separation of the flocculated soap particles and separating the solvent solution of the unsaponifiable fraction from the soap particles.

18. A process of producing a fat-soluble vitamin concentrate which comprises admixing a fat-soluble vitamin-containing oil with a lesser quantity of a water-immiscible organic solvent, bubbling nitrogen through the oil-solvent mixture, adding thereto a saponifying catalyst and at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of water-immiscible organic solvent to cause complete separation of flocculated soap particles, and separating the solvent solution of the unsaponifiable fraction from the soap particles.

19. A process of producing a fat-soluble vitamin concentrate which comprises admixing a fish liver oil with a lesser quantity of a water-immiscible organic solvent, bubbling nitrogen through the oil-solvent mixture, adding thereto an alcoholic saponifying catalyst and at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of water-immiscible organic solvent to cause complete separation of flocculated soap particles, and separating the solvent solution of the unsaponifiable fraction from the soap particles.

20. A process of producing a fat-soluble vitamin concentrate which comprises admixing a fish liver oil with a lesser quantity of ethylene

dichloride, bubbling nitrogen through the oil-solvent mixture, adding thereto a relatively small amount of isopropanol and at least the stoichiometrical quantity of alkali required to react completely with the saponifiable portion of said oil, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles, and separating the ethylene dichloride solution of the unsaponifiable fraction from the soap particles.

21. A process of producing a fat-soluble vitamin concentrate which comprises admixing ethylene dichloride and a fish liver oil in the ratio of 25 to 75 parts by weight of ethylene dichloride per 100 parts by weight of the oil, bubbling an inert gas through the oil-ethylene dichloride mixture, adding thereto a small quantity of an alcoholic saponifying catalyst and at least the stoichiometrical quantity of a concentrated aqueous solution of an alkali metal hydroxide required to react completely with the saponifiable portion of the oil, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adjusting the moisture content of the soap to within the range of 22% to 26% by the addition of water, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles, separating the ethylene dichloride solution of the unsaponifiable fraction from the soap particles and washing the separated soap with fresh ethylene dichloride to remove any residual unsaponifiable adhered thereto.

22. A process of producing a fat-soluble vitamin concentrate which comprises admixing ethylene dichloride and a fish liver oil in the ratio of 25 to 75 parts by weight of ethylene dichloride per 100 parts by weight of the oil, bubbling nitrogen through the oil-ethylene dichloride mixture, adding thereto a small quantity of isopropanol and at least the stoichiometrical quantity of a concentrated aqueous solution of potassium hydroxide required to react completely with the saponifiable portion of the oil, stirring the mass to form a heavy super-solvented emulsion, heating the emulsion to complete saponification and break the emulsion, adjusting the moisture content of the soap to within the range of 22% to 26% by the addition of water, adding a further quantity of ethylene dichloride to cause complete separation of flocculated soap particles, separating the ethylene dichloride solution of the unsaponifiable fraction from the soap particles and washing the separated soap with fresh ethylene dichloride to remove any residual unsaponifiable adhered thereto.

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