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## STABILIZATION OF OXIDIZABLE SUBSTANCES

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This invention relates to the production of antioxidants and to the stabilization of oxidizable organic substances, primarily those of an oily or fatty nature.

It is well known in the art that many oxidizable organic substances, e. g. oils, fats and waxes containing fatty acid radicals, as well as soaps thereof, tend to be deterimentally affected by exposure to atmospheric conditions for prolonged periods of time. For example, many oils and fats tend to develop considerable rancidity and undesirable tastes and odors upon prolonged exposure to air. This instability of oils and fats tends to be accentuated by conventional refining processes since in many cases the refining destroys or removes the natural antioxidants contained in such substances. This characteristic instability is particularly undesirable in connection with fat-soluble vitamin-containing oils, since these oils not only show the typical tendency to become rancid upon exposure to air, but also tend to lose a considerable portion of their valuable vitamin activity. Other oxidizable organic substances manifest their characteristic instabilities in different fashions, but in practically every case their instability is highly undesirable.

As a result of the instability shown by many oxidizable organic substances, many attempts have been made to increase the resistance of these substances to the action of oxidizing influences. For example it has been proposed to stabilize oils and fats by adding certain crude vegetable oils thereto, the theory being that since the crude vegetable oils suggested for use contain natural antioxidants, these antioxidants would serve to stabilize the oils and fats. This proposal has, however, not met with any particular success because of the fact that since the vegetable oils do not contain very high percentages of the antioxidants, disproportionately large amounts of the oils have to be added to the substances to be stabilized in order to achieve the desired antioxidant effect. Several proposals have been advanced designed to recover valuable fractions from vegetable oils, but there has been no important success achieved along these lines with regard to the production of effective antioxidants therefrom; as a matter of fact, the art has generally believed that the vegetable meals, not the oils expressed therefrom, were the most suitable source of antioxidants and has turned away from the idea of recovering antioxidants from such oils.

It has been suggested that solvents, such as ethyl alcohol, would be capable of extracting effective antioxidants from oil-free vegetable meals. This proposal has several disadvantages. In the first place, the antioxidants extracted from the meals are generally not completely oil-soluble, so that in some cases it is not possible to form completely homogeneous mixtures of these antioxidants with substances such as oils and fats. In the second place, the antioxidants extracted from vegetable meals may have extremely dark colors and unpleasant odors and are generally obtained in very poor yields. The result of these disadvantages has been that the suggested method has not met with any substantial degree of commercial success.

It has also been proposed to recover antioxidants from vegetable oils by saponifying the oils, separating the unsaponifiable portions of the oils and recovering antioxidants from these unsaponifiable portions by successive extractions and fractionations. This proposal has likewise not been commercially successful because it entails the destruction by saponification of the valuable vegetable oils, thereby rendering the process highly uneconomical, and because the saponification probably destroys the antioxidant properties of certain of the materials contained in the oils; moreover, the necessity for carrying out a number of extraction and fractionation steps is clearly disadvantageous.

Because of the many disadvantages inherent in prior processes for the production of antioxidants, there is still a considerable demand in the industry for a simple, economical and effective method for preparing antioxidants which will accomplish the desired results. Furthermore, because of the tremendous recent development in the production and use of fat-soluble vitamin-containing oils, the need for such antioxidants has become particularly acute due to the well known instability of vitamins contained in such oils.

It is an object of this invention to provide stabilized oxidizable organic substances resistant to the action of atmospheric conditions.

It is a more specific object of this invention to provide antioxidants capable of stabilizing fat-soluble vitamin-containing oils.

Another object of this invention is to provide a simple and economical process for the production of highly effective antioxidants.

I have made the surprising discovery that highly effective antioxidants may be economically produced from fatty materials with which they are associated by subjecting fatty materials con-

taining natural antioxidants to solvent extraction with a suitable solvent, whereby the antioxidants become concentrated in the solvent extract. My discovery is particularly applicable to the recovery of antioxidants from fatty oils such as vegetable and fish oils, since, contrary to all expectations, I have found that solvent extraction of such materials yields products containing antioxidants in extremely active condition. I have further found that the extracts recovered from fatty materials may be blended with oxidizable organic substances to form mixtures extremely resistant to deteriorative oxidation. My invention is primarily concerned with the stabilization of oxidizable organic substances of an oily or fatty nature, since my antioxidants may be easily blended with such substances to form completely homogeneous, stable mixtures. A preferred embodiment of my invention involves the stabilization of fat-soluble vitamin-containing oils, since the addition of my extracts to such oils not only prevents the development of undesirable rancidity and discoloration, but stabilizes the vitamin content of the oils so that there is relatively little destruction of either the vitamin A or D contained in the oils even after prolonged exposure to atmospheric conditions. My novel process has the additional advantage that the residual fatty materials from which the antioxidants have been extracted are more valuable than the fatty materials originally treated, since a certain amount of refining takes place due to a substantial removal of color and odor along with constituents responsible for the production of "break"; thus my invention not only yields valuable antioxidants, but also produces refined fatty materials suitable for a wide variety of purposes. The yields obtained in accordance with my process are excellent and the solvents employed are all readily available and comparatively inexpensive; as a result, my novel process for the preparation of antioxidants is extremely economical.

The fatty materials from which the antioxidants are extracted in accordance with my invention may be any fatty material containing naturally occurring antioxidants, or mixtures thereof; preferably crude materials containing such antioxidants are employed. The term "fatty material" is used throughout the specification and claims to include oils, fats and waxes containing fatty acid radicals. There are many such materials containing natural antioxidants known to the art. Thus, vegetable oils and fats, such as soybean oil, wheat germ oil, corn germ oil, corn oil, oat oil, rye oil, olive oil, sesame oil, cottonseed oil, palm oil, cocoa butter, palm kernel oil, coconut oil, rice oil, rice germ oil, linseed oil, oiticica oil, teaseed oil, perilla oil, alfalfa seed oil, celery seed oil, flax seed oil, groundnut oil, hemp seed oil, kapok oil, mustard seed oil, rape seed oil, poppy seed oil, sunflower seed oil, pumpkin seed oil, melon seed oils, peanut oil and the like may be treated. Another group of fatty materials which may be employed is the fish liver oils, such as cod liver oil, tuna liver oil, halibut liver oil, shark liver oil, etc., as well as other marine oils, such as menhaden oil, herring oil and sardine oil. Other oils which may be treated in accordance with my invention are tomato seed oil, grape seed oil, peach kernel oil, egg oil and whale oil. I prefer to produce my antioxidants from vegetable oils, and in the detailed description hereinafter given particular reference will be made to the treatment of such oils; however it is to be understood that other fatty materials may be used if desired.

As hereinabove pointed out, the antioxidants are recovered from fatty materials with which they are associated by extraction with a suitable solvent. The solvent employed in accordance with my invention may be selected from a large number of aliphatic solvents found to be useful as a result of extensive experimentation; the choice of the solvent will depend to some extent upon the properties of the material to be treated, as will become more evident from the detailed description hereinafter given. My results have indicated that the solvents preferably employed are members of well recognized chemical classes; I have also found that the number of carbon atoms in the solvent to be used is a particularly important factor in determining the availability thereof for use in the practice of my invention. The following table embodies the results of my experiments and sets forth the classes of solvents which I have found to be particularly useful in the recovery of antioxidants:

*Table I*

1. Aliphatic and alicyclic monohydroxy alcohols containing from 3 to 6 carbon atoms.
2. Esters formed by the reaction of aliphatic and alicyclic alcohols with aliphatic monocarboxylic acids, said esters containing not more than 8 carbon atoms.
3. Aliphatic and alicyclic aldehydes containing not more than 6 carbon atoms.
4. Aliphatic ketones containing not more than 6 carbon atoms.

Solvents falling in the classes above listed are all liquid aliphatic organic compounds having the properties of being miscible with fatty materials at temperatures above room temperature, i. e. 20° to 25° C., and partially immiscible therewith at temperatures substantially below room temperature, and my experiments have shown that solvents falling within this class of compounds may be used in the practice of my invention. In addition it will be noted that my preferred solvents possess relatively low freezing points.

In order to more fully illustrate the nature of the solvents which I may employ, a partial list thereof is herewith given; it is to be understood, however, that this list is not intended to be complete, but is merely illustrative of the solvents which may be employed. Thus I have found that the following solvents may be used: n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, n-amyl alcohol, isoamyl alcohol, secondary amyl alcohol, furfuryl alcohol, allyl alcohol, diacetone alcohol, β-hydroxy ethyl acetate, methyl formate, ethyl formate, ethyl acetate, methyl acetate, isopropyl acetate, glycol diformate, glycol diacetate, methyl levulinate, ethyl levulinate, methyl aceto acetate, ethyl aceto acetate, methyl furoate, vinyl acetate, furfural, propionaldehyde, crotonaldehyde, acetone, methyl ethyl ketone, acetonyl acetone and propylene chlorhydrin. Mixtures of these solvents may also be used. It will be noted that all these solvents belong to that class of aliphatic organic compounds which have the properties of being miscible with fatty oils at temperatures above room temperature and partially immiscible therewith at temperatures substantially below room temperature; furthermore, it will be noted that the majority of these solvents have relatively low freezing points.

Occasionally it may be found that certain of the solvents hereinabove mentioned may be too

miscible with some of the fatty materials which may be treated by my invention to effect a separation of antioxidants therefrom; thus, for example, acetone is too miscible with many fatty materials to accomplish the purposes of this invention. However, this condition may be easily corrected by diluting the solvent either with a small amount of water or with some liquid aliphatic organic solvent relatively immiscible with fatty materials. In general it may be said that the effect of diluting any of the above solvents with water will be to render the solvent more immiscible with fatty materials, so that if difficulty is encountered in effecting proper separation of the antioxidant extracts from the fatty materials, this difficulty may generally be overcome by the addition of a small amount of water to the solvent.

The solvents I prefer to employ in the practice of my invention are the aliphatic alcohols containing from 3 to 6 carbon atoms; of these solvents isopropanol and diacetone alcohol have proved to be the most successful. The presence of the hydroxyl group seems to impart to these solvents properties which make them particularly useful for my purposes; whether this factor is due to some activating influence possessed by this group is not known.

In carrying out the extraction of the antioxidants from the oils with which they are associated, the oil to be treated is first mixed with the particular solvent to be employed. The relative proportion of oil to solvent may vary widely; preferably the ratio of solvent to oil should be greater than one, and in most cases mixtures containing between about 2% and about 25% oil are most suitable. It is preferable to cause substantially all the oil to dissolve in the solvent; when employing the preferred solvents of my invention, complete solution is ordinarily effected most readily by heating the mixture to a temperature substantially above room temperature. However, it is not necessary to cause the oil to dissolve completely in the solvent, since highly active antioxidant fractions may be extracted from the oil by agitating the oil with the solvent at a temperature such that only partial solution is effected. The extraction is preferably carried out in an inert gas atmosphere; furthermore, if fat-soluble vitamins are present in the oil being extracted, it is not advisable to heat the mixture to temperatures substantially in excess of 175° C. if recovery of the vitamins is desired.

The antioxidant fraction extracted from the oil may be recovered in any suitable manner. When operating in accordance with the preferred embodiment of my invention, i. e. when the oil is completely dissolved in the solvent at somewhat elevated temperatures, the recovery of the antioxidant extract is most conveniently accomplished by cooling the solution to a temperature substantially below room temperature, e. g. between about 0° C. and about —70° C., whereby two layers form. The layer which separates from the solvent will be found to consist chiefly of the portion of the original oil insoluble in the solvent at the temperature at which the separation is carried out. This portion generally has a considerably lighter color than the original oil and in many cases has lost some of the characteristic odor of the original oil. Furthermore, in most cases it will be found that materials responsible for producing "break" have been removed from the oil by the extraction. Thus the residue from the extraction may be used for a wide variety of purposes in accordance with processes well known to the art.

The solvent layer obtained from the extraction above described may be filtered and then treated to remove the solvent therefrom, e. g. by vacuum distillation, whereby an extract is recovered containing relatively large amounts of highly active antioxidants. If desired, water may be added to the extract in order to precipitate some of the glycerides contained therein or some of the sterols may be removed; however, these steps are not essential, since the glycerides and sterols do not inhibit the antioxidant properties of the extract. If the extract contains an excessive amount of free fatty acids, these are preferably removed by treatment with alkali in a solvent medium or by other suitable methods. The extract ordinarily possesses the characteristic odor and color of the oil from which it is obtained and is generally slightly more viscous than the original oil. The tests carried out on vegetable oil extracts indicate that the iodine values of the extracts are substantially lower than those of the original oils. If a fish liver oil is employed in the practice of my invention, it will be found that the extract contains a considerable portion of the vitamins concentrated therein. This process of extracting fish liver oils is disclosed and specifically claimed in the co-pending application of Dombrow, Serial No. 343 553, filed July 2, 1940, and hence I do not intend to specifically claim the extraction of such oils in the instant case.

My novel antioxidants may be employed for the stabilization of all types of oxidizable organic substances, particularly those of a fatty nature, i. e. fatty oils, fats, waxes, soaps, vitamin concentrates, etc. Thus oils and fats of animal, vegetable or fish origin, such as cod liver oil, tuna liver oil, shark liver oil and other fish liver oils, as well as vitamin concentrates or vitamin-containing fractions obtained from such oils; corn oil, cotton seed oil, soybean oil and other vegetable oils; fats such as butter, margarine, lard, hydrogenated shortenings, palm oil, etc.; soaps of higher fatty acids; and compositions containing such fatty materials as essential ingredients, e. g. food emulsions such as mayonnaise, may all be suitably stabilized in accordance with my invention. Furthermore, substances such as sulfonated oils and other sulfonated fatty compounds, amides, mono and diglycerides and other fatty substances which tend to become rancid upon exposure to air may be treated by my invention. The amount of the extract added to the fatty material to be stabilized may vary considerably, depending upon the activity of the extract and the degree of instability of the fatty material; I have found that oils or fats containing anywhere from about 0.1% to about 20%, preferably from about 0.5% to about 5%, of my antioxidant extracts show striking improvements in their stability.

My antioxidants are particularly adapted for the stabilization of fat-soluble vitamin-containing oils or concentrates, as well as vitamin-containing fractions recoverable from such products by vacuum distillation, solvent extraction or other processes. This is extremely fortunate, for antioxidants capable of stabilizing such products have not as yet been made available on a wide scale. My antioxidants may be added to such materials in any suitable amount without imparting undesirable color, odor, taste or toxicity thereto; furthermore the incorpora-

tion of my antioxidants in such vitamin-containing products yields vitamin compositions of a stability such that they may be handled more easily and economically than compositions heretofore obtainable. These stabilized vitamin compositions may be employed in the same manner as ordinary vitamin compositions and thus may be incorporated in food materials of all types, emulsified to form valuable emulsions or put to other appropriate uses.

Substances of a fatty nature stabilized by the addition of my novel extracts thereto may be heated to elevated temperatures without substantially affecting the activity of the antioxidants; moreover, the heating of vitamin-containing oils stabilized by the addition of my extracts does not substantially reduce the vitamin activity of the oils. As a matter of fact, I have found that by adding the antioxidant extracts of my invention to substances of a fatty nature having undesirable tastes and odors and subsequently heating the mixtures to elevated temperatures, e. g. 110° to 130° C., the undesirable tastes and odors of the substances are substantially minimized.

In order to illustrate the improved stability displayed by vitamin-containing oils stabilized in accordance with my invention, the following table is submitted, which shows the relative stabilities of crude shark liver oil and shark liver oil refined to remove its odor, color and taste contrasted with these same oils containing 5% of one of the extracts of my invention. These tests were conducted by maintaining the samples at a constant temperature of 34.5° C. in the presence of air for the indicated number of days and then measuring the percentage of the vitamin A destroyed.

*Table II*

| Sample | Percent vitamin A destroyed in— | | | | |
|---|---|---|---|---|---|
| | 6 days | 14 days | 20 days | 27 days | 36 days |
| Crude shark liver oil containing 116,000 A/gm. | 8.2 | 20.2 | 32.7 | 46.2 | 68 |
| Crude shark liver oil containing 5% soybean oil extract | 2.25 | 8.6 | 10.9 | 24.2 | 27.1 |
| Refined shark liver oil containing 108,500 A/gm. | 42.6 | 73.1 | ------ | ------ | ------ |
| Refined shark liver oil containing 5% wheat germ oil extract | 0.47 | 4.2 | 15.1 | 25.2 | 37.9 |
| Refined shark liver oil containing 5% soybean oil extract | 6.66 | 22.1 | 32.2 | 42.1 | ------ |
| Refined shark liver oil containing 5% corn germ oil extract | 1.87 | 12.3 | 25.2 | 40.5 | 52.9 |

The above table clearly demonstrates the superiority of vitamin-containing oils stabilized by the addition of my novel antioxidants. It will be noted that the stabilized refined oils of my invention are even more stable than ordinary crude shark liver oil, so that it is evident my invention permits the production of vitamin oils having no undesirable color, odor or taste, and which are, nevertheless, exceedingly stable to oxidizing influences.

While it is to be understood that the process hereinabove described is preferably employed, my invention may also be carried out by contacting a fatty material containing natural antioxidants with one of the above solvents mixed with a mutual solvent, such as ether or ethylene dichloride, so as to form a homogeneous solution of the fatty material in the solvent mixture and then cooling the mixture until separation takes place. The antioxidants are concentrated in the solvent layer and may be recovered therefrom.

A modification of the process hereinabove described which I have found to be particularly successful involves extracting a mixture of a fish liver oil and a vegetable oil containing natural antioxidants with one of the above solvents. As pointed out in the copending Dombrow application hereinabove referred to, the extraction of the fish liver oil effects a concentration of the vitamins in the solvent; furthermore the antioxidants of the vegetable oil are also concentrated in the extract, so that a highly potent, extremely stable extract is recovered. A similar extraction of a mixture of a vegetable oil and a fat-soluble vitamin concentrate yields an extremely stable extract constituted chiefly of the concentrate and the antioxidants of the oil.

While my invention is primarily concerned with the stabilization of oxidizable organic substances of a fatty nature, other oxidizable organic substances, such as non-fatty substances containing vitamin C, pyrethrum, essential oils and other materials known to the art may be stabilized by treatment with my novel extracts.

The following examples are illustrative of the method of producing the extracts of my invention; amounts are given in parts by weight.

*Example I*

93 parts of cold pressed wheat germ oil having an iodine value of 127 were mixed with 320 parts of 91% isopropanol and the mixture heated to about 62° C. in a nitrogen atmosphere, whereby a homogeneous solution was formed. The solution was then cooled to —18° C. and the solvent layer withdrawn and filtered. The residue was re-extracted with 91% isopropanol as hereinabove described and the solvent layer recovered. The isopropanol was then evaporated from the solvent layers by vacuum distillation in the presence of nitrogen. Both extracts showed strong antioxidant properties. The iodine values of the first and second extracts were 119 and 124, respectively.

*Example II*

500 parts of crude corn germ oil having an iodine value of 119.2 were added dropwise to 1600 parts of 99% isopropanol heated to 60° C., the mixing being conducted in a nitrogen atmosphere. The solution thus obtained was cooled to —18° C. and the solvent layer withdrawn and filtered. The residue was re-extracted in the same manner. Upon evaporation of the isopropanol from the extracts it was found that each extract contained highly active antioxidants. The iodine values of the first and second extracts were 110.2 and 113.2, respectively.

*Example III*

500 parts of virgin soybean oil having an iodine value of 126 were mixed with 1600 parts of 99% isopropanol and the mixture heated to about 50° C. in a nitrogen atmosphere, whereby a homogeneous solution formed. The solution was then cooled to —18° C. and the solvent layer withdrawn and filtered. The residue was re-extracted with 99% isopropanol as hereinabove described. Upon evaporation of the isopropanol from the extracts, it was found that both extracts had strong antioxidant properties. The iodine values of the first and second extracts were 119.3 and 117.9, respectively.

*Example IV*

500 parts of virgin soybean oil were dissolved in 1800 parts of ethyl acetate heated to 60° C. in a nitrogen atmosphere. The solution was then cooled to —18° C. and the solvent layer withdrawn and separated. Upon evaporation of the ethyl acetate from the solvent layer, it was found that the extract possessed strong antioxidant properties.

*Example V*

500 parts of crude corn oil having an iodine value of 117.8 were dissolved in 1600 parts of 91% isopropanol heated to 60° C. in a nitrogen atmosphere. The solution was then cooled to —18° and the solvent layer withdrawn and separated. The residue was then re-extracted with 3 additional portions of 91% isopropanol. Upon evaporation of the isopropanol from the extracts, it was found that the majority of the antioxidants were concentrated in the first two extracts, the third and fourth extracts having comparatively little antioxidant value. The iodine values of the first and second extracts were 105 and 115, respectively.

*Example VI*

465 parts of cottonseed oil refined by treatment with decolorizing carbon were mixed with 1500 parts of refluxing 91% isopropanol in a nitrogen atmosphere, whereby a homogeneous solution formed. The solution was then cooled to —18° C. and the solvent layer was withdrawn and filtered. Upon evaporation of the solvent it was found that the extract possessed strong antioxidant properties.

*Example VII*

500 parts of crude peanut oil were added gradually to 1800 parts of hot diacetone alcohol in a nitrogen atmosphere, whereby a homogeneous solution was formed. The solution was then cooled to —18° C. and the solvent layer was withdrawn and filtered. Upon evaporation of the diacetone alcohol, it was found that the extract possessed strong antioxidant properties.

*Example VIII*

500 parts of raw linseed oil were added to 1600 parts of hot acetone containing about 5% water in a nitrogen atmosphere, whereby a homogeneous solution formed. This solution was then cooled to about —18° C. and the solvent layer was withdrawn and filtered. Upon evaporation of the acetone and water, an extract having strong antioxident properties was recovered.

*Example IX*

100 parts of tomato seed oil were mixed with 400 parts of 91% isopropanol in a nitrogen atmosphere and the mixture heated to about 60° C., whereby a homogeneous solution formed. The solution was then cooled to about —18° C. and the solvent layer was withdrawn and filtered. Upon evaporation of the isopropanol, it was found that the extract possessed strong antioxidant properties.

In order to specifically illustrate the improved nature of the residual oil remaining after the antioxidant extract has been removed, the following example is given:

*Example X*

200 parts of virgin soybean oil were dissolved in 640 parts of 99% isopropanol heated to 60° C. in a nitrogen atmosphere and the solution was gradually cooled to —15° C. The solvent layer was withdrawn and the insoluble residue was then extracted with two additional portions of isopropanol. The residual oil remaining from the extractions showed no darkening even upon heating to 200° or 300° C. This oil was an excellent refined "non-break" oil.

From the above description it will be evident that my invention provides a new and highly useful method for the recovery of naturally occurring antioxidants from fatty materials with which they are associated. My invention provides a process which is highly economical and which furnishes completely oil-soluble antioxidants; furthermore, since my process does not involve subjecting the fatty material being treated to saponification or any other chemical change, the residual material is particularly valuable for a wide variety of purposes after the removal of the antioxidants therefrom. Furthermore my invention provides a highly useful process for the stabilization of fat-soluble vitamin-containing oils and thus satisfies the demand of the industry for such products. My process accomplishes the separation of antioxidants from materials which were thought to contain a relatively small quantity of these antioxidants, thereby enhancing the value of the fatty materials by permitting the production of other valuable by-products therefrom. Because of these factors it will be evident that my invention will be extremely useful to all those engaged in the production and stabilization of fatty materials.

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

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

1. A process for the recovery of antioxidants from fatty materials with which they are associated, which comprises contacting the fatty material containing natural antioxidants at a temperature above room temperature with a liquid aliphatic, polar organic compound containing at least 3 carbon atoms and being miscible with fatty materials at temperatures substantially above room temperature and partially immiscible with fatty materials at temperatures substantially below room temperature, the ratio of solvent to oil being greater than one, cooling the mass to a temperature within the range of 0° C. to —70° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the fatty material.

2. A process for obtaining antioxidants from vegetable oils containing natural antioxidants, which comprises contacting a vegetable oil containing natural antioxidants with a solvent selected from the classes listed in Table I at a temperature above room temperature, cooling the mass to a temperature within the range of 0° C. to —70° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

3. A process for obtaining antioxidants from vegetable oils containing natural antioxidants, which comprises contacting a vegetable oil containing natural antioxidants with a solvent se-

lected from the classes listed in Table I at a temperature above room temperature, the ratio of solvent to oil being greater than one, cooling the mass to a temperature within the range of 0° C. to —70° C. whereby layers are formed and separating the solvent layer solution containing the highly active antioxidant extract from the remainder of the oil.

4. A process for obtaining antioxidants from vegetable oils containing natural antioxidants, which comprises contacting a vegetable oil containing natural antioxidants with an aliphatic monohydroxy alcohol containing from 3 to 6 carbon atoms at a temperature above room temperature, cooling the mass to a temperature below 0° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

5. A process for obtaining antioxidants from wheat germ oil, which comprises contacting wheat germ oil with isopropanol at a temperature above room temperature so as to form a solution of the oil in the isopropanol, cooling the solution to a temperature below 0° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

6. A process for obtaining antioxidants from corn germ oil, which comprises contacting corn germ oil with isopropanol at a temperature above room temperature so as to form a solution of the oil in the isopropanol, cooling the solution to a temperature below 0° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

7. A process for obtaining antioxidants from soybean oil, which comprises contacting soybean oil with isopropanol at a temperature above room temperature so as to form a solution of the oil in the isopropanol, cooling the solution to a temperature below 0° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

8. A process for the recovery of antioxidants from fatty materials with which they are associated, which comprises contacting a mixture of fish liver oils and vegetable oils containing natural antioxidants with a solvent selected from the classes listed in Table I at a temperature above room temperature, cooling the mass to a temperature within the range of 0° C. to —70° C. whereby layers are formed and separating the solvent layer containing the highly active antioxidant extract from the remainder of the oil.

9. A process for obtaining a refined "non-break" oil from a vegetable oil, which comprises contacting a vegetable oil with a solvent selected from the classes listed in Table I at a temperature above room temperature, cooling the mass to a temperature below 0° C. whereby layers are formed and separating the refined oil layer from the solvent layer.

10. A process for obtaining a refined "non-break" oil from a vegetable oil, which comprises contacting a vegetable oil with isopropanol at a temperature above room temperature, cooling the solution to a temperature below 0° C. whereby layers are formed and separating the refined oil layer from the solvent layer.

11. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 1.

12. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 2.

13. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 3.

14. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 4.

15. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 5.

16. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 6.

17. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 7.

18. A highly active natural antioxidant concentrate prepared in accordance with the process set forth in claim 8.

19. An oxidizable organic substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process set forth in claim 1.

20. An oxidizable organic substance of a fatty nature stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process set forth in claim 1.

21. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 1.

22. An oxidizable organic substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process set forth in claim 2.

23. An oxidizable organic substance of a fatty nature stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process set forth in claim 2.

24. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 2.

25. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 3.

26. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 4.

27. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 5.

28. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 6.

29. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 7.

30. A fat-soluble vitamin-containing substance stabilized against oxidation by the presence therein of a natural antioxidant concentrate prepared in accordance with the process of claim 8.

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