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PROCESS OF PRODUCING AN ANTIOXIDANT CONCENTRATE

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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 detrimentally affected by exposure at 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. In a few cases there has been a fair amount of success in stabilizing fatty materials against deteriorative oxidation. However, a large number of the suggested methods for producing antioxidants and stabilizing fatty materials against oxidation have not been too successful. In many cases the potency of the antioxidants obtained has been low, and as a result the stability of the fatty materials to which they were added has not been satisfactory. In some instances the antioxidants obtained have not been sufficiently miscible with the fatty materials to give a stable, desirable product. In other cases the antioxidants have had rather undesirable tastes and odors which they in turn imparted to any material to which they were added to inhibit oxidation. In view of these and other disadvantages in prior processes for producing antioxidants and stabilizing fatty materials, there is still a considerable demand for improved, potent antioxidants which will effectively stabilize fatty materials against deteriorative oxidation.

It is the object of this invention to provide an

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improved process for obtaining highly potent antioxidants.

A further object of this invention is to provide improved, highly potent antioxidants which will effectively stabilize fatty materials against oxidative changes.

Another object of this invention is to provide improved, highly potent antioxidants which will effectively prevent loss of potency in vitamin A or D containing fatty materials.

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

I have discovered that the above and other objects of the invention may be achieved by contacting a crude vegetable oil with concentrated ammonia, and subsequently fractionating the fatty material with a highly polar solvent substantially immiscible with the oil at room temperature or at temperatures above room temperature, and recovering a highly potent antioxidant concentrate from the polar solvent. Contrary to all expectations, the antioxidants are soluble in the polar solvent even though the solvent is substantially immiscible at room temperature or temperatures above room temperature with the oil. The fractionation of the crude vegetable oil wherein the antioxidants become concentrated in the polar solvent may be readily carried out at room temperature, i. e. about 10° C. to 30° C. Since the solvent and the vegetable oil are substantially immiscible, they may be easily separated by decantation, centrifugation, etc., and a highly potent antioxidant concentrate recovered from the solvent solution, e. g. by vacuum distillation of the solvent, leaving as a residue the antioxidant concentrate. Such antioxidant concentrates are particularly suitable for the stabilization of oxidizable organic substances of an oily or fatty nature since the antioxidants may be easily blended with such substances to form completely homogeneous, stable mixtures. Fat-soluble vitamin-containing materials may be stabilized very effectively with such antioxidants. Not only is the development of undesirable rancidity and discoloration in the vitamin-containing materials prevented, but also the vitamins are protected from oxidative destruction to such an extent that very little destruction thereof occurs even after prolonged exposure of the materials to atmospheric conditions.

In carrying out the process of my invention, a crude vegetable oil is first treated with concentrated ammonia. Crude vegetable oils suitable for use in the process of my invention in-

clude, among others, the crude vegetable oils contained in oil-bearing seeds and nuts such as soybeans, peanuts, corn, wheat, cottonseed, sesame seed, rice, rye, barley, oats, coconuts, etc.

In carrying out the ammonia treatment step of the process of my invention, the crude oil may be contacted with ammonia under varying circumstances. For example, the crude vegetable oil may be removed from its source material and then contacted with the ammonia; the crude vegetable oil may be contacted with ammonia prior to removal from the source material, i. e. by contacting an oil-bearing vegetable meal or other vegetable material containing the desired oil with the ammonia; or a crude vegetable oil may be added to a quantity of the same or a different type of vegetable material from which the oil was derived which vegetable material may have had none or any varying amount up to all of its original oil content previously removed therefrom, and then contacting the crude vegetable oil in such admixture with the ammonia. Naturally, of course, in the above procedures, instead of treating just one individual crude vegetable oil or a crude oil in conjunction with just one individual vegetable material, any suitable mixtures of such oils either alone, in the first case, or associated with a vegetable material or suitable mixture of such materials, in the latter two cases, may be treated. Furthermore, if desired, a vitamin-containing oil or concentrate may be admixed with the crude vegetable oil or oil-bearing vegetable material and such mixture treated in accordance with the process of the invention. By operating in such a manner, a very stable and highly potent vitamin concentrate may be produced.

When the ammonia treatment is carried out on a crude vegetable oil associated with vegetable materials, the vegetable materials are preferably ground, chopped, flaked, comminuted or otherwise finely divided prior to the ammonia treatment. Many oil-bearing vegetable materials are commercially available in the meal form such as, for example, cottonseed meal, soybean meal, sesame meal, corn meal, corn germ meal, wheat germ meal, alfalfa leaf meal, peanut meal, rice bran, and rye, barley and other similar vegetable meals. The oil content of these vegetable materials varies considerably, of course. When treating a crude vegetable oil without removing it from the original source material, it is usually preferred to employ a vegetable material which has a relatively high oil content; however, quite excellent results may be obtained by carrying out the process upon vegetable materials having a rather low oil content. In most cases, however, it is preferred to employ oil-bearing vegetable materials containing at least 5% of oil. Whenever the term "oil-bearing vegetable meal" is used in the specification and claims it is to be understood that term connotes any of the oil-bearing vegetable materials as set forth in the specification.

In the other modification of my invention, the ammonia treatment may be carried out upon a crude vegetable oil which has been admixed with the same or a different type of vegetable material from which the crude oil was derived. This vegetable material may still contain its original oil content, or it may have had any varying amount up to and including all of its original oil content removed. The crude vegetable oils may be obtained from any of the various oil-bearing vegetable materials listed above or from other sources. Likewise the vegetable materials employed may be any of those listed above or any other suitable vegetable material. The vegetable oil added to the vegetable material may be the same oil as is obtainable from the vegetable material or it may be an entirely different vegetable oil. Since it is preferred in some cases when treating a crude vegetable oil associated with a vegetable material to treat such a vegetable material containing a fairly high percentage of oil, e. g. 40% to 50% of oil, it is desirable in some instances to increase the oil content of a vegetable material which already contains in its natural state a considerable amount of oil. Thus in some cases it may be preferred to add a sufficient amount of a vegetable oil to an oil-bearing vegetable material containing, for example 20% of oil to bring its oil content up to as high as 40% or 50% or more. The vegetable oil which is added to a vegetable material already containing a considerable amount of oil may be the same oil as is obtainable from the vegetable material, or it may be an entirely different vegetable oil.

The concentrated ammonia which is employed in the process of my invention is preferably 28% aqueous ammonia. However, other concentrated aqueous solutions of ammonia as well as gaseous ammonia or liquid ammonia may be utilized. The amount of ammonia used is relatively small as compared to the amount of vegetable oil. At least about 1% by weight of 28% aqueous ammonia as compared to the weight of the material being treated should be employed. Ordinarily I prefer to employ from about 20% to about 60% of 28% aqueous ammonia based upon the weight of the material being treated. If desired, even much larger amounts of ammonia may be used, e. g. 100% or more; however, the use of such large amounts of ammonia while not being detrimental is not particularly advantageous. When other forms of ammonia are being employed, the amounts used are equivalent to that just set forth.

Preferably the crude vegetable oil is treated with the ammonia in the presence of a solvent for the oil. However, it is not necessary to carry out the treatment in the presence of a solvent, and in some cases it may be preferred not to do so. For example, in the event that ammonia gas is used, the process may be carried out in a closed vessel under pressure of the ammonia gas. The length of time of contact of the crude vegetable oil with the ammonia will vary depending upon whether or not the treatment is carried out in the presence of a solvent for the oil and whether the treatment is carried out at room temperature or at elevated temperatures. Both the presence of the solvent and increased temperatures will accentuate the action of the ammonia and thus reduce the amount of time necessary for the treatment step. When treating the crude oil in the presence of a solvent, it is preferred to heat the mixture at the reflux temperature of the solvent for a short time, e. g. half an hour to an hour although it may be heated longer, if desired. The heating may be carried out in an inert atmosphere, e. g. in the presence of nitrogen gas, if desired.

Oil solvents which may be used in the ammonia treatment step of my process include hydrocarbon and halogenated hydrocarbon solvents such as hexane, heptane, octane, ethylene dichloride, trichloroethylene, carbon tetrachloride, cyclohexane, methyl cyclohexane, benzene, etc., as

well as solvents such as acetone, isopropanol, diacetone alcohol and the like. Of these many solvents I prefer to employ acetone as it appears to give the most favorable results in the process. However, any of the other solvents will give excellent results, and they, or any desired mixtures thereof, may be used if desired.

If the process of the invention has been carried out upon a crude vegetable oil associated with a vegetable meal, or other similar vegetable material, the solvent with the crude oil dissolved therein, is separated from the vegetable meal after the ammonia treatment has been completed, and the meal is then washed with additional portions of the same oil solvent, or a different oil solvent, if desired, to completely remove the oil therefrom. If no oil solvent has been employed in the ammonia treatment step of the process, the oil containing the highly potent antioxidants may be removed from such vegetable material by washing the same with one of the oil solvents listed above. However, if desired, the treated oil-bearing vegetable material may be dried by exposure to the atmosphere, or by any other suitable means, thus removing the ammonia and the greater part of any oil solvent employed in the ammonia treatment step. The fatty material may then be removed from the treated oil-bearing vegetable material by extraction with any suitable oil solvent. Instead of removing the oil from the oil bearing vegetable material by means of solvent extraction, other conventional means of removing the oil from the oil-bearing vegetable material, e. g. the expeller process or the hydraulic process, may be employed to remove the oil in all the above cases from the oil-bearing vegetable material.

The ammonia treated oil will have dissolved therein a large amount of highly potent antioxidants. The exact nature of these antioxidants has not yet been determined. No doubt a large percentage of these antioxidants was originally present in the crude vegetable oil, and in the vegetable meal or similar vegetable material if such were employed in the process of the invention, and the effect of the ammonia treatment was to release these antioxidants with much greater efficiency than has ever been done heretofore. However, it is very probable that the ammonia also reacted with certain of the original antioxidants in such a manner as to greatly increase their potency or to produce therefrom new antioxidants of greater potency than the original antioxidants. Furthermore, it may be that the ammonia treatment converts certain compounds in the vegetable oil and vegetable meal which themselves have no antioxidant activity into materials which are excellent antioxidants. The most probable explanation is that a combination of all of the above occurs. Whatever may be the true explanation, I have discovered that the treatment as outlined hereinabove produces very highly potent antioxidants. However, since they are dissolved in a relatively large amount of oil, it is desirable that they be concentrated by separating them from the bulk of the oil.

If a crude vegetable oil has been treated in association with a vegetable meal or similar material, the treated oil may be separated from the solvent used to remove the oil from the treated oil-bearing vegetable material following the ammonia treatment step of the process by any convenient means, e. g. by distillation of the solvent under reduced pressure.

In carrying out the separation of the antioxidants from the highly potent oil solution thereof, the oil is mixed with a highly polar solvent which is substantially immiscible with fatty materials at room temperature or at temperatures substantially above room temperature. Such solvents which I have found to be suitable for use in the process of my invention include isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water. The antioxidants which it is desired to concentrate are soluble in these solvents at room temperature whereas the oil is immiscible therewith or relatively so. While these solvents have proved to be very successful in the practice of the invention, it is highly preferred to use aqueous isopropanol and particularly 80% to 90% isopropanol.

It will be noted that several of the solvents suitable for use in the fractionation step of the process may also be employed in the ammonia treatment step, and in extracting fatty material from a treated oil-bearing vegetable material, with the exception that in such steps the solvents contain very little, if any, moisture. Consequently, when one of these solvents is employed in such steps, it need not be separated from the oil prior to the fractionation step. By merely adjusting the ratio of solvent to oil, if necessary, so that it will be in proper proportion for the fractionation step, and by adjusting the water content of the solvent to the proper figure by the mere addition of water to the mass and admixing, the step of separating the oil and the solvent after the ammonia treatment and prior to the fractionation step of the process may be eliminated.

In carrying out the extraction of the antioxidants from the highly potent oil solution thereof, the oil is first mixed with the particular solvent to be employed. The relative proportion of oil to solvent may vary widely; the ratio of solvent to oil should be greater than one, and preferably two to fifty parts of solvent to one part of oil are used. If desired the solvent-oil mass may be warmed to a temperature slightly or substantially above room temperature. By so doing it is sometimes possible to obtain somewhat more intimate contact of the solvent with the fatty material and thereby obtain a more efficient and complete concentration of the antioxidants. The solvent solution and the fatty material may then be separated from each other at the elevated temperature or the mixture may first be allowed to cool to room temperature before completing this step of the process. The extraction may be carried out, if desired, in an inert gas atmosphere, e. g. in the presence of nitrogen gas. When the process of the invention is carried out on a crude vegetable oil associated with a vegetable meal, it is preferred to separate the oil from the vegetable meal prior to carrying out the fractionation step. However, such removal may be dispensed with, if desired, and the fractionation step may be carried out directly upon the treated oil-bearing vegetable material by contacting the fractionating solvent therewith.

The antioxidant concentrate separated from the oil may be recovered in any suitable manner. As the solvent and the oil are immiscible at room temperature or at temperatures substantially above room temperature, they may be separated by decantation, centrifugation or any other suitable means. The solvent solution may then be filtered and treated to remove the solvent there-

from, e. g. by vacuum distillation, whereby an antioxidant concentrate far more potent than any previously produced will be obtained. If desired, water may be added to the concentrate to precipitate any 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 concentrate. If the ammonia employed in the ammonia treatment step of the process has not already been evaporated or distilled off incidental to the previous steps of the process, it will be removed in the final step of the process when the extracting solvent is removed from the antioxidant concentrate.

Although the exact nature of these antioxidants has not yet been determined, I have observed that the antioxidant concentrates have a lower iodine value than the vegetable oils from which they are derived.

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, cottonseed 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.

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

For a fuller understanding of the nature and objects of the invention reference may 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.

Example I

Several samples of crude vegetable oils were treated with concentrated aqueous ammonia in the presence of acetone by mixing for about one hour at a temperature of about 55° C. under reflux conditions. The acetone and ammonia were removed from the oil by distillation under reduced pressure. Portions of the treated oils were then fractionated with various of the fractionating solvents listed hereinabove, two extractions being made in each case with a ratio of four parts of fractionating solvent to one part of oil. The solvent and the treated oil were contacted at room temperature, and thereafter the solvent layer was separated from that portion of the oil immiscible therewith. A highly potent antioxidant concentrate was recovered in each case upon removal of the solvent from the solvent layer by distillation under reduced pressure.

The relative potencies of these antioxidants were compared with the potencies of antioxidants prepared by the process of my U. S. Patent No. 2,396,680 patented March 19, 1946, by admixing with various samples of a refined shark liver oil amounts of the various antioxidants equal to 3% of the weight of each shark liver oil sample. The stability of these samples of refined shark liver oil was then determined by maintaining the samples at a temperature of 34.5° C. in contact with the atmosphere and measuring the percentage of vitamin A loss in each sample after a definite number of days had elapsed. A control experiment on an unstabilized sample of the shark liver oil was also conducted.

Further details and the results of the above experiments are given in the following table:

Veg. Oil	Gms. of Veg. Oil	Mls. of Conc. Ammonia (28%)	Mls. of Acetone	Solvent Used in Fractionation Step	Per Cent Yield of Extract	Per Cent Vitamin A Loss in the Vitamin-Containing Oil After—		
						6 days	14 days	20 days
	Refined Shark Liver Oil Containing No Antioxidant Concentrate.							
Soybean Oil [1]	50			83% Isopropanol	5.0	41.5		
Do	1,000	300	2,000	do	7.1	4.1	22.7	
Do. [1]	35			85% Acetone	2.14	1.9	7.7	14.3
Do	1,000	300	2,000	do	2.4	2.0	21.0	
Cottonseed Oil [1]	50			83% Isopropanol	8.0	0	5.0	6.3
Do	500	300	2,000	do	8.5	0	24.5	
Do. [1]	50			85% Acetone	2.8	0	3.9	4.1
Do	500	300	2,000	do	3.8	2.0	21.0	
Wheat Germ Oil [1]	50			83% Isopropanol	12.2	0	0	4.0
Do	500	300	2,000	do	14.6	2.2	8.7	14.0
Do. [1]	50			85% Acetone	6.4	0	0	0
Do	500	300	2,000	do	8.4	3.6	10.3	15.6
						0	0	0

[1] These examples show the use of antioxidant concentrates prepared by the process of my U. S. Patent No. 2,396,680, dated March 19, 1946.

Example II

Several samples of oil-bearing vegetable materials were treated with concentrated aqueous ammonia in the presence of acetone by mixing for about one hour at a temperature of about 55° C. under reflux conditions. The treated masses were air dried at room temperature in open trays. The treated air-dried materials were then extracted with ethylene dichloride to remove the fatty material. These solvent extracts were filtered, and the solvent removed therefrom by distillation under reduced pressure. Portions of the fatty materials were then fractionated with

various of the fractionating solvents listed hereinabove, two extractions being made in each case with a ratio of four parts of fractionating solvent to one part of fatty material being employed. The solvent and the fatty material were contacted at room temperature, and thereafter the solvent layer was separated from that portion of the fatty material immiscible therewith. A highly potent antioxidant concentrate was recovered in each case upon removal of the solvent from the solvent layer by distillation under reduced pressure.

To demonstrate the stabilizing action of these antioxidants, various samples of a refined shark liver oil were admixed with amounts of the antioxidants equal to 3% of the weight of each shark liver oil sample. The stability of these samples was then determined as in Example I. A control experiment on an unstabilized sample of shark liver oil was also conducted. To further show the potency of the antioxidant concentrates of this invention, several samples of shark liver oil were stabilized by adding thereto antioxidant concentrates prepared by the fractionation of fatty materials extracted from untreated oil-bearing vegetable materials. The stability of the vitamin A in these samples was not nearly as great as in those samples stabilized by the antioxidant concentrates of the present invention.

Further details and the results of the above experiments are given in the following table:

Vegetable Meal	Vegetable Oil	Gms. of Veg. Oil	Gms. of Veg. Meal	Mls. of Conc. Ammonia (28%)	Mls. of Acetone	Yield of Oil, gms.	Solvent Used in Fractionation Step	Percent Yield of Extract	Percent Vitamin A Loss in the Vitamin-Containing Oil After— 6 Days	14 Days	20 Days
		Refined Shark Liver Oil Containing No Antioxidant Concentrate—Control Sample #1.						52.0			
	Soybean Oil [1]	35					85% Acetone	2.14	5.4	22.6	
Linseed Oil Meal	do	1,000	1,000	300	2,000	1,160	do	3.43	0.	1.1	2.4
Rice Bran	do	1,000	1,000	300	2,000	1,052	do	3.43	0.	0.6	1.7
Soybean Meal	do	1,000	1,000	300	1,500	1,189	do	2.14	2.4	3.2	4.5
Corn Germ Meal	do	1,000	1,000	300	1,000	1,170	do	4.28	0.	0.	2.0
		Refined Shark Liver Oil Containing No Antioxidant Concentrate—Control Sample #2.						41.5			
	Cottonseed Oil [1]	50					85% Acetone	2.8	0.	2.5	11.5
Rice Bran	do	1,000	1,000	300	1,500	1,097	do	6.0	0.	0.	1.7
	Soybean Oil [1]	50					83% Isopropanol.	5.0	2.0	21.0	
Linseed Oil Meal	do	1,000	1,000	300	2,000	1,160	do	23.0	1.5	5.9	4.7
Rice Bran	do	1,000	1,000	300	2,000	1,052	do	23.3	0.	3.2	10.2
Soybean Meal	do	1,000	1,000	300	1,500	1,189	do	23.2	1.9	5.4	9.5
Corn Germ Meal	do	1,000	1,000	300	1,000	1,170	do	21.3	0.	7.9	14.5

[1] These examples show the use of antioxidant concentrates prepared by the process of my U. S. Patent No. 2,396,680, dated March 19, 1946.

Example III

Several samples of relatively oil-free vegetable materials were admixed with various crude vegetable oils, and the resulting oil-bearing vegetable materials were processed as in Example II to produce highly potent antioxidant concentrates.

The potency of the antioxidant concentrates was determined as in Example I. For purposes of comparison control experiments on unstabilized samples of shark liver oil were also conducted. Also samples of the various crude vegetable oils employed to increase the oil content of the relatively oil-free vegetable materials were fractionated, and the potency of the resulting antioxidant concentrates compared with that of the antioxidant concentrates prepared by the process of the present invention. In each case when an antioxidant concentrate was added it was added in an amount equal to 3% of the weight of the oil being stabilized.

Details and results of the above experimnts are given in the following table. In each case when the fatty material was extracted from the vegetable oil-vegetable meal mixture, three extractions with ethylene dichloride were made employing a ratio of one to one (mls./gms.) of solvent to vegetable oil-vegetable meal mixture.

Oil Bearing Veg. Material	Gms. of Oil Bearing Veg. Material	Mls. of Conc. Ammonia (28%)	Mls. of Acetone	No. of Extractions with $C_2H_4Cl_2$	Ratio of $C_2H_4Cl_2$ to Oil-Bearing Veg. Mat.	Percent Yield of Oil	Solvent Used in Fractionation Step	Percent Yield of Extract	Percent Vitamin A Loss in the Refined Shark Liver Oil After— 6 Days	14 Days	20 Days	27 Days
	Control Sample of Refined Shark Liver Oil Containing No Antioxidant Concentrate								52.0			
Ground Soybeans [1]	1,000			2	5/2	12.0	85% Isopropanol.	8.0	13.2	39.4		
Do	2,000	200	2,000	2	5/2	14.7	do	8.5	12.6	33.5		
Ground Flaxseed [1]	500			2	4/1	33.4	do	10.5	51.5			
Do	1,000	100	1,000	2	4/1	33.0	do	8.8	17.7			
Whole Wheat Germ [1]	1,000			3	5/2	9.2	do	23.4	7.8	27.8		
Do	1,000	100	500	3	5/2	9.4	do	30.9	2.6	6.1	9.2	
Do. [1]	1,000			3	5/2	9.2	85% Acetone.	11.4	7.2	22.5		
Do	1,000	100	500	3	5/2	9.4	do	15.5	1.0	0.	6.2	
Corn Germ Meal [1]	2,000			3	2/1	7.5	83% Isopropanol.	21.4	8.4	42.0		
Do	2,000	200	2,000	3	2/1	7.9	do	22.0	1.3	2.6	4.6	5.7
Do. [1]	2,000			3	2/1	7.5	85% Acetone.	14.8	4.7	39.5		
Do	2,000	200	2,000	3	2/1	7.9	do	16.8	1.0	2.4	4.9	6.7

[1] These examples show the use of antioxidant concentrates prepared by the process of my U. S. Patent No. 2,396,680, dated March 19, 1946.

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

1. In a process for producing an antioxidant concentrate, the steps comprising contacting a

crude vegetable oil with ammonia, contacting the ammonia-treated oil with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the oil.

2. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with ammonia, contacting the treated material with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the treated material.

3. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with ammonia, removing fatty material from the oil-bearing vegetable material, contacting the fatty material with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the fatty material.

4. In a process for producing an antioxidant concentrate, the steps comprising contacting a crude vegetable oil with ammonia in the presence of a solvent for fatty materials, contacting the ammonia-treated oil with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water and separating a solvent solution containing a highly active antioxidant extract from the oil.

5. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with ammonia in the presence of a solvent for fatty materials, removing fatty material from the oil-bearing vegetable material, contacting the fatty material with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the fatty material.

6. In a process for producing an antioxidant concentrate, the steps comprising contacting a crude vegetable oil with ammonia in the presence of a solvent for fatty materials, heating the mass for a short time at the reflux temperature of the solvent, contacting the ammonia-treated oil with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the oil.

7. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with ammonia in the presence of a solvent for fatty materials, heating the mass for a short time at the reflux temperature of the solvent, removing fatty material from the oil-bearing vegetable material by extraction with a solvent for fatty materials, contacting the fatty material with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, and separating a solvent solution containing a highly active antioxidant extract from the fatty material.

8. In a process for producing an antioxidant concentrate, the steps comprising contacting a crude vegetable oil with ammonia in the presence of a solvent for fatty materials, heating the mass for a short time at the reflux temperature of the solvent, contacting the ammonia-treated oil with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, the ratio of solvent to oil being greater than 1, and separating a solvent solution containing a highly active antioxidant extract from the oil.

9. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with ammonia in the presence of a solvent for fatty materials, heating the mass for a short time at the reflux temperature of the solvent, removing fatty material from the oil-bearing vegetable material by extraction with a solvent for fatty materials, contacting the fatty material with a highly polar solvent selected from the group consisting of isopropyl alcohol, n-propyl alcohol, acetone, diacetone alcohol, ethyl acetate, methyl acetate, and methyl ethyl ketone, said solvents containing at least 10% of water, the ratio of solvent to fatty material being greater than 1, and separating a solvent solution containing a highly active antioxidant extract from the fatty material.

10. In a process for producing an antioxidant concentrate, the steps comprising contacting a crude vegetable oil with concentrated ammonium hydroxide in the presence of acetone, heating the mass for a short time at the reflux temperature of the acetone, contacting the ammonia-treated oil with isopropanol containing at least 10% of water, the ratio of solvent to fatty material being greater than 1, and separating the isopropanol solution containing a highly active antioxidant extract from the oil.

11. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with concentrated ammonium hydroxide in the presence of acetone, heating the mass for a short time at the reflux temperature of the acetone, removing fatty material from the oil-bearing vegetable material by extraction with ethylene dichloride, contacting the fatty material with isopropanol containing at least 10% of water, the ratio of solvent to fatty material being greater than 1, and separating the isopropanol solution containing a highly active antioxidant extract from the fatty material.

12. In a process for producing an antioxidant concentrate, the steps comprising contacting a crude vegetable oil with concentrated ammonium hydroxide in the presence of acetone, heating the mass for a short time at the reflux temperature of the acetone, contacting the ammonia-treated oil with acetone containing at least 10% of water,

the ratio of solvent to fatty material being greater than 1, and separating the acetone solution containing a highly active antioxidant extract from the oil.

13. In a process for producing an antioxidant concentrate, the steps comprising contacting an oil-bearing vegetable material with concentrated ammonium hydroxide in the presence of acetone, heating the mass for a short time at the reflux temperature of the acetone, removing fatty materials from the oil-bearing vegetable material by extraction with a solvent for fatty materials, contacting the fatty material with acetone containing at least 10% of water, the ratio of solvent to fatty material being greater than 1, and separating the acetone solution containing a highly active antioxidant extract from the fatty material.

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