Patented May 23, 1944

2,349,274

UNITED STATES PATENT OFFICE

2,349,274

ANTIOXIDANT

Kenneth C. D. Hickman, Rochester, N. Y., assignor to Distillation Products, Inc., Rochester, N. Y., a corporation of Delaware

No Drawing. Original application March 2, 1940, Serial No. 321,913. Divided and this application October 17, 1941, Serial No. 415,425

14 Claims. (Cl. 99—163)

This invention relates to improved procedure for preparing and employing antioxidants to improved antioxidant products and stabilized substances and the like.

It is common procedure to subject various vegetable and animal oils, fats, and the like to refining treatment in order to improve color, taste, odor, etc. It has been recognized that refined oils have rather poor keeping qualities and that they are decidedly inferior in this respect to the raw or crude oils. The refining treatments employed in most cases involved reaction with chemicals and deodorization in a vacuum with inert gases such as steam. The inert gas treatment in vacuum is usually the final step in the refining process with the possible exception of those cases where the oil is to be bleached.

This invention has for its object to provide improved antioxidants. Another object is to provide antioxidants which are satisfactory for edible materials. A further object is to provide improved procedure for stabilizing unstable or oxidizable substances, particularly foods and the like. Another object is to provide improved procedure for preparing antioxidants. Other objects are to provide improvements in the art of stabilizing materials and preparation of antioxidants. Other objects will appear hereinafter.

It is well known that during the deodorization of fats and the like by vacuum and inert gas treatment, such as steam, a small amount of volatile matter is obtained as a distillate or impurity in the distillate. When steam is employed for deodorizing, the material separates as a scum on the top of the water in the discharge from the barometric condenser. I have discovered that this material when obtained from vegetable and marine oils contains substances having a high antioxidant activity. I have found that the material can be employed as an antioxidant in the original condition in which it is removed from the deodorizing equipment or it may be refined before use.

The most common method of deodorizing oils involves vacuum treatment in the presence of steam. The vacuum is usually produced by means of a steam ejector and the steam is passed through the oil being refined. The steam which is passed through the oil is usually condensed in a barometric condenser and the condensed steam permitted to flow into a sump or condenser discharge. I have found that scum having high antioxidant qualities or potency is produced in relatively large amounts by this procedure and that it can be removed from mixed steam vapors, from the barometric condenser or from the sump into which the condenser discharges. The content of the scum in antioxidant potency vitamin E activity, and sterol and other accessory substance content is often many times that of the richest crude oils from which it is derived. The scum is thus a valuable primary concentrate of accessory substances in spite of it having been considered an annoying waste product for upwards of fifty years.

Many variations of the vacuum deodorizing method are employed by the different oil manufacturers and it is to be understood that my invention is applicable to all methods of deodorization which involve the use of incipient distillations in combination with a carrier gas, and that my improved antioxidant can be separated from the vapors or gases derived from the refined oil. Separation may be accomplished in the manner set forth above but it is equally feasible to separate the vapors, sludge or scum at intermediate stages such as between the deodorizing vessel and the evacuating pumps by means of catching vessels or condensers. Such material is known as deodorizer trap sludge. It is to be understood that the word scum as used herein shall include volatilized matter produced by each of the foregoing methods.

The antioxidant material is lighter than water and coats the surface of the condenser discharge or barometric sump with a thin scum. This material is known in industry as deodorizer hot well sludge. In collecting the active material the simplest method employed is to skim the substance from the surface of the water intermittently. It also tends to collect on the walls of the tank and can be scraped therefrom. The discharge from the condenser is usually rather warm and the discharge tank is often quite small. For this reason the scum may not separate or considerable amounts of the active material remain in solution or suspension and flow to the waste discharge. I have found that the yield of active substance can be considerably increased by completely cooling the condenser discharge or the contents of the discharge tank to approximately atmospheric temperature. The yield can also be increased by substantially increasing the size of the discharge tank or even providing an outside pond to the still surface on which the scum can rise. The discharged condensate can also be treated with a solvent, scrubbers, or passed through filters or screens. Any one or all of the foregoing expedients can be employed to improve the yield of the active material.

The scum can sometimes be employed effectively as an antioxidant in its original condition, or it may be subjected to a refining treatment to remove various substances some of which are inert impurities and others of which have an antagonistic action to that of the antioxidant. In addition to the antioxidant the scum contains, among other materials, sterols, waxes, unsaturated hydrocarbons, free fatty acids, small amounts of unchanged oil and soaps formed by the reaction between the free fatty acids and the dissolved solids which ordinarily occur in water. Calcium soaps are formed by this means and the antioxidant and the globules of oil, fatty acids, etc. are attracted to and precipitated in the calcium soaps. This product as removed from the deodorization procedure is a greasy, spongy substance.

Numerous methods of refining are available but the ones which appear at the present time to offer the best product are distillation, solvent extraction, neutralization or saponification or combinations thereof preceded if necessary by a chemical treatment such as washing with mineral acid to remove iron or calcium soaps. Vacuum steam distillation analogous to that employed in the original deodorization, yields a distillate of the antioxidants relatively free of fatty acids, sterols, etc. and substantially free of soaps. Ordinary vacuum distillation of the scum can be employed and at a temperature of 150 to 330° a fraction of high antioxidant potency is obtained. The scum may also be distilled in a molecular or similar still, under high vacuum, unobstructed path distillation conditions. A distillate having high antioxidant potency is obtained at about 120 to 220° C. The distillation treatment can be preceded by neutralization of the soaps and this procedure is usually desirable.

A portion of the antioxidant substance becomes entrained in the soaps but it has been found that solvents can be employed to extract the antioxidant therefrom. The solvent extract can then be distilled either to remove the solvent or to also distill off the antioxidant from the accompanying extracted materials.

The antioxidant of my invention, namely, the sludge or the refined products derived therefrom, can be employed to stabilize a wide variety of substances. For instance, it can be added to vitamin products, such as fish oils and vitamin concentrates produced therefrom by high vacuum distillation or saponification. It can be used in foods and in edible substances in general. For instance it can be added to edible oils, shortenings, lard, margarines, etc. to protect them against rancidity. It can also be added to the fat employed to prepare foods such as potato chips and the potato chips are stabilized thereby. It is of particular interest in connection with foods because the antioxidant is derived from natural animal and vegetable materials and its presence in foods, therefore, would be free of objection. The antioxidant can be added to rubber, gasoline, or to crude materials treated to yield such substances. The antioxidant has particular value for use in its crude condition for processes wherein an oxidizable substance is treated or purified, etc. For instance, if the crude sludge is added to a fish oil which is then subjected to alkali refining, followed by molecular distillation, a distillate containing the vitamins of the fish oils and the antioxidant of the sludge is obtained in relatively pure condition free from impurities accompanying the antioxidant in the original sludge. This procedure has the added advantage that the vitamin is protected during the entire treatment. If desired the antioxidant can be returned to the oil from which it was derived in the oil refinery. In this way the stability of the original oil is made to compare favorably with that of the raw oil before it was introduced into the refinery.

Example 1.—Treatment of corn oil deodorizer hotwell sludge to obtain materials of useful antioxidant value

The sludge as recovered from the hotwell contains up to 50 percent free fatty acids and seldom less than 10 per cent. The pipes and vessels are generally made of iron and the water from the ejector barometric leg generally contains calcium. The sludge, therefore, contains calcium and iron salts, the latter being especially detrimental to its use as an antioxidant. As a first stage in refining, the sludge may be melted, the water separated, and then wet filtered from the debris and much of the soaps. Alternatively, the sludge may be melted, much of the water drained away, and the residue treated with an organic or inorganic acid, which may be acetic or some other strong organic acid, sulfuric, hydrochloric or other acid giving soluble calcium and iron salts; sulfuric is widely used to liberate free fatty acids from crude soap-stocks but hydrochloric acid is the preferred acid for my purpose.

Example 1a

100 gallons of corn oil deodorizer sludge were treated with 12 gallons of commercial concentrated hydrochloric acid and themixture brought to boil, and intimate admixture, by contact with a steam jet. The acid and soluble chlorides were then allowed to settle, and the supernatant oil was washed three times with water. The oil was decanted and passed through a centrifuge until a substantially dry, bright oil of light brown color was secured. This oil contained approximately 2 per cent gamma tocopherol and was found suitable for addition to animal feeds without further treatment.

Example 1b

Before or during the boiling with hydrochloric acid as in Example 1*a*, zinc dust was added in the proportion of 5 pounds to 100 gallons of oil. This resulted in a marked reduction in the color, and the tocopherol quinones present were altered to the reduced form of the substance. The oil was worked up as before. Other metals which react with acid to give nascent hydrogen, such as iron can be used in place of zinc. The tocopheral in vegetable oil is present in the form of the quinone and hydroquinone form so that reduction of the quonine to the hydroquinone substantially reduces loss during subsequent procedures such as distillation.

Example 1c

The oil from any of the above examples was placed in a vacuum deodorizing kettle and the process of deodorization carried out with steam at a pressure of .1 mm. and a temperature of 130° C. After three hours most of the volatile fatty acids had been removed leaving substantially all of the gamma tocopherol in the kettle. The material was withdrawn and allowed to stand at a temperature near the setting point of the mass for two days, during which time a large quantity of vegetable sterols separated and

were filtered off. The liquid portion was found to contain 2¼ per cent gamma tocopherol and had an acid value of 4. It was found suitable for addition to lard, edible vegetable oils, and vitamin-bearing products for the purpose of stabilization.

Example 1d

The oil from the preceding example instead of being withdrawn from the still after subjection to a temperature of 130° C. was continued under vacuum with the passage of steam while the temperature was raised to 170° C. Material which contained 10 per cent free fatty acid and approximately 10 per cent tocopherol was collected from the barometric leg.

This material was worked up separately for the production of pure tocopherol, or alternatively it was returned to new batches of acid-treated sludge prior to deodorization. The temperature was now raised to 200° C. and a quantity of hotwell sludge collected which was substantially free from fatty acid and contained 15 per cent gamma tocopherol. This material was entirely suitable for adding to margarine, salad oils, etc., for the purpose of stabilization. The temperature was then raised to 250° C. and a further portion to tocopherol sludge recovered. By an alternative procedure a surface condenser was placed between the deodorizer and the steam ejector, and the materials collected here instead of as hotwell sludge. The residue from the final deodorization process was found to be a dark, neutral fat. This was passed through bleaching earth and was added to a batch of crude oil about to pass through the plant on the normal cycle of refining operations.

Example 1e

In this example the sludge is treated exactly as in the foregoing example except that it is placed in the deodorizing kettle without any previous acid or other treatment except as a convenience for the removal of most of the water.

Example 2a—Recovery of tocopherol from hotwell sludge obtained from the deodorization of soybean oil

Sludge is given acid treatment as in the previous example and is placed in a large vacuum kettle under a vacuum of 1 mm. of mercury. The temperature is raised to about 100°, and a quantity of distillate withdrawn which smells strongly of terpenes. It contains free fatty acids and at least two unsaturated hydrocarbons. The fatty acids can be separated by crystallization or neutralization, and the hydrocarbons further purified by distillation. The temperature is now raised to 150° when more hydrocarbons of a similar nature come over together with a liberal proportion of free fatty acids. The temperature is now raised to 200° C. and the pressure reduced to .1 mm. A mixture of residual free fatty acids comes over containing a mixture of alpha and gamma tocopherols. The distillate is cooled to separate the majority of acids, and the liquid filtered off containing 5–10 per cent tocopherols. The temperature is raised and further quantities of tocopherol solution substantially free from free fatty acids are removed. This solution may contain as much as 25 per cent mixed alpha and gamma tocopherols. It is suitable for employment as such in medicinal preparations for vitamin E activity or for the stabilizing of oils and foods, or the distillates may be further worked up to produce the further tocopherol or tocopherol palmitate.

All the distillates from this example when cooled separate into liquid and solid portions. Besides free fatty acids, a mixture of sterols which may contain as much as 50 per cent stigmasterol can be separated. Stigmasterol may be separated from this crude sterol by the preparation of the tetra-bromides, with subsequent hydrolysis. The residue left in the still is a low grade fat, the quality of which, however, is much higher than contained in the original sludge. It may be returned to the refinery cycle or may be used directly as a low grade fat.

Figure 2b

The acid-treated sludge after treatment in a vacuum still at 130°, as in the above example, may be transferred to a batch molecular still or a continuous molecular still or any form of high vacuum unobstructed or short-path still or to a continuous high-vacuum column still, and the tocopherols removed from the majority of the other constituents. Thus, the oil may be passed over the rotating plate of a centrifugal unobstructed path still operating at a pressure of three microns. The majority of the tocopherols will distill at 180° C. or between the limits 130–230° C. There will result a distillate containing from 10–30 per cent alpha and gamma tocopherols. Where a grid or other fractionating device is employed, as in Patent 2,180,052 to Hickman and Hecker, concentrations as high as 50–60 per cent tocopherols may be obtained.

Example 3.—Alpha tocopherol from cottonseed deodorizer trap sludge

The trap sludge is melted and filtered. If the fatty acid content is below 10 per cent, the fat is given an alkali refining at this stage. In either case, the melted sludge is allowed to enter a vacuum degasser at 90° C. at a pressure of 10 mm. Volatile hydrocarbons and terpenes are separated in an attached condenser. The degassed liquid is now allowed to enter the center of a long countercurrent fractionating distillation column, which column is the middle one of a series of several columns, maintained under a vacuum of 50 microns at the top and 3 mm. at the bottom end. The bottom end is maintained at temperatures ranging from 150 to 270° C. The columns have substantially unobstructed paths, between the vaporizing and condensing surfaces. From the first column, fatty acids and hydrocarbons are withdrawn; from the second, hydrocarbons; and from the third, a distillate of tocopherol which is substantially more potent than could be secured from a single molecular distillation. This apparatus with column still is described in detail in my application 187,454, filed 1/28/38.

Example 4—Use of crude scum to stabilize vitamins during refining

5 parts of a deodorizer scum containing 2 per cent tocopherol is added to 97 parts of grayfish-liver oil containing 15,000 units per gram vitamin A, and the mixture is given alkali refining. It is then distilled, under high vacuum, unobstructed path conditions yielding a fraction containing 230,000 units per gram of vitamin A and 1–1.5 per cent tocopherol. This represents a higher concentration of tocopherol than could be obtained by distilling a blend of grayfish-liver oil and 25 per cent of an average quality crude corn oil.

Example 5

10 parts of deodorizer scum are intimately mixed with 90 parts shark stearine containing 100,000 units of vitamin A per gram. The mixture is alkali refined, filtered, and distilled as in Example 4. A distillate is secured containing 90 per cent of the vitamin A in a concentration above three-quarters of a million units per gram and in the same concentrate there is between 2–4 per cent by weight of tocopherol.

Example 6—Stabilization of vitamins

Sardine oil is vacuum distilled to yield a concentrate containing 500 units per gram of vitamine D and 3,000 units per gram vitamin A. To 90 parts of this mixture is added 10 parts of neutralized and filtered deodorizer scum. The mixture is used as a stable vitamin feed for chickens.

Example 7

A concentrate is made by vacuum distillation or steam distillation or other means, consisting of tocopherol and hard fatty acids from deodorizer scum. This is blended with a vitamin A oil and is mechanically mixed with alkali, preferably lime in just sufficient quantity to neutralize all the free acid. The mixture sets to a hard cake which may then be pulverized and added to the animal feed. The vitamin A is found to be extremely stable in such powders and the lime salts are definitely beneficial as a constituent of feed.

Example 8—Stabilization of rubber

A low temperature distillate of tocopherol from one of the preceding examples containing too much odor and fatty acid to be readily acceptable for edible purposes is added to a rubber mix on the incorporating rolls in a rubber mill in the proportion of one part of distillate to 1000 parts of rubber. The mixture is finished and moulded into commercial articles in the ordinary way.

Example 9—Stabilization of lard

One part of odorless distillate prepared as in the foregoing examples and containing approximately 20 per cent tocopherol is added to 200 parts of lard and thoroughly mixed and the mixture placed in containers for the commercial market.

Example 10—Stabilization of hardened fat

One part of steam deodorized sludge prepared as in Example 1c, substantially free from taste and odor is added to 25 parts of a hydrogenated cottonseed frying oil and is used for the frying of chipped potatoes.

In all the previous examples the starting materials and the methods of processing are interchangeable. Thus, the first examples have been given in connection with gamma tocopherol and corn oil, and the last with alpha tocopherol from cottonseed oil. Nevertheless, any one of the sludges could be handled according to any of the examples.

Due to the high stability of vitamin concentrates which are stabilized by this antioxidant, they can be dispersed in animal foodstuffs without substantial loss. Heretofore this has been unsatisfactory procedure because the vitamin is necessarily exposed to atmospheric oxygen when distributed in the foods in this manner. Rapid loss was a consequence. However, with my highly active antioxidant this procedure is feasible and little loss results therefrom.

The active material can be obtained in the manner described from the sludges and the like derived from any natural animal oil or fat or the like which contains the tocopherols. However, all oils do not contain it and for this reason all distillate by-products can not be used. For instance sesame seed oil in its original condition or in hydrogenated condition is free of this material. However, I have found that most of these oils and fats do contain these substances and do yield highly potent wastes. Oils which give particularly active wastes are corn, peanut, soybean and cottonseed oils.

Since each stage in the refining treatment of an oil results in additional destruction of the antioxidant, I have found that it is best to modify the conventional refining scheme so that the deodorization step takes place at the first of the procedure and is then followed by the other refining steps such as alkali refining hydrogenation, bleaching, etc. In this way the original antioxidant content of the oil is available for recovering in the manner described.

By another modification I have found that it is feasible to recover the antioxidant of my invention by providing means for collecting vapors removed from paint or drying oils, such as linseed oil, during the bodying or polymerization step in paint oil manufacture. If desired, steam may be blown through the oil and/or vacuum may be applied. In the conventional polymerization procedure heretofore employed the active substance has been either decomposed completely or has been discharged into the atmosphere. The antioxidants are definitely detrimental to the drying oil and their removal is advantageous for this reason and also for the reason that the polymerization rate is increased.

I am aware of Patent 2,095,740, which describes the use of a heavier than water steam distillate of hydrogenated sesame seed oil. However, this oil does not contain tocopherol. Tocopherol is lighter than water and is contained in the scum which separates at the top of steam condensate.

This application is a division of my application 321,913 filed March 2, 1940.

What I claim is:

1. The process for stabilizing a vitamin bearing substance which comprises adding thereto a lighter-than-water tocopherol-containing substance which has an antioxidant activity and which has been separated from the class consisting of vapors and scum separated from a tocopherol-bearing fat during vacuum-inert gas deodorization of said fat.

2. The process which comprises adding to a vitamin bearing fat a lighter-than-water tocopherol containing crude vapor condensate derived from the vacuum-steam deodorization of a tocopherol bearing fat, subjecting the mixture of vitamin bearing fate and vapor condensate to alkali refining and then subjecting the refined mixture to high-vacuum, unobstructed path distillation to separate the vitamin content thereof.

3. The process which comprises subjecting a tocopherol bearing fat to vacuum-inert gas deodorization treatment, separating a lighter-than-water scum containing tocopherol from the inert gas and returning at least part of the contents of this scum to the fat after deodorization is completed.

4. The process of claim 3 in which the scum is purified before being returned to the fat.

5. The process of stabilizing a fat which is unstable to atmospheric oxidation which com-

prises adding to the fat a lighter-than-water tocopherol containing vapor condensate derived from the vacuum-steam deodorization of a tocopherol bearing fat and then subjecting the mixture of vapor condensate and fat to a refining treatment whereby a refined fat of high stability is obtained.

6. The process of protecting a substance which is normally subject to oxidation which comprises adding thereto a relatively small amount of lighter-than-water tocopherol containing vapor condensate derived from the vacuum-steam deodorization of a fat which contains tocopherol, said vapor condensate being condensed and separated from the steam after it has been passed through the fat being deodorized.

7. The process defined in claim 6 in which the vapor condensate is first refined.

8. The process which comprises treating a lighter-than-water tocopherol containing scum which is condensed and separated from the steam utilized for the vacuum-steam deodorization treatment of a fat which contains tocopherol, in order to separate or concentrate the tocopherol content of the scum and then adding the concentrated material to an easily oxidizable organic material in order to protect it against oxidation.

9. As a new product an organic substance which is subject to oxidation to which has been added lighter-than-water tocopherol containing scum derived from the vacuum-steam deodorization of a vegetable fat which contains tocopherol, said scum being condensed from the steam used in the deodorization after the steam has been passed through the fat.

10. The method of stabilizing shortenings which comprises in combination subjecting a lighter-than-water tocopherol containing scum derived from the vacuum-inert gas deodorization of a tocopherol bearing fat to a refining treatment for the removal of impurities including free fatty acids, and incorporating the refined scum in the shortening, said scum being condensed from the carrier gas utilized for the vacuum deodorization.

11. The process of claim 10 in which the shortening is lard.

12. The process of stabilizing an oxidizable substance which is unstable to atmospheric oxidation which comprises adding to the oxidizable substance a lighter-than-water tocopherol containing antioxidant comprising the matter volatilized during the steam-vacuum deodorization of a member of the group consisting of tocopherol-bearing vegetable and animal fats, and then subjecting this mixture of antioxidant and oxidizable substance to an alkali refining treatment whereby a refined oxidizable substance of high stability is obtained.

13. The process of stabilizing a fat which is unstable to atmospheric oxidation which comprises adding to the fat an antioxidant comprising the lighter-than-water tocopherol-containing material volatilized during the steam-vacuum deodorization of a member of the group consisting of tocopherol-bearing vegetable and animal fats, and then subjecting this mixture to an alkali refining treatment whereby a refined fat of high stability is obtained.

14. The process of stabilizing a shortening which is unstable to atmospheric oxidation which comprises adding to the shortening an antioxidant comprising the lighter-than-water tocopheral containing material volatilized during the steam-vacuum deodorization of a member of the group consisting of tocopheral-bearing vegetable and animals fats, and then subjecting this mixture to an alkali refining treatment whereby a refined shortening of high stability is obtained.

KENNETH C. D. HICKMAN.