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COLOR STABILIZATION

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This invention relates to a method of treating polyphenolic compounds and more particularly it relates to the prevention of discoloration of polyphenols and their partial esters by iron, copper or other polyvalent metals, especially in fatty preparations.

The use of polyphenolic substances for many purposes, such as antioxidants, is seriously hampered because of their tendency to discolor on standing. Overcoming of this unfortunate property would greatly expand the field of effectiveness of polyphenols, particularly as antioxidants for fatty oils or the like.

It has now been found possible to prevent the discoloration of polyphenols, particularly gum guaiac. The process preferably comprises a combination of two procedures, but either one alone is effective to a lesser extent. The first procedure is to dissolve the phenolic material in an alkaline solution followed by the separation therefrom of any insoluble material, for example, by filtration, centrifugation, decantation, extraction, or the like. To the alkaline solution is then added an acid substantially free of polyvalent metal ions which form colored salts, to regenerate the phenolic substance. The latter may then be recovered from the solution, if desired by filtration, centrifugation, extraction, decantation, or the like. In the case of the preferred water-insoluble polyphenols, these may be readily recovered from aqueous solutions by decantation or by filtration, if in solid form either at normal or lowered temperatures. Water soluble polyphenols may be recovered by salting out of solution, or by extraction with suitable solvents. The product is greatly improved as to color stability. The second procedure which is not necessary to the first but which may be used alone or in combination with the first to give a color stability much greater than that expected for either of the procedures alone is to add an acid to the phenol, which acid is stronger than acetic acid. This treatment is preferably employed as the acidification of the alkaline solution of phenol in the first procedure, employing it in slight excess of that necessary to neutralize the solution.

The alkaline treatment may be used in combination with the alkali refining of fatty oils or fats by dissolving the polyphenols in the fatty material with or without a mutual solvent, such as acetic acid, monostearin or the like, prior to the refining step. The fatty material is then treated with a quantity of alkali solution to remove free fatty acids therein. The alkali solution with soaps therein is separated by any suitable means

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such as settling, centrifuging, or the like. The stabilized oil is then free from a tendency to discolor. The oil may be treated by any of the usual methods such as bleaching, hydrogenation, deodorization, or the like without destroying the stabilization or color resistance, and in fact with improved results as to reversion resistance of the fatty material. This combined treatment is particularly effective with relatively water-insoluble polyphenols or relatively water-insoluble partial esters of polyphenols.

A variation of this method is to dissolve the polyphenolic material in a small amount of alkali solution. Any unsoluble material may be removed at this point if desired. The aqueous solution is then added to the fatty material which may then be refined by treatment with alkali as noted hereinbefore.

These procedures are unusually effective for gum guaiac or its partial esters which react with traces of certain metals such as nickel, iron, cobalt, copper and members of the groups commonly called heavy metals to yield colored products. The formation of colorations by the addition of certain metals, their oxides or salts to these compounds containing phenolic groups, not only discolors the polyphenols and their partial esters but also materials containing them even in small percentages. The colorations normally produced by iron salts vary from yellow or brown to reds, violets and blues, depending on the phenol present. The shade and intensity of the color formed is often indicative of the particular phenol.

Natural gum guaiac contains certain quantities of phenolic material and when these encounter traces of iron, copper or the like in a fat or oil, the same fat solution assumes a pink or purple color which varies in intensity with the quantity of gum or metal present. Presence of traces of iron and nickel is particularly common since fats, oils, and other materials protected from oxidation by gum guaiac are, for the most part, processed commercially in equipment made of one or both of these metals. Copper is picked up by edible fats from copper cooking utensils.

For example, undeodorized lard containing gum guaiac after deodorization at temperatures of 90 degrees C. to 110 degrees C. gives a pink color when heated in air. The color appears at 100 degrees C. and continued heating at 125 degrees C. or so results in a gradual fading and final disappearance of the color. Deodorization at about 150 degrees C. effects a reduction in the intensity of toe color, whereas the color fails to develop if much higher deodorization temperatures are em-

ployed. The use of high temperature deodorization of animal fats in particular gives rise to off and/or reverted flavors and odors, so that such a means of preventing coloration due to iron is not recommended for all purposes.

Oleaginous materials protected from oxidation by the addition of gum guaiac forms an intense purple coloration in the presence of cupric salts. Heating in copper vessels in the presence of air at 100°–150° C. is also sufficient to generate the purple coloration. This purple color, too, disappears upon continued heating.

It has now been found that the presence of traces of acid reacting materials prevent the formation of these colorations. Such acid reacting materials are inorganic and organic acids, acid salts, and salts of bases with acids stronger than the base. These acid reacting materials preferably are added in aqueous solution and may be incorporated near the end of the deodorization. Another operable procedure is an acidified wash of the fat which operation should leave a trace or more of the acid present in the fat. Certain weak organic acids do not prevent colorations. These are generally as weak as or weaker than acetic acid. Normal fatty acids are without effect. The iron, copper, or other metal, is not removed by this treatment. The exact mechanism of the function of the acidic materials is not known.

A further improvement in the prevention of colorations due to traces of metals in substances containing gum guaiac can be effected by a previous processing of the gum guaiac. This treatment can be applied to the crude gum guaiac or in any of its purer forms resulting from the extraction of the crude gum with special solvents. This purification embodies the extraction of the gum guaiac with alkalies, filtration of the alkaline extract and subsequent precipitation with an acid reacting material capable of neutralizing the alkali used. In a variation of this procedure applied to unrefined fats, the gum guaiac is dissolved in a minimum of alkali and water and added to the crude fats, and the fat plus gum guaiac is then refined with alkali in the usual way.

The following example is given for the purpose of illustrating the principle of the present invention but is not intended to be limiting on the scope thereof.

A lard containing 0.05% of gum guaiac is alkali refined and is deodorized in a standard deodorizing vessel by treatment with steam under vacuum at a temperature of between 200° to 250° F. for about three hours. About 0.1% of a 1% aqueous solution of citric acid is added to the deodorizing vessel and the treatment continued for another fifteen minutes to remove the water. The product after this double deodorization treatment is light colored and possesses exceptional color stability.

The concentration of the polyphenol or partial ester in the material to be stabilized may be varied over a wide range, for example, between 0.001% to 1.0%. The quantity of acid which may be used in conjunction therewith likewise can be varied over a wide range from a fraction of per cent of the polyphenol to several times the quantity of the polyphenol. Among the acids which may be so used include citric acid, tartaric acid, phosphoric acid, maleic acid, fumaric acid, aconitic acid, or the like. These acids present during the deodorization also materially assist in the improvement of reversion resistance and stability of the final product.

The alkali treatment which may be used alone and along with the acid treatment usually employs solutions of caustic soda but other caustic alkalis such as potassium hydroxide, ammonium hydroxide, pyridine or the like may also be employed. The alkali refining of the fats concurrent with the deodorizing of the phenol usually is conducted with aqueous caustic soda solution.

Solvents may be employed for the polyphenols or their compounds in any of the procedures in which they will be stable. For example, monoglycerides, fatty acids or fatty alcohols may be used to incorporate gum guaiac in the fatty material, such as, prior to alkali refining or the deodorization process.

Among the preferred class materials which may be improved by the present means are olive oil, butter, lard, cottonseed oil, soy bean oil, peanut oil, tallow, sesame oil, coconut oil, palm oil, palm kernel oil, safflower oil, sunflower oil, linseed oil, chaulmoogra oil, menhaden oil, sardine oil, spermaceti, sperm oil, whale oil, fish liver oils, vitamin concentrates, beeswax, wool fat, castor oil, tall oil, almond oil, cocoa butter, cashew nut oil, cashew nut shell oil, chicken fat, kapok oil, corn oil, rape oil, oiticica oil, perilla oil, tung oil, the full and partial hydrogenated derivatives of these oils, the individual fatty acids therein and mixtures thereof, the monohydric alcohol esters of the acids therein, and the full and partial polyhydric alcohol esters therein, various other derivatives of these fatty acids, and mixtures of any of the foregoing acid esters and other derivatives.

Although this invention is particularly directed to the improvement of fatty materials, it is also possible to similarly improve the other organic substances such as petroleum, lubricating oils, cracked and natural gasoline, fuel oils, gas oils, terpenes, carotenes and other hydrocarbons; soaps, essentail oils, flavors and perfumes; synthetic polyamides, glue, zein, gelatin, casein; rosin, shellac, copal, polyvinyls, polyacrylates and other natural and synthetic resins; rubber, polychloroprene, thickol, polybutadiene, polyisoprene, chicle, and other natural and synthetic rubbers; and/or the like with or without any of the aforementioned fatty materials. The improved products may be in the form of cosmetics, such as creams; foodstuffs, such as butter, lard, hydrogenated vegetable shortenings, margarine, mayonnaise, peanut and like nut butter, baked goods, cereals, meals, flours, soup and soup stocks; lacquers, paints, inks and plastics; medicines and vitamin concentrates.

The polyhydric phenols, such as gum guaiac, or their partial esters may be used alone or in mixtures or along wtih other antioxidants and modifying agents such as ctiric acid, malic acid, phosphoric acid, salicylic acid, benzoic acid, pyrogallol-acetone condensation product, phenyl mercury nitrate, phenol mercury acetate, hexyl resorcinal, aminophenol, mono- and di-hydroxy naphthalene, and the like. Glycerol, polyglycerol, ethylene glycol, polyglycols, propylene glycols, tetrahydrofurfuryl alcohol, acetic acid, propionic acid, lactic acid and the like can also be employed as solvents for assisting in the incorporation of gum guaiac into the organic material to be stabilized. The use of the ultimate composition determines the type of agent which may be so incorporated.

Obviously, many modifications and variations

of the invention hereinbefore set forth may be made without distinguishing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process of treating oleaginous material containing gum guaiac and normally tending to become discolored in the presence of metals, which comprises incorporating in said oleaginous material an acid reacting material stronger than acetic acid in sufficient amount whereby such discoloration is substantially retarded.

2. The process of stabilizing a fatty material, which comprises, adding to said fatty material gum guaiac and an acid stronger than acetic acid, said gum guaiac being present in sufficient amount to cause substantial stabilization of the fatty material against oxidative changes and to normally cause the development of undesirable colors in said fatty material in the presence of metals, and said acid being present in sufficient amount to substantially retard said development of undesirable colors.

3. The process of stabilizing fats and glyceride oils against oxidative changes on storage and discoloration in the presence of metals, which comprises, deodorizing said fats and oils in the presence of small amounts of gum guaiac and an acid stronger than acetic acid.

4. A process according to claim 3 in which the acid comprises phosphoric acid.

5. The process of treating shortening containing gum guaiac stabilizer to minimize development of color in the presence of metals, which comprises deodorizing the gum guaiac treated shortening and adding to the product a small amount of an acid stronger than acetic acid.

6. The process of treating fatty materials, which comprises, adding gum guaiac to the fatty material in sufficient amount to substantially stabilize the material against oxidative changes, deodorizing the resulting product and adding a small amount of an acid stronger than acetic acid near the end of the deodorizing operation.

7. The process according to claim 6 in which the acid comprises citric acid.

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