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ANTIOXIDANT COMPOSITIONS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Antioxidant compositions containing a mixture of colamine and/or a higher fatty acid salt thereof and a higher fatty acid ester of ascorbic acid are disclosed.

BACKGROUND OF THE INVENTION

Antioxidants are employed to delay the decomposition of oxidation-sensitive materials such as, for example, vitamin A, carotenoids, e.g. β -carotene, fats and oils containing unsaturated, oxidisable fatty acid esters, essential oils and other aromatic materials, and the like.

The most frequently employed antioxidants are tocopherols such as α - and γ -tocopherol, and related compounds such as α -tocopheramine, N-methyl- γ -tocopheramine, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), nordihydroguaiaretic acid (NDGA), gallates, especially those esters of gallic acid with alcohols having at least 3 carbon atoms such as, for example, propyl gallate, octyl gallate, decyl gallate, dodecyl gallate, 6-ethoxy-2,2,4-trimethyl-1,2-dihydro-quinoline, as well as mixtures thereof.

Antioxidants are often employed in combination with synergists such as adrenaline, noradrenaline, betaine, serotonin, choline, creatine, creatinine, hydroxytyramine, butylamine, hexylamine, octylamine, decylamine, dodecylamine, tetradecylamine, octadecylamine, tri-isoctylamine, di-isopropylamine, triamylamine, tributylamine, diamylamine, dicyclohexylamine fatty acid salts, dialkylamines with at least 10 carbon atoms in at least one alkyl group such as colamine; dilaurylamine; alkanol-, dialkanol- and trialkanolamines and fatty acid salts thereof; 8-hydroxyquinoline, aniline derivatives such as dimethylaniline; glucamines, morpholine derivatives, benzylamine, α -alanine, arginine, glycine, lysine, tryptophan, methionine, alanine, proline, valine, aspartic acid, serine, phenylalanine, threonine, histidine, leucine, cysteine, mercaptobenzimidazole, citric acid and salts thereof, citric acid esters such as, monoisopropyl citrate; palmitoyl-citric acid, citraconic acid, ascorbic acid, sodium ascorbate, higher fatty acid esters of ascorbic acid such as ascorbyl palmitate, ascorbyl stearate, ascorbyl laurate, ascorbyl myristate; tartaric acid, oxalic acid, malonic acid, maleic acid, fumaric acid, succinic acid, aconitic acid, hydroxamic acids, phosphoric acid and its acidic salts and esters, protein hydrolysates, gelatin, egg-yolk, urea, thiourea, thiouracil, thiodipropionic acid, didodecyl and dioctadecyl esters of thiodipropionic acid; oatmeal extract, oat oils, oat phosphatides, tomato puree, tetraalkylthiuram disulphides, chelate-formers, e.g., tetraacetic acid; vitamin D, reaction products of secondary amines, of aldehydes and of phenol; decomposition products of glucose, saccharose, starches, alanine, gelatin, and casein; polyphosphates, cephalin, lecithins, phosphatides, sorbitol, saccharose, polysaccharides, gums, resins, distillation residues of spice oils, dialkylphosphonates such as tert. butyl, isopropyl, methyl, sec. butyl, isobutyl, 2-methyl-4-pentyl, 2-ethylhexyl and 2,6-dimethylheptyl phosphonates, zinc dialkyl-dithiophosphate, zinc dibutyl-dithiocarbamate, lead chro-

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mate, iron oxide, 2-hydroxy-4-n-octoxy-benzophenone and the like.

The combination of antioxidants with any one of the synergists listed results in some increase in activity.

SUMMARY OF THE INVENTION

This invention relates to antioxidants compositions containing an antioxidant synergist mixture. More particularly, this invention relates to antioxidant compositions containing as the antioxidant synergist a mixture of two synergists, e.g., colamine and/or a higher fatty acid salt thereof and a higher fatty acid ester of ascorbic acid. As used herein throughout the specification and claims "higher fatty acid" refers to monocarboxylic saturated acids having from 10 to 20 carbon atoms, e.g., capric, lauric, palmitic, stearic, and the like.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that it is possible to increase the activity of antioxidants so that it exceeds the activity of known compositions containing a single synergist, by utilizing two synergists as defined hereinafter in the antioxidant composition. This is particularly significant since no criteria exists for utilizing the inventive combination in preference to the multitude of theoretical combinations using known synergists.

In its broadest aspect, this invention comprehends an antioxidation composition containing (a) an antioxidant, (b) colamine and/or a higher fatty acid salt thereof and (c) a higher fatty acid ester of ascorbic acid.

It has been found that a particularly strong synergistic action is achieved with tocopherols, which in view of the physiological acceptability of these materials is of extraordinary importance. In this respect, α - and γ -tocopherol are advantageously utilized. Thus the preferred composition of this invention contains as the antioxidant either α - or γ -tocopherol.

Colamine can be used as the base or as a salt with a higher fatty acid having 10–20 carbon atoms. The palmitate and the stearate are the preferred salts.

The ascorbic acid esters used in accordance with the invention are esters of higher fatty acids having from 10 to 20 carbon atoms, preferably palmitic or stearic acid.

The amount of ingredients in the antioxidation compositions of this invention are suitable within broad ranges. Thus, for every part by weight of antioxidant, the amount of colamine or colamine salt can suitably be from about 0.1 to about 50 parts by weight with about 1 to about 10 parts by weight preferred and the amount of ascorbic acid ester can suitably be from about 0.5 to about 100 parts by weight with about 1 to about 10 parts by weight preferred. The amount of antioxidation composition utilized in accordance with this invention depends on the requirements of the substrate to be stabilized. Amounts between about 0.01 and about 0.1% by weight are generally sufficient with oils and fats, and amounts between about 0.5 and about 30% by weight are sufficient in the case of vitamin A preparations. Thus, in its most comprehensive embodiment, this invention contemplates the use of from about 0.01 to about 5% by weight of the antioxidant composition for the stabilization of fats and oils having a content of unsaturated oxidizable fatty acid esters, as well as of essential oils and other aromatic substances. Many foodstuffs contain such oxidation-sensitive materials only as ingredients, often only in small concentrations. Such foods are hydrophilic in their nature and are denoted as "water-based foods." Examples of such foods are, for example, vegetables, especially in comminuted form, vegetable meals and conversion products thereof, meat commodities and the like. The good dispersability in aqueous environment of the antioxidant mixture in accordance with this invention is of advantage

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in such cases. The dispersability is particularly marked when colamine and the ascorbic acid ester are used in about stoichiometric amounts.

The following examples illustrate the invention. Temperatures are in degrees C.

EXAMPLE 1

2 g. of ascorbyl palmitate, 3 g. of sodium ascorbate, 0.5 g. of α -tocopherol, 0.6 g. of colamine and 1 g. of dextrin are dispersed in 20 ml. of water at 50°. The emulsion obtained is blended into 10 kg. of sausage meat for hard sausages. The sausages manufactured therefrom have stability equivalent to those whose filling contains double the amount of ascorbyl palmitate and no colamine or α -tocopherol.

EXAMPLE 2

1.5 g. of vitamin A palmitate, 1.5 g. of sunflower oil, 50 mg. of α -tocopherol, 250 mg. of ascorbyl palmitate, 250 mg. of colamine palmitate, 200 mg. of polyoxyethylene (2) oleyl ether (HLB value 4.9) and 0.3 mg. of copper oleate are heated to 60° and homogeneously mixed. This mixture is stored in air at 45° and the vitamin A retention is measured and compared to compositions without colamine and compositions without ascorbyl palmitate. After a storage time of 600 hours, the vitamin A retention in the composition prepared according to this example is 96%. In the composition without colamine, the vitamin A retention is 0% and in compositions without ascorbyl palmitate the vitamin A retention is about 10%.

EXAMPLE 3

1.5 g. of vitamin A palmitate, 1.5 g. of sunflower oil, 50 mg. of γ -tocopherol, 250 mg. of ascorbyl stearate and 250 mg. of colamine palmitate are heated to 60° and homogeneously mixed. This mixture is stored in air at 45° and the vitamin A content determined after 600 hours and compared to compositions without colamine palmitate and compositions without ascorbyl stearate. The vitamin A retention in the composition prepared according to this example is 95% while in the composition without colamine palmitate, vitamin A retention is 0% and in the composition without ascorbyl stearate the vitamin A retention is about 10%.

EXAMPLE 4

1.5 g. of vitamin A palmitate, 1.5 g. of sunflower oil, 50 mg. of butylated hydroxy anisole, 250 mg. of ascorbyl palmitate, 50 mg. of colamine, 200 mg. of polyethylene-glycol (2) oleyl ether and 0.3 mg. of copper oleate are heated to 60° and homogeneously mixed. This mixture is stored in air at 45°. The vitamin A-content is determined after 400 hours and compared to compositions without colamine and compositions without ascorbyl palmitate. The vitamin A retention in the composition prepared according to this example is 94% while in compositions without colamine, the vitamin A retention is 0% and in the composition without ascorbyl palmitate the vitamin A retention is about 10%.

EXAMPLE 5

0.25 g. of vitamin A palmitate, 2.5 g. of sunflower oil, 10 mg. of 6-ethoxy-2,2,4-trimethyl-1,2-dihydro-quinoline, 50 mg. of ascorbyl palmitate, 10 mg. of colamine, 200 mg. of polyoxyethylene (2) oleyl ether and 10.3 mg. of copper oleate are mixed with heating to 60° and homogeneously triturated. This mixture is stored in air at 45° and the vitamin A-content determined after 600 hours and compared to compositions without colamine and compositions without ascorbyl palmitate. The vitamin A retention in the composition prepared according to this example is 97%. The vitamin A retention in the composition without colamine is 10% and in the composition without ascorbyl palmitate present, the vitamin A retention is 80%.

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EXAMPLE 6

50 mg. of β -carotene, 10 mg. of α -tocopherol, 10 mg. of ascorbyl palmitate and 5 mg. of colamine palmitate are dissolved in 100 g. of sunflower oil with heating to 80°. The content of β -carotene is measured after a storage of 750 hours at 45° in air and compared to compositions without colamine palmitate and compositions without ascorbyl palmitate. The β -carotene retention in the composition prepared in this example is 66%. The β -carotene retention in the composition without colamine palmitate is 33% and in the composition without ascorbyl palmitate the β -carotene retention is 50%.

EXAMPLE 7

1 kg. of safflower oil with a natural content of tocopherols of about 400 mg./kg. (about 320 mg. thereof α -tocopherol) is treated with 100 mg. of α -tocopheryllamine, 200 mg. of ascorbyl laurate and 20 mg. of colamine palmitate. The stabilized oil is stored open in daylight at room temperature. The time-lapse until the attainment of a peroxide-number of 10 is 3.6 times longer than that for an oil without the addition of tocopheryllamine, ascorbyl laurate and colamine palmitate, while without addition of ascorbyl laurate this protection factor is 3.3 and without colamine palmitate it is 3.1.

EXAMPLE 8

100 g. of sunflower oil, 5 mg. of α -tocopherol, 10 mg. of ascorbyl laurate and 1 mg. of colamine are stored open and in the light. In accordance with the criteria mentioned in Example 6, the stabilized sunflower oil keeps 2 times longer than non-stabilized oil. Without ascorbyl laurate the oil keeps 1.7 times longer than the non-stabilized oil and without colamine it keeps 1.8 times longer than the non-stabilized oil.

EXAMPLE 9

1 kg. of pork lard is stabilized with 50 mg. of γ -tocopherol, 100 mg. of ascorbyl laurate and 10 mg. of colamine. According to the criteria in accordance with Example 6, the keeping quality of the stabilized lard exceeds that of the non-stabilized product about 10-fold. Without ascorbyl laurate the keeping quality exceeds the non-stabilized product 1.5 times, and without colamine it keeps 3 times longer than the non-stabilized product.

EXAMPLE 10

2.5 mg. of butylated hydroxy anisole, 2.5 mg. of butylated hydroxy toluene, 10 mg. of ascorbyl palmitate and 5 mg. of colamine palmitate are added to 100 g. of orange oil and dissolved by heating the oil in an air-free atmosphere. After storage for 10 days in an open dish, the stabilized orange oil still contains no noticeable oxidation products, whilst a control sample, without addition of the antioxidation composition, is clearly oxidized after 3 days, as evident by the presence of oxidation products.

EXAMPLE 11

0.6 g. of vitamin A palmitate, 1 mg. of D,L- α -tocopherol, 50 mg. of colamine palmitate and 100 mg. of ascorbyl palmitate are mixed homogeneously. This mixture is stored in air at 45° and the content of vitamin A is determined after 500 hours and compared to compositions with one or more components of the antioxidant composition omitted. The retention of vitamin A in the composition prepared according to this example is 95%. If one or two components of the antioxidant composition are omitted, the vitamin A retention is 0%.

We claim:

1. An antioxidant composition comprising (a) a compound selected from the group consisting of α -tocopherol, γ -tocopherol or mixtures thereof; (b) colamine palmitate and (c) ascorbyl palmitate.

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2. A process for the stabilization against oxidation of oxidation sensitive materials comprises adding thereto an antioxidative amount of an antioxidant composition comprising (a) a compound selected from the group consisting of α -tocopherol, γ -tocopherol or mixtures thereof; (b) col-
amine palmitate and (c) ascorbyl palmitate.

3. A process for the stabilization against oxidation of oxidation sensitive materials which comprises adding thereto an antioxidative amount of the antioxidant composition of claim 1.

4. An oxidation stable composition containing an oxidation sensitive material and an antioxidative amount of the antioxidant composition of claim 1.

5. The process of claim 3 wherein the oxidation sensitive material is vitamin A or a derivative thereof.

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