

UNITED STATES PATENT OFFICE

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COMPOSITION USEFUL AS AN ANTIOXIDANT
FOR FATS AND OILSJames E. Magoffin, Kingsport, Tenn., assignor to
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corporation of New JerseyNo Drawing. Application May 5, 1949,
Serial No. 91,635

8 Claims. (Cl. 252-404)

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This invention relates to compositions useful as antioxidants for fats and oils. This application is a continuation-in-part of my copending application Serial No. 37,972, filed July 9, 1948, now abandoned.

It has long been known that phenols, especially the dihydroxybenzenes, such as hydroquinone, are useful as antioxidants for fats and oils (Moureu et al. "Compt. rend." 174, 258 (1922); Husa et al. "Journal of the American Pharmaceutical Association" 17, 243 (1928)). It is also known that the phenolic compounds, such as the alkylated hydroxyphenyl ethers (for example, alkylated hydroxyanisoles, etc.) can be used as antioxidants for fats and oils. It is further known that the antioxidant action of such phenolic antioxidants can be synergized with acids, e. g. citric acid, orthophosphoric acid, tartaric acid, etc. While these phenolic compounds, as well as their synergistic combinations with acids, such as citric acid, etc. have been found to be highly effective in retarding the oxidative rancidity during storage of fats and oils, they are subject to the disability in many instances of being only slightly soluble in the fatty materials to which they are added. In processing such fats and oils a considerable percentage of the effective amounts of the antioxidants are frequently lost due to this lack of sufficient solubility.

I have now found that the dispersion of these antioxidants in fats and oils can be materially improved if a concentrate of these antioxidants in propylene glycol is employed. This concentrate has the advantage of materially increasing the solubility or dispersability of the antioxidants (or mixtures thereof) in the fatty material to be stabilized, thus enabling one to secure uniformly dispersed mixtures of the antioxidant in the fatty materials and more effectively to prevent oxidation with a given proportion of antioxidant to fat.

According to my invention, one or more alkylated hydroxyphenyl ethers, can be dispersed in propylene glycol to give a concentrate which is highly useful as an antioxidant for fats and oils. Advantageously, the total weight of the alkylated hydroxyphenyl ether in the concentrate is from 10 to 60% of the total weight of the concentrate. The remainder can be propylene glycol alone, or propylene glycol plus an additional antioxidant, e. g. a p-dihydric phenol, e. g. hydroquinone, toluhydroquinone, ethylhydroquinone, n-propylhydroquinone, n-butylhydroquinone, tert. butylhydroquinone, etc., or propylene

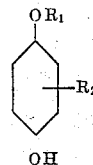
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glycol plus at least one synergizing acid, or propylene glycol plus the additional antioxidant plus at least one synergizing acid. Most advantageously, the total weight of the alkylated hydroxyphenyl ether in the concentrate is from 15 to 50% of the total weight of the concentrate.

When employed, the weight of the p-dihydric phenol is advantageously from 5 to 20% of the total weight of the concentrate. Where at least one synergizing acid is employed, the total weight of the synergizing acid is advantageously from 3 to 10% of the total weight of the concentrate. In no case, should the weight of propylene glycol be less than from 40 to 70% of the total weight of the concentrate.

Advantageously, the total weight of the alkylated hydroxyphenyl ether employed is from 1.75 to 2.25 times the total weight of the p-dihydric phenol. Advantageously, the total weight of the synergizing acid is from 0.3 to 0.7 times the total weight of the p-dihydric phenol.

The alkylated hydroxyphenyl ethers which I employ in practicing my invention can be represented by the following general formula:



wherein R₁ represents an alkyl group containing from 1 to 2 carbon atoms, and R₂ represents a tertiary alkyl group containing from 4 to 5 carbon atoms. Typical examples are: 2-tert. butyl-4-hydroxyanisole, 3-tert. butyl-4-hydroxyanisole, 2-tert. butyl-4-hydroxyphenetole, 3-tert. butyl-4-hydroxyphenetole, 3-tert. amyl-4-hydroxyanisole, 3-tert. amyl-4-hydroxyphenetole, etc.

Among the synergizing acids which I employ are citric acid, orthophosphoric acid, metaphosphoric acid, tartaric acid, ascorbic acid, etc.

An efficacious concentrate which can be prepared according to my invention is represented by the following example:

Example 1

	Parts by weight
Propylene glycol	100
Butylated hydroxyanisole	30
Hydroquinone	15
Citric acid	6

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Such a concentrate is of such composition that one pound is sufficient to stabilize one ton of lard. Such a concentrate is a homogeneous system even at temperatures as low as -20°C . It is, therefore, capable of being manufactured and handled in ordinary channels of commerce without separation of the added components. Propylene glycol is satisfactory for incorporation in edible products in concentrations much greater than result from use of this mixture. In contrast thereto, a material such as glycerin will not function in a satisfactory manner because of the difficulty of getting the above type compounds to disperse therein and like disadvantages.

In contrast to the fats stabilized against oxidative rancidity with hydroquinone without the use of propylene glycol as a dispersing medium, fats stabilized according to the method set forth in the above example contained the antioxidant uniformly dispersed throughout the entire body of the fat, thus enabling the fatty material to be stored for longer periods of time, and also to be further processed (as, for example, by cooking, etc.), without removal of the antioxidant, to give products which are also stable to the influences of oxidative rancidity.

Although the above example illustrates a composition containing hydroquinone, an alkylated hydroxyphenyl ether and a synergizing acid, my invention also contemplates a concentrate of butylated hydroxyanisole in propylene glycol, butylated hydroxyphenetole in propylene glycol, 2-tertiary amyl-4-hydroxyanisole in propylene glycol, 3-tertiary amyl-4-hydroxyanisole in propylene glycol, 2-tertiary amyl-4-hydroxyphenetole in propylene glycol, 3-tertiary amyl-4-hydroxyphenetole in propylene glycol, or mixtures of one or more (e. g. 1 to 3) of these alkylated hydroxyphenyl ethers with a p-dihydric phenol, or with at least one (e. g. 1 to 2) synergizing acid, such as citric acid, ortho-phosphoric acid, metaphosphoric acid, ascorbic acid, tartaric acid, etc., or with p-dihydric phenol plus at least one of said synergizing acids.

Moreover, in the above example, the citric acid can be replaced by 6 parts by weight of ascorbic acid, tartaric acid, metaphosphoric acid or orthophosphoric acid. Still other compositions which can be used are, for example, the following:

Example 2

	Parts by weight
Propylene glycol.....	100
Butylated hydroxyanisole.....	100

Example 3

	Parts by weight
Propylene glycol.....	100
Butylated hydroxyanisole.....	90
Orthophosphoric acid.....	10

Example 4

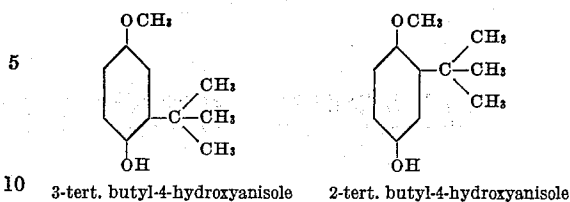
	Parts by weight
Propylene glycol.....	100
Butylated hydroxyanisole.....	35
Hydroquinone.....	15

Other fats or fatty materials, such as the glycerides of fatty acids, peanut oil, palm oil, coconut oil, cottonseed oil, soya bean oil, sunflowerseed oil, sesame oil, shortenings (especially those of the dry plastic type), fat-oil mixtures, etc. can be stabilized by dispersing therein, one of my concentrates in propylene glycol.

The butylated hydroxyanisole of the above ex-

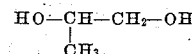
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amples is a mixture of about equal parts by weight of:



Instead of a mixture of 3-tert. butyl-4-hydroxyanisole and 2-tert. butyl-4-hydroxyanisole, like parts by weight of either of the compounds can be used in the above examples. The butylated hydroxyanisoles can be replaced with either 2-tert. butyl-4-hydroxyphenetole or 3-tert. butyl-4-hydroxyphenetole or a mixture thereof, or by 2-tert. amyl-4-hydroxyanisole or 3-tert. amyl-4-hydroxyanisole or 2-tert. amyl-4-hydroxyphenetole or 3-tert. amyl-4-hydroxyphenetole or a mixture of such tertiary amyl compounds.

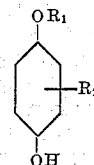
By the term "propylene glycol," I mean the compound which has the following formula:



The alkylated hydroxyphenyl ethers can be prepared by reacting p-hydroxyanisole or p-hydroxyphenetole with tert. butyl or tert. amyl alcohol, at a temperature of from 80° to 90°C ., in the presence of orthophosphoric acid as a catalyst. The alkylated hydroxyphenyl ethers can also be prepared by reacting p-hydroxyanisole or p-hydroxyphenetole with isobutylene or with isoprene in the presence of sulfuric acid.

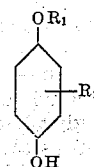
What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A concentrate containing propylene glycol and at least one alkylated hydroxyphenyl ether selected from the group consisting of those represented by the following general formula:



wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, the total weight of the alkylated hydroxyphenyl ether being from 10 to 60% of the total weight of the concentrate.

2. A concentrate containing propylene glycol, a p-dihydric phenol and at least one alkylated hydroxyphenyl ether selected from the group consisting of those represented by the following general formula:

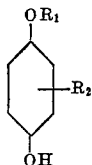


wherein R_1 represents an alkyl group containing from 1 to 2 carbon atoms and R_2 represents a tertiary alkyl group containing from 4 to 5 carbon atoms, the total weight of the alkylated hydroxyphenyl ether being from 10 to 60% of the total weight of the concentrate, and the weight of the p-dihydric phenol being from 15 to 30% of the total weight of the concentrate,

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the weight of the propylene glycol being from 40 to 70% of the total weight of the concentrate.

3. A concentrate containing propylene glycol, hydroquinone, at least one alkylated hydroxyphenyl ether selected from the group consisting of those represented by the following general formula:



wherein R₁ represents an alkyl group containing from 1 to 2 carbon atoms and R₂ represents a tertiary alkyl group containing from 4 to 5 carbon atoms, and at least one synergizing acid selected from the group consisting of citric acid, orthophosphoric acid, metaphosphoric acid, tartaric acid and ascorbic acid, the total weight of the alkylated hydroxyphenyl ether being from 10 to 60% by weight of the total weight of the concentrate, the total weight of the hydroquinone being from 15 to 30% of the total weight of the concentrate, the total weight of the synergizing acid being from 3 to 10% of the total weight of the concentrate, and the weight of the propylene glycol being from 40 to 70% of the total weight of the concentrate.

4. A concentrate containing propylene glycol, a mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole, hydroquinone and citric acid, the weight of the mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole being from 10 to 60% of the total weight of the concentrate, the weight of hydroquinone being from 15 to 30% of the total weight of the concentrate, the weight of the citric acid being from 3 to 10% of the total weight of the concentrate, and the weight of the propylene glycol being from 40 to 70% of the total weight of the concentrate.

5. A concentrate containing propylene glycol, a mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole, hydroquinone and citric acid, the weight of the mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole being from 10 to 60% of the total weight of the concentrate, the weight of the hydroquinone being from 15 to 30% of the total weight of the concentrate, the weight of the

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citric acid being from 3 to 10% of the weight of the concentrate, the weight of the propylene glycol being from 40 to 70% of the weight of the concentrate, the total weight of the mixture 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole being from 1.75 to 2.25 times the weight of the hydroquinone and the weight of the citric acid being from 0.3 to 0.7 times the weight of the hydroquinone.

6. A concentrate having the following composition:

	Parts by weight
Propylene glycol	100
Mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole	30
Hydroquinone	15
Citric acid	6

7. A concentrate having the following composition:

	Parts by weight
Propylene glycol	100
Mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole	100

8. A concentrate having the following composition:

	Parts by weight
Propylene glycol	100
Mixture of 2-tert. butyl-4-hydroxyanisole and 3-tert. butyl-4-hydroxyanisole	35
Hydroquinone	15

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