

UNITED STATES PATENT OFFICE

2,553,441

STABILIZATION OF ORGANIC MATERIALS

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No Drawing. Application March 29, 1947,
Serial No. 738,210

16 Claims. (Cl. 99-163)

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This invention relates to the stabilization of organic compounds which tend to deteriorate in storage or in use due to oxidation reactions.

Various organic compounds including motor fuel and particularly cracked gasoline and polymer gasoline, mineral oil, lubricating oil, fuel oil, drying oil, greases, rubber, edible fats and oils, etc., are adversely affected by oxygen, with the resultant formation of undesirable gum, discoloration, rancidity, or other deleterious reactions.

The invention is particularly applicable to the stabilization of edible fats and oils which generally are of animal or vegetable origin and which tend to become rancid, especially during long periods of storage prior to use. Typical representatives of these edible fats and oils include linseed oil, menhaden oil, cod liver oil, castor oil, olive oil, rapeseed oil, coconut oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, fat, lard, beef tallow, etc., as well as hydrogenated oils and fats such as are sold under various trade names including "Spry," "Crisco," "Snowdrift," etc. It is understood that other oils and fats may be treated within the scope of the present invention, including oils and fats which have previously been subjected to various treatments, such as blowing with air, heat treatment, etc.

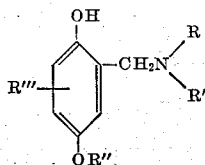
In one embodiment the present invention relates to a method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a disubstituted aminomethyl dihydroxybenzene.

In a specific embodiment the present invention relates to a method of stabilizing edible fats and oils against rancidity which comprises incorporating therein a dialkylaminomethyl-dihydroxybenzene.

In another specific embodiment the present invention relates to a method of stabilizing edible fats and oils against rancidity which comprises incorporating therein an inhibitor comprising a dialkylaminomethyl-4-alkoxyphenol.

In another specific embodiment the present invention relates to a method of stabilizing edible fats and oils against rancidity which comprises incorporating therein an inhibitor comprising a 2,5-bis-(dialkylaminomethyl)-hydroquinone.

The inhibitors of the present invention may be illustrated by the following general formula:



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Where R and R' are alkyl or cycloalkyl radicals which may also be substituted or where R and R' are carbon atoms of a heterocyclic ring, R'' is hydrogen, alkyl, aralkyl, aryl or alkaryl radical, and R''' is a disubstituted aminomethyl radical, hydrogen, alkyl, aralkyl, aryl or alkaryl radical.

Where R and R' are alkyl or substituted alkyl radicals and R'' is hydrogen, suitable compounds include 2-dimethylaminomethyl-hydroquinone, 2-diethylaminomethyl-hydroquinone, 2-dipropylaminomethyl-hydroquinone, 2-dibutylaminomethyl-hydroquinone, 2-diamylaminomethyl-hydroquinone, 2-di- β -hydroxyethylaminomethyl-hydroquinone. Derivatives in which R'' is an alkyl or substituted alkyl radical include such compounds as 2-dimethylaminomethyl-4-methoxyphenol, 2-diethylaminomethyl-4-methoxyphenol, 2-dipropylaminomethyl-4-methoxyphenol, 2-diamylaminomethyl-4-methoxyphenol, 2-dimethylaminomethyl-4-ethoxyphenol, 2-diethylaminomethyl-4-ethoxyphenol, 2-dipropylaminomethyl-4-ethoxyphenol, 2-dibutylaminomethyl-4-ethoxyphenol, 2-diamylaminomethyl-4-ethoxyphenol, 2-dimethylaminomethyl-4-propoxyphenol, 2-diethylaminomethyl-4-propoxyphenol, 2-dipropylaminomethyl-4-propoxyphenol, 2-dibutylaminomethyl-4-propoxyphenol, 2-dimethylaminomethyl-4-butoxyphenol, 2-diethylaminomethyl-4-butoxyphenol, 2-dipropylaminomethyl-4-butoxyphenol, 2-dibutylaminomethyl-4-butoxyphenol, 2-di- β -hydroxyethylaminomethyl-4-methoxyphenol, etc. Other suitable compounds of a hydroquinone or 4-alkoxyphenol type include those in which R and R' are cycloalkyl radicals as illustrated by 2-dicyclohexylaminomethyl-hydroquinone and 2-dicyclohexylaminomethyl-4-alkoxyphenols. Here again the alkoxy group may comprise ethoxy, methoxy, propoxy, butoxy, pentoxy, etc. radicals.

Also included within the scope of the present invention are compounds in which R and R' are different. Representative compounds of this category include hydroquinone or 4-alkoxyphenols substituted in the 2-position by radicals such as methylethylaminomethyl, methylpropylaminomethyl, methylbutylaminomethyl, methylamylaminomethyl, ethylpropylaminomethyl, ethylbutylaminomethyl, ethylamylaminomethyl, propylbutylaminomethyl, propylamylaminomethyl, butylamylaminomethyl, etc. and radicals in which R is an alkyl group and R' is a cycloalkyl group as in such radicals as methylcyclohexylaminomethyl and ethylcyclohexylaminomethyl.

Another class of compounds within the scope of the present invention include those in which

R and R' are carbon atoms of a heterocyclic ring. Heterocyclic rings include those derived from morpholine, piperazine, piperidine, and pyrrolidine.

Referring again to the structural formula heretofore set forth when R''' comprises a disubstituted-aminomethyl radical, it generally will be the same as the group attached in the 2-position. Suitable compounds include 2,5-bis-(dimethylaminomethyl)-hydroquinone, 2,5-bis-(morpholinomethyl)-4-hydroxyphenol, etc. and particularly 2,5-bis-(diethylaminomethyl)-hydroquinone.

It is understood that the various compounds which may be prepared and used within the broad scope of the present invention are not necessarily equivalent in their activity. In general it is preferred that the total number of carbon atoms in the inhibitor is not greater than about 25, as it has been found that, within certain limits, the potency of the inhibitor decreases with inclusion of hydrocarbon radicals of high molecular weight.

The inhibitors of the present invention may be prepared in any suitable manner. A particularly satisfactory method is to react the desired dialkylamine, formaldehyde, and either hydroquinone or the desired 4-alkoxyphenol under refluxing conditions for a time sufficient to complete the reaction. The products are separated and recovered by conventional methods. Specific details as to the preparation of these compounds are shown in the examples hereinafter set forth.

The inhibitor of the present invention is generally added to the organic material in amounts of less than 1% by weight and preferably within the range of from about 0.001% to about 0.5% by weight. The inhibitor may be used alone or in conjunction with synergists, inhibitor activators, dyes, antiknock agents, etc., depending upon the material to be treated. For example, when used in edible fats and oils, a synergist such as phosphoric acid, ascorbic acid, etc., will generally be added along with the inhibitor. When used in gasoline, lead tetraethyl, a dye and perhaps an inhibitor activator, such as certain types of alkylene polyamines, may be used.

The following examples are introduced to illustrate further the novelty and utility of the present invention, but not with the intention of unduly limiting the same.

Example 1

2,5-bis-(diethylaminomethyl)-hydroquinone was prepared as follows: hydroquinone and diethylamine were placed in a 3-necked flask fitted with a stirrer, thermometer and dropping funnel. A 35% formaldehyde-aqueous solution was added dropwise to the mixture which was stirred and maintained at a temperature of 20-30° C. The reaction product was extracted with ether, dried, the ether evaporated, and the residue recrystallized from methyl alcohol.

The 2,5-bis-(diethylaminomethyl)-hydroquinone prepared in the above manner was used to stabilize lard. The lard had a normal stability period of 1 1/4 hours as determined by the "Swift" test. This test is described in detail in the article by A. E. King, H. L. Roschen and W. H. Irwin, which appeared in the Oil and Soap vol. X, No. 6, pages 105 to 109 (1933). In general, this test comprises bubbling air through a sample of the lard until rancidity is determined organoleptically and by peroxide values.

0.02% by weight of the above inhibitor in-

creased the number of hours until the lard developed a peroxide number of 20 from 1 1/4 hours to 72 hours.

Example 2

2-dimethyl-aminomethyl-4-methoxyphenol was prepared in substantially the same manner as the inhibitor of Example 1 except that 4-methoxyphenol was used instead of hydroquinone and dimethylamine was used in place of diethylamine. This inhibitor was used to stabilize another sample of the same lard. 0.02% by weight of this inhibitor increased the stability period of the lard to reach a peroxide number of 20 from 1 1/4 hours to 35 hours.

Example 3

2-morpholinomethyl-4-methoxyphenol, likewise prepared in a similar manner, was also tested in another sample of the same lard. This inhibitor increased the stability period of the lard from 1 1/4 hours to 22 hours.

Example 4

2-dimethylaminomethyl-4-methoxyphenol was used to stabilize Pennsylvania cracked gasoline which had a blank induction period of 105 minutes. Upon the addition of 0.05% by weight of this inhibitor, the induction period of the cracked gasoline was increased from 105 minutes to 435 minutes. The induction period is determined by the Oxygen Bomb Stability Test which is a standard method for evaluating the storage stability of gasoline.

Example 5

0.05% by weight of 2,5-bis-(morpholinomethyl)-hydroquinone increased the induction period of another sample of the Pennsylvania cracked gasoline used in Example 4 from 105 minutes to 505 minutes.

I claim as my invention:

1. A method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a disubstituted aminomethyl-dihydroxybenzene.

2. A method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a dialkylaminomethyl-dihydroxybenzene.

3. A method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a dialkylaminomethyl-4-alkoxyphenol.

4. A method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a 2,5-bis-(dialkylaminomethyl)-hydroquinone.

5. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an inhibitor comprising a 2,5-bis-(dialkylaminomethyl)-hydroquinone.

6. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an inhibitor comprising 2,5-bis-(diethylaminomethyl)-hydroquinone.

7. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an inhibitor comprising a dialkylaminomethyl-dihydroxybenzene.

8. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an

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inhibitor comprising 2-dimethylaminomethyl-4-methoxyphenol.

9. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an inhibitor comprising 2 - morpholinomethyl - 4-methoxyphenol.

10. An organic compound tending to deteriorate due to oxygen containing a disubstituted-aminomethyl-dihydroxybenzene in an amount sufficient to retard said oxidative deterioration.

11. Edible fats and oils tending to become rancid containing a 2,5-bis-(dialkylaminomethyl)-hydroquinone in an amount sufficient to retard rancidity.

12. Edible fats and oils tending to become rancid containing 2,5-bis-(diethylaminomethyl)-hydroquinone in an amount sufficient to retard rancidity.

13. A method of stabilizing an organic material subject to oxidative deterioration which comprises adding thereto an inhibitor selected from the group consisting of a disubstituted aminomethyl-dihydroxybenzene and a dialkylaminomethyl-4-alkoxyphenol.

14. A method of stabilizing edible fats and oils against rancidity which comprises incorporating therein from about 0.005% to about 0.1% of an

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inhibitor selected from the group consisting of a disubstituted aminomethyl - dihydroxybenzene and a dialkylaminomethyl-4-alkoxyphenol.

15. An organic compound tending to deteriorate due to oxygen-containing an inhibitor selected from the group consisting of a disubstituted aminomethyl-dihydroxybenzene and a dialkylaminomethyl-4-alkoxyphenol in an amount sufficient to retard said oxidative deterioration.

16. Edible fats and oils tending to become rancid containing an inhibitor selected from the group consisting of a disubstituted aminomethyl-dihydroxybenzene and a dialkylaminomethyl-4-alkoxyphenol in an amount sufficient to retard rancidity.

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