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STABILIZATION OF ORGANIC COMPOUNDS

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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 are unstable in storage or during treatment and form undesirable gums, undergo discoloration, form sludges or otherwise deteriorate due to oxidation, polymerization or other undesired reactions. Included among the organic compounds which undergo such deterioration are gasoline, Diesel oil, mineral oil, transformer oil, lubricating oil, fuel oil, drying oil, greases, edible fats and oils, acetylenes and particularly vinyl acetylene, butadiene, isoprene, styrene and other vinyl aromatics, various unsaturated alcohols, acids, esters, ethers, ketones, etc.

This invention is particularly applicable to the stabilization of unsaturated gasoline and still more particularly cracked and polymer gasoline. In storage or during treatment these unsaturated gasolines tend to form undesirable gums. The invention is also applicable to the treatment of aviation gasolines which tend to undergo deterioration due to the addition of tetraethyl lead fluid or due to other components in the gasoline.

The invention is also 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, soya bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, fat, lard, beef tallow, etc. It is understood that other oils and fats may be treated within the scope of the present invention, including oils and fats which previously have been subjected to various treatments, such as blowing with air, heat treatment, hydrogenation, etc.

In another embodiment the present invention is particularly applicable to the treatment of crops by dusting or spraying in order to preserve food accessory factors such as carotene, vitamins, various fatty acids, alcohols, 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 2,6-dialkyl-alkoxyphenol.

In a specific embodiment the present invention relates to the stabilization of motor fuel normally tending to deteriorate in storage which comprises

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adding thereto from about 0.001% to about 0.5% by weight of 2,6-dimethyl-4-methoxyphenol.

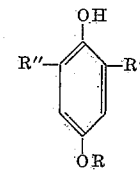
In another specific embodiment the present invention relates to a method of stabilizing edible fats and oils normally subject to oxidative deterioration which comprises adding thereto from about 0.001% to about 0.5% by weight of 2-methyl-6-tertiary-butyl-4-methoxyphenol.

In another specific embodiment the present invention relates to an organic material subject to oxidative deterioration containing, as an inhibitor for such deterioration, a 2,6-dialkyl-4-alkoxyphenol.

In still another embodiment the present invention relates to a novel composition of matter comprising a 2,6-dialkyl-alkoxyphenol and particularly 2,6-dimethyl-4-methoxyphenol, 2-methyl-6-tertiary-butyl-4-methoxyphenol and 2-methyl-6-secondary-butyl-4-methoxyphenol.

The 2,6-dialkyl-alkoxyphenols require special methods of preparation and cannot be prepared, for example, by the alkylation of an alkoxyphenol or of a 2-alkyl-4-alkoxyphenol by an olefin or alcohol as this results in the formation of a 2,5-dialkyl-4-alkoxyphenol.

The 2,6-dialkyl-4-alkoxyphenols of the present invention may be represented by the following general formula:



where R, R' and R'' comprise alkyl radicals.

The preferred inhibitors of the present invention comprise those in which R is an alkyl radical of not more than 4 carbon atoms, R' is a branched chain alkyl radical of from 3 to 10 carbon atoms, and R'' is an alkyl radical of not more than about 4 carbon atoms. Preferred inhibitors include 2-methyl-6-isopropyl-4-methoxyphenol, 2-methyl-6-isopropyl-4-ethoxyphenol, 2-methyl-6-tertiary-butyl-4-methoxyphenol, 2-methyl-6-secondary-butyl-4-methoxyphenol, 2-methyl-6-tertiary-amyl-4-methoxyphenol, 2-methyl-6-tertiary-hexyl-4-methoxyphenol, 2-methyl-6-tertiary-heptyl-4-methoxyphenol, 2-methyl-6-tertiary-octyl-4-methoxyphenol, 2-methyl-6-tertiary-butyl-4-ethoxyphenol, 2-methyl-6-secondary-butyl-4-ethoxyphenol, 2-methyl-6-tertiary-amyl-4-ethoxyphenol, 2-methyl-6-tertiary-amyl-4-ethoxyphenol, 2-methyl-6-tertiary-hexyl-4-ethoxyphenol, 2-methyl-6-tertiary-butyl-4-pro-

poxyphenol, 2-methyl-6-tertiary-amyl - 4 - propoxyphenol, 2-methyl-6-tertiary-butyl-4-butoxyphenol, 2-methyl-6-tertiary-amyl-4-butoxyphenol, 2-ethyl-6-tertiary - butyl-4-methoxyphenol, 2 - ethyl - 6 - tertiary amyl - 4 - methoxyphenol, 2-ethyl - 6 - tertiary-heptyl - 4 - methoxyphenol, 2-propyl - 6 - tertiary-butyl - 4 - methoxyphenol, 2-propyl - 6 - tertiary-amyl - 4 - methoxyphenol, 2-butyl-6-tertiary - butyl-4-methoxyphenol, etc. Other satisfactory but not necessarily equivalent compounds include 2,6-dimethyl-4-methoxyphenol, 2,6-dimethyl-4-ethoxyphenol, 2,6-dimethyl 4-propoxyphenol, 2,6-diethyl-4-methoxyphenol, 2,6-diethyl-4-ethoxyphenol, 2,6 - diethyl-4-propoxyphenol, 2,6-dipropyl-4-methoxyphenol, 2,6-dipropyl - 4 - ethoxyphenol, 2,6-dipropyl-4-propoxyphenol, 2,6-dibutyl-4-methoxyphenol, 2,6-dibutyl-4-ethoxyphenol, 2,6-dibutyl-4-propoxyphenol, 2-methyl - 6 - ethyl - 4 - methoxyphenol, 2-methyl-6-ethyl-4-ethoxyphenol, 2-methyl-6-ethyl - 4 - propoxyphenol, 2-methyl - 6 - ethyl-4-butoxyphenol, 2-methyl-6-propyl-4-methoxyphenol, 2 - methyl - 6 - propyl - 4 - ethoxyphenol, 2-methyl-6-propyl-4-propoxyphenol, 2-propyl-6-butyl - 4 - methoxyphenol, 2 - propyl-6-butyl-4-ethoxyphenol, 2-propyl-6-butyl-4-propoxyphenol, etc.

While the 2,6-dialkyl-4-alkoxyphenols may be prepared in any suitable manner, special methods of preparation are required because they cannot be manufactured by usual methods of preparation as hereinbefore set forth. A preferred method of manufacturing these compounds is by the use of the Mannich reaction. For example, when 2,6-dimethyl-4-methoxyphenol is desired, it may be prepared by the reaction of 4-methoxyphenol with formaldehyde and a suitable dialkyl amine such as dimethyl amine, diethyl amine, dipropyl amine, etc. In some cases, ammonia may be employed instead of the dialkyl amine but usually improved results are obtained with the dialkyl amine. In this particular preparation, it is desired to introduce two methyl groups in the aromatic ring and, therefore, at least 2 mols of formaldehyde are employed per mol of 4-alkoxyphenol. In general, it is also desirable to use an excess of dialkyl amine and this generally will be over 2 mols per mol of the alkoxy phenol. When the dialkyl amine comprises diethyl amine, the resultant product will be a diethyl-aminomethyl derivative. When an ethyl group or diethyl groups are desired, acetaldehyde will be used in place of formaldehyde. Similarly, when propyl or dipropyl groups are desired, propaldehyde is utilized, etc.

When 2-methyl-6-tertiary-butyl-4-methoxyphenol is desired, this is readily prepared by starting with 2-tertiary-butyl-4-methoxyphenol and reacting the same with formaldehyde in the presence of a suitable dialkyl amine. In this instance, at least one mol of formaldehyde per mol of alkoxyphenol is required. The 2-tertiary-butyl-4-methoxyphenol is readily prepared by the alkylation of 4-methoxyphenol with tertiary butyl alcohol in the presence of a phosphoric acid catalyst. Thus, 4-methoxyphenol may be reacted with tertiary butyl alcohol at a temperature of 75–80° C. in the presence of a catalyst comprising 85% phosphoric acid.

The dialkyl amine derivative of 4-alkoxyphenol is hydrogenated to form the desired 2,6-dialkyl-4-alkoxyphenol. The hydrogenation may be effected in any suitable manner, a preferred method being in the presence of hydrogen and a nickel catalyst at a temperature of from about 125° to about 200° C. or more, preferably at a substantial superatmospheric pressure which generally will range from 100 pounds to 1000 pounds or more per square inch.

The inhibitor of the present invention is generally added to organic materials in an amount of less than 1% by weight and preferably within the range of from about 0.001% to about 0.5%. When used in gasoline, it is understood that the inhibitor may be used in conjunction with various dyes, inhibitor activators, metal deactivators, antiknock agents such as tetraethyl lead, etc. When used in edible fats and oils, it is understood that the inhibitor may be used in conjunction with a synergist, such as phosphoric acid, ascorbic acid, etc.

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 I

2,6-dimethyl-4-methoxyphenol was prepared by reacting 4-methoxyphenol with formaldehyde and diethyl amine at room temperature. Over 2 mols of formaldehyde and over 2 mols of diethyl amine were used per mol of 4-methoxyphenol. The reaction occurred readily at room temperature and the product was extracted with caustic to remove unreacted methoxyphenol. The resultant product was then distilled to remove excess diethylamine and finally was recovered by extraction in acid to separate the desired product from by-products of the reaction. The product was washed and then hydrogenated in a pentane solvent with 10–20 weight percent of nickel catalyst, 1000 pounds per square inch of hydrogen at a temperature of 150° C. for a period of 6 hours.

0.02% by weight of the 2,6-dimethyl-4-methoxyphenol, prepared in the above manner, was added to a Pennsylvania cracked gasoline having a blank induction period of 90 minutes and this served to increase the induction period thereof to 395 minutes.

0.02% by weight of the 2,6-dimethyl-4-methoxyphenol was added to a lard having a normal stability period of 3½ hours and served to increase the stability period thereof to 18.75 hours.

Example II

2-methyl-6-tertiary-butyl - 4 - methoxyphenol was prepared in substantially the same manner as described in Example I except that 2-tertiary-butyl-4-methoxyphenol was utilized in place of 4-methoxyphenol as the primary reactant.

0.02% by weight of the 2-methyl-6-tertiary-butyl-4-methoxyphenol, prepared in the above manner, was added to another sample of the Pennsylvania cracked gasoline and served to increase the induction period thereof to 380 minutes.

When 0.02% by weight of the 2-methyl-6-tertiary-butyl-4-methoxyphenol was added to another sample of the lard having a normal stability period of 3½ hours, it served to increase the stability period thereof to 35 hours.

Example III

2 - methyl -6- secondary - butyl -4- methoxyphenol was prepared in substantially the same manner as described in the preceding examples. In this instance, 2-secondary-butyl-4-methoxyphenol was utilized as one of the primary reactants.

0.02% by weight of the 2-methyl-6-secondary-butyl-4-methoxyphenol was added to another sample of the cracked gasoline and served to increase the induction period thereof to 350 minutes.

0.02% by weight of the 2-methyl-6-secondary-butyl-4-methoxyphenol, when added to another sample of the lard, increased the stability period thereof to 24 hours.

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 2,6-dialkyl-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms.

2. A method of stabilizing motor fuel subject to oxidative deterioration which comprises adding thereto a 2,6-dialkyl-4-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms.

3. A method of stabilizing edible fats and oils subject to oxidative deterioration which comprises adding thereto an inhibitor comprising a 2,6-dialkyl-4-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms.

4. A method of stabilizing lard subject to oxidative deterioration which comprises adding thereto from about 0.001% to about 0.5% by weight of 2-methyl-6-tertiary-butyl-4-methoxyphenol.

5. Organic material subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2,6-dialkyl-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms. deterioration containing not more than 1% by

6. Edible fats and oils subject to oxidative weight of a 2,6-dialkyl-4-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms.

7. Lard subject to oxidative deterioration containing from about 0.001% to about 0.5% by weight of 2-methyl-6-tertiary-butyl-4-methoxyphenol.

8. Motor fuel subject to oxidative deterioration containing not more than about 1% by weight of a 2,6-dialkyl-4-alkoxyphenol in which one of the alkyl groups is a branched chain alkyl radical of from about 3 to about 10 carbon atoms, the other alkyl group contains not more than about 4 carbon atoms, and the alkoxy group contains not more than about 4 carbon atoms.

9. A method of stabilizing motor fuel subject to oxidative deterioration which comprises adding thereto from about 0.001% to about 0.5% by weight of 2-methyl-6-tertiary-butyl-4-methoxyphenol.

10. Gasoline subject to oxidative deterioration containing from about 0.001% to about 0.5% by weight of 2-methyl-6-tertiary-butyl-4-methoxyphenol.

11. Organic material subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2 - alkyl -6- tertiary - butyl - 4-ethoxyphenol, said alkyl group containing not more than about 4 carbon atoms.

12. Edible fats and oils subject to oxidative deterioration containing no more than 1% by weight of 2-methyl -6- tertiary-butyl -4- ethoxyphenol.

13. Organic material subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2 - alkyl - 6 - tertiary - amyl - 4-ethoxyphenol, said alkyl group containing not more than about 4 carbon atoms.

14. Edible fats and oils subject to oxidative deterioration containing no more than 1% by weight of 2-methyl-6-tertiary-amyl-4-methoxyphenol.

15. Organic material subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2 - alkyl - 6 - tertiary - octyl - 4-alkoxyphenol, said alkyl group containing not more than about 4 carbon atoms.

16. Edible fats and oils subject to oxidative deterioration containing no more than 1% by weight of 2-methyl-6-tertiary-octyl-4-methoxyphenol.

17. Organic material subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2,6-di-tertiary-alkyl-4-alkoxyphenol, one of said alkyl groups containing from about 3 to about 10 carbon atoms, the other alkyl group containing not more than about 4 carbon atoms, and the alkoxy group containing not more than about 4 carbon atoms.

18. Edible fats and oils subject to oxidative deterioration containing, as an inhibitor for said deterioration, a 2,6-di-tertiary-butyl-4-methoxyphenol.

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