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STABILIZATION OF ORGANIC COMPOUNDS

Ralph B. Thompson, Hinsdale, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

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1

This application is a continuation-in-part of my copending application Serial No. 5,209, filed January 29, 1948, now abandoned, and 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, 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, ketones, etc.

The invention is particularly applicable to the stabilization of unsaturated gasolines and still more particularly cracked and polymer gasolines. 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, olive oil, rapeseed oil, coconut 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 have previously been subjected to various treatments, such as blowing with air heat treatment, 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.

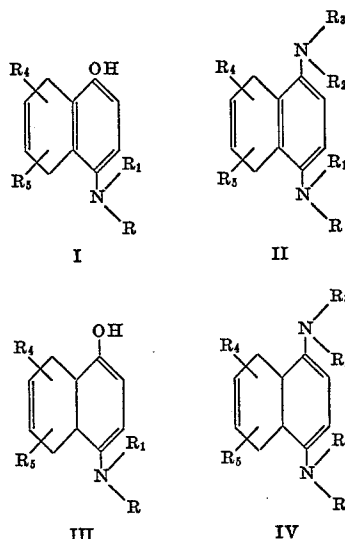
In one embodiment the present invention relates to an organic material subject to oxidative deterioration containing an inhibitor prepared by reacting an aliphatic amine with a member of the group consisting of 1,4-dihydroxy-5,8-dihydronaphthalene and 1,4-dihydroxy-5,6,7,8-tetrahydronaphthalene.

In a specific embodiment the present invention

2

relates to motor fuel normally tending to deteriorate in storage containing from about 0.001% to about 0.5% by weight of N-sec-butyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene.

The novel inhibitors of the present invention may be represented by the following general structure:



R, R₁, R₂, R₃, R₄, and R₅ may comprise hydrogen or alkyl radicals. When these groups comprise alkyl radicals, they preferably are selected so that the total number of carbon atoms in the inhibitor does not exceed about 25. Still more particularly, these compounds preferably comprise alkyl radicals containing from about 1 to about 4 carbon atoms and include such groups as methyl, ethyl, propyl and butyl.

General structure I above illustrates a 1-hydroxy - 4 - amino-5,8-dihydronaphthalene. Preferred inhibitors of this class include those in which R comprises an alkyl group and comprise such compounds as 1-hydroxy-4-methylamino-5,8 - dihydronaphthalene, 1 - hydroxy - 4 - ethylamino - 5,8 - dihydronaphthalene, 1 - hydroxy-4 - propylamino - 5,8 - dihydronaphthalene, 1-hydroxy - 4 - butylamino - 5,8 - dihydronaphthalene, 1 - hydroxy - 4 - dimethylamino - 5,8 - dihydronaphthalene, 1 - hydroxy - 4 - diethylamino - 5,8 - dihydronaphthalene, 1 - hydroxy-4 - dipropylamino - 5,8 - dihydronaphthalene, 1 - hydroxy - 4 - dibutylamino - 5,8 - dihydronaphthalene, N - ethyl - N - methyl - 1 - hydroxy-4 - amino - 5,8 - dihydronaphthalene, N - propyl-

3

N - methyl - 1 - hydroxy - 4 - amino - 5,8 - dihydronaphthalene, N - butyl - N - methyl - 1 - hydroxy - 4 - amino - 5,8 - dihydronaphthalene, N - propyl - N - ethyl - 1 - hydroxy - 4 - amino - 5,8 - dihydronaphthalene, N - butyl - N - ethyl - 1 - hydroxy - 4 - amino - 5,8 - dihydronaphthalene, etc.

Structure II illustrates a 1,4-diamino-5,8-dihydronaphthalene. Preferred inhibitors in this class include 1,4 - diamino - 5,8 - dihydronaphthalene, 1,4 - dimethylamino - 5,8 - dihydronaphthalene, 1,4 - diethylamino - 5,8 - dihydronaphthalene, 1,4 - dipropylamino - 5,8 - dihydronaphthalene, 1,4 - dibutylamino - 5,8 - dihydronaphthalene, 1 - methyl - amino - 4 - ethylamino - 5,8 - dihydronaphthalene, 1 - methylamino - 4 - propylamino - 5,8 - dihydronaphthalene, 1 - methylamino - 4 - butylamino - 5,8 - dihydronaphthalene, 1-ethylamino - 4 - propylamino - 5,8 - dihydronaphthalene, 1 - ethylamino - 4 - butylamino - 5,8 - dihydronaphthalene, 1 - propylamino - 4 - butylamino - 5,8 - dihydronaphthalene, etc. In the case of the di (alkylamino) compounds it is desirable that at least one of the alkyl groups is a sec-alkyl group such as isopropyl or sec-butyl.

Structure III illustrates a 1-hydroxy-4-amino-5,6,7,8 - tetrahydronaphthalene. Preferred inhibitors of this class include 1-hydroxy-4-methylamino-5,6,7,8 - tetrahydronaphthalene, 1 - hydroxy-4 - ethylamino-5,6,7,8 - tetrahydronaphthalene, 1-hydroxy-4-propylamino-5,6,7,8-tetrahydronaphthalene, 1-hydroxy-4-butylamino-5,6,7,8 - tetrahydronaphthalene, 1 - hydroxy-4-dimethylamino-5,6,7,8 - tetrahydronaphthalene, 1-hydroxy-4-diethylamino - 5,6,7,8 - tetrahydronaphthalene, 1-hydroxy-4-dipropylamino-5,6,7,8-tetrahydronaphthalene, 1-hydroxy - 4 - dibutylamino-5,6,7,8-tetrahydronaphthalene, N - ether - N - methyl-1-hydroxy-4-amino-5,6,7,8 - tetrahydronaphthalene, N-propyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene, N-butyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene, N-propyl-N-ethyl - 1 - hydroxy-4-amino-5,6,7,8 - tetrahydronaphthalene, N-butyl-N-ethyl-1-hydroxy - 4,5,6,7,8 - tetrahydronaphthalene, etc.

Structure IV illustrates a 1,4-diamino-5,6,7,8-tetrahydronaphthalene. Preferred inhibitors of this class include 1,4-diamino-5,6,7,8-tetrahydronaphthalene, 1,4-dimethylamino - 5,6,7,8 - tetrahydronaphthalene, 1,4 - diethylamino - 5,6,7,8-tetrahydronaphthalene, 1,4-dipropylamino-5,6,7,8-tetrahydronaphthalene, 1,4-dibutylamino-5,6,7,8 - tetrahydronaphthalene, 1 - methylamino-4-ethylamino - 5,6,7,8 - tetrahydronaphthalene, 1-methylamino-4-propylamino-5,6,7,8 - tetrahydronaphthalene, 1 - methylamino-4-butylamino-5,6,7,8 - tetrahydronaphthalene, 1 - ethylamino-4-propylamino - 5,6,7,8 - tetrahydronaphthalene, 1 - ethylamino - 4 - butylamino - 5,6,7,8-tetrahydronaphthalene, 1 - propylamino - 4 - butylamino-5,6,7,8-tetrahydronaphthalene, etc.

It is understood that the compounds hereinbefore set forth comprise preferred inhibitors and that compounds of these general structures otherwise substituted by suitable groups are also included within the scope of the present invention. For example, other satisfactory and in fact in many cases preferred inhibitors include those in which one or both of the hydrogen atoms attached to each nitrogen atom are replaced by alkyl groups. Specific examples of compounds of this class are specified in the list of preferred compounds of the class illustrated in general

4

Structures I and III. Similar di-substituted compounds of the diamino compounds illustrated by general Structures II and IV are comprised within the scope of the present invention. However, as hereinbefore set forth, it is preferred that the total number of carbon atoms in the inhibitors does not exceed about 25.

It is understood that the inhibitors of the present invention may comprise the specific compounds named herein in admixture with various isomers thereof. For example, in the dihydro-compound the isomers may comprise corresponding compounds in which the double bond in the non-aromatic ring has shifted to a conjugated position and/or those in which the hydroxy and amino groups have interchanged positions with respect to an alkyl group positioned on the non-aromatic ring. In the tetrahydro compounds, the isomers will be of the latter type.

The inhibitors of the present invention may be prepared in any suitable manner. In general, these inhibitors are prepared by the reaction of a 1,4-dihydroxy-5,8-dihydronaphthalene or 1,4-dihydroxy-5,6,7,8 - tetrahydronaphthalene with a suitable aliphatic amine. Suitable aliphatic amines include methyl amine, ethyl amine, propyl amine, isopropyl amine, n-butyl amine, isobutyl amine, sec-butyl amine, etc. The reaction is generally effected by heating the reactants at an elevated temperature and recovering the products by extraction in suitable solvents. As a typical example, a specific method of preparation is hereinafter set forth.

In one method of preparing 1-hydroxy-4-sec-butylamino - 5,8 - dihydronaphthalene and 1,4-di-sec-butylamino - 5,8 - dihydronaphthalene, 1,4-dihydroxy - 5,8 - dihydronaphthalene may be heated in a sealed tube with sec-butylamine at an elevated temperature of about 200° C. When the dialkylamino compound is desired the amount of sec-butylamine and the reaction time are increased in order to effect reaction of the amine with both of the hydroxy groups. After the reaction has proceeded to the desired extent, the product may be dissolved in an organic solvent, such as ether-petroleum ether, and then extracted with a dilute aqueous sodium hydroxide solution to remove the unreacted starting material. The product is subsequently extracted with Claisen solution to remove the 1-hydroxy-4-sec-butyl-5,8-dihydronaphthalene and to thereby separate it from 1,4-di-sec-butylamino-5,8-dihydronaphthalene. The other alkylamino substituted compounds may be prepared in a similar manner by varying the starting reagents as desired. Similarly the tetrahydro substituted compounds are made in substantially the same manner by starting with 1,4-di-hydroxy-5,6,7,8-tetrahydronaphthalene.

When it is desired to produce compounds containing two alkyl groups attached to the same nitrogen atom, the monoalkyl substituted compound may be treated with a suitable alkylation agent such as dimethyl sulfate, diethyl sulfate, propyl chloride, etc. in order to produce the desired tertiary amine.

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, synergists, metal deactivators, anti-knock 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, citric acid, etc.

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

EXAMPLE I

The inhibitors used in the following runs were prepared in a manner similar to that heretofore set forth. These inhibitors were tested in a Pennsylvania cracked gasoline which had an induction period of 100 minutes. The inhibitor was added in a concentration of 0.01% by weight to different samples of the gasoline and gave the results as shown in Table I.

Table I

Inhibitor	Induction Period, Minutes
1-hydroxy-4-sec-butylamino-5,8-dihydronaphthalene.....	290
1-hydroxy-4-sec-butylamino-5,6,7,8-tetrahydronaphthalene.....	285
1,4-di-sec-butylamino-5,6,7,8-tetrahydronaphthalene.....	345
N-sec-butyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene.....	650

It will be noted that inhibitors of the present invention increased the induction period from 100 minutes to at least 285 minutes and that the last mentioned compound, which comprised a tertiary amine, increased the induction period to 650 minutes. The inhibitor of the present invention therefore preferably contains a tertiary amine grouping.

EXAMPLE II

The inhibitors used in the following run were prepared in a manner similar to that heretofore set forth. These inhibitors were added to lard which had a normal stability period of 9 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 and reporting the number of hours until the lard develops a peroxide value of 20. 0.02% by weight of the inhibitors were added to this sample of the lard and gave the results as shown in Table II.

Table II

Inhibitor	Stability Period, Hours
1-hydroxy-4-sec-butylamino-5,8-dihydronaphthalene.....	>111
N-sec-butyl-N-methyl-1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene.....	>111

It will be noted that the inhibitors of the present invention increased the stability period of the lard from 9 hours to greater than 111 hours.

I claim as my invention:

1. An organic material normally subject to oxidative deterioration containing, as an inhibitor for said deterioration, a small amount of an inhibiting compound selected from the group consisting of a 1-hydroxy-4-amino-5,8-dihydronaphthalene, a 1,4-diamino-5,8-dihydronaphthalene, a 1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene, and a 1,4 - diamino - 5,6,7,8 - tetrahydronaphthalene.

2. Unsaturated gasoline normally tending to deteriorate in storage containing, as an inhibitor for said deterioration, a small amount of a 1-hydroxy-4-amino-5,8-dihydronaphthalene.

3. Unsaturated gasoline normally tending to deteriorate in storage containing, as an inhibitor for said deterioration, a small amount of a 1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene.

4. Unsaturated gasoline containing a small amount of a 1-hydroxy-4-alkylamino-5,8-dihydronaphthalene.

5. Unsaturated gasoline containing a small amount of a 1-hydroxy-4-alkylamino-5,6,7,8-tetrahydronaphthalene.

6. Cracked gasoline containing from about 0.001% to about 0.5% by weight of N-sec-butyl-N - methyl - 1 - hydroxy - 4 - amino - 5,8 - dihydronaphthalene.

7. Cracked gasoline containing from about 0.001% to about 0.5% by weight of N-sec-butyl-N - methyl - 1 - hydroxy - 4 - amino - 5,6,7,8 - tetrahydronaphthalene.

8. Edible fats and oils normally tending to deteriorate in storage containing, as an inhibitor for said deterioration, a small amount of a 1-hydroxy-4-amino-5,8-dihydronaphthalene.

9. Edible fats and oils normally tending to deteriorate in storage containing, as an inhibitor for said deterioration, a small amount of a 1-hydroxy-4-amino-5,6,7,8-tetrahydronaphthalene.

10. Lard containing from about 0.001% to about 0.5% by weight of N-sec-butyl-N-methyl-1-hydroxy-4-amino-5,8-dihydronaphthalene.

11. Lard containing from about 0.001% to about 0.5% by weight of N-sec-butyl-N-methyl-1 - hydroxy - 4 - amino - 5,6,7,8 - tetrahydronaphthalene.

12. A composition as defined in claim 1 further characterized in that said organic material comprises unsaturated gasoline.

13. A composition as defined in claim 1 further characterized in that said organic material comprises a fatty substance.

14. A composition as defined in claim 1 further characterized in that said organic material comprises lard.

RALPH B. THOMPSON.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
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