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STABILIZATION OF ORGANIC COMPOUNDS

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This invention relates to the stabilization of organic compounds and more particularly to a novel method of improving the effectiveness of oxidation inhibitors in retarding deterioration of organic compounds.

Various organic compounds are unstable in storage or use, while being transported or during treatment, and form undesirable gums, undergo discoloration, become rancid or otherwise deteriorate due to oxidation, polymerization and/or other undesired reactions. Included among the organic compounds which undergo such deterioration and which are intended for treatment according to the present invention are, for example, motor fuel, diesel oil, mineral oil, lubricating oil, fuel oil, drying oil, edible fats and oils, greases, rubber, acetylenes, and particularly vinyl acetylenes, butadiene, isoprene, styrene, and other vinyl aromatics, various unsaturated alcohols, acids, ketones, etc.

The invention is particularly applicable to the stabilization of unsaturated gasoline and still more particularly cracked and polymer gasolines. In storage or during treatment, these unsaturated gasolines tend to form undesirable gums and undergo discoloration. 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, marine 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 lard, 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, 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 treatment such as blowing with air, hydrogenation, heat treatment, etc.

Still another use for inhibitors is in the treatment of forage crops to prevent loss of vitamins and food accessory factor content.

In order to retard such undesirable deterioration it is general practice to add an oxidation inhibitor to the organic compound. The oxidation inhibitor is usually added in amounts of less than 1% by weight and generally within the range of from about 0.001% to about 0.1% by weight.

As applied to gasoline, preferred inhibitors comprise aromatic amino compounds and still more particularly p-phenylene diamines such as N,N'-di-secondary-butyl-p-phenylene diamine and p-aminophenols such as N-n-butyl-p-aminophenol. It is understood that other oxidation inhibitors include aromatic amino compounds in which different alkyl groups are included. Other satisfactory but not necessarily equivalent inhibitors include phenol, alkylphenols, and particularly the trialkyl phenols such as 2,4-dimethyl-6-tertiary-butylphenol, 2,6-ditertiary-butyl-4-methylphenol, hydroquinone, catechol, wood tar naphthol, naphthalene diol, hydroxycoumaran, hydroxychroman, hydroxyquinoline, etc.

As applied to the stabilization of edible fats and oils, the oxidation inhibitor employed must meet certain severe requirements. The inhibitor must function to prevent or retard rancidity, it must be non-toxic, it must not impart an undesirable odor, taste or color, and it must be readily soluble in the edible fats and oils. A number of oxidation inhibitors meet the requirements hereinbefore set forth in varying degrees. A particularly preferred inhibitor for edible fats and oils comprises a 2-tertiary-alkyl-4-alkoxyphenol and still more particularly 2-tertiary-butyl-4-methoxyphenol and 2-tertiary-butyl-4-ethoxyphenol. Other preferred inhibitors include N. D. G. A. (nordihydroguaiaretic acid), gum guiac and propyl gallate. Still other inhibitors include dialkylaminoalkyl-hydroquinones and particularly 2,5-bis-dimethylaminomethyl hydroquinone, dihydroxynaphthalenes, hydroxy-alkoxy-alkyl-dihydronaphthalenes and particularly 1-hydroxy-4-ethoxy-7-methyl-5,8-dihydronaphthalene, and related compounds. It is understood that the novel features of the present invention are applicable to any oxidation inhibitor which is suitable for use in organic compounds.

Regardless of the particular oxidation inhibitor employed, it has been found that the addition of certain compounds, to be hereinafter set forth in detail, serves to increase the effectiveness of the inhibitor beyond that which would normally be expected. Thus, the improved potency exceeds the additive effects of the oxidation inhibitor and of the additional compound. This unexpected improvement is referred to as a "synergistic effect" and the compound which produces this effect is referred to as a "synergist."

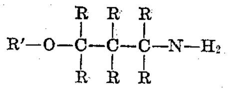
As will be shown by the examples appended to this specification, the synergist of the present invention possesses substantially no inhibitor potency when used alone. It is only through the mutual and inter-related effect with the oxidation inhibitor that the synergist serves to produce these improved results. This offers a particular advantage in permitting the use of smaller amounts of both the oxidation inhibitor and of the synergist to obtain satisfactory stabilization than is obtained with the use of oxidation inhibitor alone. The use of the combination of oxidation inhibitor and synergist also finds particular advantage in the treatment of certain organic compounds which are not as readily receptive to inhibitor addition as are other organic compounds.

In one embodiment the present invention relates to a method of stabilizing an organic compound subject to oxidative deterioration which comprises adding thereto an oxidation inhibitor and a synergist comprising an alkoxypropylamine.

In another embodiment the present invention relates to an organic material subject to oxidative deterioration containing an oxidation inhibitor and an alkoxypropylamine.

In still another embodiment the present invention relates to a stabilizing composition comprising an oxidation inhibitor and an alkoxypropylamine.

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



$$R'-O-\overset{R}{\underset{R}{C}}-\overset{R}{\underset{R}{C}}-\overset{R}{\underset{R}{C}}-N-H_2$$

where R' is an alkyl group and R is selected from the groups consisting of hydrogen and a hydrocarbon group. It is understood that the hydrocarbon group may be substituted by a non-hydrocarbon group including groups containing oxygen, nitrogen and/or sulfur.

It is a particular feature of the present invention that the alkoxy group and the nitrogen group are separated by 3 carbon atoms in straight chain arrangement. Preferred synergists comprise those in which R in the above formula is hydrogen and thus includes such compounds as methoxypropylamine, ethoxypropylamine, propoxypropylamine, butoxypropylamine, pentoxypropylamine, hexoxypropylamine, heptoxypropylamine, octoxypropylamine, etc. In general it is preferred that the alkoxy group contains not more than 4 carbon atoms, although for some uses compounds containing alkoxy groups of a larger number of carbon atoms may be advantageous. Furthermore, it generally is preferred that the total number of carbon atoms in the synergist compound does not exceed about 15 carbon atoms for most purposes.

When at least one of the R's in the above general formula is a hydrocarbon group, the synergist may include such compounds as 2-amino-4-methoxybutane, 2-amino-4-ethoxybutane, 2-amino-4-propoxybutane, 2-amino-4-butoxybutane, etc., 2-methoxy-4-aminobutane, 2-ethoxy-4-aminobutane, 2-propoxy-4-aminobutane, 2-butoxy-4-aminobutane, etc., 2-aminomethyl-3-methoxypropane, 2-aminomethyl-3-ethoxypropane, 2-aminomethyl-3-propoxybutane, 2-aminomethyl-3-butoxypropane, etc., 3-amino-5-methoxypentane, 3-amino-5-ethoxypentane, 3-amino-5-propoxypentane, 3-amino-5-butoxypentane, etc., 3-methoxy-5-aminopentane, 3-ethoxy-5-aminopentane, 3-propoxy-5-aminopentane, 3-butoxy-5-aminopentane, etc., 3-aminomethyl-4-methoxybutane, 3-aminomethyl-4-ethoxybutane, 3-aminomethyl-4-propoxybutane, 3-aminomethyl-4-butoxybutane, etc., 2-amino-4-alkoxypentanes, 3-amino-4-alkoxyhexanes, etc. 3-alkoxy-5-aminohexanes, etc., 2-amino-2-methyl-4-alkoxy-4-methylpentanes, 3-amino-3-methyl-5-alkoxy-5-methylhexanes, etc., 2-amino-2-methyl-4-alkoxy-4-methylhexanes, etc., 1-amino-1-phenyl-3-alkoxypropanes, 1-amino-2-phenyl-3-alkoxypropanes, 1-alkoxy-1-phenyl-3-aminopropanes, etc. It is understood that the alkoxy groups may contain from 1 to 6 carbon atoms or more and preferably contain from 1 to 4 carbon atoms. It is understood that the specific compounds herein set forth are merely representative and, in many cases, the preferred compounds of the large number which may be employed in accordance with the present invention and that these various compounds are not necessarily equivalent in their activity but all of them will exhibit a synergistic effect with oxidation inhibitors.

The synergist of the present invention may be prepared in any suitable manner. For example, methoxypropylamine may be prepared by the reaction of acrylonitrile with methyl alcohol followed by reduction. When ethoxypropylamine is desired, ethyl alcohol will be utilized, and so on.

The synergists of the present invention will generally be utilized in a concentration of from about 0.0001% to about 0.1% by weight of the organic material to be stabilized. In general the amount of synergist employed will be lower than the amount of oxidation inhibitor utilized . It is understood that the synergist may be used with two or more different oxidation inhibitors and/or with other compounds such as citric acid, phosphoric acid, alkyl amines, alkylene polyamines, 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

The synergist used in this example comprised methoxypropylamine. The substrate used in this example was a Pennsylvania cracked gasoline which had a blank induction period of 90 minutes. The oxidation inhibitor employed was N,N'-di-secondary-butyl-p-phenylene diamine which, when added in a concentration of 0.005% by weight to the cracked gasoline, served to raise the induction period thereof to 435 minutes.

The addition of 0.01% by weight of methoxypropylamine to the cracked gasoline not containing the oxidation inhibitor had substantially no effect and resulted in an induction period of 105 minutes. However, upon the addition of 0.01% by weight of methoxypropylamine to another sample of the cracked gasoline containing 0.005% by weight of the oxidation inhibitor, the induction period was increased to 645 minutes.

From the above data it is apparent that the methoxypropylamine had no inhibitor potency as such, but that its use in conjunction with the oxidation inhibitor served to considerably increase the induction period of the gasoline.

Example II

The oxidation inhibitor used in this example was N-n-butyl-p-aminophenol and, when added in a concentration of 0.01% by weight, increased the induction period of the cracked gasoline described in Example I from 90 to 340 minutes. When using 0.01% by weight of the oxidation inhibitor and 0.01% of methoxypropylamine, the induction period of the gasoline was increased to 500 minutes. Here it is again seen that the combination of oxidation inhibitor and synergist served to increase the induction period of the gasoline to a considerably greater extent than obtained only with the oxidation inhibitor.

Example III

The synergist used in this example was propoxypropylamine. When added in a concentration of 0.01% by weight to another sample of the Pennsylvania cracked gasoline, in the absence of the oxidation inhibitor, this compound had substantially no effect and resulted in an induction period of 95 minutes. When added in a concentration of 0.01% to another sample of the gasoline described in Example I, containing 0.005% by weight of the oxidation inhibitor described in Example I, the induction period of the gasoline was increased to 615 minutes.

Example IV

When propoxyproylamine was added in a concentration of 0.01% to another sample of the gasoline described in Example I but containing 0.01% of the oxidation inhibitor described in Example II, the induction period of the gasoline was increased to 495 minutes.

Example V

This example illustrates the beneficial effects obtained when using ethoxypropylamine along with an oxidation inhibitor in the stabilization of lard. The oxidation inhibitor may comprise 2-tertiary-butyl-4-methoxyphenol and is utilized in a concentration of 0.02% by weight. When this oxidation inhibitor is utilized in conjunction with 0.005% by weight of ethoxypropylamine, the stability period of the lard is considerably increased over and above that obtained by the oxidation inhibitor alone. The stability period is determined by measuring the number of hours until the lard reaches a peroxide number of 20 and this in turn is reported as the A. O. M. time.

I claim as my invention:

1. Gasoline normally subject to oxidative deterioration containing from about 0.001% to about 1% by weight of an oxidation inhibitor selected from the group consisting of a phenylene diamine and an aminophenol and from about 0.0001% to about 0.1% by weight of an unsubstituted alkoxypropylamine in which the alkoxy group contains not more than 4 carbon atoms.

2. Cracked gasoline containing from about 0.001% to about 0.1% by weight of a phenylene diamine inhibitor and from about 0.0001% to about 0.1% by weight of methoxypropylamine.

3. Cracked gasoline containing from about 0.001% to about 0.1% by weight of a phenylene diamine inhibitor and from about 0.0001% to about 0.1% by weight of ethoxypropylamine.

4. Cracked gasoline containing from about 0.001% to about 0.1% by weight of a phenylene diamine inhibitor

and from about 0.0001% to about 0.1% by weight of propoxypropylamine.

5. Cracked gasoline containing from about 0.001% to about 0.1% by weight of an aminophenol inhibitor and from about 0.0001% to about 0.1% by weight of methoxypropylamine.

6. Cracked gasoline containing from about 0.001% to about 0.1% by weight of an aminophenol inhibitor and from about 0.0001% to about 0.1% by weight of ethoxypropylamine.

7. Cracked gasoline containing from about 0.001% to about 0.1% by weight of an aminophenol inhibitor and from about 0.0001% to about 0.1% by weight of propoxypropylamine.

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