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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 or other reactions.

The novel method of the present invention is utilized for the stabilization of organic materials which are unstable in storage, during treatment and/or in use, and include motor fuel, particularly unsaturated gasoline, jet fuel, diesel oil, mineral oil, lubricating oil, fuel oil, drying oil, greases, waxes, plastics, resins, rubber, edible fats and oils, forage crops, monomers including styrene, butadiene, isoprene, acetylenes, etc., various unsaturated alcohols, acids, ketones, aldehydes, etc. These materials are adversely affected by oxygen, with the resultant formation of undesirable gum, discoloration, rancidity or other deleterious reaction products.

The invention is particularly applicable to the stabilization of hydrocarbons, including motor fuel and still more particularly unsaturated gasolines including cracked gasoline, coker distillate, polymer gasoline, etc. In storage or during transportation and/or treatment, these unsaturated gasolines tend to form undesirable gum and/or undergo discoloration. The invention also is 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 stabilization of greases, either of synthetic or petroleum origin. The synthetic greases generally are referred to as lithium base grease, sodium base grease, calcium base grease, barium base grease, strontium base grease, aluminum base grease, etc. These greases are solid or semi-solid gels and, in general, are prepared by the addition to mineral oils of hydrocarbon-soluble metal soaps or salts of higher fatty acids as, for example, lithium stearate, calcium stearate, aluminum naphthenate, etc. The grease may contain thickening agents such as silica, carbon black, polyacrylates, talc, etc. Another type of grease is prepared from oxidized petroleum wax, to which the saponifiable base is combined with the proper amount of the desired saponifying agent, and the resultant mixture processed to produce a grease. Other types of greases in which the features of the present invention are usable include petroleum grease, whale grease, wool grease, etc., and those made from inedible fats, tallow, butcher's waste, etc.

The present invention also is particularly applicable to the stabilization of lubricating oils, including those of petroleum or synthetic origin. The synthetic lubricants are of varied types including aliphatic esters, polyalkylene oxides, silicones, esters of phosphoric and silicic acids, highly fluorine-substituted hydrocarbons, etc. Of the aliphatic esters, di-(2-ethylhexyl) sebacate is being used on a comparatively large commercial scale. Other aliphatic esters include dialkyl azelates, dialkyl suberates, dialkyl pimelates, dialkyl adipates, dialkyl glutarates, etc. Specific examples of these esters include dihexyl azelate, di-(2-ethylhexyl) azelate, di-3,5,5-trimethylhexyl glutarate, di - 3,5,5 - trimethylpentyl glutarate, di-(2-ethylhexyl) pimelate, di-(2-ethylhexyl) adipate, triamyl tricarballylate, pentaerythritol tetracaproate, dipropylene glycol dipelargonate, 1,5-pentanediol-di-(2-ethylhexanonate), etc. The polyalkalene oxides and derivatives include polyisopropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diester, etc. The silicones include methyl silicone, methylphenyl silicone, etc., and the silicates include, for example, tetraisooctyl silicate, etc. The highly fluorinated hydrocarbons include fluorinated oil, perfluorohydrocarbons, etc.

The invention also may find particular use in the stabilization of fatty materials including the stabilization of edible fats and oils, which may be of animal, vegetable or mineral origin and which tend to become rancid especially during long periods of storage prior to use. Typical representatives of 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, 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 may be applied 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 against deterioration which comprises incorporating therein a stabilizing concentration of an aminocarbazole inhibitor.

In a specific embodiment the present invention relates to a method of stabilizing cracked gasoline which comprises incorporating therein from about 0.0001% to about 1% by weight of 3-isopropylaminocarbazole.

In another specific embodiment the present invention relates to a method of stabilizing synthetic grease which comprises incorporating therein from about 0.1% to about 3% by weight of 3-octylaminocarbazole.

The novel inhibitor of the present invention comprises an aminocarbazole. Included are 1-aminocarbazole, 2-aminocarbazole, 3-aminocarbazole, 4-aminocarbazole, 5-aminocarbazole, 6-aminocarbazole, 7-aminocarbazole, 8-aminocarbazole, etc. Also included are the polyaminocarbazoles including 1,2-diaminocarbazole, 1,3-diaminocarbazole, 1,4-diaminocarbazole, 1,5-diaminocarbazole, 1,6-diaminocarbazole, 1,7-diaminocarbazole, 1,8-diaminocarbazole, 2,3-diaminocarbazole, 2,4-diaminocarbazole, 2,5-diaminocarbazole, 2,6-diaminocarbazole, 2,7-diaminocarbazole, 3,4-diaminocarbazole, 3,5-diaminocarbazole, 3,6 - diaminocarbazole, 1,3,6,8 - tetraaminocarbazole, 2,3,6,7-tetraaminocarbazole, etc. While these carbazoles are effective inhibitors, in some cases they are not soluble to the desired extent in certain substrates. In such cases, it is preferred to utilize aminocarbazoles containing a substituent group as hereinafter set forth.

The substituted carbazoles preferably contain a hydrocarbon substituent attached to one or more of the amino nitrogens. Illustrative inhibitors in this class include 1-ethylaminocarbazole, 1-propylaminocarbazole, 1-butylaminocarbazole, 1-amylaminocarbazole, 1-hexylaminocarbazole, 1-heptylaminocarbazole, 1-octylaminocarbazole, 1-nonylaminocarbazole, 1-decylaminocarbazole, 1-undecylaminocarbazole, 1-dodecylaminocarbazole, 3-ethylaminocarbazole, 3-propylaminocarbazole, 3-butylaminocarbazole, 3-amylaminocarbazole, 3-hexylaminocarbazole, 3-heptylaminocarbazole, 3-octylaminocarbazole, 3-nonylaminocarbazole, 3-decylaminocarbazole, 3-undecylaminocarbazole, 3-dodecylaminocarbazole, etc., 3,6-diethylaminocarbazole, 3,6-dipropylaminocarbazole, 3,6-dibutylaminocarbazole, 3,6-diamylaminocarbazole, 3,6-dihexyl-

aminocarbazole, 3,6-diheptylaminocarbazole, 3,6-dioctylaminocarbazole, 3,6-dinonylaminocarbazole, 3,6-didecylaminocarbazole, 3,6-diundecylaminocarbazole, 3,6-didodecylaminocarbazole, etc., 1,3,6,8-tetraethylaminocarbazole, 1,3,6,8-tetrapropylaminocarbazole, 1,3,6,8-tetrabutylaminocarbazole, 1,3,6,8-tetraamylaminocarbazole, 1,3,6,8-tetrahexylaminocarbazole, 1,3,6,8-tetraheptylaminocarbazole, 1,3,6,8-tetraoctylaminocarbazole, etc., 2,3,6,7-tetraethylaminocarbazole, 2,3,6,7-tetrapropylaminocarbazole, 2,3,6,7,-tetrabutylaminocarbazole, 2,3,6,7-tetraamylaminocarbazole, 2,3,6,7-tetrahexylaminocarbazole, 2,3,6,7-tetraheptylaminocarbazole, 2,3,6,7-tetraoctylaminocarbazole, etc. It is understood that the specific compounds set forth above are illustrative and that corresponding compounds having the substitutions in other positions may be utilized.

In another embodiment, aminocarbazoles also having a substituent attached to the imino nitrogen may be used. The imino nitrogen is the heterocyclic nitrogen in the 5-membered ring. Illustrative examples of inhibitors in this class include N-ethyl-3-ethylaminocarbazole, N-ethyl-3-propylaminocarbazole, N-ethyl-3-butylaminocarbazole, N-ethyl-3-amylaminocarbazole, N-ethyl-3-hexylaminocarbazole, N-ethyl-3-heptylaminocarbazole, N-ethyl-3-octylaminocarbazole, etc., N-propyl-3-ethylaminocarbazole, N-propyl-3-propylaminocarbazole, N-propyl-3-butylaminocarbazole, N-propyl-3-amylaminocarbazole, N-propyl-3-hexylaminocarbazole, N-propyl-3-heptylaminocarbazole, N-propyl-3-octylaminocarbazole, etc., N-butyl-3-ethylaminocarbazole, N-butyl-3-propylaminocarbazole, N-butyl-3-butylaminocarbazole, N-butyl-3-amylaminocarbazole, N-butyl-3-hexylaminocarbazole, N-butyl-3-heptylaminocarbazole, N-butyl-3-octylaminocarbazole, etc., N-amyl-3-ethylaminocarbazole, N-amyl-3-propylaminocarbazole, N-amyl-3-butylaminocarbazole, N-amyl-3-amylaminocarbazole, N-amyl-3-hexylaminocarbazole, N-amyl-3-heptylaminocarbazole, N-amyl-3-octylaminocarbazole, etc., N-hexyl-3-ethylaminocarbazole, N-hexyl-3-propylaminocarbazole, N-hexyl-3-butylaminocarbazole, N-hexyl-3-amylaminocarbazole, N-hexyl-3-hexylaminocarbazole, N-hexyl-3-heptylaminocarbazole, N-hexyl-3-octylaminocarbazole, etc., N-ethyl-3,6-dipropylaminocarbazole, N-propyl-3,6-dipropylaminocarbazole, N-butyl-3,6-dipropylaminocarbazole, N-amyl-3,6-dipropylaminocarbazole, N-hexyl-3,6-dipropylaminocarbazole, etc., N-ethyl-2,3,6,7-tetraethylaminocarbazole, N-ethyl-2,3,6,7-tetrapropylaminocarbazole, N-ethyl-2,3,6,7-tetrabutylaminocarbazole, N-ethyl-2,3,6,7-tetraamylaminocarbazole, N-ethyl-2,3,6,7-tetrahexylaminocarbazole, etc., N-propyl-2,3,6,7-tetraethylaminocarbazole, N-propyl-2,3,6,7-tetrapropylaminocarbazole, N-propyl-2,3,6,7-tetrabutylaminocarbazole, N-propyl-2,3,6,7-tetraamylaminocarbazole, N-propyl-2,3,6,7-tetrahexylaminocarbazole, etc., N-propyl-1,3,6,8-tetrapropylaminocarbazole, N-propyl-1,3,6,8-tetrabutylaminocarbazole, etc. Here again, it is understood that the specific compounds set forth above are illustrative and that other compounds containing an alkyl substituent attached to the imino nitrogen and also those containing this substituent and alkyl substituents attached to one or more of the amino nitrogens may be employed.

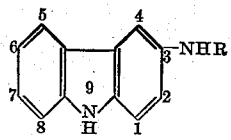
In another embodiment, the amino or alkylaminotetrahydrocarbazoles may be employed. Illustrative examples of compounds in this class include 6-propylamino-1,2,3,4-tetrahydrocarbazole, 6-butylamino-1,2,3,4-tetrahydrocarbazole, 6-amylamino-1,2,3,4-tetrahydrocarbazole, 6-hexylamino-1,2,3,4-tetrahydrocarbazole, etc.

While the alkyl-substituted amino or polyaminocarbazoles are preferred, it is understood that substituted amino or polyamino carbazoles in which the substituent comprises other groups may be employed. The other groups preferably comprise hydrocarbon groups and will be selected from cycloalkyl, aryl, alkaryl or aralkyl. In some cases, the substituent may comprise an alkenyl or cycloalkenyl group. In still other cases, the alkyl or other hydrocarbon group may contain non-hydrocarbon components including those comprising oxygen, nitrogen and/or sulfur.

It is understood that mixtures of compounds may be employed. In fact, during the preparation of some of these compounds, a mixture containing two different amino, alkylamino, polyamino or polyalkylamino compounds is formed, and such mixture may be used.

It is apparent that numerous compounds may be prepared and utilized in accordance with the present invention. However, all of these compounds are not necessarily equivalent and may be of different effectiveness in the same or different substrates. The particular compound to be used will depend upon the specific substrate to be inhibited and also upon the cost and availability of the inhibitor or of the reactants utilized in the preparation thereof.

In view of an apparent discrepancy in the literature as to the numbering of carbazole compounds, the structural formula of a representative inhibitor compound of the present invention is set forth below to illustrate the numbering system used in the present specifications and claims.



The particular carbazole compound illustrated is a 3-alkylaminocarbazole. Again, it is understood that this formula is merely for illustrative purposes and that other suitable amino and alkylamino, including poly-substituted compounds, may be employed.

The inhibitor compounds of the present invention may be prepared in any suitable manner. For example, aminocarbazole may be prepared by nitration of carbazole to form the nitro-substituted compound, followed by reduction of the nitro group to the amino group and, when desired, by reductive alkylation to form the alkylaminocarbazole. The alkyl substitution preferably is of secondary configuration; that is, the alkyl group is attached to the nitrogen atom at an intermediate carbon atom of the alkyl group. This substitution is obtained by utilizing a ketone in the reductive alkylation reaction. When a primary alkyl group is desired, an aldehyde is used in the reductive alkylation step.

The inhibitor compound of the present invention generally is incorporated in the organic material to be stabilized in an amount of below about 5% by weight and preferably in an amount within the range of from about 0.0001% to about 1% by weight in some substrates as, for example, gasoline, lard, etc., and from about 0.1% to about 3% in other substrates as, for example grease, rubber, etc. When used in gasoline, it is understood that the inhibitor compound may be utilized in conjunction with various dyes, synergists, metal deactivators, antiknock agents, such as tetraethyl lead, iron carbonyl, etc., rust inhibitors, etc. When used in edible fats and oils, the inhibitor compound may be used in conjunction with synergists such as citric acid, phosphoric acid, ascorbic acid, etc., and/or in combination with other inhibitors and other compounds added for specific purposes. The inhibitor may be utilized as such or in a suitable solvent, including hydrocarbons, alcohols, glycols, ethers, ketones, etc. When desired, the inhibitor compound may be marketed as a solution along with other additives to be incorporated in the organic materials.

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 inhibitor compound of this example is 3-isopropylaminocarbazole. This compound had a melting point of 181–182° C. and a boiling point of 170–190° C. at 1 mm.

pressure. This additive was utilized for the stabilization of Pennsylvania cracked gasoline having a blank induction period of about 100 minutes. 0.01% by weight of the additive was incorporated in a sample of the cracked gasoline and this served to increase the induction period thereof to 705 minutes. It thus is seen that the additive of the present invention served to increase considerably the induction period of the gasoline.

Example II

The additive used in this example is 3,6-diisopropylaminocarbazole, this compound having a boiling point of 170–230° C. at 1 mm. pressure. 0.01% by weight of this additive was incorporated in another sample of the cracked gasoline described in Example I, and this served to increase the induction period of the gasoline to 705 minutes. Here again, it will be noted that the additive served to increase considerably the induction period of the gasoline.

Example III

The additive used in this example is 6-isopropylaminotetrahydrocarbazole. This additive is incorporated in another sample of the cracked gasoline described in Example I serves to increase the induction period thereof.

Example IV

The additive used in this example is N-ethyl-3-aminocarbazole. This additive is incorporated in another sample of the gasoline described in Example I and likewise serves to increase the induction period of the gasoline.

Example V

The additive used in this example was 3-octylaminocarbazole and was utilized for the stabilization of a lithium grease commercially available in the open market. The stability of the grease was tested according to a modified Norma Hoffman method, in which a sample of the grease is placed in a bomb and oxygen is charged thereto. The bomb then is heated to 212° F., and the time required for a drop of 5 pounds pressure is taken as the induction period. In this run, a control sample of the grease (not containing this additive) had an induction period of 10 hours. On the other hand, a sample of the grease containing 1% by weight of 3-octylaminocarbazole had an induction period of 31 hours. Thus, it is seen that the inhibitor of the present invention served to improve considerably the stability of the grease.

Example VI

The run described in Example V was continued until a pressure drop of 30 pounds per square inch was obtained. In the control sample, this drop occurred after 23 hours. However, the sample containing 3-octylaminocarbazole ran for 122 hours before reaching the 30 pound pressure drop.

Example VII

1-(2-octylamino)-carbazole was utilized in a concentration of 0.02% by weight to stabilizing lard having a normal stability period of 6 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 Oil and Soap, vol. X, No. 6, pages 105–109 (1933), and modified as described in the article by R. W. Reimenschneider, J. Turner and R. M. Spec, which appeared in Oil and Soap, pages 169–171 (September 1943). In general, this test comprises bubbling air through a sample of the lard and determining rancidity organoleptically and by peroxide number. The results of these tests are reported as A. O. M. stability period, which is the number of hours required to reach a peroxide number of 20. 0.02% of the above additive served to increase the A. O. M. stability period to 22 hours.

I claim as my invention:

1. Gasoline subject to deterioration in storage containing a stabilizing concentration of an alkylaminocarbazole inhibitor.

2. Gasoline subject to deterioration in storage containing a stabilizing concentration of a polyalkylaminocarbazole inhibitor.

3. Cracked gasoline tending to deteriorate in storage containing a stabilizing concentration of 3-isopropylaminocarbazole.

4. Cracked gasoline tending to deteriorate in storage containing a stabilizing concentration of 3,6-diisopropylaminocarbazole.

5. Cracked gasoline tending to deteriorate in storage containing a stabilizing concentration of 3-octylaminocarbazole.

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