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STABILIZATION OF HYDROCARBONS

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This application is a continuation-in-part of copending application Serial No. 425,755, filed April 26, 1954, now abandoned, and relates more particularly to a novel method of preventing and/or retarding deterioration of hydrocarbons.

While the novel features of the present invention are particularly useful in the stabilization of gasoline, they also have particular utility in the stabilization of higher boiling hydrocarbons including, for example, naphthas, kerosene, mineral oil, lubricating oil, cutting oil, rolling oil, electrical oil, insulating oil, hydraulic oil, transmission oil, transformer oil, steam turbine oil, diesel oil, burner oil, fuel oil, petroleum greases, petroleum waxes, petrolatum, etc. As will be hereinafter set forth, the inhibitors of the present invention are comparatively nonvolatile and readily soluble in hydrocarbons. Therefore, these inhibitors also are especially suitable for use in heavier hydrocarbonaceous materials.

In one embodiment the present invention relates to a method of stabilizing a hydrocarbon which comprises incorporating therein a stabilizing amount of an N,N'-di-sec-aliphatic-p-phenylene diamine inhibitor in which both aliphatic groups contain at least 8 carbon atoms each.

In a specific embodiment the present invention relates to a method of stabilizing gasoline which comprises incorporating therein from about 0.001% to about 1% by weight of N,N'-di-3-(5-methylheptyl) - p - phenylene diamine.

In another specific embodiment the present invention relates to a method of stabilizing petroleum wax which comprises incorporating therein from about 0.0001% to about 5% by weight of N,N'-di-4-(2,6-dimethylheptyl)-p-phenylene diamine.

In another embodiment the present invention relates to a hydrocarbon stabilized with an N,N'-di-sec-aliphatic-p-phenylene diamine in which both aliphatic groups contain at least 8 carbon atoms each.

It will be noted that the inhibitor of the present invention comprises a specific type of N,N'-di-aliphatic-p-phenylene diamine. Both aliphatic groups must contain at least 8 carbon atoms each and preferably from 8 to about 20 carbon atoms each. Furthermore, the aliphatic group must be attached to the nitrogen atom at an intermediate carbon atom of the aliphatic group, and this is designated by identifying the aliphatic groups as sec-aliphatic. Inhibitors having this composition and configuration appear to be of higher potency and to offer other advantages over the use of substituted phenylene diamine compounds of shorter chain alkyl groups and those in which the alkyl groups are attached at terminal carbon atoms to the nitrogen atoms.

As an illustration of a particular advantage offered by the inhibitor compounds of the present invention as compared to similar compounds containing shorter chain alkyl groups, the inhibitor compounds of the present invention reduce the intake manifold deposits in an automobile engine to approximately one-half of that obtained when using compounds containing shorter alkyl groups.

This will be illustrated in Example III of the present application. The reduction of intake manifold deposits obviously is of importance because it permits long time operation of the engine and will not result in plugging of the manifold and accordingly failure of the engine in a shorter period of time.

As hereinbefore set forth, the inhibitors of the present invention are of improved potency in retarding deterioration of hydrocarbons, particularly deterioration caused by oxidation. These inhibitors are comparatively nonvolatile and thereby are retained satisfactorily in the hydrocarbonaceous material. The inhibitors are substantially non-toxic and therefore may be handled safely during preparation and use. Also, the inhibitors may be used safely in petroleum waxes which subsequently are utilized for coating material for containers or wrappers of food products. Still further, these inhibitors are substantially water insoluble and, therefore, will not be lost in the event that the hydrocarbonaceous material contacts water.

The inhibitors of the present invention may be prepared in any suitable manner. In a preferred method, these inhibitors are prepared by the reductive alkylation of p-phenylene diamine or p-nitroaniline with a suitable ketone. When using a ketone for effecting the reductive alkylation, it will be noted that the resultant aliphatic group will be attached at an intermediate carbon atom to the nitrogen atom. Representative ketones suitable for use in the reductive alkylation include methyl isohexyl ketone, methyl heptyl ketone, methyl octyl ketone, methyl nonyl ketone, methyl decyl ketone, methyl undecyl ketone, methyl dodecyl ketone, methyl tridecyl ketone, methyl tetradecyl ketone, methyl pentadecyl ketone, methyl hexadecyl ketone, methyl heptadecyl ketone, methyl octadecyl ketone, methyl nonadecyl ketone, methyl eicosyl ketone, etc., ethyl amyl ketone, ethyl hexyl ketone, ethyl heptyl ketone, ethyl octyl ketone, ethyl nonyl ketone, ethyl decyl ketone, ethyl undecyl ketone, ethyl dodecyl ketone, etc., propyl butyl ketone, propyl amyl ketone, propyl hexyl ketone, propyl heptyl ketone, propyl octyl ketone, propyl nonyl ketone, propyl decyl ketone, propyl undecyl ketone, etc., dibutyl ketone, butyl amyl ketone, butyl hexyl ketone, butyl heptyl ketone, butyl octyl ketone, butyl nonyl ketone, butyl decyl ketone, etc., diamyl ketone, amyl hexyl ketone, amyl heptyl ketone, amyl octyl ketone, amyl nonyl ketone, amyl decyl ketone, etc., dihexyl ketone, hexyl heptyl ketone, hexyl octyl ketone, hexyl nonyl ketone, hexyl decyl ketone, etc.

The reductive alkylation may be effected in any suitable manner. A suitable catalyst for effecting the reaction comprises a mixture of the oxides of chromium, copper and barium, although other suitable catalysts may be employed. Other catalysts include those containing cobalt, nickel, platinum, palladium, molybdenum, etc. In general, the reaction is effected at an elevated temperature of from about 100° to about 250° C. and a hydrogen pressure of from about 5 to about 200 atmospheres.

Preferred inhibitor compounds prepared in the above manner include N,N'-di-3-(5-methylheptyl)-p-phenylene diamine prepared by the reductive alkylation of p-nitroaniline with ethyl isoamyl ketone, N,N'-di-4-(2,6-di-methylheptyl)-p-phenylene diamine prepared by the reductive alkylation using diisobutyl ketone, N,N'-di-2-nonadecyl-p-phenylene diamine prepared by the reductive alkylation using methylheptadecyl ketone formed from stearic and acetic acids. Other representative compounds include N,N'-di-2-(5-methylheptyl)-p-phenylene diamine, N,N'-di-2-octyl-p-phenylene diamine, N,N'-di-2-(6-methyloctyl)-p-phenylene diamine, N,N'-di-2-nonyl-p-phenylene diamine, N,N'-di-2-(7-methylnonyl)-p-phenylene diamine, N,N'-di-2-decyl-p-phenylene diamine, N,N'-di-2-(4-methyldecyl)-p-phenylene diamine, N,N'-di-2-(8-methyldecyl)-

p-phenylene diamine, N,N'-di-2-(4,8-di-methyldecyl)-p-phenylene diamine, N,N'-di-2-undecyl-p-phenylene diamine, N,N'-di-2-(5,10-di-methylundecyl)-p-phenylene diamine, N,N'-di-2-dodecyl-p-phenylene diamine, N,N'-di-2-(4-methyldodecyl)-p-phenylene diamine, N,N'-di-2-(4,9-di-methyldodecyl)-p-phenylene diamine, N,N'-di-2-(4,7,10-trimethyldodecyl)-p-phenylene diamine, etc., N,N'-di-3-octyl-p-phenylene diamine, N,N'-di-3-(5-methyloctyl)-p-phenylene diamine, N,N'-di-3-(5,7-dimethyloctyl)-p-phenylene diamine, N,N'-di-3-nonyl-p-phenylene diamine, N,N'-di-3-(7-methylnonyl)-p-phenylene diamine, N,N'-di-3-decyl-p-phenylene diamine, N,N'-di-3-(5,9-dimethyldecyl)-p-phenylene diamine, N,N'-di-3-(6-ethyldecyl)-p-phenylene diamine, N,N'-di-3-undecyl-p-phenylene diamine, N,N'-di-3-(9-methylundecyl)-p-phenylene diamine, N,N'-di-3-(6,9-di-ethylundecyl)-p-phenylene diamine, N,N'-di-3-dodecyl-p-phenylene diamine, N,N'-di-3-(6-methyldodecyl)-p-phenylene diamine, N,N'-di-3-(10-ethyldodecyl)-p-phenylene diamine, N,N'-di-3-(5-ethyl-11-methyldodecyl)-p-phenylene diamine, etc.

When the aliphatic groups comprise alkenyl groups, the inhibitor may be prepared by the reaction of p-phenylene diamine or p-nitroaniline with a suitable unsaturated ketone including, for example, vinyl amyl ketone, phorone, vinyl hexyl ketone, vinyl heptyl ketone, vinyl octyl ketone, vinyl nonyl ketone, vinyl decyl ketone, vinyl undecyl ketone, vinyl dodecyl ketone, vinyl tridecyl ketone, vinyl tetradecyl ketone, vinyl pentadecyl ketone, etc. Representative examples of inhibitors in this class are N,N'-di-3-(1-octenyl)-p-phenylene diamine, N,N'-di-4-(2,6-di-methyl-2,5-heptadienyl)-p-phenylene diamine, etc. This reaction is effected in substantially the same manner as hereinbefore set forth and, depending upon the extent of hydrogenation, the product may comprise N,N'-di-alkenyl-p-phenylene diamine or a mixture of an N,N'-di-alkenyl-p-phenylene diamine and N,N'-di-alkyl-p-phenylene diamine.

It is understood that the various inhibitors which may be prepared and used in accordance with the present invention are not necessarily equivalent in the same or different hydrocarbons but all of them will be effective in retarding oxidative deterioration thereof.

The inhibitor of the present invention may be incorporated in the hydrocarbon in any suitable manner. When the hydrocarbon is a liquid, the inhibitor compound may be readily dissolved therein and preferably is followed by suitable mixing in order to obtain complete mixing of the inhibitor with the hydrocarbon. Similarly, when the hydrocarbon is a solid, the inhibitor may be dissolved therein by suitable mixing and, when desired, mild heating of the hydrocarbon followed by suitable mixing. When the inhibitor compound is a solid, it may be dissolved in the hydrocarbon as such or it may be dissolved in a suitable solvent including hydrocarbon, ketone, ether, etc., or the inhibitor compound may be heated to liquefy it and then utilized as a liquid.

In general, the inhibitor will be used in an amount of from about 0.0001% to about 5% by weight of the hydrocarbon, although in some cases lower or higher concentrations may be employed. The exact concentration to be used will depend upon the particular hydrocarbon fraction being treated. In most cases, concentrations of from about 0.0001% to about 1% and more particularly from about 0.001% to about 1% by weight generally will be employed.

When desired, the inhibitor of the present invention may be used along with other additives incorporated in the hydrocarbon fraction. The other additives will depend upon the particular hydrocarbon fraction being treated. For example, in gasoline a metal deactivator, tetraethyl lead, dye, etc., may be incorporated in the gasoline. When incorporated in wax for subsequent use in contact food products, various supplementary non-toxic inhibitors, synergists, etc. are employed. In any event, it is understood that other antioxidants may be used along with the inhibitor of the present invention and, when desired, the inhibitor and other additives may be prepared as a mixture with one or more of these additives and incorporated in this manner in the hydrocarbon fraction.

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

N,N'-di-3-(5-methylheptyl)-p-phenylene diamine is used in a concentration of 0.01% by weight to stabilize a Pennsylvania cracked gasoline having an uninhibited induction period of 100 minutes. Upon the addition of the inhibitor as hereinbefore set forth, the induction period of the gasoline is increased sufficiently for satisfactory use of the gasoline.

Example II

0.05% by weight of N,N'-di-4-(2,6-di-methylheptyl)-p-phenylene diamine is incorporated in petroleum wax. This serves to retard oxidative deterioration of the wax.

Example III

As hereinbefore set forth, a particular advantage to the use of the inhibitor compounds of the present invention is the reduction in intake manifold deposits. This illustrated in comparative tests conducted with a gasoline comprising a blend of catalytic reformed, straight run and thermally cracked gasolines, the blend having an ASTM gum content of 6 mg. These runs were made in a Chevrolet engine operated at the following conditions:

Speed	r.p.m.	2500
Load	B.H.P.	30
Jacket temp.	° F.	95
Oil temp.	° F.	65
Air-fuel ratio	° F.	14.5
Duration	hours	60

Three samples of the gasoline were employed. One sample was utilized without the addition of inhibitor compound. To a second sample of the gasoline, N,N'-di-sec-butyl-p-phenylene diamine was incorporated in a proportion of 10 pounds of inhibitor per 1000 barrels of gasoline. To the third sample of the gasoline, N,N'-di-3-(5-methylheptyl)-p-phenylene diamine was incorporated in a proportion of 10 pounds of inhibitor per 1000 barrels of gasoline. The three gasoline samples then were run in the engine as above described and the intake manifold deposits were measured. These results are reported below:

Additive:	Deposit, grams
None	24.9
N,N'-di-sec-butyl-p-phenylene diamine	12.4
N,N'-di-3-(5-methylheptyl)-p-phenylene diamine	6.2

From the above data, it will be noted that the intake manifold deposits were reduced approximately one-half by the addition of N,N'-di-sec-butyl-p-phenylene diamine. While this is an important reduction in the intake manifold deposits, it will be noted that N,N'-di-3-(5-methylheptyl)-p-phenylene diamine reduced the intake manifold deposits to approximately one-quarter of that obtained with the control sample of gasoline and to approximately one-half of that obtained with the gasoline containing N,N'-di-sec-butyl-p-phenylene diamine. As hereinbefore set forth, this reduction in intake manifold deposits is of importance and serves to prolong the satisfactory operation of the engine.

We claim as our invention:

1. Gasoline comprising a substantial proportion of cracked gasoline normally subject to oxidative deterioration and containing a stabilizing amount of a compound selected from the group consisting of N,N'-di-3-(5-meth-

ylheptyl) p-phenylene diamine and N,N'-di-2-octyl-p-phenylene diamine.

2. Gasoline containing from about 0.00001% to about 5% by weight of a compound selected from the group consisting of N,N'-di-3-(5-methylheptyl)-p-phenylene diamine and N,N'-di-2-octyl-p-phenylene diamine.

3. Gasoline containing from about 0.00001% to about 1% by weight of N,N'-di-2-octyl-p-phenylene diamine.

4. Cracked gasoline normally subject to oxidative deterioration containing a stabilizing amount of N,N'-di-3-(5-methylheptyl)-p-phenylene diamine.

5. Gasoline containing from about 0.0001% to about 1% by weight of N,N'-di-3-(5-methylheptyl)-p-phenylene diamine.

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