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## STABILIZED COMPOSITIONS CONTAINING HYDROGENATED QUINOLINES WITH OXIDATION INHIBITORS

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This invention relates to an improved class of oxidation inhibitors consisting of hydrogenated quinolines. The invention also concerns an improved combination of oxidation inhibitors consisting of a mixture of hydrogenated quinolines and conventional types of oxidation inhibitors. In accordance with this invention, an oxidation unstable material, such as gasoline or lubricating oil, may be inhibited against deterioration normally caused by oxidation, by incorporating therein small quantities of the oxidation inhibitors of this invention. The invention also has particular application to the stabilization of lead antiknock compounds to prevent the precipitation of these lead compounds in concentrated lead fluids or in gasoline compositions containing these lead antiknock compounds.

In the petroleum industry, it is generally desirable in order to prepare a superior quality of gasoline or lubricant, to stabilize these materials against degradation caused by oxidation. In general, hydrocarbon mixtures falling in the gasoline or lubricating oil boiling range, if unstabilized, will, over a period of time, be subject to gum formation, sludge formation, the formation of acids or objectionable color bodies. Furthermore, if lead antiknock agents are incorporated in the hydrocarbon mixture, it is generally desirable to stabilize the lead compounds against precipitation. At the present time, therefore, it is generally the practice to incorporate in a lubricating oil, a gasoline, or similar hydrocarbon mixture, a suitable agent which will inhibit oxidation of these mixtures. These agents are generally called oxidation inhibitors or antioxidants and presently consist of compounds selected from the classes consisting of amines or phenols. For example, suitable oxidation inhibitors known to the art consist of: α-naphthol, β-naphthol, mixed xylenols, 2,4-di-tert.-butyl-4-methyl phenol, hydroquinone, aniline, α-naphthylamine, phenyl-β-naphthylamine, N,N'-di-sec.-butyl-p-phenylene diamine, diphenyl p-phenylene diamine, N,n-butyl-p-aminophenol and 2,4-diamine phenol. While all of the above indicated inhibitors are more or less successful in reducing the instability of hydrocarbon mixtures, none of the inhibitors is effective in actually preventing all degradation indefinitely. Thus, while the degree of stability afforded by each of the above inhibitors varies somewhat, each of the inhibitors is ouly successful in partially stabilizing hydrocarbon mixtures over a period of time. It is, therefore, the principal object of this invention to provide an improved type of oxidation inhibitor which will more effectively stabilize hydrocarbon mixtures against oxidation.

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The discovery on which this invention is based is that the hydrogenated quinolines as a class have remarkable oxidation inhibiting properties. Thus hydrogenated quinolines may be employed by themselves as inhibitors with beneficial results. More basically, however, it has been discovered that hydrogenated quinolines in some manner act with conventional types of antioxidants to provide a synergistic effect remarkably enhancing the antioxidant properties of these compounds. In accordance with this invention, therefore, hydrogenated quinolines may be used by themselves or preferably in combination with conventional inhibitors of the classes indicated above to provide oxidation inhibitors of improved effectiveness.

While, as indicated, it is contemplated that hydrogenated quinolines may beneficially be employed in combination with any of the conventional antioxidants, the preferred combination is the combination of a hydrogenated quinoline and an amino phenol. Of the alkyl phenols, the tri alkyl phenols and specifically the 2,4,6 tri alkyl phenols are preferred. Still more specifically, 2,4,6 tri alkyl phenols having a tertiary butyl group in either or both of the 2 and 6 positions either with or without a normal alkyl group of 1–4 carbon atoms in the 4 positions may be employed. Similarly in the case of diamine type inhibitors, the para phenylenediamine inhibitors are preferred and particularly para phenylenediamine inhibitors having alkyl groups of 3–5 carbon atoms on the amino groups. Again in the case of amino phenol inhibitors, 3–5 carbon atom alkyl groups may be positioned on the nitrogen atom. As will be disclosed, it now appears that a hydrogenated quinoline may be used in combination with any of these inhibitors to provide a synergistic antioxidant effect.

The hydrogenated quinolines which may be employed in the practice of this invention are generally any compound derived from the hydrogenation or reduction of quinoline or substituted

quinoline. The class of compounds within the scope of this invention comprises quinolines having either the heterocyclic ring or both the heterocyclic and benzene rings of the compound saturated with hydrogen, for example, 1,2,3,4-tetrahydroquinoline and decahydroquinaldine. This class of compounds also consists of the hydrogenated quinolines just described which have alkyl, cycloparaffinic, or aryl groups attached to either the heterocyclic or benzene nucleus. Specific compounds falling within the scope of this invention are: 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroquinaldine, decahydroquinoline and decahydroquinaldine. As stated above, any of these compounds may be utilized by itself or combinations of these compounds may be employed as oxidation inhibitors. However, it is preferred that any one or any combination of the above compounds be employed with one or more of the conventional oxidation inhibitors formerly indicated falling in the broad classes of amines or phenols.

The total amount of antioxident to be employed in a given application may generally be stated to be that amount employed according to current practices. This amount varies widely depending upon the particular application of the antioxidant. For example, in the stabilization of gasolines, in general, about one half to ten pounds per 5000 gallons of inhibitor are employed to prevent gum formation during the storage of the gasoline. Again in the case of the stabilization of lubricating oils, up to several per cent of antioxidant may be employed in order to prevent the formation of sludge, varnish or acidic materials during the service life of the lubricant. Similarly, in the application of antioxidants to stabilize concentrated mixtures of lead antiknock agents against precipitation, about 0.05 to 1.0 per cent of antioxidant may be employed. It is apparent that the above indicated ranges of antioxidant to be employed in any particular application may be varied as desired and it is furthermore apparent that many other applications of antioxidants may be made within and without the petroleum industry. Thus, it is contemplated that the oxidation inhibitors of this invention may be employed to stabilize synthetic or natural rubber, plastics, greases, waxes, edible fats and oils, etc. Any proportional combination of inhibitors may be employed according to the broad concept of this invention. In general, it is contemplated that mixtures of any hydrogenated quinoline and conventional antioxidants may be used in which the ratio of the hydrogenated quinoline to conventional antioxidant falls substantially within the range of 0.1 to 10 by weight. However, it is preferred that in order to obtain the optimum synergistic effect provided by the unique combination of antioxidants, that the hydrogenated quinoline should be used in approximately equal proportions with the conventional antioxidant for most applications.

The nature of this invention will be more fully understood from a consideration of the following examples embodying the principles of this invention.

As an example of this invention, a turbine oil was tested for stability without any oxidation inhibitors, with a conventional phenolic inhibitor, with a hydrogenated quinoline, and with combinations of the hydrogenated quinoline and the phenolic inhibitor. The turbine oil tested was a petroleum neutral oil having a viscosity of about 43 Saybolt seconds at 210° F. and containing 0.06 weight per cent of zinc naphthenate as a corrosion inhibitor. The stability of this oil alone and with the addition of the above additives was determined by means of a modified Staeger test. In this test a sample of the oil is placed in a beaker with a polished copper strip and maintained at a temperature of 110° C. during the test period in an oven equipped with a rotating shelf. The performance of the oil is determined by measuring the time for the neutralization number of the sample to increase by 0.20 mg. KOH/gram over the neutralization number of the original sample at the start of the test. This value is determined by periodically extracting samples from the beaker container in the oven and the value obtained is ordinarily designated as the Staeger life. The results of the indicated test are presented in Table I.

TABLE I

*Modified Staeger test for turbine oils*

[Petroleum neutral oil +0.06 wt. percent zinc napthenate]

| Inhibitor | Staeger Life, Hours [1] |
|---|---|
| None | 72 |
| 0.4 wt. percent 2,6-Di-t-butyl-4-methyl phenol | 445 |
| 0.4 wt. percent 1,2,3,4-Tetrahydroquinaldine | 315 |
| 0.2 wt. percent 2,6-Di-t-butyl-4-methyl phenol +0.2 wt. percent 1,2,3,4-Tetrahydroquinaldine | 520 |

[1] Time to reach an increase in neutralization number over original sample of 0.20 mg. KOH/g.

It will be noted from this table that the turbine oil tests, when the oil contained no oxidation inhibitor, had a Staeger life of 72 hours. By incorporating 0.4 weight per cent of the conventional inhibitor, 2,6-di-t-butyl-4-methyl phenol, in the turbine oil, the Staeger life was increased to 445 hours. Similarly, when incorporating 0.4 weight per cent of 1,2,3,4-tetrahydroquinoline in the oil, the Staeger life was found to be 315 hours. Finally, in the last line of the table, when employing 0.2 weight per cent of each of the above indicated inhibitors, it was found that the Staeger life was 520 hours. It will be noted that the stability of the oil indicated by these tests was unexpectedly greater when 50/50 proportions of the two inhibitors were employed over the case when the same total amount of either of the inhibitors was used.

As a further example of this invention, several hydrogenated quinolines were evaluated alone and with a conventional gasoline antioxidant in an uninhibited motor fuel. The oxidation stability of the gasoline was determined by means of the ASTM induction period method which is normally used for determining the oxidation stability of gasolines. The ASTM test designation is D 525—46. The gasoline employed in the test constituted a commercial blend of thermally cracked stock, catalytically cracked stock and straight run gasoline distillate containing about 1 ml. of tetraethyl lead per gallon. The conventional oxidation inhibitor employed in these experiments, identified in Table II as "Antioxidant," was N,N'-di-sec. butyl-para-phenylenediamine. The hydrogenated quinolines employed, identified in Table II as "Synergist," were tetrahydroquinoline, decahydroquinoline, tetrahydroquinaldine and a mixture of hydroquinaldines consisting of about 60% tetrahydroquinal-

dine and 40% decahydroquinaldine. The results of these tests are indicated in Table II below:

TABLE II

*ASTM oxidation test results*

| Antioxidant Concentration, lb./5,000 gal. | 0 | 5 | 5 |
|---|---|---|---|
| Synergist Concentration, lb./5,000 gal. | 10 | 0 | 5 |

| Synergist | Induction Period, Min.[1] | | | Net Gain[2] |
|---|---|---|---|---|
| None | 60 | 845 | | |
| Tetrahydroquinoline | 140 | 845 | 1,240 | 355 |
| Decahydroquinoline | 75 | 845 | 1,175 | 320 |
| Tetrahydroquinaldine | 110 | 845 | 995 | 125 |
| Mixed Hydroquinaldines [a] | 130 | 845 | 960 | 80 |

[a] Approximately 60% tetrahydroquinaldine and 40% decahydroquinaldine.
[1] Average of two or more determinations.
[2] Increase in induction period over base gasoline due to combination of additives (10 lbs./5,000 gals.) minus the sum of the induction period increase due to each additive (5 lbs./5,000 gals.)

It will be noted that the antioxidant effect of the combination of the conventional antioxidant and any of the hydrogenated quinolines was appreciably greater than that which would be expected based upon the antioxidant activity of the hydrogenated quinolines alone or the conventional antioxidant alone. It has been found convenient to express the synergistic activity of the hydrogenated quinolines as the increase in induction period over that of the base gasoline due to the combination of additives minus the sum of the induction period increase due to each of the component additives. As an example, considering the effect of the tetrahydroquinoline: the uninhibited gasoline had an induction period of 60 minutes while the gasoline containing 10 lbs./5000 gals. of tetrahydroquinoline had an induction period of 140 minutes, indicating an increase in induction period of about 40 minutes for 5 lbs./5000 gals. of the tetrahydroquinoline. Similarly the increase in induction period due to 5 lbs./5000 gals. of N,N'-di-sec.-butyl-paraphenylenediamine was 785 minutes while the increase due to 5 lbs. of both of the additives was 1180 minutes. The net gain in induction period due to the synergistic combination of these additives was therefore 1180—(785+40) or about 355 minutes. Thus, it may be seen from the table above that there is a net gain in the ASTM induction period of 80 to 355 minutes when the combination of a hydrogenated quinoline and N,N'-di-sec.-butyl-p-phenylenediamine is employed. It is particularly notable that each of the four hydrogenated quinoline samples tested exhibited this synergistic effect with this conventional gasoline antioxidant.

A further evaluation of the synergistic antioxidant activity of hydrogenated quinolines was made employing a gasoline similar to that described in the preceding example. In this example other conventional gasoline antioxidants of the amino phenol and trialkyl phenol classes were employed. The particular compounds employed were tetrahydroquinoline and tetrahydroquinaldine as examples of hydrogenated quinolines, and N-n-butyl-p-aminophenol and 2,6-ditertiary butyl-4-methylphenol, which are examples of the classes of conventional antioxidants formerly identified.

TABLE III

*ASTM oxidation test results*

| | N-n-butyl-p-aminophenol | | | 2,6,di-t-butyl-4-methyl phenol | |
|---|---|---|---|---|---|
| Antioxidant Concentration: lb./5,000 gal. | 0 | 2.5 | 2.5 | 2.5 | 2.5 |
| Synergist Concentration: lb./5,000 gal. | 5 | 0 | 2.5 | 0 | 2.5 |

| Synergist | Induction Period[1] | | Net Gain[2] | Induction Period[1] | | Net Gain[2] |
|---|---|---|---|---|---|---|
| None | 60 | 300 | | 180 | | |
| Tetrahydroquinoline | 110 | 300 | 465 | 140 | 180 | 240 | 35 |
| Tetrahydroquinaldine | 100 | 300 | 410 | 90 | 180 | 225 | 35 |

[1] Average of two determinations.
[2] Increase in induction period over base gasoline due to combination of additives (5 lbs./5,000 gals.) minus the sum of the induction period increase due to each additive (2.5 lbs./5,000 gals.).

Thus, it is apparent from Table III above that with both of these conventional gasoline antioxidants in combination with each of the hydrogenated quinolines, a synergistic effect was observed which resulted in a net gain in the ASTM induction period.

As one further example of this invention, the oxidation inhibitors of this invention were tested in a somewhat different application. In this example, a concentrated lead fluid was employed consisting of one theory of ethylene dibromide and pure tetraethyl lead. One theory of ethylene dibromide identifies the amount of dibromide required to form lead bromide in stoichiometric proportions. This mixture of tetraethyl lead and ethylene dibromide is very similar to the mixture normally employed in aviation gasolines. Normally this mixture is characterized by a tendency for lead precipitation during storage of sufficient magnitude to cause severe difficulties in engine operation after long periods of storage, particularly in hot climates. This precipitation may occur either with the concentrated lead mix or with leaded gasolines. While the mechanism of the lead decomposition is not thoroughly understood, it appears that the lead precipitation may be initiated by oxidation. In any case, it has been established that lead precipitation can be substantially minimized by employing a suitable antioxidant either to prevent precipitation in the concentrated lead fluid or in the gasoline containing lead. In order to demonstrate the inhibiting action of a hydrogenated quinoline-conventional antioxidant combination for preventing the undesirable lead precipitation just described, samples of a mixture of pure tetraethyl lead and pure ethylene dibromide were stored with a steel strip in brown glass bottles kept in a bath maintained at a constant temperature of 120° F. The samples that were stored included one to which no antioxidant had been added, one in which 0.1 weight percent of tetrahydroquinaldine was added, one which contained 0.1 weight percent of 2,6-di-tertiary-butyl-4-methyl-phenol, and one containing 0.05 weight percent each of the hydrogenated quinoline and the phenol. The extent of degradation of the tetraethyl lead fluid was determined by periodically examining the samples and visually estimating the amount of lead precipitation present. It has been found convenient to express the stability of the various samples as the time in days required to reach a precipitation level arbitrarily

chosen as "moderate." The results of the test just described are shown in the following table.

TABLE IV

*Storage tests of tetraethyl lead fluid at 120° F.*[1]

[Brown bottles—Steel strip.]

| Additive | Wt. percent | Days required to reach "Moderate" amount of deposit |
|---|---|---|
| Description: | | |
| Tetrahydroquinaldine | 0.1 | 6 |
| 2,6-Di-t-butyl-4-methylphenol | 0.1 | 10 |
| Tetrahydroquinaldine | 0.05 | 93+ |
| 2,6-Di-t-butyl-4-methylphenol | 0.05 | |
| None | | 1 |

[1] Commercial grade of antiknock agent containing tetraethyl-lead and one theory or molar-equivalent of ethylene dibromide.

Thus it can be seen that the time required to reach the moderate precipitation level is greatly extended by the use of either tetrahydroquinaldine or 2,6-di-tertiary-butyl-4-methyl phenol. The combination of these two additives added to the lead mix in the same total concentration even more remarkedly improved the stability of the lead mixture. Thus the synergistic activity of a hydrogenated quinoline when employed with a trialkyl phenol is clearly demonstrated in this application of retarding lead precipitation.

What is claimed is:

1. A hydrocarbon composition normally characterized by oxidation instability containing small quantities of a hydrogenated quinoline selected from the class consisting of tetrahydroquinoline, tetrahydroquinaldine, decahydroquinoline, and decahydroquinaldine and an oxidation inhibitor consisting of N-n-butyl paramino phenol, said composition containing a weight ratio of said hydrogenated quoline to said inhibitor ranging from 0.1 to 10.

2. A hydrocarbon composition normally characterized by oxidation instability containing small quantities of a hydrogenated quinoline selected from the class consisting of tetrahydroquinoline, tetrahydroquinaldine, decahydroquinoline, and decahydroquinaldine in synergistic combination with an oxidation inhibitor compound selected from the group consisting of N-n-butyl para-amino phenol, N-N'-di-secondary butyl para-phenylene diamine and 2,6-di-tertiary butyl-4-methyl phenol, said composition containing a weight ratio of hydrogenated quinoline to inhibitor ranging from 0.1 to 10.

3. A hydrocarbon composition normally characterized by oxidation instability containing small quantities of a hydrogenated quinoline selected from the class consisting of tetrahydroquinoline and tetrahydroquinaldine and an oxidation inhibitor selected from the class consisting of N-n-butyl para-amino phenol, N-N'-di-secondary butyl para-phenylene diamine and 2,6-di-tertiary butyl-4-methyl phenol, said composition containing a weight ratio of said hydrogenated quinoline to said inhibitor ranging from 0.1 to 10.

4. A composition according to claim 3 in which the hydrocarbon composition is gasoline and in which the total weight percentage of the hydrogenated quinoline and the inhibitor is about 0.05 to 25 pounds per 1,000 gallons of gasoline.

5. A composition according to claim 4 in which the oxidation inhibitor is N-n-butyl para-amino phenol and the hydrogenated quinoline is tetrahydroquinaldine.

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