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SYNERGISTIC ANTIOXIDANT COMPOSITION AND USE

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The present invention relates to synergistic antioxidant mixtures, particularly for liquid hydrocarbon-type fuels that are subject to deterioration by contact with oxygen.

Gosoline and diesel fuels are subject to deterioration sometimes fairly rapidly, when exposed to air. The deterioration is evidenced by the formation of gum which deposits on surfaces, with which these fuels are in contact. These gums interfere with the filtering of the fuels as by clogging the filters and even cause fuel control valves to stick and spark plugs to become fouled.

The gums result from the polymerization of olefins present in the fuel, which polymerization is catalyzed or caused by reaction with oxygen. Over the past years these fuels have come to contain increasing amounts of olefins so that the gum formation has increased in significance, especially where the fuels are likely to be stored for an extended time. Antioxidants have heretofore been added to such fuels for the purpose of inhibiting and/or postponing the deterioration. However, where fuels contain about 15 percent or more olefin content, the standard antioxidants, to comply with technical requirements, would have to be added in such large amounts as to interfere with the proper operation of some engines.

Among the objects of the present invention is the provision of novel antioxidant mixtures that are more effective than the piror art antioxidants.

Additional objects of the invention include the provision of mixtures of olefin-type liquid hydrocarbon fuels with a synergistic antioxidant mixture that can be used in reduced concentration.

The above as well as still further objects of the present invention will be more clearly understood from the following description of several of its exemplifications.

It has been discovered that antioxidants of the class consisting of N-alkylated-p-phenylenediamines and N-alkylated aminophenols have their antioxidant effect unexpectedly increased when they are mixed with a bis-(dialkylaminoalkyl)-hydroquinone. The synergistic effect appears to extend to mixtures having about 25 to 80 percent by weight of the above phenylenediamines or aminophenols, the balance being essentially the above hydroquinones. Best results are obtained, however, with a mixture having about twice as much of the phenylenediamine or aminophenol as the hydroquinone.

The following examples are typical of the improvements resulting from the present invention. In these examples the deterioration tendency has been measured by determining the induction period various samples of materials require before beginning to react with oxygen under accelerated reaction conditions. The specific method used is a standard one adopted by the American Society of Testing Materials for determination of the Oxidation Stability of Gasoline (Induction Period Method), ASTM Designation: D525–46, and is fully described in part III–A, ASTM Standards for 1946. According to this method, the induction period is the period during which there is no absorption of oxygen by the test material as indicated by a time delay before the pressure

drops in a testing bomb containing the test material at 100° C. with oxygen at an initial pressure of 100 pounds per square inch gauge.

All percentages given below are by weight, except where indicated otherwise, and tests were made with a commercial gasoline normally tending to deteriorate in the presence of oxygen or ozone having the following characteristics:

Hydrocarbon type (percent by volume):	
Olefins	15.8
Aromatics	16.4
Paraffins	57.0
Naphthenes	10.8
Dissolved gum—mgs./100 ml.	1.00
Total sulfur—percent	0.015
Gravity—° API	61.3
Vapor pressure, ° F.—pounds per square inch	5.8
Distillation range, ° F. (29.3 inches of mercury):	
Initial	104
5	139
10	153
15	163
20	179
30	192
40	213
50	234
60	256
70	277
80	299
85	312
90	326
95	342
Final	375

The antioxidant effects of various additions to this gasoline are:

Protecting additive	Induction Period in Minutes
None	50
0.00375% N,N'-di-sec-butyl-p-phenylenediamine A	380
0.0075% A	585
0.005% A plus 0.0025% 2,5-bis-(dimethylaminomethyl)-hydroquinone	680
0.0025% A plus 0.00125% 2,5-bis-(diethylaminomethyl)-hydroquinone	515
0.005% A plus 0.0025% 2,5-bis-(diethylaminomethyl)-hydroquinone	945

It should be noted that the bis-(dialkylaminoalkyl)-hydroquinones shown above to have a synergistic antioxidant effect when combined with the N,N'-di-sec-butyl-p-phenylenediamine have when used by themselves an antioxidant behavior which is very small, being about one-seventh that of the N,N'-di-sec-butyl-p-phenylenediamine.

Although the above examples show the value of the present invention in connection with a stock gasoline, the same general improvements are obtainable with other gasolines as well as with olefin-type diesel fuels that tend to deteriorate in the presence of oxygen. The effect with gasolines is obtained whether or not the gasoline is colored with dyes or leaded, that is contains added tetraethyllead along with its usual lead scavenger complement, as for example ethylene dibromide or ethylene dichloride.

When other alkylated p-phenylenediamines are substituted for the N,N'-di-sec-butyl-p-phenylenediamine, equally good synergistic improvement is obtained. Specific examples of such suitable alkylated p-phenylenediamines showing the synergism are those in which either or both amine groups are alkylated, as for example, N,N'-dimethyl-p-phenylenediamine, N-ethyl-p-phenylene-diamine, N-methyl-N'-n-propyl-p-phenylenediamine, N-stearyl-p-phenylenediamine, N-methyl-N'-lauryl-p-phen-

ylenediamine. Ortho, meta or para aminophenols in which the amino nitrogen is substituted with one or two alkyl groups ranging from methyl to cetyl also show the above types of synergistic effect when used in place of the p-phenylenediamines. In general, the use in the synergistic antioxidants of the present invention of N,N'-dialkyl-p-phenylenediamines wherein the alkyl groups each contain up to about eight carbon atoms is preferred.

Other dialkylamino alkyl hydroquinones are also effective synergists when used in the above combination instead of the above-mentioned bis-(dimethylaminomethyl) and bis-(diethylaminomethyl) compounds. 2,3-bis-(N-methyl-N-isopropylaminomethyl)-hydroquinone, 2,6-bis-(di-isopropylaminobutyl)-hydroquinone, 2-dimethylaminomethyl, 5-di-n-propylaminoethyl hydroquinone are some of such other synergists. It is preferred that the alkyl and alkylene groups of these compounds have no more than four carbon atoms each.

A feature of the present invention is that it reduces the solubility problems arising when the separate ingredients of the mixture are used independently. Thus, not only is the antioxidant effect of any given percentage of addition increased, but moreover the amounts of the individual ingredients are even further reduced so that they are more readily dissolved in the gasoline or other hydrocarbon fuel by conventional blending operations. Solvents such as ethanol, acetone or the like can be used to further improve the solubility of the synergistic mixture without significantly affecting the above described results. The mixtures of the present invention can be dissolved as a fairly highly concentrated solution in these solvents and then be readily mixed with the hydrocarbon fuel to give a uniformly dispersed product from which the antioxidants do not settle out. About 1 percent of the solvent based on the weight of the final gasoline formulation can be so incorporated. Thus, by adding such mixtures dissolved in a solvent to an inherently unstable hydrocarbon fuel in the requisite amount and shaking, stirring or otherwise agitating the resulting blend, a homogeneous improved fuel composition protected against the deleterious effects of oxygen or ozone is obtained.

In all the above modifications, the same general formulation of ingredient proportion is effected. The concentration of an antioxidant mixture in the material being protected can be varied from about 0.01 percent down to the smallest concentration that will be effective. Concentrations larger than 0.01 can be used but are not desirable.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof, except as defined in the appended claims.

What is claimed is:

1. Olefin-containing gasoline normally tending to deteriorate in the presence of oxygen containing about 0.00375 to about 0.01 percent by weight of a mixture of an N,N'-dialkyl-p-phenylene diamine wherein the alkyl groups each contain up to about 8 carbon atoms and a bis-(dialkylaminoalkyl)-hydroquinone having no more than 4 carbon atoms in each of the alkyl groups, said phenylene diamine being from about 25 to 80 percent by weight of said mixture.

2. An olefinic gasoline in which the olefin content is at least about 15 percent, said gasoline containing about 0.00375 to about 0.01 percent by weight of a mixture of N,N'-di-sec-butyl-p-phenylene diamine and 2,5-bis-(dimethylaminomethyl)-hydroquinone, the former constituting from about 25 to 80 percent by weight of the mixture.

3. An olefinic gasoline in which the olefin content is at least about 15 percent, said gasoline containing about 0.00375 to about 0.01 percent by weight of a mixture of N,N'-di-sec-butyl-p-phenylene diamine and 2,5-bis(diethylaminomethyl)-hydroquinone, the former constituting about 25 to 80 percent by weight of the mixture.

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