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SYNERGISTIC ANTIOXIDANTS AND THEIR USE

Eugene F. Hill, Birmingham, Mich., assignor to Ethyl Corporation, New York, N. Y., a corporation of Delaware

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The present invention relates to the protection of materials that are subject to deterioration by contact with oxygen in any of its forms.

Certain hydrocarbon-type materials in wide use are subject to deterioration, sometimes fairly rapidly, when exposed to air and particularly where the air might have some ozone content. By way of example, gasolines and diesel engine fuels now enjoying wide-spread use are for practical reasons manufactured with a relatively high content of olefinic-type hydrocarbons. These materials, upon standing, will react with oxygen and will at least be partially converted to a form that is not desirable. Thus, olefinic gasolines will show a strong tendency to deposit gums which will interfere with the filtering of the gasoline by clogging up the filters and even cause fuel-passing valves to stick. In addition, gummy deposits often foul spark plugs and thereby cause misoperation of the engine. These same general type of difficulties are experienced with diesel fuels.

In the past it has been found desirable to add antioxidants to the above types of oxygen-sensitive materials. However, with the progress of time, fuels have come to contain more and more olefins and engines have become more efficient and powerful so that the engine and fuel specifications are more rigid. The continuous use of prior art antioxidants accordingly results in the build-up of the antioxidant concentration to the point where it cannot be tolerated by some engines.

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

Additional objects of the invention include the provision of mixtures of olefin-type hydrocarbons with a synergistic antioxidant composition that makes possible more effective protection of the hydrocarbons.

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 standard antioxidants selected from the class consisting of phenylenediamines, aminophenols and trialkylphenols, when mixed with a compound of the class consisting of ascorbic acid and its esters, show an unexpectedly high antioxidant effect in protecting olefin-type hydrocarbons that are subject to deterioration by oxygen. This effect is particularly significant inasmuch as ascorbic acid and its esters show very little or no antioxidant value in connection with these materials when used as a primary antioxidant. The synergistic effect appears to extend to antioxidant compositions having from 10 to 80 percent of ascorbic acid or its ester, the balance being essentially one or more of the above-named standard antioxidants. Best results are obtained, however, with an antioxidant composition having about twice as much of the standard antioxidant as ascorbic acid or its esters.

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 are by weight.

Hydrocarbon Material Tested	Protecting Addition	Induction Period in Minutes
G1 Gasoline	None	118
Do	0.0075% N,N'-di-sec-butyl-p-phenylenediamine A.	394
Do	0.005% A +0.0025% ascorbic acid	533
G3 Gasoline	None	90
Do	0.00375% A	260
Do	0.0025% A +0.00125% ascorbic acid	315
Do	0.0075% A	340
Do	0.005% A +0.0025% ascorbic acid	400
Do	0.0025% A +0.00125% ascorbyl palmitate	350
Do	0.005% A +0.0025% ascorbyl palmitate	430
G2 Gasoline	None	140
Do	0.00375% A	310
Do	0.0025% A +0.00125% ascorbyl palmitate	355
Do	0.0075% A	400
Do	0.005% A +0.0025% ascorbyl palmitate	490

In the above examples the G1, G2, and G3 gasolines are standard commercially available automotive gasolines which, when untreated, are normally susceptible to deterioration in the presence of oxygen. The characteristics of the above gasolines are as follows:

	G1	G2	G3
Distillation Range, ° F.		Initial 80; 10% 107; 50% 217; 90% 330; Final 389 (29.5 in. Hg)	Initial 94; 10% 137; 50% 268; 90% 341; Final 380 (29.2 in. Hg)
Hydrocarbon-Type		Olefins 26.7%; Aromatics 18.1%; Paraffins 41.7%; Naphthenes 13.5%	Olefins 18.4%; Aromatics 23.6%; Paraffins 36.5%; Naphthenes 21.5%
Vapor Pressure (Millimeters of Hg at ° F.).		12.1	10.1
Gravity, ° API	54.7	62.6	58.7
Bromine Number	56	64.0	57.6
Acid Heat (1:2) ° F.	105	99.0	105
Percent Sulfur	0.021	0.097	0.023
Gum, mg./100 ml.:			
Cu Dish	105.8	13.0	22.7
High Temp	0.6		2.0
Dissolved	0.6	0.6	2.0

It should be noted that the ascorbic acid shown above to have a synergistic antioxidant effect when combined with the N,N'-di-sec-butyl-p-phenylenediamine has when used by itself an antioxidant behavior which is very small, being about one-tenth that of the N,N'-di-sec-butyl-p-phenylenediamine. The ascorbyl palmitate of these examples has, when used alone, no appreciable antioxidant effect.

Although the above examples show the value of the present invention in connection with stock gasolines, the same general improvements are obtainable with other olefin-type materials such as diesel fuels that tend to deteriorate in the presence of oxygen. The effect with gasolines is obtained whether or not the gasoline is leaded, that is contains added tetraethyllead along with its usual

lead scavenger complement, as for example ethylene dibromide or ethylene dichloride.

When other of the above mentioned prior art standard antioxidants are substituted for the N,N'-di-sec-butyl-p-phenylenediamine equally good synergistic improvement is obtained. Specific classes of suitable prior art antioxidants showing the synergism when admixed or otherwise used in conjunction with ascorbic acid and esters thereof are phenylenediamines, aminophenols and trialkylphenols. Illustrative examples of the phenylenediamines include such materials as unsubstituted p-phenylenediamine, unsubstituted o-phenylenediamine, as well as derivatives of these materials in which either or both amine groups are alkylated such as N,N'-dimethyl-p-phenylenediamine, ethyl-p-phenylenediamine, N-methyl-N' - n - propyl - p-phenylenediamine, stearyl-p-phenylenediamine, N-methyl-N'-lauryl-p-phenylenediamine, N,N'-diethyl-o-phenylenediamine, N-methyl-o-phenylenediamine, N-butyl-N'-isopropyl-o-phenylenediamine, N-stearyl - o - phenylenediamine, N-methyl-N'-lauryl-o-phenylenediamine, 2-aminodiphenylamine, 4-aminodiphenylamine, and the like. Illustrative examples of aminophenols which can be employed in the synergistic antioxidant compositions of the present invention include unsubstituted p-aminophenol, unsubstituted o-aminophenol, unsubstituted m-aminophenol, and any of the above aminophenols in which the amino nitrogen is substituted with an alkyl group ranging from methyl to cetyl. The trialkylphenols which can be utilized in the synergistic antioxidant compositions of the instant invention are exemplified by such materials as 2,4-dimethyl-6-t-butylphenol, and other 2,4,6-trialkylphenols in which some or all of the alkyl groups are the same, or they are all different, and the groups range from methyl to decyl.

Instead of the ascorbic acid or ascorbyl palmitate other ascorbic acid esters can be used to give the equivalent results. Such other esters include such substances as ascorbyl formate, ascorbyl acetate, ascorbyl lactate, ascorbyl succinate, ascorbyl maleate, ascorbyl propionate, ascorbyl picrate, ascorbyl benzoate, ascorbyl salicylate, ascorbyl monomalonate, ascorbyl dimalonate, and the like.

In all the above modifications, the same general formulation of ingredient proportion is effected. The concentration of antioxidant composition 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 the invention may be made without departing from the spirit and scope hereof, it is understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. Gasoline normally tending to deterioriate in the presence of oxygen, and containing a mixture of an N,N'-dialkyl phenylene diamine antioxidant and a synergist selected from the class of ascorbic acid and ascorbyl palmitate, said synergist being present in an amount of from 10 to 80 percent of the total amount of the mixture, the total mixture being present in an amount sufficient to stabilize the gasoline.

2. The combination of claim 1 in which the N,N'-dialkyl phenylene diamine is N,N'-di-sec-butyl-p-phenylene diamine.

3. The combination of claim 2 in which the synergist is ascorbic acid.

4. The combination of claim 2 in which the synergist is ascorbyl palmitate.

5. A leaded olefinic gasoline containing about 0.005 to about 0.01 percent by weight of a mixture of two parts of N,N'-di-sec-butyl-p-phenylenediamine with one part of a synergist selected from the class of ascorbic acid and ascorbyl palmitate.

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