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SYNERGISTIC ANTIOXIDANT COMPOSITION

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1

This invention relates to the stabilization of organic materials normally susceptible to deterioration. More particularly our invention relates to the inhibition of attack by oxygen and the prolongation of the useful life of oxygen-sensitive materials. This invention is further disclosed in applicants' co-pending application, Serial Number 277,336.

Hydrocarbon fuels for internal combustion engines may be broadly classified into three categories, according to the use for which they are intended; fuels for automotive spark ignition engines, fuels for aircraft spark ignition engines, and fuels for compression ignition engines. Although each such fuel is composed essentially of hydrocarbons, the stability characteristics during the manufacturing process and subsequent storage and use, particularly in the presence of oxygen, differs considerably for each type. For example, typical automotive fuels contain straight and branched chain aliphatics, olefins, naphthenes and some aromatics, while typical aircraft fuels contain smaller proportion of olefins. In recent years fuels for compression ignition engines have contained an increased proportion of cracked stocks, resulting in a higher olefin content and consequent increase in the susceptibility to gum formation. The effect of the deterioration of the fuel upon each type of engine may differ, but equivalent processes of deterioration occur in each fuel. For example, the formation of gum in fuels designed for use in spark ignition engines interferes with normal operation of the ignition system and valves, while the formation of such gummy materials in compression ignition engine fuels interferes with the normal operation of the fuel filters and injectors in such engines.

In general, the hydrocarbons present in automotive gasolines are more susceptible to degradation than those comprising aircraft fuels. However, both automotive and aircraft fuels are commonly blended with tetraethyllead before use. Such blending imposes a further point of instability in the finished fuel, since the tetraethyllead is susceptible to some deterioration by contact with oxygen during the blending, storage and handling operations, with consequent formation of haze, loss of some antiknock value, and lessened performance in the engine. This point of attack is often overlooked and is ordinarily unimportant in automotive fuels, as the protective measures necessary for the base stock are usually more than sufficient to protect the tetraethyllead. If, however, a stabilizing ingredient were added which is capable of protecting only the fuel, the attack upon the tetraethyllead would then become apparent. In aircraft fuels the protection must center upon the antiknock additive, as the fuel itself is relatively

2

stable. Furthermore, this phase of the problem becomes relatively more important in aircraft fuels, since the tetraethyllead content of such fuels is generally several times that present in automotive fuels.

Heretofore, the protection of fuels for internal combustion engines effectively against the two above-described separate but related deleterious effects of contact with oxygen during the refining, manufacturing, blending, storage and handling operations has been accomplished only with difficulty. Furthermore, because of the specifications imposed on such fuels by the rigid requirements of present day engines, particularly aircraft engines, it is essential that any material used to protect such fuels against deterioration be effective in extremely small quantities, on the order of one pound of additive per five thousand gallons of fuel, so that secondary problems do not arise through their use.

Similarly, synthetic and natural elastomers are susceptible to absorption of oxygen with consequent destruction of certain useful physical properties and with the introduction of certain properties which render articles manufactured from such elastomers of limited utility. By absorption of oxygen such elastomers deteriorate prematurely, lose tensile strength and flexibility, and become discolored and embrittled. While certain materials have been proposed for the protection of such elastomers from the deleterious action of oxygen, most of such protective substances, as for example β-naphthol, possess the serious disadvantage, particularly with respect to light colored stocks, that their own degradation products are themselves colored and hence interfere with the color fastness of the stocks being protected.

Further examples of materials which must be protected from the deleterious effects of oxygen include mineral oils, such as lubricating oils, soaps, certain perishable foodstuffs, such as animal and vegetable oils and fats, and synthetic unsaturated organic materials. In general, such organic substances may require protection at any time during the processes of manufacturing, handling, storage and use when they become exposed to and absorb oxygen with deleterious effects.

It is therefore an object of our invention to provide means for protecting such organic substances which deteriorate in or are affected adversely by oxygen. It is a further object of our invention to provide a class of mixtures which provides the required protection against the formation of gummy oxidation and polymerization products of unstable hydrocarbons on contact with oxygen at reduced levels of additive. Another object of our invention is to provide means for increased stabilization of hydrocarbon fuels

for internal combustion spark, and compression ignition engines during the manufacturing, handling and storage of such fuels prior to their use without increasing the total amount of stabilizing additive. Likewise, it is an object of our invention to provide means for reducing the antioxidant requirement of unstable organic materials. A still further object of our invention is to provide hydrocarbon fuels containing tetraethyllead which do not deteriorate in contact with oxygen with the resultant formation of gum, haze and tetraethyllead oxidation products. It is also an object of our invention to provide fuels containing tetraethyllead in which there is essentially no loss in performance characteristics due to such deterioration of the tetraethyllead during blending, storage and handling. Likewise it is an object of our invention to provide means for preventing embrittlement, discoloration, loss of tensile strength and other harmful effects in elastomers during the milling, compounding, fabrication, storage, handling and use of such elastomer stocks. A further object of our invention is to provide means for protecting other perishable natural or synthetic organic materials from the adverse effects of contact with oxygen. Still further objects of our invention will appear from the description of our invention as hereinafter disclosed.

The above objects can be accomplished by practicing our invention which comprises adding to oxygen-sensitive organic materials a small proportion of a composition comprising arylamine antioxidant materials and substances derived from the class of mercaptans.

We have made the discovery that certain organic mercaptans, themselves incapable of protecting organic materials from deterioration in the presence of oxygen, have the property of greatly increasing the effectiveness of previously known antioxidants of the arylamine type. Such mercaptans we refer to hereinafter as synergists. The mercaptans of our invention include those which contain hydrocarbon radicals, selected heterocyclic radicals, and certain functionally substituted hydrocarbon radicals. Among the hydrocarbon radicals which we have found to be effective substituents of the mercaptans of our invention are alkyl, aryl and aralkyl. As examples of heterocyclic radicals effective in our mercaptans we include the furfuryl group and the imidazolidine group. The functionally substituted hydrocarbon radicals of our synergistic mercaptans include carbalkoxy groups, as in the alkyl thioglycolates.

We have found that the replacement of a portion of the arylamine antioxidant of a stabilized composition with an equal weight of our synergistic mercaptans, themselves incapable of providing oxygen stabilization, results in a stabilized composition which is more resistant to attack by oxygen. Furthermore, to attain a specified degree of oxygen stability the required amount of our arylamine-mercaptan mixture is less than the required amount of the arylamine antioxidant alone. For convenience in referring to known antioxidants hereinafter the following letters are assigned thereto:

N,N'-di-sec.-butyl-p-phenylenediamine ------ A
N-n-butyl-p-aminophenol ------ B
N-isobutyl-p-aminophenol ------ C
N,N'-di-β-naphthyl-p-phenylenediamine ----- D

The absorption of oxygen by hydrocarbon fuels can be measured directly by the standard method of the American Society of Testing Materials for determination of the oxidation stability of gasoline (induction period method), ASTM designation: D525-46, as 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 drop in pressure, when placed in a testing bomb maintained at a temperature of 100° C. with an initial pressure of 100 pounds per square inch gauge of oxygen. The induction period increase (IPI) is the increase in the duration of this period caused by the addition of a protective substance, and is a direct measure of the protection afforded by such additive. Thus, the longer the IPI the more effective is the stabilizer. On the contrary, certain substances exert a prooxidant effect in which a negative IPI is obtained, that is, the duration of the induction period, or period of no absorption of oxygen, is less than in the absence of the additive.

It is well known in the art of protecting gasoline from oxidation that the susceptibility to oxidation of gasoline varies significantly with different types of gasolines. Furthermore, it is likewise well known that the efficiency of any antioxidant, and, therefore, the minimum concentration required, will vary greatly from gasoline to gasoline. Therefore, in order to show the general applicability of the compounds of our invention to the solution of this problem, and at the same time not present in detail the large amount of data so obtained, we have listed in Tables I and II representative induction period increases obtained with a variety of test gasolines. The gasolines used in obtaining the data presented herein were all commercial blending stocks or finished gasolines and included the following types: An average-response gasoline containing 20 per cent olefins and 14 per cent aromatics, the remainder being paraffins and naphthenes; a gasoline containing approximately 38 per cent olefins, 33 per cent aromatics, and the remainder paraffins and naphthenes; a gasoline containing 18 per cent olefins and 24 per cent aromatics; a high-sulfur gasoline containing 0.21 per cent sulfur; and a gasoline containing 28 per cent olefins and 18 per cent aromatics with medium sulfur content.

The ASTM method employed to illustrate the activity of the compounds of our invention as in Tables I and II is a reliable indication of the efficiency of a stabilizing material within the test limits of plus 10 minutes and minus 10 minutes. Materials exhibiting an effect near these limits are essentially inert. To obtain the results shown herein, 6 milligrams of the additive was dissolved in 100 milliliters of the gasoline. Where the solubility characteristics of the material were such that this concentration could not be obtained, a small amount of a solubilizing agent, such as ethyl or isopropyl alcohol, was added in amount up to 2 per cent of the gasoline.

TABLE I

Effect on induction period increase of gasolines

Synergist	IPI
Amyl mercaptan	−15
Dodecyl mercaptan	−65
Furfuryl mercaptan	−20
2-mercapto-imidazolidine	+20
Isopropyl thioglycolate	−70

From Table I it is clear that the synergizing components of the antioxidant mixtures of our invention are essentially inert or act as pro-oxidants. Other mercaptans of our invention which do not exhibit an antioxidant effect when employed alone in gasoline include allyl mercaptan, t-butyl mercaptan, benzyl mercaptan, 2-mercapto-4-methyl-imidazolidine, ethyl thioglycolate and butyl thioglycolate.

The effectiveness of the mercaptans of our invention as synergists is shown in Table II, wherein the mercaptans were added to the test gasoline in admixture with known antioxidants. We have listed in Table II the increase in the induction period of the so-treated gasoline at a total concentration of 6 milligrams of the synergistic mixture per 100 milliliters of gasoline, and the increase in the induction period of the test gasoline treated with the arylamine antioxidant alone at the same concentration of 6 milligrams per 100 milliliters of gasoline.

TABLE II

Effect on induction period increase of gasoline

No.	Synergist	Antioxidant	Percent of Synergist in mixture	IPI with 6 mg./100 ml. of antioxidant	IPI with 6 mg./100 ml. of synergistic mixture
1	Amyl mercaptan	A	33	250	365
2	t-Butyl mercaptan	A	25	300	485
3	Dodecyl mercaptan	A	25	300	470
4	Dodecyl mercaptan	A	50	235	325
5	Furfuryl mercaptan	A	33	250	370
6	2-mercapto-imidazolidine	A	33	250	380
7	Ethyl thioglycolate	A	25	300	480
8	Isopropyl thioglycolate	B	33	340	405
9	Isopropyl thioglycolate	C	33	335	410
10	Butyl thioglycolate	A	25	365	550

By reference to Table II the increase in protection afforded to an unstable gasoline at the same total weight of additive, achieved by replacing a portion of the known antioxidant material by the mercaptans of our invention, is apparent. Thus, for example, replacing 25 per cent of antioxidant A with an equal weight of t-butyl mercaptan increases the induction period increase of the fuel over 60 per cent. Stated differently, 6 milligrams of synergistic mixture No. 2 in Table II is equivalent to almost 10 milligrams of antioxidant A, although t-butyl mercaptan alone is not an antioxidant. Thus, to obtain an IPI of 300, as in No. 2, only 3.8 milligrams of our mixture would be required, containing 2.85 milligrams of antioxidant A and 0.95 milligrams of t-butyl mercaptan. Similar considerations apply in each of the examples of the table. Further examples of the compounds of our invention which produce a synergistic effect with antioxidant materials include allyl mercaptan, benzyl mercaptan, 3-propyl-2-mercapto-imidazolidine and octyl thioglycolate.

We have demonstrated the efficiency of the synergistic mixtures of our invention in preventing undue formation of gum in automotive gasolines by storing such gasolines containing them for long periods, and determining from time to time the gum content of the fuel. The quantity of gum so-formed was compared with that formed in the presence of known antioxidants and in the untreated gasoline. Two commercial motor gasolines, consisting of 27 and 38 per cent olefins and initially containing 0.6 and 0.8 milligram of gum per 100 milliliters, were employed. For each demonstration duplicate amber quart bottles were filled with one pint of the gasoline with or without an additive. The bottles were stoppered and stored in the dark at a temperature of 110° F. Every four weeks the bottles and their contents were cooled to room temperature and the stoppers were removed for two hours to permit access to the air. Every 8 weeks a sample of the fuel mixture was removed and the dissolved gum therein was determined by the so-called "air-jet evaporation" method, ASTM designation: D381–46, fully described in ASTM Standards for 1946, Part III–A.

TABLE III

Effect on gum in motor gasoline

No.	Additive	Conc., mg./100 ml.	Increase in gum content, mg./100 ml.			
			8 weeks	16 weeks	24 weeks	32 weeks
	(Gasoline #1)					
1	Antioxidant A (50%)+2-mercapto-imidazolidine (50%).	3	1.2	1.0	3.8	3.7
2	Antioxidant A	1.5	2.5	2.3	5.3	7.3
3	None		3.1	15.0	109.4	407.9
	(Gasoline #2)					
4	Antioxidant A (50%)+ethyl thioglycolate (50%).	3.0	2.3	3.5	4.6	5.2
5	Antioxidant A	1.5	1.0	2.5	6.9	7.3
6	None		8.1	43.1	131.6	326.1

As shown in Table III by incorporating the mercaptans of our invention, which by themselves are not antioxidants, into gasoline containing materials known to be antioxidants, a substantial reduction in the amount of gum formed during storage was obtained compared to the gasoline containing the antioxidant alone. In this comparison, our synergists were used in addition to known antioxidants, and resulted in

improved storage stability of the fuel. As a further embodiment we have replaced part of the antioxidant material with our synergists, thereby obtaining equivalent protection but utilizing for the purpose a smaller quantity of the antioxidant.

To illustrate the protection afforded to hydrocarbon solutions of tetraethyllead by the compounds of our invention we conducted a series of tests in which hot-acid isooctane containing 4.6 milliliters of tetraethyllead per gallon was heated at a temperature of 100° C. in a stainless steel bomb with oxygen added to an initial pressure of 100 pounds per square inch gauge. Under these conditions the pressure in a bomb containing only isooctane and a tetraethyllead antiknock mixture underwent a sharp drop after four hours, indicating absorption of oxygen by the fuel mixture. Various amounts of known antioxidants and our synergistic mixtures were thereupon added until it was determined at what minimum concentration the pressure in the bomb did not drop during a period of 16 hours at a temperature of 100° C. Thus, the effective concentration shown in Table IV is the minimum quantity of additive required, expressed as milligrams per 100 milliliters of fuel, to afford at least a four-fold increase in the stability of the fuel.

TABLE IV

Stabilization of isooctane containing tetraethyllead

No.	Additive	Effective conc., mg./100 ml.
1	Antioxidant A (67%)+2-mercapto-imidazolidine.	0.2
2	Antioxidant A	0.4
3	2-Mercapto-imidazolidine	>2.3

By reference to Table IV it is clear that by replacing one-third of the arylamine antioxidant by a synergist of our invention, the mixture is effective at one-half the concentration required for the antioxidant alone. This result is obtained with a synergist which, when employed alone, fails to protect the fuel at over eleven times the effective concentration of the mixture of our invention.

A further class of organic substances sensitive to oxygen comprises the elastomers, natural and synthetic. To illustrate the utility of the synergistic mixtures of our invention in protecting such substances we selected a natural rubber compounded into a typical tire-tread formula. One requisite of such stocks is that the desirable properties incorporated therein by careful selection of the compounding ingredients and cure time shall be maintained during extended periods of storage or use in the presence of oxygen. Comparison of various rubber stocks is best carried out on stocks initially having the same state of cure. The most reliable means for determining the state of cure is by the T–50 test, ASTM designation: D599–40T, described in the ASTM standards for 1946, Part III–B. This test measures the temperature at which a test piece recovers its elasticity when it is stretched at room temperature, frozen at a sufficiently low temperature to cause it to lose its elastic properties, and then gradually warmed. In practice the temperature noted is that at which the sample recovers to 50 per cent of the original elongation and is, therefore, referred to as the T–50 value. In the examples that follow stocks for testing and comparison were cured for a time sufficient to have a T–50 value of +1° C., so that a valid comparison of the properties could be made. The accelerated aging was conducted by the procedure of ASTM designation: D572–42, described in the ASTM Standards for 1946, Part III–B, for a period of 96 hours at a temperature of 70° C., with an initial oxygen pressure in the test bomb of 300 pounds per square inch gauge on specimens showing the following composition:

	Parts by weight
Smoked sheet	100.00
Carbon black	45.00
Zinc oxide	5.00
Stearic acid	3.00
Pine tar oil	2.00
Sulfur	3.00
Mercapto-benzothiazole	0.65
Stabilizing ingredient	1.00
	159.65

To demonstrate the protection afforded to the rubber by the mixtures of our invention, the tensile strength and the ultimate elongation of stocks prepared with the addition of a synergistic mixture of our invention were determined before and after aging. These properties were compared with the same properties determined on an identical rubber stock protected by the arylamine antioxidant alone, and finally with a stock not protected by an inhibitor. Both of these properties were determined by means of the test procedure of ASTM designation: D412–41, fully described in ASTM Standards for 1946, Part III–B. The tensile strength is the tension load per unit cross-sectional area required to break a test specimen, while the ultimate elongation is the elongation at the moment of rupture of a test specimen. A decrease in the values for either of these properties upon aging represents a decrease in the usefulness of the article fabricated therefrom, so that the degree to which these properties are retained is a direct measure of the utility of the protective substance.

TABLE V

Effect on aging properties of rubber

No.	Antioxidant	Percent of original retained after aging	
		Tensile Strength	Ultimate Elongation
1	Antioxidant D(67%)+2-mercapto-imidazolidine (33%).	53.7	83.0
2	Antioxidant D	43.8	80.4
3	None	24.5	55.0

By referring to Table V it is apparent that both Nos. 1 and 2 are effective in promoting retention of the tensile strength and ultimate elongation over the control which contained no protective additive (No. 3). However, by replacement of one-third of the known antioxidant by the synergistic material of our invention, not only was protection maintained, but an increase in retention of the original physical properties resulted.

The quantities of the mixtures of our invention incorporated in the materials to be stabilized are not critical and depend largely upon the type of material being stabilized and the conditions under which the exposure to oxygen occurs. For example, with gasolines, tetraethyllead, mineral oils and similar materials the mixtures of our

invention are preferably employed in concentrations between the limits of approximately 0.1 and 15 milligrams per 100 milliliters of material to be stabilized. For other materials, such as for example elastomers, both natural and synthetic, somewhat larger amounts of the stabilizers of our invention are preferred and can be tolerated. Thus, in such materials we employ between approximately 0.1 and 2 parts of synergistic mixture per 100 parts of oxidizable material. Thus, our mixtures can be satisfactorily employed in a wide range of concentrations, and we do not intend that our invention be restricted to the specific quantities mentioned herein.

Furthermore, we do not mean to be restricted by the ratios of synergistic mercaptan to arylamine antioxidant employed in the specific embodiments of our invention disclosed herein by way of examples. Such ratios will be determined in part by the nature of the material to be stabilized, in part by the specific arylamine employed and in part by the specific synergistic mercaptan. In general, however, we prefer to employ between about 30 and 100 parts by weight of mercaptan to 100 parts by weight of arylamine.

We have disclosed a number of preferred embodiments of our invention and illustrated several means whereby protection can be afforded to organic materials sensitive to attack by oxygen. Our invention is not intended to be limited to the specific embodiments of our invention herein or to the means described herein for obtaining the advantages possible in employing our synergistic mixtures, as other methods of practicing our invention will be apparent to those skilled in the art.

We claim:

1. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials, said composition consisting essentially of a lower alkyl-p-phenylene diamine and a sulfur compound selected from the group consisting of alkyl mercaptans containing from 4 to 12 carbon atoms, furfuryl mercaptan, the lower alkyl esters of thioglycolic acid, 2-mercapto imidazolidine and lower alkyl 2-mercapto imidazolidines, said sulfur compound being present in amount by weight between about 25 per cent and about 50 per cent of said synergistic antioxidant compound.

2. The composition of claim 1 in which the arylamine antioxidant is N,N'-di-sec.-butyl-p-phenylenediamine.

3. The composition of claim 2 in which the sulfur compound is an alkyl mercaptan containing from 4 to 12 carbons.

4. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials consisting essentially of 100 parts of N,N'-di-sec.-butyl-p-phenylenediamine and between about 30 and 100 parts of t-butyl mercaptan.

5. The composition of claim 2 in which the sulfur compound is furfuryl mercaptan.

6. The composition of claim 2 in which the sulfur compound is a lower alkyl ester of thioglycolic acid.

7. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials consisting essentially of 100 parts of N,N'-di-sec.-butyl-p-phenylenediamine and between about 30 and 100 parts of ethyl thioglycolate.

8. The composition of claim 2 in which the sulfur compound is a lower alkyl 2-mercapto imidazolidine.

9. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials consisting essentially of 100 parts of N,N'-di-sec.-butyl-p-phenylenediamine and between about 30 and 100 parts of 3-propyl-2-mercapto imidazolidine.

10. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials consisting essentially of 100 parts of N,N'-di-sec.-butyl-p-phenylenediamine, and between about 30 and 100 parts of 2-mercaptoimidazolidine.

11. A composition consisting essentially of at least one hydrocarbon that normally tends to deteriorate in the presence of oxygen, and an effective amount of a synergistic antioxidant mixture of an arylamine antioxidant and a sulfur compound, as defined by claim 1, said sulfur compound being present in amount between about 30 and 100 parts per 100 parts of said arylamine antioxidant by weight.

12. A petroleum hydrocarbon fuel for internal combustion engines, normally subject to deterioration in the presence of oxygen, containing as a principal antioxidant ingredient a synergistic antioxidant mixture consisting essentially of an arylamine antioxidant and a sulfur compound as defined in claim 1, said sulfur compound being present in amount between about 30 and 100 parts per 100 parts of said arylamine antioxidant, and said synergistic mixture present in amount between about 0.1 to 15 milligrams per 100 milliliters of said hydrocarbon fuel.

13. A fuel for internal combustion engines containing petroleum hydrocarbons stable to oxygen, an antiknock additive substance comprising tetraethyllead, the presence of which tends to increase the deterioration of the resulting fuel blend in the presence of oxygen, and as a principal antioxidant ingredient the synergistic mixture of claim 1, in amount between about 0.1 to 15 milligrams per 100 milliliters of said fuel composition.

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