Patented Nov. 3, 1953

2,657,983

UNITED STATES PATENT OFFICE

2,657,983

SYNERGISTIC STABILIZING COMPOSITIONS

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No Drawing. Application March 18, 1952, Serial No. 277,336

16 Claims. (Cl. 44—70)

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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 application is a continuation of co-pending application Serial No. 135,044, filed December 24, 1949.

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

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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 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.

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 hydroxy arylamino antioxidant materials and substances derived from the class of esters of thioglycolic acid.

We have made the discovery that esters of thioglycolic acid themselves incapable of protecting organic materials from deterioration in the presence of oxygen, have the property of greatly increasing the effectiveness of hydroxyarylamino antioxidants. Such esters we refer to hereinafter as synergists. The synergistic thioglycolic esters of our invention include those wherein the esterifying radical is a hydrocarbon. Such radicals comprise aryl and aliphatic radicals. Thus, among the aryl esters we contemplate, for example, phenyl, α-naphthyl, β-naphthyl, and other polynuclear aromatic radicals as well as substituted aryl radicals, such as tolyl, xylyl, ethylphenyl, cumyl, tetralin, methylnaphthyl and the like. Among the aliphatic thioglycolic esters which provide synergism in accordance with our invention we include alkyl esters such as methyl, propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, the isomeric amyl, hexyl, heptyl, octyl, nonyl and the like up to and including about eighteen carbon atom alkyl radicals such as lauryl, stearyl and the like; alkenyl esters such as vinyl, allyl, methallyl, crotyl, phtyl, oleyl, undecenyl, and the like; cycloalkyl esters, such as cyclobutyl, cyclopentyl, cyclohexyl, methylcyclohexyl and the like; and aralkyl esters, such as benzyl, phenethyl, 2-phenylpentyl and the like. The lower alkyl esters are among our preferred synergists.

The hydroxy arylamino antioxidant components of our synergistic mixtures are well known, and include those employed in many antioxidant applications such as foodstuffs, fats, oils, greases, soaps, petroleum products, natural rubbers, synthetic hydrocarbon rubbers, such as the butyl, styrene and butadiene rubbers, as well as those of the chloroprene, thiokol, acrylonitrile, and silicone types, and plastics, for example, the vinyl, cellulosic, polyethylene types, etc. Typical hydroxy arylamino antioxidants include p-aminophenol, N-n-butyl-p-aminophenyl, 1-amino-4-hydroxy-naphthalene, N-isobutyl-p-aminophenol, N-isopropyl-p-aminophenol, 1-N-butylamino-4-hydroxy-naphthalene, N-phenyl-p-aminophenol, N-cyclohexylamino-p-aminophenol, N-(p-hydroxyphenyl)-p-phenylenediamine and the like. Where the hydroxy arylamino antioxidant can be considered as a naphthalene derivative we prefer to employ modifications wherein the hydroxy and amino groups are on the same aromatic nucleus. In general we prefer to employ the aminophenol type of antioxidant with our thioglycolic ester synergists.

We have found that the replacement of a portion of the hydroxy arylamine antioxidant of a stabilized composition with our synergistic thioglycolates, themselves incapable of providing oxygen stabilization, results in a stabilized composition which is remarkably resistant to attack by oxygen. Furthermore, to attain a specified degree of oxygen stability the required amount of our hydroxy arylamino-thioglycolic ester mixture is less than the required amount of the hydroxy arylamine antioxidant alone.

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 pro-oxidant 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 obtained representative Induction Period Increases 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 gaso-

line containing 28 per cent olefins and 18 per cent aromatics with medium sulfur content.

In general, the synergistic component of our novel antioxidant compositions is ineffective as an antioxidant. When tested by the above-mentioned ASTM method we obtain results ranging from zero IPI or insignificant values, such as 10 to 20 minutes, to negative values of IPI. That is, the synergistic component may actually be an oxidizing material, or a pro-oxidant. Typical of such results is that obtained with isopropyl thioglycolate, which at a level of 6 milligrams per 100 milliliters of test gasoline actually reduced the induction period of the untreated fuel by 70 minutes.

Other thioglycolate esters of our invention which do not exhibit an antioxidant effect when employed alone in gasoline include methyl thioglycolate, n-butyl thioglycolate, isobutyl thioglycolate, cyclohexyl thioglycolate, phenyl thioglycolate, amyl thioglycolate, benzyl thioglycolate, allyl thioglycolate, lauryl thioglycolate, n-dodecyl thioglycolate, and α-naphthylthioglycolate.

The effectiveness of typical synergistic mixtures of our invention is shown by adding to the test gasoline a total concentration of 6 milligrams of the synergistic mixture per 100 milliliters of gasoline, and comparing the increase in the induction period of the test gasoline obtained with that obtained with the arylamine antioxidant alone at the same total concentration of 6 milligrams per 100 milliliters of gasoline. Thus, employing a mixture comprising 2.0 milligrams of isopropyl thioglycolate and 4.0 milligrams of N-n-butyl-p-aminophenol per 100 milliliters of gasoline an IPI of 405 minutes was obtained, while in a similar determination using 6.0 milligrams of N-n-butyl-p-aminophenol an IPI of only 340 minutes was obtained. Thus, replacing one-third of the antioxidant with a pro-oxidant actually increased the effectiveness of the remaining antioxidant by thirty-three per cent. Similar results were obtained with a mixture comprising 33 per cent isopropyl thioglycolate and 67 per cent N-isobutyl-p-aminophenol at a total concentration of 6 milligrams per 100 milliliters of gasoline. The IPI of the so-treated fuel was 410 minutes, while using 6 milligrams of N-isobutyl-p-aminophenol alone per 100 milliliters of gasoline produced an IPI of only 335 minutes. Like results are obtained by employing equal parts of N-n-butyl-p-aminophenol and ethyl thioglycolate, 33 per cent cyclohexyl thioglycolate and 67 per cent N-cyclohexyl-p-aminophenol, 25 per cent phenyl thioglycolate and 75 per cent 1-(methylamino)-4-hydroxy naphthalene, equal parts of allyl thioglycolate and N-(4-hydroxyphenyl)-p-phenylenediamine, and 30 per cent stearyl thioglycolate and 70 per cent N-isopropyl-p-aminophenol.

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 milligrams 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. Thus, by incorporating our thioglycolate esters, 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 comparsion, 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.

Our synergists likewise afford protection to hydrocarbon solutions of tetraethyllead as shown by 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 are thereupon added until it is determined at what minimum concentration the pressure in the bomb does not drop during a period of 16 hours at a temperature of 100° C. By using our mixtures, nearly a two-fold increase in effectiveness can be obtained, compared to the hydroxy arylamine antioxidant alone at a reduced concentration of total additive.

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 a natural rubber compounded into a typical tire-tread formula is convenient. 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 these tests stocks for testing and comparison are cured for a time sufficient to have a T–50 value of +1° C., so that a valid comparison of the properties can be made. The accelerated aging is 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 having 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 are determined before and after aging. These properties are 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 decrese 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. When the following typical mixtures of the synergists of our invention are so-tested as much as a 100 per cent increase in the tensile strength and a 50 per cent increase in the ultimate elongation is obtained: 33 per cent isopropyl thioglycolate, 67 per cent 4-hydroxy-α-naphthyl amine; 25 per cent α-naphthyl thioglycolate, 75 per cent N-(p-hydroxyphenyl)-p-phenylenediamine; 30 per cent cyclohexylthioglycolate, 70 per cent N-butyl-1-amino-5-hydroxy naphthalene; and 33 per cent ethyl thioglycolate, 67 per cent N-n-butyl-p-aminophenyl.

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, lubricating oils, diesel fuels, 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, soaps, fats and greases, 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. For plastics, foodstuffs, etc., we prefer to employ between about 0.05 and 1 part of synergistic mixture per 100 parts of perishable 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 thioglycolic ester to hydroxy 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 thioglycolic ester to 100 parts by weight of hydroxy 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 consisting essentially of a hydroxy arylamine antioxidant and an ester of thioglycolic acid.

2. A synergistic antioxidant composition effective in inhibiting oxidation in oxygen-sensitive organic materials consisting essentially of between about 30 and 100 parts by weight of alkyl thioglycolate and about 100 parts by weight of an aminophenol.

3. A composition consisting essentially of an organic material tending to deteriorate in the presence of oxygen, and a synergistic antioxidant mixture, present in quantity sufficient to inhibit such deterioration, said antioxidant mixture consisting essentially of a hydroxy arylamine antioxidant and an ester of thioglycolic acid.

4. The composition of claim 1 wherein said hydroxy alkylamine antioxidant is 4-hydroxy-α-naphthyl amine and said ester of thioglycolic acid is isopropyl thioglycolate.

5. The composition of claim 1 wherein said hydroxy alkylamine antioxidant is N-(p-hydroxyphenyl)-p-phenylenediamine and said ester of thioglycolic acid is α-naphthyl thioglycolate.

6. The composition of claim 1 wherein said hydroxy alkylamine antioxidant is N-butyl-1-amino-5-hydroxynaphthalene and said ester of thioglycolic acid is cyclohexylthioglycolate.

7. The composition of claim 1 wherein said hydroxy alkylamine antioxidant is N-n-butyl-p-aminophenol and said ester of thioglycolic acid is ethyl thioglycolate.

8. 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 mixture consisting essentially of a hydroxy arylamine antioxidant and an ester of thioglycolic acid, said ester being present in amount between about 30 and 100 parts per 100 parts of said hydroxy arylamine and said synergistic mixture present in amount between about 0.1 to 15 milligrams per 100 milliliters of said hydrocarbon fuel.

9. The composition of claim 8 wherein said

hydroxy arylamine antioxidant is N-n-butyl-p-aminophenol and said ester of thioglycolic acid is isopropyl thioglycolate.

10. The composition of claim 8 wherein said hydroxy arylamine antioxidant is N-isobutyl-p-aminophenol and said ester of thioglycolic acid is isopropyl thioglycolate.

11. The composition of claim 8 wherein said hydroxy arylamine antioxidant is N-n-butyl-p-aminophenol and said ester of thioglycolic acid is ethyl thioglycolate.

12. 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 a hydroxy arylamine antioxidant and an ester of thioglycolic acid, said ester being present in amount between about 30 and 100 parts per 100 parts of said hydroxy arylamine antioxidant by weight and said synergistic mixture being present between about 0.1 and 2 parts by weight per 100 parts of said elastomer.

13. The composition of claim 12 wherein said ester is isopropyl thioglycolate and said hydroxy arylamine is 4-hydroxy-α-naphthylamine.

14. The composition of claim 12 wherein said ester is α-naphthyl thioglycolate and said hydroxy arylamine is N-(p-hydroxyphenyl)-p-phenylenediamine.

15. The composition of claim 12 wherein said ester is ethyl thioglycolate and said hydroxy arylamine is N-n-butyl-p-aminophenol.

16. The composition of claim 12 wherein said ester is cyclohexylthioglycolate and said hydroxy arylamine is N-butyl-1-amino-5-hydroxynaphthalene.

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