

UNITED STATES PATENT OFFICE

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STABILIZED ORGANIC COMPOSITIONS

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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 such materials.

Hydrocarbon fuels for use in internal combustion, spark ignition engines may be classified broadly into three categories, according to the type of engine for which they are manufactured and marketed, such as automotive, aircraft and diesel fuels. Although each type of fuel is composed essentially of hydrocarbons, the type and stability characteristics of the individual hydrocarbon types comprising each fuel differ considerably, as do the relative proportions of the various types in each fuel. For example, typical automotive fuels contain straight and branched chain aliphatics, olefins, naphthenes and some aromatics, typical aircraft fuels are particularly low in olefins and typical diesel fuels contain principally saturated hydrocarbons with a smaller proportion of olefins.

During the refining, manufacturing and blending processes, and during subsequent storage and handling operations, it is unavoidable that these fuels or their ingredients, such as cracked blending stocks, or the highly olefinic stocks for reforming and alkylation, are brought into contact with oxygen. The result of such contact is the formation, by oxidation or polymerization or a combination thereof, of gummy materials which interfere with the efficient utilization of said fuels in the engine.

Automotive gasolines are, in general, more susceptible to this type of degradation by oxygen than aircraft fuels, while in recent years the degradation of fuels for use in compression ignition engines has become more significant. The presence of gummy materials in fuels for spark ignition engines causes valve sticking, lowered spark plug efficiency, piston varnish and associated troubles, while such deteriorated fuels, when used in diesel engines, interferes with the operation of the fuel filters and injectors.

Because of the specifications imposed on fuels by the rigid requirements of present day engines, particularly aircraft engines, it is essential that any material capable of protecting 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.

Many other materials in extensive use require protection from the adverse effects of contact with oxygen. One such class of materials is the elastomers, both natural and synthetic. Upon absorption of oxygen such elastomers deteriorate prematurely, lose tensile strength and

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flexibility and become discolored and embrittled. This absorption can occur during manufacturing operations, fabrication, storage or use. While certain materials have been proposed for the protection of such elastomers from the deleterious action of oxygen, many of such protective substances possess the serious disadvantage, particularly with respect to light colored stocks, that the decomposition products are themselves colored and hence interfere with the color fastness of the stocks being protected.

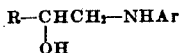
Further examples of materials which require protection from the effects of oxygen include certain foodstuffs, such as animal and vegetable oils and fats, which upon exposure to oxygen develop rancidity, color and odor. Still further examples include mineral oils, lubricating oils, soaps, and diverse synthetic unsaturated organic materials. In general, our invention is useful in protecting those organic substances which, during the process of manufacturing, handling, storage or use 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 substances which prevents the formation of gummy oxidation and polymerization products of unstable hydrocarbons on contact with oxygen. Another object of our invention is to provide means for stabilizing hydrocarbon fuels for internal combustion spark and compression ignition engines during the manufacturing, handling and storage of such fuels prior to their use. 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, and which do maintain for long periods the qualities inherent in such finished fuels at the time of manufacture. 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 this invention is to provide means for protecting foodstuffs and 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 the addition to organic materials of a protective amount of an ethanalamine resulting from the reaction of 1,2-epoxy compounds or their equivalents, with aromatic aminophenols or aromatic diamines.

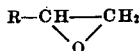
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We have made the discovery that the substances obtained by condensation of a 1,2-epoxy compound with an aromatic compound of the benzene series containing two substituents, one of which is an amino group and the other is either a second amino group or a hydroxy radical, located in the para position, have the property of markedly improving the resistance of unstable organic materials to the deleterious action of oxygen. Such substances, comprising the compounds of our invention, are characterized by the structure

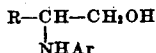


wherein R is associated with the 1,2-epoxy reactant and Ar is associated with the amino reactant.

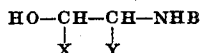
By 1,2-epoxy compounds we refer to organic substances described by the general formula



Such materials react with amino compounds to produce the above-described substituted ethanolamines. In addition to the ethanolamine structure shown above, condensation may take place to form products having the isomeric structure



although such compounds are obtained in lesser proportion. It is, however, within the scope of our invention to employ compounds of this structure in our stabilized compositions, and certain of our preferred antioxidants comprise a mixture of the two isomeric forms. Thus, the antioxidants of our invention may be described by the general formula



wherein one of X and Y is hydrogen and the other is alkyl, aryl, alkoxymethylene or aryloxymethylene, as described hereinafter, and B is an aromatic group containing hydroxy or amino substituents as further defined below.

Other raw materials for the manufacture of the antioxidants of our invention can be used and will occur to those skilled in such art. In general, compounds capable of yielding a 1,2-epoxy-containing substance during the condensation reaction with the amine can be employed. For example, alkene chlorhydrins and bromhydrins react with amines to form substituted ethanolamines. Thus, for the purpose of practicing our invention, alkene chlorhydrins and bromhydrins are such examples of compounds equivalent to 1,2-epoxy compounds. Therefore, although 1,2-epoxy compounds will be employed hereinafter to describe our invention, we do not mean to be limited to this embodiment thereof.

As the 1,2-epoxy constituent of the reaction products of our invention we have successfully employed compounds in which R is an aromatic substituent, as for example, in phenylethylene oxide. Further examples of the group R comprise alkyl substituents, as typified in 1,2-propylene oxide, and 1,2-butylene oxide. As a further example, the R group may be an alkoxymethylene group, as in glycidyl methyl ether and, glycidyl propyl ether or phenoxyethylene, as in glycidyl phenyl ether.

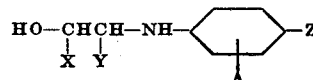
As the second constituent of the reaction mixtures producing the antioxidant materials of our

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invention we employ an aromatic amine substituted in the para position with either an additional amino group or an hydroxy group. Examples of the former include p-phenylenediamine, and 2,5-diaminotoluene. Examples of the latter include p-aminophenol, 2-amino-5-hydroxytoluene, and 2-pentadecyl-4-hydroxyaniline.

From the foregoing examples, it is evident that the second amino group of this constituent of the reaction mixture, or the hydroxyl group thereof, are important features of the resulting antioxidant material. In the absence of such group, the reaction product does not exhibit inhibiting properties. Thus, aniline when reacted with the 1,2-epoxy compounds of our invention, produces an inert material. It is not essential, however, that the second amino group be unsubstituted, as we have obtained excellent results when alkyl or aryl substituents occur thereon. For example, the ethanolamine obtained by condensation of phenylethylene oxide and 4-amino-diphenylamine is an effective antioxidant. Conversely, however, it is preferred that the hydroxy group of the reactants of our invention be not substituted. Thus, when we reacted p-anisidine with phenylethylene oxide, we obtained a product which exhibited no appreciable antioxidant effect.

Therefore, we can describe the compounds of our invention by the formula



wherein each of X and Y has the meaning defined above. A is selected from hydrogen or alkyl, and Z is a hydroxy group or an amino or alkyl-substituted amino group.

As shown above, inclusion of an alkyl group substituted on the aromatic nucleus of the diamine or aminophenol comprises a preferred embodiment of our invention. Although such alkyl groups are not believed to contribute an antioxidant effect, they do impart the important property of appropriate solubility. Thus, an antioxidant material for certain uses, such as, for example, stabilizers for gasoline, diesel fuels, and lubricating oils, must exhibit relatively high solubility in hydrocarbons and extremely low solubility in water, to prevent extraction thereby. Likewise, a rubber antioxidant must possess certain compatibility and miscibility characteristics with the stock being protected. Similar considerations pertain for each class of substances for which our compounds are useful antioxidants. These functions are performed by such alkyl substituent. However, for certain applications, notably in stabilizing gasoline, we prefer to rely upon the choice of the substituent X or Y to provide high hydrocarbon solubility and low water solubility. By so adjusting the solubilizing groups at these points in the antioxidant molecule, instead of on the aminophenol or arylenediamine, we have found that the antioxidant effectiveness is impaired to a lesser degree. Thus, while it is important to achieve practical solubility characteristics, it is preferred not to accomplish this by sacrificing antioxidant effectiveness. In that embodiment of our invention wherein Z is an amino group, we have found that the substitution of an alkyl group thereon contributes more than mere solubility to the resulting antioxidant material, and in a particular manner. Thus, a methyl group increases the antioxidant activity.

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Upon increasing the carbon chain of such alkyl group this effect continues to be felt, but to a diminishing extent, and as groups above propyl are so-employed the prime contribution is one of solubilizing.

We have found that alkylene diamines, dialkylamines and alkanolamines do not produce anti-oxidant materials when substituted for the phenylenediamines and aminophenols of our invention. Thus, the products obtained by reacting ethylenediamine or dimethylamine with phenylethylene oxide do not stabilize gasoline against attack by oxygen.

The compounds of our invention may be further defined by reference to the following methods of preparation, which, while not restricting the scope of the variations possible in different embodiments of our invention, are representative of methods which we have employed in preparing the specific materials described herein. All quantities referred to herein are parts by weight.

EXAMPLE I

Reaction of phenylethylene oxide with p-aminophenol

In a reaction vessel provided with agitating, heating and refluxing means and means for introducing liquid reactants was placed 24 parts of p-aminophenol and 40 parts of anhydrous methanol. The resulting suspension was agitated while a solution of 27 parts of phenylethylene oxide in 40 parts of anhydrous methanol was introduced over a period of one hour, maintaining the reaction mixture at a temperature of approximately 25° C. The reaction mixture was heated for a further period of six hours at the reflux temperature after addition was complete, and then allowed to remain at a temperature of 25° C. for a period of fifteen hours. The resulting mixture was transferred to a distillation apparatus, containing 1 part of phenylacetylene. The methanol was removed by distillation at atmospheric pressure, and the pressure was thereupon reduced to 2 millimeters of mercury absolute, and the product distilled at a temperature of 230 to 240° C. The product so-obtained, 19.5 parts, was an oil which solidified on standing, the resulting solid having a melting point of 76 to 78° C. The product contained 6.87 per cent nitrogen.

EXAMPLE II

Reaction of phenylethylene oxide with p-phenylene diamine

Following the procedure of Example I, 21.6 parts of p-phenylene diamine in 40 parts of methanol was reacted with 24 parts of phenylethylene oxide in 40 parts of methanol. In this example, the product, 20 parts, distilled at a temperature of 250 to 255° C., at a pressure of 1 millimeter of mercury absolute. The product contained 11.65 per cent nitrogen.

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 drop in pressure, indicating no absorption of oxygen when the test material is 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.

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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.

Our invention is illustrated by reference to Table I wherein are listed the IPI of a number of substances, determined by the above-described method. 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 alcohol, was added in amount up to 2 per cent of the gasoline.

It is well known in the art of protecting gasoline from oxidation that the susceptibility to oxidation of gasolines varies significantly with different types of gasolines. Furthermore, it is likewise well known that the efficiency of any anti-oxidant, 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, there are listed in Table I the average IPI obtained with from one to three test gasolines, so chosen as to be typical of the variety encountered in commercial gasolines.

The ASTM method employed to illustrate the activity of the compounds of our invention as in Table I is a reliable indication of the efficiency of a stabilizing material within the test limits of plus 10 minutes and minus 10 minutes. However, a compound or substance which produces an induction period increase of less than 50 minutes is not considered an effective antioxidant.

Referring to Table I, it is readily apparent that compounds 1 through 6 inclusive, are extremely effective antioxidants, while compounds 7 through 10, inclusive, are either so mild as not to be truly effective, or are essentially inert. The requirements and limitations of the reactants employed in the manufacture of the compounds of our invention, described heretofore, are illustrated by the materials listed in Table I.

TABLE I

Effect on induction period increase of gasolines

No.	Reactants		IPI, min.
	Epoxy	Amino	
1.....	Phenylethylene oxide...	p-Aminophenol.....	500
2.....	Glycidyl propyl ether...	p-Aminophenol.....	379
3.....	Phenylethylene oxide...	p-Phenylenediamine...	250
4.....	Phenylethylene oxide...	4-Aminodiphenylamine...	230
5.....	Phenylethylene oxide...	2-Amino-5-hydroxytoluene...	215
6.....	Glycidyl phenyl ether...	p-Aminophenol.....	110
7.....	Phenylethylene oxide...	Ethylenediamine.....	45
8.....	Phenylethylene oxide...	p-Anisidine.....	25
9.....	Phenylethylene oxide...	Dimethylamine.....	25
10.....	Phenylethylene oxide...	Aniline.....	0

We have demonstrated the efficiency of the compounds of our invention in preventing undue formation of gum in automotive gasolines by storing such gasolines for long periods in the presence and absence of our antioxidants and

determining from time to time the gum content of the fuels. For such demonstration duplicate amber quart bottles were filled with one pint of the gasoline and sufficient additive was dissolved therein to be equivalent to 4.5 milligrams of stabilizer per 100 milliliters of gasoline. 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. At the end of 24 weeks, and again after 32 weeks a sample of the fuel mixture was removed and the dissolved gum therein was determined by the "air-jet evaporation" method, ASTM designation: D381-46, fully described in ASTM Standards for 1946, part III-A. In the same manner the gum formed in the fuel under these conditions, but in the absence of the antioxidants of our invention, was determined by storing, aerating and sampling the untreated fuel as above. For example, the gum in a gasoline so-treated with the reaction product of phenylethylene oxide and p-aminophenol increased by only 5.1 and 7.8 mg. per 100 ml. of gasoline after storage periods of 24 and 32 weeks, respectively, while the increase of gum in the untreated fuel was 130 and 325 mg. per 100 ml. at the same periods. Thus, it is readily apparent that the amount of gum formed in the presence of our stabilizing materials was insignificant, and, furthermore, that this protection was afforded to a sensitive fuel, under conditions whereby very large quantities of gum were formed in the untreated fuel.

The utility of the compounds of our invention in preventing deterioration of hydrocarbon fuels by the action of oxygen is not impaired by the co-presence of other additives which may be added thereto. Thus, tetraethyllead and halogen-containing scavengers therefor, commonly present in finished gasoline, will not interfere with the protection afforded by our antioxidants. In fact, it is usually desirable to add one of our antioxidants to gasoline prior to blending the gasoline with the tetraethyllead composition, to protect the gasoline during the blending operation. The protection so-provided to the finished fuel is useful during subsequent handling, storage and use of the fuel. For example, we determined the induction period of a commercial gasoline containing 3 ml. of tetraethyllead per gallon to be 150 minutes, by the method described hereinbefore. The same fuel mixture to which we added 3 mg. of the reaction product of phenylethylene oxide and p-aminophenol exhibited an induction period of 555 minutes, a more than two-fold increase.

A further class of organic substances sensitive to oxygen comprises the elastomers, natural and synthetic. To illustrate the utility of the compounds 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 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 compounds of our invention, the tensile strength and the ultimate elongation of stocks prepared with the addition of antioxidants of our invention were determined before and after aging and were compared with the same properties determined on an identical rubber stock not protected by such compounds but having the same state of cure. 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. Thus, the degree to which these properties are retained is a direct measure of the utility of the protective substance.

TABLE II
Effect on aging properties of rubber

No.	Reaction product of (1) with (2)		Per cent of original retained after aging	
	(1)	(2)	Tensile Strength	Ultimate Elongation
1.....	Phenylethylene oxide.....	p-Phenylenediamine.....	39.8	61.6
2.....	do.....	p-Aminophenol.....	37.3	67.2
3.....	No antioxidant.....		18.9	53.5

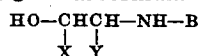
By referring to Table II it is at once apparent that the samples containing representative members of the compounds of our invention (Nos. 1 and 2) showed a remarkable increase in the retention of the original tensile strength and ultimate elongation over the control which contained no protective additive (No. 3).

The quantities of the compounds 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, diesel fuels, mineral oils and similar materials the compounds 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 soaps and natural and synthetic elastomers, 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 antioxidant per 100 parts of oxidizable material. Thus, our compounds 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.

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 herein or to the means described herein for obtaining the advantages possible in employing our compounds, as other methods of practicing our invention will be apparent to those skilled in the art.

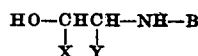
We claim:

1. A new composition stable to oxidation consisting essentially of an organic material normally tending to deteriorate in the presence of oxygen, and a substituted ethanolamine, present in quantity sufficient to inhibit such deterioration, having the general formula



wherein one of X and Y is hydrogen, and the other is selected from the group consisting of alkyl, phenyl, alkoxymethylene and phenoxy-methylene, and B is selected from the group consisting of p-aminophenyl, p-hydroxyphenyl, p-(N-alkylamino)phenyl, and 2- and 3-alkyl-4-hydroxyphenyl.

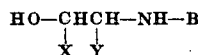
2. A petroleum hydrocarbon fuel for use in internal combustion engines stable to oxidation, consisting essentially of a petroleum hydrocarbon fuel normally tending to deteriorate in the presence of oxygen, and a substituted ethanolamine, present in quantity sufficient to inhibit such deterioration, having the general formula



wherein one of the X and Y is hydrogen, and the other is selected from the group consisting of alkyl, phenyl, alkoxymethylene and phenoxy-

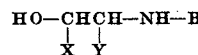
methylene, and B is selected from the group consisting of p-aminophenyl, p-hydroxyphenyl, p-(N-alkylamino)phenyl, and 2- and 3-alkyl-4-hydroxyphenyl.

3. A new composition stable to oxidation consisting essentially of an elastomer composition normally tending to deteriorate in the presence of oxygen and a substituted ethanolamine, present in quantity sufficient to inhibit such deterioration, having the general formula



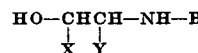
wherein one of X and Y is hydrogen, and the other is selected from the group consisting of alkyl, phenyl, alkoxymethylene and phenoxy-methylene, and B is selected from the group consisting of p-aminophenyl, p-hydroxyphenyl, p-(N-alkylamino)phenyl, and 2- and 3-alkyl-4-hydroxyphenyl.

4. The composition of claim 1 wherein the ethanolamine has the following formula



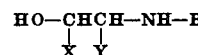
wherein one of X and Y is hydrogen and the other is phenyl, and B is p-hydroxyphenyl.

5. The composition of claim 1 wherein the ethanolamine has the following formula



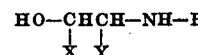
wherein one of X and Y is hydrogen and the other is propoxymethylene, and B is p-hydroxyphenyl.

6. The composition of claim 1 wherein the ethanolamine has the following formula



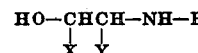
wherein one of X and Y is hydrogen and the other is phenyl, and B is p-aminophenyl.

7. The composition of claim 1 wherein the ethanolamine has the following formula



wherein one of X and Y is hydrogen and the other is phenyl, and B is p-(N-phenylamino)phenyl).

8. The composition of claim 1 wherein the ethanolamine has the following formula



wherein one of X and Y is hydrogen and the other is phenyl, and B is 4-hydroxy-2-methylphenyl.

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The following references are of record in the file of this patent:

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