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ORTHOALKYLPHENOL-SULFUR DICHLORIDE REACTION PRODUCTS

Calvin J. Worrel, Detroit, Mich., assignor to Ethyl Corporation, New York, N.Y., a corporation of Virginia

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This invention relates to new compositions of matter, more particularly to new sulfur and chlorine-containing reaction products.

Some phenolic compounds have found utility as antioxidants in various organic media. The ability of such compounds to act as antioxidants is dependent on a delicate balance of properities such as molecular weight, solubility, steric hindrance of the hydroxyl group and others which have yet to be defined.

Certain sulfur and chlorine-containing compounds have found utility as anti-wear and extreme pressure agents. Effectiveness as such is due in part to the affinity of such compounds for metal surfaces. Bearings in contact with an oil containing such compounds are protected from wear by the coating action of the additive. The anti-wear agent coats the bearing to remove it physically from the oil.

Thus the mechanisms by which the two types of additives function can be contrasted. On the one hand, antioxidants function by intimately co-acting with the medium, for example oil, to react with oxygen and perioxides, thus stabilizing the oil. On the other hand, anti-wear agents are more effective where their affinity for metal surfaces is greater than their affinity for oil. They act not chemically as to antioxidants with oxygen and peroxides but rather act physically on metal surfaces or bearings in the oil. Attempts have been made in the past to find antioxidants which will also act as anti-wear agents. Such a task is made difficult by the fact that the respective functions are accomplished by contrasting mechanisms. In order to accomplish such a task a delicate balance must be achieved whereas the solubility, molecular weight, configuration, affinity and other properties of the compounds must be such as to allow the compound to function in both capacities. This is not an easy task. Previous attempts have resulted in compounds which are not effective in either capacity.

It is an object of this invention to provide new compositions of matter. A further object is to provide highly effective sulfur and chlorine-containing phenolic reaction products. Another object is to provide a new process for preparing these sulfur and chlorine-containing reaction products. Still another object is to provide new compositions of matter which comprise various organic media, particularly mineral oils, containing the sulfur and chlorine-containing reaction products of this invention. Other objects of this invention will be apparent from the ensuing description.

Applicant has discovered a certain class of sulfur and chlorine-containing phenolic material which, contrary to the properties of either phenolic or sulfur and chlorine-containing material, are not only excellent and highly effective antioxidants in a large and varied range of organic media but also act effectively as anti-wear and extreme pressure agents for liquid organic media when such media are in contact with a metal surface.

Further, this dual role is accomplished without resort to the use of metal salts. This is very significant. The use of metal-containing additives in lubricating oil results in a buildup of metallic deposits in various parts of the engine. As a result additional additives have to be resorted to in order to aid removal of these metallic deposits, many times unsuccessfully. Applicant's invention in its lubricating oil embodiment avoids the necessity of such additional additives since no metallic ash is formed upon its burning.

The fact that the products of this invention act not only as antioxidants but also as highly effective anti-wear and extreme pressure agents is completely unexpected from the nature of the reactants. Anti-wear and extreme pressure agents act by coating the metal surface or bearing in the oil. However, these agents protect not only by presenting a shield against chemical reaction but also by their physical presence, preventing contact of the metal surface with abrasive particles in the oil. These abrasive particles can be metallic in nature or they can be reaction or deterioration products of the oil.

Further, applicant's products have excellent oil solubility. Solubility is extremely important to the usefulness of a product as an oil additive. Products which have only limited solubility in oil tend to deposit out when the oil is subjected to extermes of temperatures and pressure. This handicap is usually associated with products containing sulfur or chlorine. Applicant's products, however, have excellent oil solubility and do not form deposits when the oil is subjected to harsh treatment.

Thus applicant's products possess two outstanding advantages. They are antioxidants and anti-wear and extreme pressure agents combined and are most superior in each capacity.

In accordance with the present invention new compositions of matter are provided which consist of the sulfur and chlorine-containing phenolic product obtained by reaction between (1) a phenolic compound having, ortho to the phenolic hydroxyl group, an alkyl group of from 3–8 carbon atoms and (2) sulfur dichloride; there being at least about 1.0 mole of said sulfur dichloride per mole of phenol as reactants.

The sulfur and chlorine-containing phenolic products of this invention are substantially involatile, oil soluble, clear, reddish-yellow, viscous semi-solids or resins. These products are complex in chemical structure. When subjected to elemental chemical analyses they do not correspond to any specific chemical formula. To further characterize the product, infrared as well as visible and ultraviolet spectra techniques were attempted. However, they afforded little help. Characteristic bands for sulfur-phenol and chlorine-phenol bonds are weak at best.

Elemental analysis, however, does afford a means for further characterizing the products of this invention. Thus applicant's invention can be defined in terms of its carbon, hydrogen, sulfur and chlorine content as well as its average molecular weight. Thus, the products of this invention can be described as antioxidant material containing 50 to 62 percent carbon, 4.5 to 7.2 percent hydrogen, 34 to 11 percent sulfur, and having a molecular weight of from 500 to 740.

Accordingly, an embodiment of this invention is a substantially involatile, reddish-yellow polynuclear phenolic compound containing 2 to 5 phenolic nuclei wherein each phenolic nuclei contains one hydroxyl radical and one alkyl group of 3–8 carbon atoms ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from those carbon atoms ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said compound containing about 50 to 62 percent carbon, about 4.5 to 7.2 percent hydrogen, about 34 to 11 percent sulfur, and about 16 to 5 percent chlorine, said compound having an average molecular weight of about 500 to 740, and said compound being soluble in hydrocarbon mineral oil.

The novel sulfur and chlorine-containing reaction products of this invention possess a number of outstanding advantages. They very effectively improve the performance characteristics of a wide variety of organic media

when incorporated therein, for example, when used as additives in lubricating oil. Further, these products are readily prepared in good yield from starting materials which are available as articles of commerce. Also, these products possess high solubility and compatibility with most organic media, especially petroleum hydrocarbon oils. Therefore, these products are easily blended with liquid hydrocarbons and with other organic media and can be used at high concentrations, with no solubility problems occurring when liquid hydrocarbons containing these products are stored at low temperatures for long periods of time. Furthermore, the products of this invention possess unusual resistance against hydrolysis and thus can be effectively used as additives for organic media which come in contact with or contain water. Moreover, the products of this invention are very stable at elevated temperatures such as are encountered in operating gasoline engines. Thus when used as mineral oil additives for crankcase lubricants and the like no appreciable deterioration of the products occur during engine service.

Further, these compounds have the unusual advantage of possessing antioxidant properties as well as anti-wear and extreme pressure properties. They also are used in their original form and need not be combined with metallic salts. Advantages attendant with the use of such products have not heretofore been achieved.

Another part of this invention is the process of preparing sulfur and chlorine-containing products which comprise reacting (1) a phenolic compound having, ortho to the phenolic hydroxyl group, an alkyl group of from 3–8 carbon atoms and (2) sulfur dichloride; there being at least about 1.0 mole of said sulfur dichloride per mole of phenol as reactants.

It is important that the molar concentration of the sulfur dichloride reactant be at least equivalent to the molar concentration of the alkylated phenol reactant. If concentrations of less than molar equivalence are used, an ineffective product results. For example, when I use a product prepared from a reaction in which the molar ratio of SCl_2 to phenol is 1.0, I obtain excellent antioxidant protection. There is no definite upper limit except that which is convenient. In other words, it is merely important to have a stoichiometric equivalent or excess of sulfur dichloride present so as to insure complete reaction. Applicant has found that excesses up to 1.5 molar ratio of sulfur dichloride to alkylated phenol result in reactions that are easy to control and yield products which need no inordinate purification. The use of higher amounts will result in effective products but the presence of excessive and unreacted sulfur dichloride gives rise to purification problems. Further, a slight excess would be desirable so as to insure complete reaction with reasonable heating and reaction time. Accordingly, a molar ratio of sulfur dichloride to alkyl phenol of from 1.1 to 1.5 is desirable. Applicant has found that best results are obtained when a ratio of about 1.5 is used.

In carrying out the present process hydrogen chloride gas is evolved. It is, therefore, desirable to employ an inert solvent to act as a carrier and assist in the liberation of this gas. Suitable solvents for this purpose include: hydrocarbons such as petroleum ether, hexane, isooctane, benzene, toluene, xylene, pseudocumene; inert chlorinated hydrocarbons such as carbon tetrachloride, chloroform, trichloroethylene, chlorobenzene, ethylene dichloride, etc.; nitro hydrocarbons such as nitromethane, nitrobenzene, etc.; and the like. The choice of solvent should be such that the particular reactants employed will be dissolved therein sufficiently to react effectively under the particular reaction conditions.

The above reactions can be conducted conveniently from 0 to 100° C. at reaction times of from a few minutes to about a day or more, such that the particular phenolic reactant chosen will effectively react to form the desired product as described above. Reaction temperatures of 15–65° C. have been found to be most convenient giving high yields in a reasonable time. Further, reaction temperatures of 40–65° C. are preferable since excellent yields are obtained in a minimum of reaction time. Applicant has found that by introducing the sulfur dichloride reagent over a period of time, for example, one hour at a temperature of 40–45° C. and subsequently allowing the temperature to rise to 60–65° C. for an additional hour produces the most favorable yields in a reasonable time.

The reactions can be conducted in an open vessel. In commercial operation where recovery of the hydrochloric acid byproduct is desired, reaction may be conducted in a vessel equipped with such recovery means. Further, a nitrogen sweep may be used to aid in removing the hydrochloric acid gas.

The product obtained by the above process can be used very effectively by itself in various organic media without need of further purification. However, the compound can be increased in effectiveness and its solubility in various media increased by the use of various treatments.

The products can be purified by washing with Na_2S, Na_2CO_3, NaOH solutions or mixtures thereof. Also the products can be purified by heat treating them to strip the volatiles. Another method of purification is to dissolve the products in petroleum ether, filter the resulting insolubles and subsequently strip the petroleum ether to yield the purified product. A further method is to dissolve the product in mineral oil and filter the insolubles from the mineral oil. If it is desired to use the products as an additive for lubricating oils, this last procedure is preferred. The products of this invention are highly soluble and 50 weight percent can be dissolved in mineral oil. After filtration of the insolubles a 50 weight percent mixture remains which can be incorporated directly into the lubricating oil. Further combinations of the above processes can be used. Thus the product can be heat treated, dissolved in mineral oil and the insolubles filtered to yield a 50 weight percent mixture of mineral oil and product. This last procedure is particularly preferred since it yields products which are exceptionally soluble and most highly effective as antioxidants, anti-wear and extreme pressure agents. Illustrations of the above various treating procedures can be found in the ensuing examples.

Examples of the phenolic reactants used pursuant to this invention include: 2-n-hexylphenol; 2-n-butylphenol; 2-sec-butylphenol; 2-tert-butylphenol; 2-(3′-heptyl)phenol; 2-n-propylphenol; 2-isopropylphenol; 2-n-amylphenol; 2-isobutylphenol and 2-n-octylphenol.

Preferred phenolic reactants are those having, ortho to the phenolic hydroxyl group, an alpha-branched alkyl group having from 3–8 carbon atoms. These are preferred because of the ease of their reaction and superiority of the products obtained by their use. Examples of such compounds include: 2-isopropylphenol; 2-sec-butylphenol; 2-(3′-octyl)phenol; 2-tert-amylphenol; 2-(2′-heptyl)phenol; 2-(2′-hexyl)phenol and 2-tert-octylphenol.

Thus another embodiment of this invention is a substantially involatile, reddish-yellow polynuclear phenolic material containing 2 to 5 phenolic nuclei wherein each phenolic nuclei contains one hydroxyl radical and an alpha-branched alkyl group of 3–8 carbon atoms ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from those carbon atoms ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said compound containing about 50 to 62 percent carbon, about 4.5 to 7.2 percent hydrogen, about 34 to 11 percent sulfur, and about 16 to 5 percent chlorine,

said compound having an average molecular weight of about 500 to 740, and said compound being soluble in hydrocarbon mineral oil.

A particularly preferred phenolic reactant is 2-tert-butylphenol. This reactant is preferred because it is readily available, allows convenient reaction time and conditions and its use results in a most superior and efficacious product.

The antioxidant material prepared from 2-tert-butylphenol has certain characteristic analytical parameters. These products can be described as antioxidant material containing about 52 to 54 percent carbon, about 5 to 5.5 percent hydrogen, about 24 to 12 percent sulfur, about 14 to 6 percent chlorine and having a molecular weight of about 540 to 590. Thus a still further embodiment of this invention is a substantially involatile, reddish-yellow polynuclear phenolic compound containing 2 to 5 phenolic nuclei wherein each phenolic nuclei contains one hydroxyl radical and one tertiary butyl group ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from those carbon atoms ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said compound containing about 52 to 54 percent carbon, about 5 to 5.5 percent hydrogen, about 24 to 12 percent sulfur and about 14 to 6 percent chlorine, said compound having a molecular weight of about 540 to 590, and said compound being soluble in hydrocarbon mineral oil.

The sulfur and chlorine-containing phenolic products of this invention and the process for their preparation will be further apparent from the following specific examples in which all parts and percentages are by weight, unless otherwise indicated.

EXAMPLE 1

In a reaction vessel equipped with stirring means, heating means and temperature measuring means was placed a solution of 150 parts (1.0 mole) of 2-tert-butylphenol in 315 parts of ethylene dichloride. The solution was stirred at 45° C. and a solution of 154 parts (1.5 moles) of sulfur dichloride in 165 parts of ethylene dichloride was added over a period of 55 minutes. The temperature was allowed to rise to 60° C. and maintained at 60–65° C. during the addition and for one hour afterward. The solvent was distilled off at 89 mm. pressure to a temperature of 137° C. A resionous material resulted which will be called product 1–A. A portion of product 1–A was then diluted with oil to 50 weight percent and filtered hot through Celite filter-aid. This will be called product 1–B and contains 50 percent active ingredient.

One hundred parts of product 1–A were stripped of volatiles up to 140° C. at 25 microns pressure. The loss amounted to three parts. The resulting product will be called product 1–C. Total analysis of product 1–A is 52.5 percent carbon, 5.39 percent hydrogen, 22.6 percent sulfur, 11.6 percent chlorine, 1.0 percent 2-tert-butyl-4-chlorophenol, 0.2 percent 2-tert-butyl-6-chlorophenol and 0.9 percent 2-tert-butyl-4,6-dichlorophenol. The molecular weight was found to be 549. Analysis of product 1–C is 52.6 percent carbon, 5.46 percent hydrogen, 23.3 percent sulfur, 10.9 percent chlorine, 0.1 percent 2-tert-butyl-4,6-dichlorophenol. Molecular weight was found to be 580. Polarographic analysis revealed the presence of polysulphides of at least three sulfur atoms, and that about one-fourth of the sulfur was present as monosulphide and the rest as polysulphide.

EXAMPLE 2

In a reaction vessel equipped with stirring means, heating and cooling means, hydrochloric acid gas exit trap and temperature measuring means are added a solution of 60 parts (0.4 mole) of 2-tert-butylphenol in 126 parts ethylene dichloride. The temperature was lowered to 15–20° C. and maintained at that temperature while a solution of 46 parts (0.44 mole) of sulfur dichloride in 63 parts of ethylene dichloride was added over a period of 1.25 hours. The mixture was allowed to come to room temperature, about 23° C., then heated to 35° C. and maintained at that temperature for one hour. Hydrochloric acid was collected in the gas exit trap and amounted to 75 percent of theory. Volatiles were stripped from the reaction mixture at about 90–95° C. under aspirator pressure to obtain a reddish-yellow resin of this invention. Analysis: 19.5 percent sulfur, 8.17 percent chlorine.

EXAMPLE 3

The procedure of Example 2 was repeated yielding a reddish-yellow resin analyzing 21.6 percent sulfur and 10.7 percent chlorine. This will be called product 3–A. A 40-part portion of product 3–A was treated with 260 parts of petroleum ether (boiling point of 38–40° C.) which dissolved all but a small residue. The residue was recovered by filtration and the solvent was stripped, leaving 31.4 parts of a resinous semisolid of this invention. This will be called product 3–B. Analysis: 21.1 percent sulfur, 11.5 percent chlorine.

Another portion of product 3–A was diluted with benzene and washed successively with cold water, a solution containing 10 parts sodium hydroxide, 10 parts sodium sulphide and 80 parts water, a 10 percent aqueous sodium hydroxide solution and cold water to neutrality (4 washes were needed). The product was dried and then stripped at 0.5 mm., 25° C. to a constant weight. Analysis: 12.5 percent sulfur, 12.3 percent chlorine. This will be called product 3–C.

EXAMPLE 4

In a reaction vessel equipped with stirring means, heating and cooling means, temperature measuring means, gas inlet and outlet tubes, hydrogen chloride gas exit trap and a nitrogen source were placed 150 parts (1.0 mole) of 2-tert-butylphenol in 189 parts of ethylene dichloride. The vessel was flushed with nitrogen and the temperature lowered to 15–20° C. One hundred thirteen and three tenths (1.1 moles) parts of sulfur dichloride in 151 parts of ethylene dichloride were added dropwise over a period of 1.5 hours with stirring. The temperature was raised to room temperature, about 25° C., then heated to 35° C. and maintained at that temperature with stirring for one hour. Hydrogen chloride gas, amounting to 73 percent of theory, was trapped in the gas exit trap. The mixture was then stripped at reduced pressure yielding a dark reddish-yellow transparent resin. Two hundred forty parts of petroleum ether (boiling point of 38–40° C.) were added and the mixture was stirred until only a small amount of insoluble material remained. An additional 320 parts of petroleum ether were added to insure complete extraction from the insoluble material and to facilitate handling. The mixture was filtered and stripped of solvent at 90–95° C. under aspirator pressure yielding a reddish-yellow resin residue of this invention. Analysis: 22.1 percent sulfur, 6.55 percent chlorine. Infrared analysis showed the spectrum to be qualitatively identical to the spectrum of the product of Example 3.

Fifty parts by volume of the above product were dissolved in 50 parts by volume of mineral oil at about 90–95° C. The material remained in oil solution after standing for 48 hours with no separation or precipitation observed. The oil solution was heated at 90–95° C. for 40 minutes with a polished copper strip. The strip remained essentially untarnished.

EXAMPLE 5

To demonstrate the unobvious and unexpected properties of the products of applicant's invention, two materials

were prepared falling outside the scope of applicant's invention.

One product, which shall be called 5–A, was prepared by reacting 150 parts (1 mole) of 4-tert-butylphenol with 113.3 parts (1.1 moles) of sulfur dichloride following the procedure of Example 4.

Another product, which shall be called 5–B, was prepared by reacting 150 parts (1 mole) of 2-tert-butylphenol with 92.63 parts (0.9 mole) of sulfur dichloride following the procedure of Example 4. Thus, product 5–A is in all respects the same as the product of Example 4 except the starting material is 4-tert-butylphenol instead of 2-tert-butylphenol. Also product 5–B is in all respects the same as the product of Example 4 except the molar ratio of sulfur dichloride to phenol is 0.9, whereas the corresponding molar ratio of the product of Example 4 and of 5–A is 1.1.

Products 5–A, 5–B and the product of Example 4 were tested in a modified Polyveriform oxidation stability test. The normal Polyveriform oxidation stability test is described in the paper entitled "Factors Causing Lubricating Oil Deterioration in Engines," Ind. and Eng. Chem., anal. ed. 17, 302 (1945). See also "A Bearing Corrosion Test for Lubricating Oils and Its Correlation With Engine Performance," Anal. Chem. 21, 737 (1949). This test evaluates the performance of lubricating oil antioxidants. The test equipment and procedure employed are discussed in the first paper cited above.

One modification was that the steel sleeve and copper test piece described in this publication were omitted from the apparatus. In these tests an initially additive-free, 105.5 V.I. solvent-refined SAE–20 crankcase oil was used. The principal conditions consisted of passing 48 liters of air per hour through the test oil for a total period of 120 hours while maintaining the oil at a temperature of 300° F. Oxidative deterioration of the oil was further promoted by employing as oxidation catalysts 0.10 percent by weight of lead bromide, based upon the weight of oil employed. In addition a copper lead bearing is submerged in the oil as an additional catalyst. At the end of the test the loss in weight of the copper lead bearing is determined. When no loss in weight has occurred, a small increase in weight is generally observed. This increase in weight is generally within the experimental error of the test. It can also be attributed to the formation of a slight amount of varnish which is expected from the harsh conditions of the test. Such a determination gives good correlation with actual engine tests.

Lubricating oils were prepared by blending 0.5 weight percent of effective compound, based on the weight of the test oil, with individual portions of the test oil. These compositions were then subjected to the above stringent oxidation test. The results are shown in Table I. The nature of the reactants and ratios of sulfur to phenol are also given in the table.

Table I

EFFECT ON A COPPER-LEAD BEARING IN LUBRICATING OIL (0.5 WEIGHT PERCENT EFFECTIVE COMPONENT)

Additive	Phenol Reactant	Sulfur Dichloride/ Phenol Molar Ratio	Bearing Weight Loss, mg.[1]
Example 4	2-tert-butylphenol	1.1	+2.5
Example 5A (outside of invention).	4-tert-butylphenol	1.1	787
Example 5B (outside of invention).	2-tert-butylphenol	0.9.1	698

[1] An average of two tests.

It can be seen from the data that products having the same reactants but in a molar ratio of 0.9:1 are ineffective. Further, products having the same molar ratio but an isomeric reactant are ineffective. Thus the superiority of applicant's invention is completely unobvious and unexpected.

EXAMPLE 6

In a reaction vessel equipped with stirring means, heating and cooling means, hydrochloric acid gas exit trap and temperature measuring means were placed a solution of 300 parts (2.0 moles) of 2-tert-butylphenol in 630 parts of ethylene dichloride. The solution was stirred at 15–20° C. and maintained at that temperature while a solution of 268 parts (2.6 moles) of sulfur dichloride in 286 parts of ethylene dichloride was added over a period of one hour. The mixture was allowed to come to room temperature, about 25° C., and then heated to 35° C. and maintained at that temperature for one hour. Hydrochloric acid was collected in the gas exit trap and amounted to 83.5 percent of theory. The volatiles were stripped from the reaction mixture at about 90–95° C. under aspirator pressure to obtain a reddish-yellow resin. Analysis: 20.5 percent sulfur, 11.7 percent chlorine. This product will be called 6–A.

The above procedure was repeated except that the temperature at which the sulfur dichloride was added was maintained at 40–45° C. Analysis: 20.4 percent sulfur, 7.5 percent chlorine. The amber colored resin produced will be called 6–B.

The above procedure was repeated again except that the temperature during addition of the sulfur dichloride was maintained at 60–65° C. The clear amber colored resin produced will be called 6–C.

Again the last-described procedure was repeated, that is, the temperature at which sulfur dichloride was added was maintained at 60–65° C. The resinous product was diluted with benzene and washed successively with cold water, a 10 percent aqueous sodium carbonate solution and cold water to neutrality. The product was dried and then stripped at 0.5 mm., 25° C., to a constant weight. This will be called 6–D.

In order to demonstate the consistent antioxidant effectiveness of the products produced by this invention within the preferred range of the reaction conditions, the modified Polyveriform oxidation stability test described in Example 5 was run using the products 6–A, B, C and D. The following table summarizes the results.

Table II

EFFECT OF REACTION VARIABLES ON ANTIOXIDANT ACTIVITY (0.5 WEIGHT PERCENT EFFECTIVE COMPONENT)

[Molar ratio of 1.3 : 1-sulfur-dichloride/phenol]

Product	Preparation Temperature, ° C.	Treatment	Bearing Weight Loss, mg.
6A	15–20		0
6B	40–45		6
6C	60–65		4
6D	60–65	Na_2CO_3 Wash	1

As can be seen from the table the products of this invention show uniform results within the experimental error of the test. A comparison with the results for Example 5–A and 5–B in Table I immediately reveal the superiority of all the products 6A–D.

EXAMPLE 7

In a reaction flask equipped with stirring means, heating and cooling means and temperature measuring means are placed a solution of 192 parts (1.0 mole) of 2-(2'-heptylphenol) in 200 parts of n-hexane. The temperature is lowered to 0° C. A solution of 103 parts (1 mole) of sulfur dichloride in 88 parts of n-hexane is added. The reaction is allowed to proceed for several minutes. The volatiles are then stripped at about 90–95° C. under aspirator pressure. A reddish-yellow resin of this inven-

tion results which has excellent oil solubility and antioxidant properties.

EXAMPLE 8

In a reaction vessel equipped with stirring means, heating and cooling means and temperature measuring means are placed 272 parts (2 moles) of o-isopropylphenol in 480 parts of iso-octane. The solution is heated to 40° C. and maintained at that temperature while a solution of 288 parts (2.8 moles) of sulfur dichloride in 210 parts of iso-octane is added over a period of 20 minutes. The mixture is heated for an additional 30 minutes. Volatiles are stripped from the reaction mixture at about 90–95° C. under aspirator pressure. The residue is then treated with 1,000 parts of petroleum ether (boiling point of 38–40° C.). The resulting solution is filtered and the solvent is stripped leaving a resinous material of this invention which has excellent anti-wearing properties.

EXAMPLE 9

In a reaction vessel equipped with stirring means, heating and cooling means and temperature measuring means is placed a solution of 206 parts (1.0 mole) of 2-(3'-octyl)phenol in 320 parts of nitrobenzene. The mixture is heated to 60° C. and maintained at that temperature while a solution of 206 parts (2.0 moles) of sulfur dichloride in 140 parts of nitrobenzene is added over a period of one hour. The mixture is then heated to 100° C. and maintained at that temperature for 24 hours. The volatiles are then stripped under reduced pressure to yield a resinous material of this invention which has excellent anti-wear properties.

The above procedures is repeated using as the phenol reactants 2-sec-butylphenol. The product of this invention which results has excellent antioxidant properties.

EXAMPLE 10

In a reaction vessel equipped with stirring means, heating and cooling means and temperature measuring means are placed a solution of 750 parts (5.0 moles) of 2-isobutylphenol in 1,000 parts of iso-octane. The solution is heated to 50° C. and maintained at that temperature while a solution of 565 parts (5.5 moles) of sulfur dichloride in 440 parts of iso-octane is added over a period of 120 minutes. The temperature is then raised to 70° C. and maintained at that temperature for 10 hours. The temperature is then raised to 95–100° C. and stripped of volatiles under aspirator pressure. A clear, reddish-yellow resinous solid of this invention results which has excellent extreme pressure properties.

EXAMPLE 11

In a reaction vessel equipped with heating and cooling means, stirring means, temperature measuring means, gas inlet and outlet tubes and a nitrogen source are placed a solution of 178 parts (1.0 mole) of 2-(2'-hexyl)phenol in 250 parts of chlorobenzene. The vessel is flushed with nitrogen, the temperature raised to 65° C. and maintained at that temperature while a solution of 175 parts (1.7 moles) of sulfur dichloride in 110 parts of chlorobenzene is added dropwise over a period of 45 minutes with stirring. The mixture is heated for an additional 2 hours at 65° C. while nitrogen is swept through the vessel. The mixture is then heated to 130° C. under aspirator pressure and stripped of volatiles. A resinous material results which is diluted with benzene and washed successively with cold water, a solution containing 10 parts sodium hydroxide and cold water to neutrality. The material is dried and then stripped at 0.5 mm., 25° C., to a constant weight. The product of this invention has excellent solubility, antioxidant and anti-wear properties.

The above procedure is repeated using the phenolic reactant 2-n-propylphenol. The resulting product of this invention has excellent solubility, antioxidant, anti-wear and extreme pressure properties.

EXAMPLE 12

To the reaction vessel of Example 7 is added a solution of 82.0 parts (0.5 mole) of 2-tert-amylphenol in 120 parts of toluene. The solution is heated with stirring to 40–45° C. A solution of 82.4 parts (0.8 mole) of sulfur dichloride in 85 parts of toluene is added dropwise over a period of 60 minutes. The temperature is allowed to rise to 60–65° C. and maintained during the addition and for 5 hours afterward. The temperature is then raised to 90–95° C. and volatiles are removed under reduced pressure. A resinous reddish yellow solid of this invention results which can be used as an oil antioxidant.

EXAMPLE 13

In a reaction vessel equipped with stirring means, heating and cooling means and temperature measuring means is placed a solution of 51.5 parts (0.25 mole) of 2-tert-octylphenol in 70 parts of carbon tetrachloride. The mixture is cooled to 15° C. and maintained at that temperature while a solution of 46.4 parts (0.45 mole) of sulfur dichloride in 40 parts of carbon tetrachloride are added over a period of 55 minutes. The temperature is then raised to 80° C. and the mixture stirred at that temperature for 2 hours. The mixture is subjected to reduced pressure at that temperature and the volatiles removed. A resinous solid of this invention results which imparts stability to lubricating oil.

The above procedure is repeated using as the phenol reactant 2-n-octylphenol. The product of this invention which results has excellent solubility and antioxidant properties and can be incorporated into a wide variety of organic media.

EXAMPLE 14

To the reaction vessel of Example 13 is added a solution of 164 parts (1.0 mole) of 2-n-amylphenol in 280 parts of xylene. The temperature is lowered to 10° C. and stirred at that temperature while a solution of 196 parts (1.9 moles) of sulfur dichloride in 180 parts of xylene is added over a period of 20 minutes. The mixture is then heated to 30° C. and maintained at that temperature with stirring for one hour. The temperature is then raised to 70° C. and the solvent distilled off under reduced pressure. A resinous material of this invention results which has excellent anti-wear properties.

The above material is diluted with an equal weight of mineral oil, heated to about 100° C. and filtered through Celite-filter air resulting in an oily product of this invention containing 50 percent active ingredient.

When various phenols are reacted in accordance with this invention the product obtained has a carbon, hydrogen, sulfur, chlorine and molecular weight analysis in the ranges of 50 to 62 percent carbon, 4.5 to 7.2 percent hydrogen, 34 to 11 percent sulfur, 16 to 5 percent chlorine and 500 to 740 molecular weight.

The products of this invention are outstanding antioxidants. Therefore, an embodiment of this invention is a new composition of matter which comprises organic material normally tending to undergo oxidative deterioration in the presence of air, oxygen or ozone, containing an appropriate quantity, from 0.001 up to about 5 percent, and preferably from about 0.25 to about 2 percent, of a product of this invention.

The products of this invention find important utility as antioxidants in a wide variety of oxygen sensitive materials. Thus, liquid hydrocarbon fuels such as gasoline, kerosene and fuel oil are found to possess increased storage stability by the use of a product of this invention. Likewise, liquid hydrocarbon fuels such as gasoline which contain organometallic additives such as tetraethyllead, as well as other organometallic compounds which are used as fuel additives, attain appreciably increased oxidative stability by the practice of this invention. In addition, lubricating oils and functional fluids, both those derived from naturally occurring hydrocarbons and those syn-

thetically prepared, are greatly enhanced by the practice of this invention. The addition of small quantities of the products of this invention to such materials as turbine, hydraulic, transformer and other highly refined industrial oils, waxes, soaps and greases, plastics, synthetic polymers such as polyethylene and polypropylene, organometallic compositions such as tetraethyllead and tetraethyllead antiknock fluids, elastomers (including natural rubber), crankcase lubricating oils, lubricating greases, and the like, greatly increase their resistance to deterioration in the presence of air, oxygen or ozone.

The products of this invention are also very effective antioxidants for high molecular weight unsaturated hydrocarbon polymers, such as polybutadiene, methyl rubber, polybutene rubber, natural rubber, butyl rubber, GR–S rubber, GR–N rubber, piperylene rubber, dimethyl butadiene rubber and the like.

As noted, the products of this invention are useful in preventing oxidative deterioration in lubricating oil compositions. Thus, a preferred embodiment of this invention is a lubricating oil normally susceptible to oxidative deterioration containing a small antioxidant quantity, up to 5 percent, of a product of this invention as defined above.

To prepare the lubricants of this invention, an appropriate quantity—from about 0.001 to about 5 percent and preferably from about 0.25 to about 2 percent—of a product of this invention is blended with the base oil to be protected. Suitable base oils include mineral oils and also synthetic diester oils, such as sebacates, adipates, etc. which find particular use as aircraft instrument oils, hydraulic and damping fluids and precision bearing lubricants. All of these base oils are normally susceptible to oxidative deterioration, especially at elevated temperature.

The finished lubricants of this invention have much greater oxidation stability and many other improved performance characteristics as compared with the corresponding base oils. The following examples illustrate the preferred lubricating oil compositions of this invention.

EXAMPLE 15

To illustrate the outstanding advantages achieved by the practice of the preferred embodiments of this invention, particularly when the compositions are subjected to elevated temperature, experiments were conducted using the panel coker test. This test measures the oxidative stability of oils which are maintained at elevated temperatures in the presence of air, the oils periodically coming in contact with a hot metal surface. The test is described in the Aeronautical Standards of the Departments of Navy and Air Force, Spec. MIL–L–7808c, dated November 2, 1955. In these tests an initially additive-free 95 V.I. solvent-refined SAE 10 crankcase oil was used. The panel coker apparatus was operated at 600° F. for 10 hours on a cycling schedule—the splasher being in operation for 5 seconds followed by a quiescent period of 55 seconds. On completion of these tests the extent by which the various test oils were decomposed under these high-temperature oxidizing conditions was determined by weighing the amount of deposit which formed on the metallic panel. The results are given in Table III.

Table III

PANEL COKER DATA

Additive	Concentration, Percent	Panel Weight Gain, mg.
None		434
Product 3B	1.0	37

It can be seen from the above results that the products of this invention provide outstanding resistance to oxidative deterioration.

EXAMPLE 16

As a further illustration of the advantages achieved by the practice of this invention a standard Polyveriform test was run. The test conditions are described in the references discussed in Example 5. The present test is not modified as was the one in Example 5. This test effectively evaluates the performance of lubricating oil antioxidants. The procedures employed and correlations of the results with engine performance are discussed in the first-named paper in Example 5. As in Example 5 a modification was that the steel sleeve and copper test piece described in the publication were omitted from the apparatus. In its place .05 percent by weight of the test oil of ferric oxide (as ferric 2-ethylhexoate) and 0.10 percent by weight of the test oil of lead bromide were added as oxidation catalysts. In these tests an initially additive-free 95 V.I. solvent-refined SAE 10 crankcase oil was used. The principal test conditions consisting of passing 48 liters of air per hour through the test oil for a total period of 20 hours while maintaining the oil at a temperature of 300° F.

Lubricating oils of this invention were prepared by blending products of this invention with the oil described above. These compositions were compared in the Polyveriform test with a sample of the oil not containing an antioxidant. As can be seen from the results listed in Table IV oils containing a product of this invention gave much superior results than base oils containing no additive.

Table IV

Additive	Additive Concentration, Weight Percent	Acid No.	Percent Viscosity Increase, SUS at 100° F.
None		6.2	113
Product of Example 2	1.0	1.4	13
Product 3A	1.0	1.7	22
Product 3B	1.0	2.3	23
Product 3C	1.0	2.6	31

EXAMPLE 17

To illustrate the anti-wear and extreme pressure properties of the products of this invention a lubricant composition of this invention was tested in a four ball extreme pressure machine to determine the lubricity of the respective lubricant compositions relative to a base line of the unprotected lubricant. The four ball extreme pressure machine is described by Lawson and Perry in the "Transactions of the A.S.M.E.," January 1945, pp. 45–50. The machine operates in the load range of 40 to 800 kilograms.

The four ball extreme pressure machine utilizes four balls of equal size arranged in an equilateral tetrahedral formation. The bottom three balls are held in a non-rotatable ball holder which is essentially a universal chuck that holds the balls in abutting relation to each other. Since the bottom three balls are of equal size the centers form the apices of an equilateral triangle. The top ball is affixed to a rotatable spindle whose axis is positioned perpendicular to the plane of the ball holder and in line with the center point of the triangle whose apices are the centers of the three bottom stationary balls. In operation, the four balls are immersed in the lubricant composition to be tested and the ball holder is moved upwardly so as to bring the three fixed lower balls into engagement with the upper rotating ball. As the load is increased, the ball holder is moved upwardly and axially of the rotating spindle affixed to the upper ball.

The lubricity of the lubricant under test is determined by the amount of wear occurring at the contact points between the three upper rotating balls and the three fixed lower balls under the conditions of the test. If the lubricant is completely effective, the amount of wear will be small. On the other hand, if the lubricant is not com-

pletely effective under the test conditions, the upper ball may fuse or weld to the lower balls due to heat or friction at the contact points or the upper ball may form circular scars in the lower balls along their line of contact. If scars are formed in the lower balls the average diameter of the circular scar is measured so as to give a quantitative basis for comparing the test results with those of other tests in which circular scars were formed. As the severity of the test conditions are increased with a given lubricant composition the likelihood of scarring the lower balls is increased. Thus the formation of scars does not indicate that the lubricant composition is unsatisfactory but rather serves only to indicate its degree of effectiveness under certain test conditions.

In the present test the ball affixed to the rotatable spindle is rotating at 1800 r.p.m. Separate tests were conducted at loads of from 40 to 150 kilograms, each test lasting one minute. The results are listed in Table V.

Table V

FOUR BALL EXTREME PRESSURE TEST

Load (kg.)	Scar (mm.)	
	Base	Base plus 1 Weight Percent Product of Example 4
40	0.37	0.37
60	2.80	0.41
80	3.32	0.65
100	3.23	1.82
120	weld	----------
150	----------	2.16

Referring to Table V it can be seen that the presence of an additive compound of this invention in lubricating oil substantially reduces the amount of scar on the steel balls used in the test. Further, while the unprotected oil welded at a load of 120 kilograms the lubricant composition of this invention did not weld even after a load of 150 kilograms was applied.

EXAMPLE 18

To 1,000 parts of a solvent refined neutral oil (95 V.I. and 200 SUS at 100° F.) containing 6 percent of a commercial methacrylate type V.I. improver which gives the finished formulation of a V.I. of 140 and a viscosity of 300 SUS at 100° F. is added 5 percent of the product of Example 14.

EXAMPLE 19

To an additive-free solvent refined crankcase lubricating oil having a viscosity index of 95 and an SAE viscosity of 10 is added 0.001 percent of product 1–A.

EXAMPLE 20

To 100,000 parts of a petroleum hydrocarbon oil having a gravity of 30.3° API at 60° F., viscosity of 178.8 SUS at 100° F., a viscosity index of 154.2 and which contains 0.2 percent sulfur, is added 200 parts of product 6–D. The resulting oil possesses greatly enhanced resistance to oxidative deterioration and possesses excellent wear properties.

EXAMPLE 21

To 100,000 parts of a commercially available pentaerythritol ester having a viscosity at 100° F., of 22.4 centistokes, and known in the trade as "Hercoflex 600" is added 400 parts (0.4 percent) of the product of Example 8. The resulting finished oil possesses markedly improved resistance against oxidative deterioration, and has excellent wear properties.

EXAMPLE 22

To 100,000 parts of a dioctyl sebacate having a viscosity of 210° F., of 36.7 SUS, a viscosity index of 159 and a molecular weight of 426.7 is added 250 parts (0.25 percent) of product 1–B.

The saturated hydrocarbon synthetic polymers which achieve greatly enhanced oxidative stability by the practice of this invention, include polymers obtained from the polymerization of a hydrocarbon monoolefin having up to 4 carbon atoms. Examples of such monomers are ethylene, propylene, butene-1, butene-2 and isobutylene. Thus the polymers are homopolymers and copolymers of ethylene, propylene, butene-1, butene-2 and isobutylene.

The concentration of the products of this invention in the polymers is from 0.001 up to 5 percent, and preferably from about 0.25 to about 2 percent.

Polyethylene is a hydrocarbon polymer derived from the polymerization of ethylene. This polymerization can be accomplished by a great variety of methods which lead to products of diverse properties. Polyethylene of any nature may advantageously be utilized for preparing compositions according to the present invention. The polymers of ethylene which are employed may, for example, be similar to those which may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerization-favoring quantities of oxygen under relatively high pressures in excess of 500 or 1,000 atmospheres at temperatures between 150 and 275° C. Or, if desired, they may be similar or identical to the essentially linear and unbranched polymers ordinarily having greater molecular weights which may be obtained under relatively low pressures of 1 to 100 atmospheres using such catalysts to polymerize the ethylene as mixtures of strong reducing agents and compounds of groups IVB, VB and VIB metals of the periodic system; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt.

The polyethylene which results from these various polymerization processes may have a molecular weight in the range from 1300 to over 1,000,000 depending on the particular conditions of polymerization employed.

There are several methods available for preparing the inhibited hydrocarbon polymer compositions of this invention. Thus, the blending of the antioxidant with a polymer such as, for example, polyethylene, may be carried out on open rolls, on internal mixers or may be accomplished by mixing with extrusion. It is also possible to prepare concentrated batches of the polymer containing excessive amounts of the antioxidant and then mix the concentrate with additional polymer to prepare a composition of this invention. The preferred method of compounding the polymers is by milling on heated open rolls at slightly elevated temperatures by methods well-known to the art. The temperature range employed is sometimes critical as certain polyethylenes will not melt at low temperatures and tend to stick to the rolls at high temperatures. The antioxidant may be initially mixed with the polymer in the dried state or it may be first dissolved in a suitable solvent, then sprayed on the polymer and milled in.

Examples of the hydrocarbon polymer compositions of this invention prepared as described above, follow. All parts and percentages are by weight in these examples.

EXAMPLE 23

To 1,000 parts of polyethylene produced by oxygen catalyzed reaction under a pressure of 20,000 atmospheres and having an average molecular weight of 40,000 is added and mixed 2 parts of the product of Example 10. The resulting composition has greatly increased oxidative stability.

EXAMPLE 24

With 200 parts of polyisobutylene having an average molecular weight of 100,000 is blended 1.0 part of product 6–A.

EXAMPLE 25

To a master batch of high molecular weight polyethyl-

ene having an average molecular weight of about 1,000,000, a tensile strength of 6,700 p.s.i., a Shore D hardness of 74 and a softening temperature under low load of 150° C. is added 5 percent of the product of Example 12.

EXAMPLE 26

A linear polyethylene having a high degree of crystallinity (about 93 percent) and below 1 ethyl branched chain per hundred carbon atoms, a density of about 0.96 gram per milliliter and which has about 1.5 double bonds per 100 carbon atoms is treated with 50×10^{-6} roentgens of β-radiation. To the thus irradiated polymer is added 0.005 percent of the product of Example 7 and the resulting product has better stability characteristics.

EXAMPLE 27

To a polyethylene having an average molecular weight of 1500, a melting point of 88–90° C. and a specific gravity of 0.92 is added 1 percent of product 1–C. After milling in the antioxidant an extremely oxidation resistant product results.

EXAMPLE 28

Two parts of the product of Example 13 are added with milling to 100 parts of a low density polyethylene prepared by high pressure polymerization and which has an average molecular weight of about 20,000. The resulting product is vastly improved in its oxidative stability.

EXAMPLE 29

To 10,000 parts of a polyethylene having an average molecular weight of about 100,000 and which has a tensile strength of 5400 p.s.i., a Shore D hardness of 70 and a softening temperature of 130° C. under low load is added 10 parts of product 6–B to prepare a composition of outstanding oxidative stability.

EXAMPLE 30

To the polyethylene in Example 17 is added 0.05 percent of the product of Example 11. The resulting composition has improved antioxidant characteristics.

EXAMPLE 31

To a polyisobutylene polymer having an average molecular weight of 35,000 is added a sufficient amount of product 6–C to give a composition containing 0.03 percent of the antioxidant. The composition has improved antioxidant properties due to the presence of product 6–C.

EXAMPLE 32

To a polypropylene having a specific gravity of 0.90, a tensile strength of 4300 p.s.i., a Rockwell hardness of 85 and a heat distortion temperature of 210° F. under a pressure of 66 p.s.i. is added 0.06 weight percent of the product of Example 4. The resulting polymer is stable against the deleterious effects of oxygen.

EXAMPLE 33

To a polybutene, prepared from the polymerization of butene-1, and having an average molecular weight of 15,000, is added 0.15 weight percent of the product of Example 9 give a polymer of outstanding oxidation stability.

EXAMPLE 34

To a polybutene, prepared from the polymerization of butene-2, and having a molecular weight of 25,000 is added 0.10 weight percent of product 1–A to yield a polymer with exceptional oxidative stability.

EXAMPLE 35

To the polyisobutylene polymer of Example 31 is added 0.07 percent of the product of Example 10.

EXAMPLE 36

To the polypropylene of Example 32 is added 0.02 percent of product 3–C.

EXAMPLE 37

To the polybutene of Example 33 is added 0.03 percent of product 3–C.

EXAMPLE 38

To the polybutene of Example 34 is added 0.08 percent of the product of Example 14.

In addition to an antioxidant product of this invention the saturated hydrocarbon polymers of this invention may contain other compounding and coloring additives including minor proportions of carbon black, elastomers, polyvinyl compounds, carboxylic acid esters, urea-aldehyde condensation products, flame retarding agents such as antimony trioxide and chlorinated hydrocarbons and various pigment compositions designed to impart color to the finished product.

The products of this invention are very useful in protecting petroleum wax—paraffin wax and micro-crystalline wax—against oxidative deterioration. They also find use in the stabilization of edible fats and oils of animal or vegetable origin which tend to become rancid especially during long periods of storage because of oxidative deterioration. Typical representatives of these edible fats and oils are linseed oil, cod liver oil, castor oil, soybean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter fat, lard, beef tallow and the like.

The products of this invention are also very useful in protecting vitamins against degradation, especially those vitamins which are incorporated in an oil base. Thus an embodiment of this invention is vitamins protected from degradation by incorporating said vitamins into an oil base containing a compound of this invention.

The products of this invention are also useful as additives to functional fluids and automatic transmission fluids. The primary constituent of a functional fluid is a refined mineral lubricating oil having a carefully selected minimum viscosity of 49 Saybolt Universal seconds (SUS) at 210° F. and a maximum viscosity of 7,000 SUS at 0° F., generally a distillate oil, lighter than an SAE 10 motor oil. The oil usually amounts to between about 73.5 to about 97.5 percent by weight of the finished fluid. Preferably, the base oil is selected from a paraffin base distillate such as a Pennsylvania crude.

The fluids usually contain compounds which are characterized by containing one or more organic components which may be alkyl, aryl, alkaryl or aralkyl groups that are bonded to one or more metal atoms through coupling groups such as sulfonate, hydroxyl, carboxyl and mercaptan. The metal atoms may be aluminum, calcium, lithium, barium, strontium, and magnesium. The organic components contain oil solubilizing groups such as high molecular weight straight or branched chain paraffins, aromatic or naphthenic rings, or contain a halogen. These metal compounds are present in the compounded fluid in a concentration range of between about 0.1 to about 5 percent by weight. These compounds include alkaline-earth metal salts or phenyl-substituted long chain fatty acids, alkaline-earth metal salts of the capryl or octyl esters of salicylic acid, the alkaline-earth metal salts of petroleum sulfonic acids, the alkaline-earth metal salts of alkyl-substituted phenol sulfides, the salt of aluminum or the alkaline-earth metals with cetyl phenol, and the metal salts of wax-substituted phenol derivatives. Another class of additives are the so-called overbased phenates and sulfonates, which can be prepared by reaction between an alkyl phenol or alkyl phenol sulfide and an alkaline-earth metal oxide or hydroxide at an elevated temperature. The overbased

phenate formed from the reaction contains up to two or three times as much metal as the normal phenate.

In addition, functional fluids may contain additional components which improve the properties of the fluid. Typical components include anti-squawk additives, pour point depressants, foam inhibitors, rust preventatives, extreme pressure agents, metal deactivators and viscosity index improvers.

The following examples show typical functional fluids of this invention. The fluids are formed by mixing the ingredients together, while heating the oil to a temperature up to 200° F.

EXAMPLE 39

A fluid of this invention is prepared by blending 80 parts of a conventionally-refined Pennsylvania mineral oil (99 SUS at 100° F.), 2 parts of product 1–C, 5 parts of barium petroleum sulfonate, 10 parts of a polyacrylate having a molecular weight of approximately 7,000 derived from a fatty alcohol such as cetyl or lauryl alcohol, 0.1 part of a dimethyl silicone polymer anti-foam agent, 2 parts of a dialkyl zinc dithiophosphate and 0.9 part of a dark, viscous liquid having a viscosity of 560 SUS at 210° F., a flash point of 420° F., a pour point of 30° F. and a specific gravity of 60/60° F. of 0.919.

EXAMPLE 40

Another such fluid consists of 95 parts of a solvent refined, light acid-treated, clay-contacted, solvent dewaxed paraffin base distillate mineral oil (110 SUS at 100° F.); 0.1 part of the product of Example 9, 0.1 part of calcium octylphenol sulfide; 2 parts of a sulfurized sperm oil having a sulfur content between 10–12 percent, a viscosity of 210° F. of 200 SUS and a pour point of 65° F.; 0.3 part of an ester of an aromatic acid and wax-alkylated phenol having a molecular weight of approximately 450; 2.5 parts of a linear pale color isobutylene polymer of a controlled molecular weight having a viscosity of 3,000 SUS at 210° F., a specific gravity of 60/60° F. of 0.875.

Liquid hydrocarbon fuels employed in the operation of spark ignition combustion engines are also vastly improved in their storage ability by the practice of this invention. Table VI, below, gives the compositions of a number of typical commercial gasolines which may be stabilized against oxidative deterioration by the inclusion therein of a product of this invention.

Table VI

GASOLINE COMPOSITIONS

Gasoline	Percent Aromatics	Percent Olefins	Percent Saturates	Gravity, °API
A	26.6	20.8	52.6	62.1
B	8.6	7.9	83.5	68.5
C	20.0	41.2	38.8	62.9
D	20.5	32.9	46.6	63.5
E	38.1	7.3	54.6	59.3

EXAMPLE 41

To 1,000 parts of gasoline A, as described in Table VI, is added 10 parts of product 6–A.

EXAMPLE 42

To 10,000 parts of gasoline B is added 50 parts of product 1–B.

EXAMPLE 43

To 500 arts of gasoline C, as described in Table VI, is added 10 parts of product 3–A.

EXAMPLE 44

To 2,000 parts of gasoline D is added 15 parts of the product of Example 7.

EXAMPLE 45

To 10,000 parts of gasoline E is added 500 parts of the product of Example 13.

Antiknock compositions and spark ignition internal combustion engine fuels containing mixtures of organolead antiknock agents and cyclopentadienyl manganese tricarbonyls are also vastly improved in their storage stability by the practice of this invention. Such compositions are described more fully in U.S. Patent No. 2,818,417.

In the compositions of this invention the concentrations of the prime ingredients will vary. Thus the finished fuels of this invention can contain from about 0.2 to about 6.4 grams of lead per gallon as an organolead antiknock agent. The manganese or nickel concentrations therein can range from about 0.005 to about 6 grams per gallon as a cyclopentadienyl manganese tricarbonyl or cyclopentadienyl nickel nitrosyl respectively. On a cost effectiveness basis, finished motor fuels containing per gallon from about 1 to about 4 grams of lead and from 0.05 to about 2 grams of manganese or nickel are preferred. In all of these finished fuels the concentration of the above compounds of this invention can be from about 0.0002 to about 0.01 weight percent based on the fuel. Expressed in different units these concentrations correspond respectively to about 0.5 to about 25 pounds per thousand barrels of fuel. These concentrations are sufficient to inhibit the deterioration which would occur in the absence of the compounds of this invention.

In formulating finished fuels it is common practice to employ concentrated gasoline solutions of the additives. These stock solutions are then cut with or metered into the remainder of the gasoline to achieve the appropriate concentration in the finished fuel. A feature of this invention is that such concentrated stock solutions are likewise very effectively stabilized by the presence therein of the above compounds of this invention. Consequently, the concentrations of the above ingredients can be as much as 10 times as high as those set forth above. The choice of concentrations is within the discretion of the refiner and takes into consideration the quantities of gasoline being processed, the storage temperatures to be accounted, the length of storage involved, etc. The specific concentrations given above are for illustrative purposes only and are not to be considered as limitations upon this invention.

Another embodiment of this invention is an antiknock fluid composition adopted for use as an additive to gasoline, which composition consists essentially of an organolead antiknock agent, a cyclopentadienyl manganese tricarbonyl or cyclopentadienyl nickel nitrosyl and a product of this invention as defined above, there being present in the composition from about 0.00078 to about 30 parts by weight of manganese or nickel per part of lead and from about 0.001 to about 5 weight percent of the compounds of this invention based on the weight of the organolead antiknock agent. These compositions possess greater stability by virtue of the presence therein of a compound of this invention. Furthermore, these compositions provide an excellent vehicle by which the finished fuels of this invention can be formulated.

The foregoing compositions of this invention can also contain other additives known in the art. Halogen scavengers for the organolead antiknock agents (ethylene dibromide and/or ethylene dichloride, etc.) corrective agents (phosphorus, arsenic and antimony compounds, etc.), dyes, solvents and/or diluents are illustrative of the types of additives which can be co-present.

The following examples illustrate the compositions of this invention and the methods by which they are prepared.

EXAMPLE 46

To 1000 gallons of a commercial gasoline having a grav-

ity of 59.0° API, an initial boiling point of 98° F. and a final boiling point of 390° F. are added 3.18 grams per gallon of lead as tetraethyllead, 0.6 theory (based on the lead) of bromine as ethylene dibromide, 1.0 theory (based on the lead) of chlorine as ethylene dichloride, 0.25 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl and 0.0002 weight percent (based on the gasoline) of the product of Example 12. The resultant fuel possesses enhanced stability characteristics.

EXAMPLE 47

With a gasoline having an initial boiling point of 93° F., a final boiling point of 378° F., an API gravity of 56.2° and a tetraethyllead content equivalent to 0.2 gram of lead per gallon are blended cyclopentadienyl nickel nitrosyl to a concentration of 0.05 gram of nickel per gallon and product 3–B to a concentration of 0.005 weight percent (based on the gasoline). The finished fuel so formed possesses improved stability properties.

EXAMPLE 48

To a gasoline having an API gravity of 51.5° C., an initial boiling point of 91° F. and a final boiling point of 394° F. are blended 6.4 grams of lead per gallon as tetrabutyllead, 2 grams of manganese per gallon as octylcyclopentadienyl manganese tricarbonyl and 0.0008 weight percent (based on the gasoline) of the product of Example 2. The resultant fuel possesses very good stability.

EXAMPLE 49

With a gasoline having an initial boiling point of 93° F. and a final boiling point of 410° F. are blended 2 grams of lead per gallon as tetraphenyllead, 6 grams of nickel as diethylcyclopentadienyl nickel nitrosyl, 1 theory (based on the lead) of bromine as ethylene dibromide and 0.01 weight percent (based on the gasoline) of the product of Example 4. The finished fuel has very good storage stability.

This invention also extends to the use in the above compositions of manganese pentacarbonyl (i.e., dimanganese decacarbonyl).

The products of this invention are also very effective antioxidants for high molecular weight unsaturated hydrocarbon polymers, such as polybutadiene, methyl rubber, polybutene rubber, natural rubber, butyl rubber, GR–S rubber, GR–N rubber, piperylene rubber, dimethyl butadiene rubber and the like. Thus a preferred embodiment of the present invention is a rubber containing as an antioxidant therefor, a product of this invention as defined above. Another part of this invention is the method of preserving rubber which comprises incorporating therein a product of this invention as defined above. The stabilizer is incorporated into the rubber by milling, Banbury mixing, or similar processes, or is emulsified and the emulsions added to the rubber latex before coagulation. In the various embodiments of this invention the stabilizer is used in small amounts, generally ranging from about 0.01 to about 5.0 percent, based on the rubber.

As used in the description and claims, the term "rubber" is employed in a generic sense to define a high molecular weight plastic material which possesses high extensibility under load coupled with the property of forcibly retracting to approximately its original size and shape after the load is removed. It is preferable that the rubber be a sulfur-vulcanizable rubber, such as India rubber, reclaimed rubber, balata, gutta-percha, rubbery conjugated diene polymers and copolymers exemplified by the butadiene-styrene (GR–S) and butadiene-acrylonitrile (GR–N or Paracril) rubbers and the like, although the invention is applicable to the stabilization of any rubber, high molecular weight organic material which is normally susceptible to deterioration in the presence of oxygen, air, or ozone. The nature of these rubbers is well known to those skilled in the art.

Among the definite advantages provided by this invention is that the present rubber compositions possess unusually great resistance against oxidative deterioration. Moreover, these compositions exhibit excellent non-staining and non-discoloration characteristics. Furthermore, the novel stabilizer is relatively inexpensive and easily prepared, and possesses the highly beneficial property of low volatility. As is well known, a highly desirable feature of a rubber antioxidant is that it have a low volatility so that it remains admixed with the rubber during vulcanization and related process steps.

The rubber compositions of the present invention are illustrated by the following specific examples wherein all parts and percentages are by weight.

EXAMPLE 50

To illustrate the enhanced oxygen resistance of the rubber compositions of this invention and their excellent non-staining and non-discoloration characteristics, a light-colored stock is selected for test. This stock has the following composition:

Pale crepe rubber	100.00
Zinc oxide filler	50.00
Titanium dioxide	25.00
Stearic acid	2.00
Ultramarine blue	0.12
Sulfur	3.00
Mercaptobenzothiazole	1.00
	181.12

To the above base formula is added one part by weight of product 6–B and individual samples are cured for 20, 30, 45 and 60 minutes at 274° C. using perfectly clean molds with no mold lubricant. Another set of samples of the same base formula which do not contain an antioxidant are cured under the same conditions.

EXAMPLE 51

To a synthetic rubber master batch comprising 100 parts of GR–S rubber having an average molecular weight of 60,000, 50 parts of mixed zinc propionate-stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole is incorporated 1.5 parts of the product of Example 8. This batch is then cured for 60 minutes at 45 p.s.i. of steam pressure.

EXAMPLE 52

Natural rubber stock is compounded according to the following formula:

	Parts
Thick gristly crepe natural rubber	100
Wax	2
Ultramarine dye	0.1
Zinc oxide	70
Titanium dioxide	20
Sulfur	3
Stearic acid	1.2
Product 6–C	1
Benzothiazyl disulfide	0.4
Amine activator	0.5

This stock is then vulcanized for 60 minutes at 280° F.

EXAMPLE 53

A butadiene-acrylonitrile copolymer is produced from butadiene-1,3 and 32 percent of acrylonitrile. Two percent (based on the dry weight of the copolymer) of the product of Example 10, is added as an emulsion in sodium oleate solution to the latex obtained from emulsion copolymerization of the monomers. The latex is coagulated with a pure grade of aluminum sulfate and the coagulum, after washing, is dried for 20 hours at 70° C.

Each of the above illustrated rubber compositions of this invention possesses greatly improved resistance against oxidative deterioration as compared with the cor-

responding rubber compositions which are devoid of an antioxidant. Moreover, the light-colored stocks of the above examples exhibit virtually no discoloration or staining characteristics even when subjected to severe weathering conditions and the like. The methods of formulating the improved rubber compositions of this invention will now be clearly apparent to those skilled in the art.

The amount of stabilizer employed in the rubber compositions of this invention varies from about 0.001 to about 5 percent by weight based on the weight of the rubber. The amount used depends somewhat upon the nature of the rubber being protected and the conditions of service to be encountered. Thus, in the stabilization of natural and synthetic rubber to be used in the manufacture of tires which are normally subjected to exposure to the elements, as well as the action of sunlight, frictional heat, stress and the like, the use of relatively high concentrations of this inhibitor is advantageous. On the other hand, when the article of manufacture is not to be subjected to such severe conditions, relatively low concentrations can be successfully utilized. Generally speaking, amounts ranging from about 0.25 to about 2 percent by weight give uniformly satisfactory results.

Other rubbers and elastomers which can be prepared according to this invention are the rubbery polymerizates of isoprene, butadiene-1,3 piperylene; also the rubbery copolymer of conjugated dienes with one or more polymerizable monoolefinic compounds which have the capability of forming rubbery copolymers with butadiene-1,3, outstanding examples of such monoolefinic compounds being those having the group $CH_2=C<$, exemplified by styrene. Examples of such monoolefinics are styrene, vinyl naphthalene, alpha methyl styrene, p-chlorostyrene, dichlorostyrene, acrylic acid, methyl acrylate, methyl methacrylate, methacrylonitrile, methacrylamide, methyl vinyl ether, methyl vinyl ketone, vinylidine chloride, vinyl carbazole, vinyl pyridines, alkyl substituted vinyl pyridines, etc. In fact, excellent stabilization is achieved by incorporating a product of this invention in any of the well known elastomers which are normally susceptible to deterioration in the presence of air, such as elastoprenes, elastolenes, elastothiomers, and elastoplastics.

I claim:

1. As a composition of matter a reddish-yellow polynuclear phenolic material containing 2 to 5 phenolic nuclei wherein each phenolic nucleus is mono-ortho-alkylated and contains one hydroxyl radical and one alkyl group of 3–8 carbon atoms ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from those carbon atoms ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said phenolic material containing about 50 to 62 percent carbon, about 4.5 to 7.2 percent hydrogen, about 34 to 11 percent sulfur, and about 16 to 5 percent chlorine, said phenolic material having an average molecular weight of about 500 to 740, and said phenolic material being soluble in hydrocarbon mineral oil.

2. As a composition of matter a substantially involatile, reddish-yellow polynuclear phenolic material containing 2 to 5 phenolic nuclei wherein each phenolic nucleus is mono-ortho-alkylated and contains one hydroxyl radical and an alpha-branched alkyl group of 3–8 carbon atoms ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from those carbon atoms ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said phenolic material containing about 50 to 62 percent carbon, about 4.5 to 7.2 percent hydrogen, about 34 to 11 percent sulfur, and about 16 to 5 percent chlorine, said phenolic material having an average molecular weight of about 500 to 740, and said phenolic material being soluble in hydrocarbon mineral oil.

3. As a composition of matter a substantially involatile, reddish-yellow polynuclear phenolic material containing 2 to 5 phenolic nuclei wherein each phenolic nucleus is mono-ortho-alkylated and contains one hydroxyl radical and one tertiary butyl group ortho to said hydroxyl radical, said phenolic nuclei being linked together in a straight chain, each of said nuclei being linked to the adjacent nuclei through 1–6 sulfur atoms in sulphide linkages, said linkages being between carbon atoms of said nuclei selected from positions ortho and para to said hydroxyl group, at least one of the terminal nuclei of said chain containing a chlorine atom, said phenolic material containing 52 to 54 percent carbon, 5 to 5.5 percent hydrogen, 24 to 12 percent sulfur and 14 to 6 percent chlorine, said phenolic material having a molecular weight of 540 to 590, and said phenolic material being soluble in hydrocarbon mineral oil.

4. Process of preparing a sulfur and chlorine-containing phenolic material which comprises reacting (1) a mono-ortho-alkylated phenolic compound having, ortho to the phenolic hydroxyl group, an alkyl group of from 1–12 carbon atoms and (2) sulfur dichloride; conducting said reaction at a temperature and for such a time that at least one terminal nucleus of said phenolic material is substantially chlorinated and said phenolic material contains from 5–16 percent chlorine; there being at least about 1.0 mole of said sulfur dichloride per mole of phenolic compound as reactants.

5. Process of claim 4 wherein said reaction is partially conducted at a temperature of 40–45° C., said temperature is allowed to rise to 60–65° C. and then the remainder of said reaction is conducted at 60–65° C.

6. Process of claim 4 wherein said phenolic compound and said sulfur dichloride are reacted at a temperature of from between 0° and 100° C.

7. Process of claim 6 wherein said alkyl group is alpha-branched and has from 3–12 carbon atoms.

8. Process of claim 7 wherein said alkyl group is tertiary butyl.

9. Process of claim 8 wherein there is from about 1.1 to about 1.5 moles of sulfur dichloride per mole of phenolic compound.

10. Process of claim 9 wherein there is about 1.5 moles of sulfur dichloride per mole of phenolic compound.

11. Process of claim 10 wherein said reaction is partially conducted at a temperature of 40–45° C., said temperature is allowed to rise to 60–65° C. and then the remainder of said reaction is conducted at 60–65° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,239,534	Mikeska et al.	Apr. 22, 1941
2,362,293	McNab et al.	Nov. 7, 1944
2,409,687	Rogers et al.	Oct. 22, 1946
2,569,122	Adelson	Sept. 25, 1951
2,621,172	Teeter	Dec. 9, 1952
2,767,163	Peters	Oct. 16, 1956
2,812,307	Saives	Nov. 5, 1957