United States Patent Office 3,043,775 Patented July 10, 1962

3,043,775

ORGANIC MATERIAL CONTAINING A 4,4'-METHYLENEBIS PHENOL

Thomas H. Coffield, Heidelberg, Germany, and Allen H. Filbey, 2290 Robell Drive, Walled Lake, Mich.

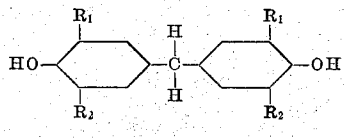
No Drawing. Filed July 24, 1959, Ser. No. 829,201
26 Claims. (Cl. 252—52)

This invention relates to novel chemical compounds having utility in the chemical arts, and particularly useful as antioxidants.

In particular, this invention relates to novel composition containing 4,4'-methylenebis(2,6-dialkylphenol) compounds which are eminently suited for use as antioxidants. These compounds have also been referred to as 1,1-bis-(3,5-dialkyl-4-hydroxphenyl) methanes.

Among the objects of this invention is that of providing new chemical compounds useful for the above and other purposes. A principal object is to provide compositions of matter protected against oxidative deterioration. Another object is to provide a hydrocarbon oil normally tending to deteriorate in the presence of oxygen containing these new compounds in amount sufficient to inhibit this deterioration. Another object is to provide lubricating oil normally tending to deteriorate in the presence of oxygen containing in amount sufficient to inhibit such deterioration a small antioxidant quantity of novel and highly effective antioxidants. Still another object is to provide organic polymers, particularly polypropylene, stabilized agenst oxidative deterioration by the presence therein of a small antioxidant quantity of novel and highly effective antioxidant. A still further object is to provide improved antiknock fluids. Another object is to provide stabilized edible material. Other objects will be apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing, as new compositions of matter, organic material tending to deteriorate in the presence of air, oxygen or ozone, protected by an antioxidant quantity of a 4,4'-methylenebis(2,6-dialkylphenol) in which all of the alkyl groups contain from 3 to 8 carbon atoms, which alkyl groups are all branched on their respective alpha carbon atoms. These 4,4'-methylenebis(2,6-dialkylphenol) compounds are represented by the general formula:



wherein the groups designated by R_1 and R_2 are alkyl groups containing from 3 to 8 carbon atoms and are further characterized by being branched on their alpha carbon atoms.

A preferred embodiment of this invention relates to 4,4'-methylenebis(2,6-di-tert-alkylphenol) compounds in which the tert-alkyl groups all contain from 4 to 8 carbon atoms. This preferred embodiment encompasses compounds which are particularly effective antioxidants for oxygen-sensitive oils, such as lubricating oil, transformer oil, turbine oil, gear oil, greases containing the aforesaid type of oils and the like.

A particularly preferred embodiment of this invention is 4,4'-methylenebis(2,6-di-tert-butylphenol). This compound is a superlative antioxidant for a wide variety of oxygen-sensitive organic material, particularly oils and greases of the type described above as well as antiknock fluids, polymers and fatty material.

Above and beyond the superlative antioxidant characteristics of 4,4'-methylenebis(2,6-di-tert-butylphenol) is the fact that it is a powerful inhibitor of engine wear when used as an additive to engine lubricants and transmission fluids. This wear inhibiting property, which is unique and totally unexpected since the chemical structure of the compound does not conform with previous concepts of wear inhibitors, was established by means of engine tests discussed hereinafter.

Typical compounds of this invention include 4,4'-methlene bis(2,6-diisopropylphenol); 4,4'methylenebis(2,6-di-sec-butylphenol); 4,4'-methylenebis(2-isopropyl - 6-tert-butylphenol); 4,4'-methylenebis[2,6-di - (2 - octyl)-phenol]; 4,4'-methylenebis[2-sec-butyl - 6 - (2 - hexyl)-phenol]; 4,4'-methylenebis[2-isopropyl-6-(1,1,3,3 - tetramethylbutyl)phenol], and the like.

The preferred class of compounds of this invention includes 4,4'-methylenebis(2-tert-butyl-6-tert - amylphenol); 4,4'-methylenebis(2,6-di-tert-amylphenol); 4,4' - methylenebis[2,6-di-(1,1,3,3 - tertramethylbutyl)phenol]; 4,4'-methylenebis[2-tert-butyl-6-(1,1,2,2 - tetramethylpropyl)-phenol] and the like.

As indicated above, 4,4'-methylenebis(2,6-di-tert-butylphenol) is a particularly preferred additive of this invention.

The additive compounds of this invention are white crystalline solids and are soluble in various organic solvents and in gasolines, diesel fuels, hydrocarbons oils and the like. These compounds are further characterized by being relatively stable, non-hygroscopic, readily crystallizable materials.

The compositions of this invention find important utility as antioxidants in a wide variety of oxygen sensitive materials; thus, liquid and solid products derived from petroleum crude are found to possess greatly increased storage stability by the use of an antioxidant of this invention. For example, gasoline, jet fuel, kerosene, fuel oil, turbine oils, insulating oils, motor oils and various waxes have increased oxidative stability when they contain an antioxidant of this invention. Likewise, liquid hydrocarbon fuels which contain organometallic additives such as tetraethyllead and other organometallic compositions which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. Furthermore, such fuels which contain halogen and phosphorus-containing scavengers for these organometallic compounds are benefited by the practice of this invention. In addition to increased storage stability, lubricating oils and functional fluids, such as automatic transmission and hydraulic fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, achieve a high degree of resistance to oxidation during use at elevated temperatures by the practice of this invention. It has been found that lubricating oils may be employed at extremely high temperatures without undergoing oxidative degradation when protected by an antioxidant of this invention. The addition of small quantities of the compositions of this invention to such materials as hydraulic, transformer and other highly refined

industrial oils as well as crankcase lubricating oils and lubricating greases prepared from these oils by the addition of metallic soaps, greatly increase their resistance to deterioration in the presence of air, oxygen or ozone. Furthermore, the organic soaps used in the preparation of lubricating greases are themselves stabilized by the practice of this invention.

Organometallic compositions such as tetraethyllead and tetraethyllead antiknock fluids containing halohydrocarbon scavengers, dyes and which may contain various phosphorus compounds and other organometallic additives are stabilized against deterioration during storage by the addition thereto of an antioxidant quantity of the compositions of this invention.

The compositions of this invention are also extremely effective antioxidants for elastomers including high molecular weight unsaturated hydrocarbon polymers both derived from naturally occurring sources and those synthetically prepared. Thus, natural rubbers and synthetic rubbers, including oil extended rubbers and sulfur vulcanized rubbers are greated benefited by the practice of this invention. Examples of the synthetic rubbers protected by the practice of this invention include such synthetics as polybutadiene, methyl rubber, polybutadiene rubber, butyl rubber, GR–S rubber, GR–N rubber piperylene rubber and dimethylbutadiene rubber.

The practice of this invention is also useful in protecting paraffin and micro-crystalline petroleum waxes against the oxidative deterioration which leads to rancidity. Furthermore, the compositions of this invention are extremely useful in the stabilization of fats and oils of animal or vegetable origin which become rancid during periods of storage due to oxidative deterioration. Typical animal fats benefited by the practice of this invention include butter fat, lard, beef tallow, fish oils—such as cod liver oil—as well as various foods containing or prepared in animal fats which tend to deteriorate. These include, for example, potato chips, fried fish, donuts, crackers, and various types of pastry such as cakes and cookies. Furthermore, fat fortified animal feeds and fish meals used as animal feeds are greatly benefited by the practice of this invention. Not only are these compositions protected against oxidative deterioration but the inclusion of a composition of this invention in such materials inhibits the degradation of vitamins A, D and E and certain of the B complex vitamins. Examples of compositions containing oils derived from vegetable sources which are benefited by the practice of this invention include castor oil, soy bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, citrus oils, cotton seed oil and various compositions containing these including peanut butter, peanuts and other whole nuts, salad dressings, margarine and other vegetable shortenings.

The compositions of this invention are also outstanding antioxidants for various organic compounds and polymeric materials including polystyrene, polyvinylchloride, polyvinyl acetate, various epoxide resins and polyester resins and polymers including the alkyds. However, in particular the compositions of this invention are outstanding antioxidants for saturated hydrocarbon synthetic polymers derived from polymerization of an aliphatic monoolefin hydrocarbon compound having preferably up to 5 carbon atoms and only a single unit of unsaturation per monomeric molecule. Examples of such monomers include ethylene, propylene, butylene, isobutylene, 2-methyl-4-butene, 2-methyl-3-butene and the like. Thus the polymers are homopolymers and copolymers of ethylene, propylene, butylene, isobutylene and the pentenes and are usually solid. Polyethylene and polypropylene are preferred polymers in the practice of this invention and they are derived from the polymerization of ethylene and propylene respectively.

An embodiment of this invention involves providing a lubricating oil normally susceptible to oxidative deterioration containing, in amount sufficient to inhibit such deterioration, a small antioxidant quantity of the above 4,4′-methylenebis(2,6-dialkylphenol). It has been found in actual practice that small amounts of these compounds very effectively stabilize lubricant compositions—e.g. petroleum hydrocarbon oils and synthetic diester oils—against oxidative deterioration.

To prepare the lubricants of this invention an appropriate quantity—from about 0.001 to about 2 percent and preferably from about 0.25 to about 2 percent—of a compound 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 temperatures.

The finished lubricants of this invention have much greater oxidation stability and many other improved performance characteristics as compared with the corresponding base oils. In the case of lubricating oils containing 4,4′-methylenebis(2,6-ditert-butylphenol), spectacular improvements are afforded, including markedly reduced engine wear characteristics, greatly improved oxidation stability and greatly reduced bearing corrosion properties.

EXAMPLE 1

Engine tests were used to demonstrate the unique properties of 4,4′-methylenebis(2,6-di-tert-butylphenol) in causing very substantial reductions in engine wear when used in motor oils. One such series of tests was the Chevrolet L–4 test (as described in "CRC Handbook," Coordinating Research Council, New York, J. J. Little and Ives Co., 1946), in which the individual piston rings were weighed before and after the tests in order to determine ring wear. A series of concentrations of 4,4′-methylenebis(2,6-di-tert-butylphenol) in the range of 0.40 to 1.50 percent by weight were tested. The base oil in these tests was a non-additive SAE 20 blend of solvent-refined neutral and bright stock having a viscosity index of 109 and a viscosity of 372 Saybolt Universal seconds (SUS) at 100° F. A bulk-oil temperature of 280° F. was maintained throughout each 36 hour test period and in addition to the weight measurement of the piston rings, two copper-lead bearings were weighed before and after each test in order to measure bearing corrosion. The effectiveness of the additive as an antioxidant was also determined by making standard inspections of the properties of the used oils.

The tremendous effectiveness of 4,4′-methylenebis(2,6-di-tert-butylphenol) in inhibiting engine wear is shown by the results of these tests in which ring wear was reduced in a linear relationship with additive concentration.

It was also found that rings from the base oil were severely scuffed while the rings from the tests using the higher concentrations of 4,4′-methylenebis(2,6-di-tert-butylphenol) showed almost no wear as evidenced by the clearly visible original tool marks on the top piston ring faces which were essentially unaltered during the test.

In the above L–4 tests substantial reductions in oil oxidation and bearing corrosion occurred, and especially when 4,4′-methylenebis(2,6-di-tert-butylphenol) was used at concentrations of 0.75 and 1.5 percent by weight.

EXAMPLE 2

Further proof of the outstanding wear inhibiting potency of 4,4′-methylenebis(2,6-di-tert-butylphenol) was provided by Chevrolet "full throttle" tests.

In order to increase the severity of the L–4 conditions, tests were performed in the Chevrolet engine using the L–4 operating conditions of speed, and sump and jacket temperatures, but substituting full-throttle operation for the L–4 part-throttle condition. This change doubled

the fuel consumption of the engine and increased the brake horsepower from 30 to 70, thereby raising the temperatures in the ring zone.

The base oil in these tests was the same as used in the L–4 tests in Example 1; it was compared with a blend containing 1.5 percent of 4,4'-methylenebis(2,6-di-tert-butylphenol). The results are shown in Table I.

Table I

EFFECT OF 4,4'-METHYLENEBIS (2,6-DI-TERT-BUTYLPHENOL) IN "FULL THROTTLE" CHEVROLET TEST

	Base oil	Oil + 1.5 percent 4,4'-methylenebis (2,6-di-tert-butylphenol)
Piston ring weight loss in grams—Avg. of 6 rings:		
Top ring	.48	.15
Second ring	.26	.07
Oil ring	.21	.05
Piston ring gap increase in inches—Avg. of 6 rings:		
Top ring	.017	.008
Second ring	.012	.004
Oil ring	.038	.013
Copper-lead bearing corrosion—Avg. grams per bearing	.584	.199
Engine cleanliness:		
Piston skirt varnish	8.4	8.9
Total varnish rating	45.2	46.9
Total engine rating	91.2	93.3
36-hour used oil properties:		
Acid number	3.3	1.0
Percent increase in viscosity at 100° F	29	13

When the base oil was used, the rings were severely scuffed and the wear rate was several times greater than in the L–4 test. 4,4'-methylenebis(2,6-di-tert-butylphenol) again demonstrated very effective wear inhibition as measured by ring-weight loss and ring-gap increase. Also, satisfactory oxidation and bearing-corrosion inhibition and a measurable improvement in piston-skirt varnish rating were observed for the oil containing 4,4'-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 3

Other engine tests still further demonstrated the unique characteristic of 4,4'-methylenebis(2,6-di-tert-butylphenol) in markedly reducing engine wear. In these tests use was made of the Chevrolet FL–2 procedure, a low jacket-temperature, high load test which has been used to evaluate fuel cleanliness. In this 40 hour test, engine speed is 2500 revolutions per minute, brake horsepower output is 45, and the water-jacket inlet temperature is 90° F. Corrosive-type ring and bore wear is usually associated with such a low jacket temperature. Tests were conducted using the same fuel and base oil as in the Chervolet L–4 test. Two concentrations of 4,4'-methylenebis(2,6-di-tert-butylphenol) were employed, viz., 0.75 and 1.5 percent by weight.

Both additive concentrations of 4,4'-methylenebis(2,6-di-tert-butylphenol) showed a large reduction in ring wear when compared with the base oil. For example, the top piston ring weight loss in terms of grams per six rings was reduced from 0.65 to 0.42 by the lower concentration and to 0.41 by the higher concentration.

EXAMPLE 4

In order to further evaluate the antiwear properties of 4,4'-methylenebis(2,6-di-tert-butylphenol) under other conditions of engine design and operation and with the use of a different wear-measurement technique, a series of tests were undertaken in a single-cylinder engine fitted with a radioactive top piston ring. The engine was an overhead-valve prototype of the 1951 Oldsmobile engine. The radioactivity detection system was of the flow-monitored type.

The tests were conducted on an operating schedule that is conducive to ring scuffing:

2500 r.p.m.
95 lb./hr. air flow (supercharger source)
0.080 *F/A* ratio (constant injection system)
180° F. jacket water temperature
100° F. air intake temperature
200° F. oil sump temperature
Ignition cycle—
  2.5 minutes at 30° BTC (max. power)
  10 seconds at 100° BTC (60 percent power)
Test time—20 hours
Test per evaluation—three tests per evaluation, preceded and followed by baseline tests

The fuel was technical grade isooctane containing 3 milliliters of tetraethyllead per gallon as 62 mix and 0.05 percent by weight of sulfur as disulfide oil.

Because of the development of very high engine temperatures and the need to disperse wear debris for circulation through the detection system, a detergent was used with the antioxidant in these tests. This provided an opportunity to evaluate 4,4'-methylenebis(2,6-di-tert-butylphenol) in combination with detergents. For comparative purposes, a similar oil blend containing a well-known antioxidant—zinc dithiophosphate—in combination with a detergent was subjected to the same test.

The oil in these tests was a blend of a solvent-refined neutral oil (95 VI and 200 SUS at 100° F.) with 6 percent of a commercial methacrylate-type VI improver. This formulation, which is typical of blends used in multiple-viscosity-grade oils, had a VI of 140 and a viscosity of 300 SUS at 100° F.

In the first series of tests, the base oil contained 4 percent of a commercial barium phenol sulfide detergent-antioxidant. A comparison was made with two concentrations of 4,4'-methylenebis(2,6-di-tert-butylphenol) in the base oil-phenate blend. 4,4'-methylenebis(2,6-di-tert-butylphenol) concentrations of 0.75 percent and 1.50 percent caused an equal and significant reduction in the rate of ring wear, the top piston ring wear rate being reduced by about 30 percent.

In the second series of tests, a typical commercial oil formulation containing a balanced blend of 4 percent barium sulfonate and 1 percent zinc dithiophosphate was compared with the same base oil containing 4 percent barium sulfonate and 1.5 percent of 4,4'-methylenebis(2,6-di-tert-butylphenol). In effect, 4,4'-methylenebis(2,6-di-tert-butylphenol) was substituted for the zinc dithiophosphate. A significantly lower rate of ring wear was observed with the oil containing 4,4'-methylenebis(2,6-di-tert-butylphenol) than with the oil containing zinc dithiophosphate.

These results provide another example of engine conditions and wear measurement technique in which 4,4'-methylenebis(2,6-di-tert-butylphenol) effectively minimized abrasive ring wear. They also show that this antiwear effect was obtained in the presence of the two most widely used types of commercial motor oil detergents.

EXAMPLE 5

To further illustrate the useful properties of the novel compounds of this invention, recourse is had to the Polyveriform oxidation stability test as 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 effectively evaluates the performance of lubricating oil antioxidants. The test equipment procedure employed and correlations of the results with engine performance are discussed in the first paper above cited. By employing various compounds of this invention in oxygen-sensitive lubricating oil,

effective inhibition of oxidation deterioration is achieved.

To demonstrate the preeminence of the particularly preferred compound of this invention—4,4'-methylenebis(2,6-di-tert-butylphenol)—as an antioxidant for industrial lubricants, comparative tests were conducted using the method and apparatus essentially as described in the publication first above mentioned. One minor 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, 95 V.I. solvent-refined SAE–10 crankcase oil was used. The principal test conditions consisted of passing 70 liters of air per hour through the test oil for a total period of 20 hours while maintaining the oil at a temperature of 280° F. Oxidation deterioration of the oil was further promoted by employing as oxidation catalysts 0.05 percent by weight of ferric oxide (as ferric 2-ethyl hexoate) and 0.10 percent by weight of lead bromide, both of these amounts being based upon the weight of oil employed. A lubricating oil of this invention was then prepared by blending 1 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol) with another portion of the above lubricating oil. This composition was then subjected to the above stringent oxidation test. To another portion of the same lubricating oil was added 1 percent by weight of 2,6-di-tert-butyl-4-methylphenol, a commercial antioxidant which has found widespread use in lubricating oils. This sample was then subjected to the same test procedure. The results of these tests are shown in Table II.

Table II

EFFECT OF ANTIOXIDANTS ON OXIDATION OF LUBRICATING OIL

Test No.	Additive	Neutralization number	Viscosity at 100° F., SUS [1]	Viscosity index increase at 100° F., percent
1	None	8.5	547.7	174
2	4,4'-methylenebis (2,6-di-tert-butylphenol).	0.3	213.7	6.5
3	2,6-di-tert-butyl-4-methyl phenol.	4.7	349.9	75.5

[1] Saybolt universal seconds.

By referring to the data presented in Table II, it is immediately apparent that 4,4'-methylenebis(2,6-di-tert-butylphenol) exhibits a striking and unexpected potency in suppressing oxidative deterioration of lubricating oil. Furthermore, comparison of the results obtained in test 2 with those of test 3 shows that the compound of this invention is about 11 times as effective as a presently used commercial lubricating oil antioxidant. That this is particularly unexpected is still further apparent from the fact that 2,6-di-tert-butyl-4-methylphenol bears a superficial resemblance insofar as chemical structure is concerned to the compound of this invention.

EXAMPLE 6

To still further demonstrate the preeminence of 4,4'-methylenebis(2,6-di-tert-butylphenol) as an antioxidant for use in lubricating oil, another series of comparative tests was conducted. In this instance the test procedure used was essentially as described above in Example 5 with the exception that still more stringent test conditions were employed. These conditions were brought about by conducting the Polyveriform oxidation stability test at a temperature of 300° F. In these tests, comparisons were made among a sample of the above-described, additive-free crankcase lubricating oil; a separate portion of this oil with which had been blended one percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol); and a third sample of this oil with which had been blended two percent by weight of 2,6-di-tert-butyl-4-methylphenol. The results of these tests are shown in Table III.

Table III

EFFECT OF ANTIOXIDANTS ON OXIDATION OF LUBRICATING OIL

Test No.	Additive	Additive conc., percent by weight	Neutralization number	Viscosity at 100° F. SUS	Viscosity increase at 100° F. percent
1	None		5.1	420	109
2	4,4'-methylenebis(2,6-di-tert-butylphenol)	1.0	0.5	224	11.5
3	2,6-di-tert-butyl-4-methylphenol	2.0	2.2	280	39.5

It is clearly evident from the data shown in Table III that even under more stringent oxidizing conditions 4,4'-methylenebis(2,6-di-tert-butylphenol) is four times as effective as 2,6-di-tert-butyl-4-methylphenol. The clear-cut superiority of 4,4'methylenebis(2,6-di-tert-butylphenol) as compared with 2,6-di-tert-butyl-4-methylphenol is still further apparent by the fact that this substantial difference in effectiveness was brought about by the use of only one-half of the concentration of 4,4'-methylenebis(2,6-di-tert-butylphenol) in relation to the amount of 2,6-di-tert-butyl-4-methylphenol used.

The compounds of this invention are particularly effective antioxidants for use in steam turbine oils. This is demonstrated by making use of the standard test procedure of the American Society for Testing Materials bearing ASTM designation D–943–54. According to this test procedure, 300 milliliters of a suitable test oil is placed in contact with 60 milliliters of water and the resulting oil-water system is maintained at a temperature of 95° C. while passing oxygen therethrough at a rate of three liters per hour. Oxidation is catalyzed by the use of iron and copper wire. Periodically measurements are made of the acid number of the test oil and failure of an antioxidant is indicated by an acid number in excess of 2.0. It is found that when the various compounds of this invention are added in small antioxidant quantities to steam turbine oils, substantial resistance against oxidative deterioration results.

EXAMPLE 7

The outstanding effectiveness of the particularly preferred compound of this invention—4,4'-methylenebis-(2,6-di-tert-butylphenol)— as an inhibitor of oxidative deterioration of steam turbine oils was demonstrated by conducting a series of comparative tests according to the above ASTM test procedure. In these tests a 95 VI solvent-refined SAE–10 hydrocarbon oil was used as the test oil. Steam turbine oil compositions of this invention were formulated by blending 0.7 and 1.0 percent by weight of 4,4'-methylene-bis(2,6-di-tert-butylphenol) with this test oil. For comparative purposes, identical concentrations of 2,6-di-tert-butyl-4-methylphenol were blended with the same test oil. The results of these tests are shown in Table IV.

Table IV

EFFECT OF ANTIOXIDANTS ON THE OXIDATIVE DETERIORATION OF STEAM TURBINE OIL

Additive	Conc. percent by weight	Acid number, hours				
		500	600	700	800	900
4,4'-methylenebis(2,6-di-tert-butylphenol	0.7	0.5	0.5	0.6	0.6	18.9
2,6-di-tert-butyl-4-methylphenol	0.7	0.3	0.5	0.5	11.2	23.0
4,4'-methylenebis(2,6-di-tert-butylphenol)	1.0	0.6	0.5	0.6	0.4	1.0
2,6-di-tert-butyl-4-methylphenol	1.0	0.4	0.5	0.6	8.8	17.8

Referring to the data of Table IV, it is clearly apparent that 4,4'-methylenebis(2,6-di-tert-butylphenol) is much

more effective in inhibiting oxidative deterioration of steam turbine oil than is 2,6-di-tert-butyl-4-methylphenol.

EXAMPLE 8

The compounds of this invention are very effective antioxidants for grease. The potency of the compounds of this invention in this respect is demonstrated by conducting the norma-Hoffman grease oxidation stability test, ASTM Test Procedure D–942–50. It is found that the presence of minor proportions of the compounds of this invention in conventional greases greatly inhibits oxidative deterioration. By way of example an initially antioxidant-free lithium base grease was modified to the extent that it contained 0.5 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol) and was subjected to the above oxidation stability test. It was found that the presence of 4,4'-methylenebis(2,6-di-tert-butylphenol) greatly retarded oxygen absorption by the grease. Thus, after maintaining this grease composition in the oxygen bomb for 376 hours under the standard test conditions, the oxygen bomb pressure had been reduced from 110 p.s.i. to 98 p.s.i. This represents a very small diminution of oxygen pressure in the light of the severe test conditions employed and is indicative of an extremely small amount of oxygen absorption.

EXAMPLE 9

The compounds 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 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 bounded 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 of 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 salts 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 and their concentration range in the fluid are as follows:

From about 1 to about 5 percent of an anti-squawk additive, usually a sulfurized oil, such as sulfurized sperm oil, sulfurized lard, sulfurized vegetable oil, sulfurized glyceride, or a sulfurized ester of fatty acids.

From about 0.05 to about 2 percent of a pour point depressant. Typical types of additives are wax-substituted naphthalenes, esters of wax-substituted phenol, polymerized unsaturated esters and acrylic polymers such as polymerized esters of methacrylic acid.

About 0.005 to about 0.1 percent of a foam inhibitor. Foam inhibitors include fatty acids and fatty acid esters, pine oil, alkyl lactates, higher ethers such as 2-(di-tert-amyl phenoxy) ethanol and mixtures of materials such as glycerol and sodium bis(2-ethylhexyl)sulfosuccinate.

From about 0.03 to about 0.1 percent of a rust preventive such as carboxylic acid derivatives including alkylated succinic acid, esters and partial esters of di- and polycarboxylic acids, esters and partial esters of hydroxy-substituted di- and polycarboxylic acids and alkyl-substituted acids containing at least two carboxylic acid groups joined by nitrogen, oxygen or sulfur esters of acids derived from oxidized petroleum; amine derivatives including hydroxy amines, hydroxy amidines, amine salts of partial esters of phosphorus acids, hydroxy amine salts of oxidized petroleum acids, hydroxy amine salts of fatty acids and long chain alkyl amines; organic sulfonates; long chain alkyl ketones; organic phosphates and phosphites; morpholine derivatives and phosphatides including lecithin and fatty acids.

About 0.1 to about 2 percent of an extreme pressure agent. These include organic compounds containing chlorine, phosphorus and sulfur, such as chlorinated waxes or a P_2S_5-terpene reaction product; organic phosphates and phosphites such as for example, tricresylphosphate or a zinc di-alkyl dithiophosphate and lead soaps such as lead naphthenate.

From about 0.05 to about 0.2 percent of a metal deactivator. Such compounds include complex organic nitrogen and sulfur-containing compounds, as for example, amines and sulfides. Also included are such compounds as organic dihydroxyphosphines, trialkyl and triaryl phosphites, certain diamines and soaps containing a metal such as tin, nickel, chromium, thallium or titanium.

From about 1 to about 10 percent of a viscosity index improver such as a polymerized olefin or isoolefin, butylene polymer or alkylated styrene polymer.

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 10

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 4,4'-methylenebis-(2,6-di-tert-butylphenol), 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 11

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 4,4'-methylenebis(2,6-diisopropyl phenol); 0.1 part of calcium octyl phenol 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 60/60° F. of 0.875.

EXAMPLE 12

An automatic transmission fluid is made by mixing 97 percent of an oil blend comprising 59.0 parts of a sol-

vent-extracted, Coastal oil, 40 SUS at 210° F.; 1.0 part of 4,4'-methylenebis(2,6-di-tert-butylphenol); 1.0 part of a barium phenol sulfide containing 2.4 percent barium, 2 percent calcium and 3.5 percent sulfur, having a viscosity of 126 SUS at 210° F., a flash point of 430° F., a pour point of 10° F. and a specific gravity 60/60° F. of 0.97; and 1.0 part of sulfurized sperm oil.

EXAMPLE 13

96 parts of a conventionally-refined Pennsylvania mineral oil (99 SUS at 100° F.); 2 parts of 4,4'-methylenebis(2,6-di-tert-butylphenol); 2 parts of a mixed barium phenol sulfide-calcium sulfonate containing 5.7 percent barium, 0.68 percent calcium and 2.9 percent sulfur, having a viscosity of 92 SUS at 210° F., a flash point of 410° F., a pour point of 10° F. and a specific gravity 60/60° F. of 0.988 are blended into an effective fluid of this invention.

EXAMPLE 14

A standard, modern automatic transmission was used to evaluate the tremendous effectiveness of 4,4'-methylenebis(2,6-di-tert-butylphenol) as an antioxidant for oils used in automatic transmission fluid service. The test schedule consisted of continuous operation of the transmission at 1800 r.p.m. input shaft speed, 275° F. sump temperature, and an eight-second shifting cycle between third and fourth gear. An Eagle multipulse timer, utilizing a synchronous motor-driven cam that activated a microswitch, provided an accurate eight-second cycle signal to the transmission shifter arm air cylinder solenoid valve. Oil sump temperature was controlled at 275±3° F. by means of a water-cooled heat exchanger. Each test was carried out for 140 hours. On completion of each test, the transmissions were dismantled and the various operating parts were visually inspected for sludge and varnish formation. The stability of the transmission oil was also determined by means of used oil analyses.

The base oil in these tests was a commercially available automatic transmission fluid, the oil having a viscosity at 100° F. of 202.6 SUS and 50.9 SUS at 210° F. The tests were run on the above automatic transmission fluid and on individual portions thereof which had been treated with 4,4'-methylenebis(2,6-di-tert-butylphenol) at concentrations of 0.5 and 1.0 percent by weight. The results of these tests are shown in Table V.

Table V

AUTOMATIC TRANSMISSION FLUID OXIDATION TESTS

Conc. of 4,4'-methylenebis (2,6-di-tert-butylphenol), percent by weight.	Percent change in oil viscosity during test, when measured at—		Pentane insoluble sludge in oil after test, percent by weight.	Acid number of used oil, mg. KOH/g. of oil
	100° F.	210° F.		
None	14.7	6.1	2.69	3.3
0.5	−3.7	−5.1	0.79	1.8
1.0	3.1	−4.7	0.39	0.1

As seen by the data in Table V, the automatic transmission fluids containing 4,4'-methylenebis(2,6-di-tert-butylphenol) were much more resistant to oxidative deterioration than the base oil. For example, the base oil possessed a very significant increase in viscosity on completion of the test, this being a direct indication that a substantial amount of polymerization had occurred in the oil. On the other hand, the transmission fluids containing 4,4'-methylenebis(2,6-di-tert-butylphenol) in most instances showed reductions in viscosity indicating that these oils had not undergone destructive polymerization reactions during the tests. The eminent superiority of the transmission fluids containing 4,4'-methylenebis (2,6-di-tert-butylphenol) was also shown by the substantial reductions in pentane insoluble matter and in acid number in the used oils as compared with the base oil. Particularly noteworthy was the fact that the transmission parts when operated on the base transmission fluid were very heavily sludged and were coated with a moderate amount of varnish. However, the transmission parts, after operation on the automatic transmission fluids of this invention were absolutely free from sludge and varnish.

The compounds of this invention are outstanding antioxidants for synthetic oils, particularly diester oils of the type described in Industrial and Engineering Chemistry, 39, 481–91 (1947). Thus, the compounds of this invention can be used to very effectively stabilize diesters formed by the esterification of straight chain dibasic acids containing from 4 to about 16 carbon atoms with saturated aliphatic monohydric alcohols containing from 1 to about 10 carbon atoms. Generally speaking, diester lubricants that are prepared from branched chain alcohols and which have molecular weights ranging from about 300 to about 600 are especially effective lubricants and are very effectively stabilized by the compounds of this invention. Thus, in the diester lubricant embodiments of this invention, use can be made of oxalates, malonates, succinates, adipates, pimelates, suberates, azelates, sebacates, and the like.

EXAMPLE 15

To demonstrate the outstanding utility of the compounds of this invention in diester lubricants, a series of panel coking tests was conducted. The panel coking apparatus (described in "Lubrication," 40, No. 4 (1945)), is used to qualify synthetic lubricants for jet engines. The method involves the splashing of a lubricant onto a heated aluminum panel which is maintained at a controlled temperature. The weight of deposit formed on the panel is a measure of the oxidation stability of the lubricant. For the following tests, the panel temperature was 600° F.; the time was 10 hours; and the splasher was operated for 5 seconds each minute.

When a commercially available, antioxidant-free dioctyl sebacate was subjected to this test procedure, the panel deposit weight was 140 milligrams. However, when the same diester oil contained concentrations of 0.5, 1.0, 2.0 and 3.0 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol), the extent of coke formation on the panel was very effectively minimized. For example, the oil containing 0.5 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol) produced 25 milligrams of deposit. Less than 5 milligrams of deposit was formed when the oil contained 2 percent and 3 percent of this additive. In contrast, the use in the same diester oil of 4-methyl-2,6-di-tert-butylphenol at concentrations of 1.0, 2.0 and 3.0 percent by weight failed to measure up to this performance. In fact, there were about 200 percent as much panel deposits when the oil contained 3.0 percent of 4-methyl-2,6-di-tert-butylphenol as compared with the oil containing only 0.5 percent of 4,4'-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 16

The compounds of this invention are also especially valuable as antioxidants for diesel engine lubricants. For example, 4,4'-methylenebis(2,6-di-tert-butylphenol) is employed in concentrations ranging from about 0.2 to about 1.5 percent by weight in railroad diesel oils, very effective inhibition of oxidative deterioration is achieved. This is reflected by the greatly reduced acid content of the used oil and its much smaller viscosity change as compared with the unused oil. This, in turn, reduces maintenance problems and permits the use of poorer grades of diesel fuels without sacrificing trouble-free engine operating time.

The results described above are merely illustrative of the effectiveness of the compounds of this invention when

employed as antioxidants. The compounds of this invention effectively inhibit oxidation in industrial lubricants of the hydrocarbon type, such as lubricating oil, turbine oil, transformer oil, transmission fluids, glass annealing oil, gear and machine lubricants, hydraulic lubricants and other industrial oils, grease and the like. As pointed out above, the compounds of this invention as a class are effective antioxidants. The preferred compounds of this invention—those which contain tert-alkyl groups containing from 4 to 8 carbon atoms—are more effective antioxidants than are the remainder of the compounds of this invention. As brought out by the experimental results described above, 4,4'-methylenebis(2,6-di-tert-butylphenol) is a superlative antioxidant and wear inhibitor.

In the compositions of this invention effective use can be made of other additives which are known to the art, such as other inhibitors, detergent dispersants, pour point depressants, viscosity index improvers, anti-foam agents, rust inhibitors, oiliness or film strength agents, dyes and the like. Of the inhibitors which can be effectively used in combination with the compounds of this invention are sulfurized sperm oil, sulfurized terpenes, sulfurized paraffin wax olefins, aromatic sulfides, alkyl phenol sulfides, licithin, neutralized dithiophosphates, phosphorus pentasulfide-terpene reaction products, diphenylamine, phenylnaphthyl amine, β-naphthol, pyrogallol and the like. Typical of the detergent additives that can be used in the lubricant compositions of this invention are metallic soaps of high molecular weight acids, such as aluminum naphthenates, calcium phenyl stearates, calcium alkyl salicylates, alkaline earth metal petroleum sulfonates, alkaline earth metal alkyl phenol sulfides (barium amyl phenol sulfide, calcium octyl phenol disulfide, etc.), metal salts of wax-substituted phenol derivatives and the like. Of the viscosity index improvers and pour point depressants, effective use can be made of polymers of the esters of methacrylic acids and higher fatty alcohols and the corresponding polymers of esters of acrylic acid and higher fatty alcohols. These and other additives which can be employed in the lubricant compositions of this invention will now be well known to those skilled in the art.

The compounds of this invention very effectively enhance the oxidation resistance of such diester oils as diethyl oxalate; di-sec-butyl malonate; di-(2-hexyl)succinate; di-(isoheptyl)pimelate; di-(3-decyl)suberate; di-sec-amyl glutarate; di-(isobutyl)glutarate; di-(2-ethylbutyl)glutarate; di-(2-ethylhexyl)glutarate; di-sec-amyl adipate; di-(3-methylbutyl)adipate; diethyl adipate; di-2-ethylhexyl adipate; di-sec-amyl azelate; di-(isobutyl)-azelate; di-(2-ethylbutyl)azelate; di-(2-ethylhexyl)-azelate; di-sec-amyl sebacate; di-sec-butyl sebacate; di-(2-ethylhexyl)sebacate; the glutarates, adipates, azelates and sebacates of branched chain secondary alcohols, such as undecanol, tetradecanol; etc., and, in general, diesters of the type described in the literature as useful for synthetic lubricant purposes.

As noted above, the compounds of this invention are also excellent antioxidants for saturated hydrocarbon polymers.

Polyethylene and polypropylene are, for example, hydrocarbon polymers derived from the polymerization of ethylene and propylene. This polymerization can be accomplished by a great variety of methods which lead to products of diverse properties. Polymers of any nature may advantageously be utilized for preparing compositions according to the present invention. The polymers 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 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 polymer 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.

EXAMPLE 17

The benefits derived from the practice of this invention are demonstrated by comparative oxidation tests of uninhibited polyethylene and polyethylene containing an antioxidant of this invention. These tests are conducted as follows: The selected amount of antioxidant is blended with the polyethylene by milling a weighed quantity of plastic pellets on a warm roll-mill. The weighed quantity of antioxidant is added to the mill after the polyethylene has been pre-milled for a short period of time. The plastic containing the antioxidant is then added in weighed quantity to a standard size vessel and melted to give a surface of reproducible size. The vessel is then inserted into a chamber which may be sealed and which is connected to a capillary tube leading to a gas buret and leveling bulb. The apparatus is flushed with oxygen at room temperature, sealed, and the temperature is raised to 150° C. The oxygen pressure is maintained at 1 atmosphere by means of the leveling bulb. The oxygen uptake at the elevated temperature is recorded for the duration of the test. This procedure has been adopted since it has been found that many compounds may inhibit the oxidation for a certain induction period after which time a very sharp increase in the rate of oxygen uptake occurs indicating that the antioxidant has been exhausted. In a test of this nature 0.05 percent of the preferred antioxidant of this invention, 4,4'-methylenebis(2,6-di-tert-butylphenol) was added to one sample of the polyethylene. Another sample of the polyethylene was tested uninhibited. The induction period of the sample containing the 4,4'-methylenebis(2,6-di-tert-butylphenol) had an induction period of 40 hours, whereas the uninhibited sample had no induction period and took up oxygen immediately. After 20 hours of heating the uninhibited sample had absorbed over 45 ml. of oxygen.

The outstanding results obtainable with the antioxidant compounds of this invention in contrast to those obtained with the uninhibited polyethylene are demonstrated by a test which was conducted with 4,4'-methylenebis(2,6-di-tert-butylphenol), the preferred compound of this invention. When 0.2 percent of this compound was compounded with the same polyethylene as used in the above test, the induction period did not expire until 40 hours of heating at 150° C. That is to say, the sample of polyethylene had absorbed essentially no oxygen until after 40 hours of heating. Thus, the compounds of this invention are outstandingly superior antioxidants for saturated hydrocarbon polymers.

There are several methods available for preparing the inhibited hydrocarbon polymer compositions of this invention. Thus the blending of the additives of this invention, 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 additive 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 additive may be initially mixed with the polymer in the dried state or 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 18

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 4,4'-methylenebis(2,6-diisopropylphenol). The resulting composition has a greatly increased oxidative stability.

EXAMPLE 19

To 100 parts of polyisobutylene having an average molecular weight of 100,000 is added 0.5 part of 4,4'-methylenebis(2,6-di-tert-butylphenol). The oxidative stability of the polymer is greatly increased by the addition of this compound.

EXAMPLE 20

To a master batch of high molecular weight polyethylene 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 4,4-methylenebis(2-isopropyl-6-tert-butylphenol). Polyethylene of improved oxidative stability results.

EXAMPLE 21

A linear polyethylene having a high degree of crystallinity (up to 93 percent) and below 1 ethyl branched chain per 100 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 4,4'-methylenebis(2,6-di-tert-butylphenol), and the resulting product has improved stability characteristics.

EXAMPLE 22

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 4,4'-methylenebis-[2-isopropyl-6-(1,1,3,3-tetramethylbutyl)phenol]. After milling in the antioxidant an extremely oxidation resistant product results.

EXAMPLE 23

Two parts of 4,4'-methylenebis(2-tert-butyl-6-tert-amylphenol) 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 24

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 4,4'-methylenebis(2,6-di-tert-butylphenol), to prepare a composition of outstanding oxidative stability.

EXAMPLE 25

To a polyisobutylene polymer having an average molecular weight of 35,000 is added sufficient 4,4'-methylenebis[2-tert-butyl-6-(1,1,2,2-tetramethylpropyl)phenol] to give a composition containing 0.03 percent of the antioxidant. The composition has improved antioxidant properties due to the presence of 4,4'-methylenebis[2-tert-butyl-6-(1,1,2,2-tetramethylpropyl)phenol].

EXAMPLE 26

To 1,000 parts of a solid polypropylene polymer having a density of 0.905 and a Rockwell hardness greater than 85 and which is isotactic, is added and blended to 5 parts of 4,4'-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 27

To an isotactic polypropylene having a tensile strength greater than 4300 p.s.i. and a compressive strength of about 9,000 p.s.i. is added sufficient 4,4'-methylenebis-(2-isopropyl-6-tert-butylphenol) to give a composition containing 0.1 percent antioxidant.

EXAMPLE 28

To a wax-like polypropylene having a melting point above 130° C. and a molecular weight of about 4,000, a density of 0.913 is added 0.2 percent of 4,4'-methylenebis(2,6-diisopropylphenol). The antioxidant is added to the polypropylene in the molten state and the mixture is allowed to solidify into the desired shape. A polypropylene product of outstanding oxidative stability results.

In addition to the additive of this invention, saturated hydrocarbon polymers 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.

Other hydrocarbon polymers which are stabilized against oxidative deterioration according to this invention include natural rubber, GR–S and GR–N rubbers, butyl rubber, methyl rubber, polybutene rubber, butadiene rubbers, piperylene rubbers, dimethylbutadiene rubbers, polystyrene, polybutadiene, polyisobutylene, polyethylene, isobutylene-styrene copolymer and, in general elastomeric hydrocarbon polymers which are normally susceptible to oxidative deterioration. (The above polymers are well-known as shown for instance in the Schildknecht text "Vinyl and Related Copolymers," copyright 1952, by John Wiley and Sons, New York. GR–S rubber, for example, is described in pages 98 and 102 as a butadiene-styrene rubbery copolymer.) Such polymers are well known in the art and besides being susceptible of oxidative deterioration are characterized by having molecular weights above about 10,000. The problem resulting from heat, light and catalyst promoted oxidative deterioration in such hydrocarbon polymers is intensified because of free radical formation within the polymers. This leads to various forms of physical and chemical degradation such as chain scission, autocatalytic oxidation, reduction in molecular weight and loss of original physical properties. The net result is that the desirable useful and necessary properties of the polymers which are associated with their original chemical structure and molecular weights are lost to a greater or lesser extent unless the polymers are stabilized against such deterioration.

Typical stabilized hydrocarbon polymers of this invention are illustrated by the following specific examples wherein all parts and percentages are by weight.

EXAMPLE 29

To a synthetic rubber master batch comprising 100 parts of GR–S rubber having an average molecular weight of 60,000, 5 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 4,4'-methylenebis[2-isopropyl-6-(1,1,3,3-tetramethylbutyl)phenol]. This batch is then cured for 60 minutes at 45 pounds per square inch of steam pressure.

EXAMPLE 30

To the master batch described in Example 29 is added 0.5 percent of 4,4'-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 31

One percent of 4,4'-methylenebis(2,6-di-tert-butylphenol) is added to a synthetic rubber master batch comprising 100 parts of GR–S rubber having an average molecular weight of 100,000, 5 parts of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole. This batch is then cured as described in Example 29.

EXAMPLE 32

Two parts of 4,4'-methylenebis[2,6-di-(1,1,3,3-tetramethylbutyl)phenol] is incorporated in 100 parts of raw butyl rubber prepared by the copolymerization of 90 percent of isobutylene and 10 percent of isoprene and having an average molecular weight of 100,000.

EXAMPLE 33

To 200 parts of raw butyl rubber having an average molecular weight of 600,000 and prepared by copolymerizing 95 percent of isobutylene and 5 percent of butadiene is added 1.5 parts of 4,4'-methylenebis[2,6-di-(2-octyl)phenol].

EXAMPLE 34

To a master batch of GR–N synthetic rubber comprising 100 parts of GR–N rubber having an average molecular weight of 75,000, 5 parts of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 2 parts of mercaptobenzothiazole is added 5 percent based on the weight of the batch of 4,4'-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 35

A dry blend of polystyrene and 4,4'-methylenebis(2-tert-butyl-6-tert-amylphenol) is prepared by mixing 1 part of this phenol with 100 parts of polystyrene having an average molecular weight of 50,000.

EXAMPLE 36

0.25 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol) is incorporated in polybutadiene having an average molecular weight of 50,000.

EXAMPLE 37

To natural rubber (Hevea) is added 0.02 percent of 4,4'-methylenebis(2,6-diisopropylphenol).

The above examples illustrate the improved compositions of this invention. Other such compositions and the methods of preparing the same will now be apparent to one skilled in the art.

EXAMPLE 38

To illustrate the enhanced oxygen resistance of the hydrocarbon polymer compositions of this invention, a natural rubber compounded into a typical tire-tread formula is selected for test. 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 D–599–40T, described in the ASTM Standards for 1952, Part 6. 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 percent of the original elongation and is, therefore, referred to as the T–50 value. In the examples that follow, stocks for testing and comparison are cured for a time sufficient to have a T–50 value of —4.5° C. so that a valid comparison of the properties can be made. The accelerated aging is conducted by the procedure of ASTM designation D–572–52, described in the ASTM Standards for 1952, Part 6, 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 sheets	100.00
Carbon black	45.00
Zinc oxide	5.00
Stearic acid	3.00
Pine tar oil	2.00
Sulfur	3.00
Mercaptobenzothiazole	0.65
	158.65

To demonstrate the protection afforded to the rubber by the inhibitors of our invention, the tensile strength and the ultimate elongation of stocks prepared by the addition of an inhibitor of our invention is determined before and after aging. These properties are compared with the same properties determined on an identical rubber stock not protected by an inhibitor. Both of these properties are determined by means of the test procedure of ASTM designation D–412–51T, fully described in ASTM Standards for 1952, Part 6. The tensile strength is the tension load per unit cross-sectional area required to break a test specimen, while the ultimate elongation is the elongation at the moment of rupture of a test specimen. A decrease in the values for either of these properties upon aging represents a decrease in the usefulness of the article fabricated therefrom, so that the degree to which these propertes are retained is a direct measure of the utility of the protective substance.

EXAMPLE 39

The inhibitors of this invention find particular utility in the stabilization of light colored hydrocarbon polymers where non-staining characteristics of the inhibitor are essential. To illustrate the non-staining characteristics of the above described phenolic inhibitors in the protection of light colored stocks the following base formula is used.

	Parts by weight
Pale crepe rubber	100.00
Zinc oxide filler	50.00
Titanium dioxide	25.00
Stearic acid	2.00
Ultramarine blue	0.10
Sulfur	3.00
Mercaptobenzothiazole	1.00
	181.10

To the above base formula is added 1 part by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol) and the sample is cured for 45 minutes at 274° F. using perfectly clean molds with no mold lubricant. After curing, a sample of the above protected light colored stock is exposed for 24 hours using a discoloration weatherometer so as to determine the amount of discoloration which occurs during this period of time. It is found that the presence of 4,4'-methylenebis(2,6-di-tert-butylphenol) in this light colored stock causes essentially no discoloration.

Another cured sample of the above light colored stock containing 4,4'-methylenebis(2,6-di-tert-butylphenol) is subjected to a test procedure designed to determine the amount of migration staining. In this test, a piece of the above cured sample is placed beween two steel panels which had been painted with enamel and allowed to dry.

This sample is then exposed for 48 hours at 212° F. in a hot air oven using a 5 pound weight on the panels to maintain rubber-to-metal contact. On completion of this test it is found that essentially no migration staining has occurred.

The amount of inhibitors of this invention employed in hydrocarbon polymers varies from about 0.01 to about 5 percent by weight of the polymer stabilized depending upon the nature of the polymer 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 to the action of sunlight, frictional heat, stress and the like, the use of relatively high concentrations of our inhibitors is advantageous. On the other hand, when the article of manufacture is not to be subjected to such severe conditions, such as in the case of molded goods fabricated from polyethylene, relatively low concentrations of our inhibitor can be successfully utilized.

As noted above the stabilizers of this invention are also excellent additives to tetraalkyllead antiknock compositions. The tetraalkyllead antiknock agents which are stabilized according to this invention are represented by such compounds as tetramethyllead, tetraethyllead, tetrapropyllead, dimethyldiethyllead, trimethylethyllead, and the like, or mixtures thereof. Such compounds containing from 4 to about 12 carbon atoms, one atom of lead and a plurality of lead-to-carbon bonds, are capable of increasing the octane quality of gasoline when employed therein in antiknock quantities—0.5 to 6.5 grams of lead per gallon. Halogen-containing compounds such as triethyllead bromide may also be stabilized according to this invention.

The scavengers which are preferably, but not necessarily, present in the antiknock compositions of this invention are organic halide compounds which react with the lead during combustion in the engine to form volatile lead halide. The halogen of these scavengers has an atomic weight between 35 and 80; that is, the active scavenging ingredient is chlorine and/or bromine. Such scavengers include carbon tetrachloride, propylene dibromide, 2-chloro-2,3-dibromobutane, 1,2,3-tribromopropane, hexachloropropylene, mixed bromoxylenes, 1,4-dibromobutane, 1,4-dichloropentane, β,β'-dibromodiisopropyl ether, β,β'-dichlorodiethyl ether, trichlorobenzene, dibromotoluenes, and in general those disclosed in U.S. Patents 1,592,954; 1,668,022; 2,364,921; 2,479,900; 2,479,901; 2,479,902; 2,479,903; and 2,496,983. In short, we prefer to employ scavengers containing only elements selected from the group consisting of carbon, hydrogen, bromine, chlorine and oxygen. The amount of scavenger used is from about 0.5 to about 2.0 theories, a theory being defined as the quantity required to react with the lead to form lead halide—i.e. 2 atoms of halogen per atom of lead. When we use mixtures of bromine-containing and chlorine-containing scavengers, particularly bromo and chlorohydrocarbons, we can employ concentrations and proportions as described in U.S. Patent 2,398,281. Such concentrations are sufficient to control the amount of deposits formed in the engine.

Representative tetraalkyllead antiknock compositions of this invention are presented in Table VI following. The figures following the representative ingredients are parts by weight. The two figures following the stabilizing ingredient show respectively the amounts which are used to obtain a composition containing 0.1 and 1.0 percent by weight of stabilizer based on the lead alkyl antiknock agent. It will be apparent that if the lower figure is halved, the resulting composition will contain 0.005 percent by weight of the stabilizing ingredient based on the lead alkyl, whereas doubling the second figure will provide a composition containing 2.0 percent. Should other concentrations be desired, the proper adjustments are evident.

Table VI

ANTIKNOCK FLUID COMPOSITIONS

Antiknock agent	Scavenger	Stabilizer
Tetramethyllead 267	None	4,4' - methylenebis[2,6 - di - (1,1,3,3 - tetramethylbutyl)phenol], 0.27–2.67.
Do	Ethylene dibromide 226	4,4' - methylenebis(2,6 - diisopropylphenol), 0.27–2.67.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	4,4' - methylenebis(2 - isopropyl - 6 - tert - butylphenol), 0.27 – 2.67.
Tetraethyllead 323	None	4,4' - methylenebis[2 - isopropyl - 6 - (1,1,3,3-tetramethylbutyl) phenol], 0.32–3.23.
Do	Ethylene dibromide 188.	4,4' - methylenebis(2,6 - di - tert - butylphenol), 0.32–3.23.
Do	Ethylene dibromide 94 and ethylene dichloride 99.	4,4' - methylenebis(2,6 - di - tert - amylphenol), 0.32–3.23.
Do	Mixed dibromotoluenes 200.	4.4' - methylenebis(2,6 - di - tert - butylphenol) 0.32–3.23.
Do	Mixed dibromotoluenes 125 and ethylene dichloride 99.	4,4' - methylenebis[2,6 - di - (1,1,3,3 - tetramethylbutyl)phenol], 0.32–3.23.
Do	Mixed dibromotoluenes 150 and 1,2,4-trichlorobenzenes 175.	4,4' - methylenebis(2,6 - diisopropylphenol), 0.32–3.23.
Do	Ethylene dibromide 94 and mixed trichlorobenzenes 146.	4,4' - methylenebis(2,6 - di - tert - butylphenol), 0.32–3.23.
Do	1,4 - dibromobutane 216.	4,4' - methylenebis[2,6 - di - (1,1,3,3 - tetramethylbutyl)phenol], 0.32–3.23.
Do	1,4 - dibromobutane 108 and 1,4 - dichlorobutane 127.	4,4' - methylenebis(2 - tert - butyl - 6 - tert - amyl - phenol), 0.32–3.23.
Tetrapropyllead 379	Acetylene tetrabromide 346.	4,4' - methylenebis[2,6 - di - (2 - octyl)phenol], 0.38–3.79.
Dimethyldiethyllead 295.	β,β' - Dibromodiethyl ether 232.	4,4' - methylenebis[2 - tert - butyl - 6 - (1,1,2,2-tetramethylpropyl) phenol], 0.30–2.54.
Methyltriethyllead 309.	β,β' - Dibromodiisopropyl ether 130 and β,β' - dichlorodiethyl ether 143.	4,4' - methylenebis(2,6 - di - tert - butylphenol) 0.31–3.09.

The antiknock fluid compositions shown in the above table are presented for illustrative purposes only. Other such compositions will be apparent to one skilled in the art. In all instances, the presence of the compound of this invention enhances the stability characteristics of the formulation over those prevailing in the absence of our stabilizer.

To demonstrate the unexpected potency of the compounds of this invention and particularly 4,4'-methylenebis(2,6-di-tert-butylphenol) as tetraalkyllead stabilizers, recourse was had to accelerated fluid storage tests. Portions of an antiknock fluid consisting essentially of tetraethyllead, 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride were placed in glass bottles containing 80 percent outage; that is, the bottles contained 80 percent by volume of air. In one instance, 4,4'-methylenebis(2,6-di-tert-butylphenol) was blended with the above antiknock fluid so that the concentration of this stabilizer was 0.06 percent by weight based upon the weight of the tetraethyllead present. The sample was stored at 50° C. for a period of 168 hours. The amount of antiknock fluid decomposition which occurred during this stringent storage test was found by determining the ammonia-soluble lead contents of the samples by chemical analysis. Basically the method involves extracting from the samples all lead salts formed during storage by means of an ammonia-ammonium acetate solution and assaying the amount of such salts in the extract by conventional means. Thus, the method provides a reliable measure of the amount of decomposition which has occurred during the storage test described above. The results of this test show that the compound

is an excellent stabilizer for tetraethyllead containing antiknock fluids.

Another method of demonstrating the benefits of this invention is to conduct storage test procedures. For example, antiknock fluid compositions of this invention and comparable formulations not containing our stabilizer are placed in glass or cold rolled steel containers which are then stored at a constant temperature of 122° F. under air. Periodic inspection and analysis of the samples shows that the unprotected antiknock fluid compositions continually deteriorate with the formation of insoluble sludges and other decomposition products, whereas those formulations of this invention remain practically unchanged.

The tetraalkyllead antiknock compositions of this invention may contain other ingredients such as dyes for identification purposes, metal deactivators, diluents and the like.

Antiknock compositions containing tetraalkyllead antiknock agents are employed by adding them to gasoline to improve the antiknock quality thereof. Such gasolines both before and after addition of the antiknock fluid are benefited by the practice of this invention. Thus gasolines to which have been added a compound of this invention are found to be more stable upon prolonged periods of storage.

The following examples illustrate gasoline embodiments of this invention.

EXAMPLE 40

To 10,000 parts of a grade 115/145 aviation gasoline containing 4.5 ml. of tetraethyllead per gallon which has an initial boiling point of 110° F. and a final boiling point of 330° F. and an API gravity of 71.0° is added .5 percent of 4,4′-methylenebis(2,6-di-tert-butylphenol).

EXAMPLE 41

To a gasoline containing 26.6 percent aromatics, 20.8 percent olefins and 52.6 percent saturates and which has an API gravity of 62.1° is added 0.1 percent of 4,4′-methylenebis(2,6-diisopropylphenol).

Similarly, other compounds of this invention may be added with benefit to gasoline of whatever nature and however processed.

As noted above the compounds of this invention are also extremely useful in inhibiting and stabilizing non-petroleum fats and oils normally subject to the deteriorating effect of oxidative rancidity. In particular, compounds of this invention are excellent stabilizers for animal fats and oils, especially lard, against the effects of rancidity. The compounds of this invention may be used in concentrations from 0.001 to about 0.1 weight percent in this embodiment of the invention. In addition, an acid synergist may be employed to promote the activity of the additives of this invention. These synergists which mutually cooperate with the compounds of this invention, particularly 4,4′-methylenebis(2,6-di-tert-butylphenol), to produce a disproportionately large increase in effectiveness in stabilizing fatty materials include citric acid, phosphoric acid, abscorbic acid, ethyl acid phosphate, glucuronolactone, phytic acid, tartaric acid and aconitic acid.

In formulating the stabilized non-petroleum fats and oils of this invention, the additive or combination of additives is incorporated by appropriate means into the substrate to be stabilized. Thus, in the case of animal, vegetable and fish oils, the additive or combination of additives is added in appropriate quantity and the resulting mixture agitated to insure homogeneity. Where the substrate is a solid at room temperatures—e.g., fats, butter, etc.—the mixing is preferably carried out at temperatures above the melting point of the substrate. When a combination of additives is used, they can be mixed with the substrate as a preformed mixture or can be separately blended therewith in either order. Generally speaking, it is desirable to first dissolve the additive or additive combination in high concentration in a small portion of the material to be stabilized. The resulting concentrated solution is then blended with the remaining bulk. Another way of facilitating the formulation of the composition of this invention is to pre-dissolve the additive or combination of additives in a suitable solvent, such as ethanol, glycerol, propylene glycol, etc. and then mix the resultant solution with the material to be stabilized. However, the preferred way of formulating the compositions of this invention is to pre-dissolve the additive or additive mixture in a fatty acid partial ester of a polyhydroxy compound, notably a monoglyceride, and then blend this mixture with the material to be stabilized. The nature of these monoglyceride compositions is well known in the art and may be made from either animal or vegetable fats, with or without previous hydrogenation. These compositions generally contain about 40 percent of the monostearyl, monooleyl, and/or monopalmityl glycerides or mixtures thereof with the balance comprising a mixture of di- and tri-glycerides. Molecularly distilled monoglycerides may also be used for this purpose. These compositions will be apparent from the following examples.

EXAMPLE 42

With 1,000 parts of melted lard is mixed 1 part (0.1 percent) of 4,4′-methylenebis(2,6-di-tert-butylphenol). After cooling the lard can be stored for long periods of time without the development of rancidity.

EXAMPLE 43

With 5,000 parts of cottonseed shortening is blended 0.05 part (0.001 percent) of 4,4′-methylenebis(2-isopropyl-6-tert-butylphenol). The resulting shortening has improved resistance against oxidative rancidity.

EXAMPLE 44

In 2.5 parts of propylene glycol is dissolved with stirring 1 part of 4,4′-methylenebis(2,6-di-tert-butylphenol). The resulting mixture is then added with stirring to 10,000 parts of cod liver oil. The resultant oil containing 0.01 percent of 4,4′-methylenebis(2,6-di-tert-butylphenol) possesses increased resistance against oxidative deterioration.

EXAMPLE 45

To 10,000 parts of corn oil are added with stirring 5 parts (0.05 percent) of 4,4′-methylenebis(2,6-di-tert-amylphenol) and 2 parts (0.02 percent) of ascorbic acid. The resulting corn oil has improved storage stability characteristics.

EXAMPLE 46

To 100 parts of monoglyceride (prepared from a partially hydrogenated vegetable oil) heated to 180° F. is added with stirring 5 parts of 4,4′-methylenebis(2,6-di-tert-butylphenol) and 4 parts of citric acid. Ten parts of the resultant monoglyceride formulation are added with stirring to 10,000 parts of melted prime steam lard. The lard composition so formed which contains 0.005 percent of 4,4′-methylenebis(2,6-di-tert-butylphenol) and 0.004 percent of citric acid can be stored at room temperature for long periods of time without developing rancidity.

Those skilled in the art will now clearly understand the various methods of preparing the improved compositions of this invention.

To illustrate the outstanding results achieved by the practice of this invention, a series of experiments was carried out using lard. In these experiments, the standard accelerated test known as the active oxygen method (AOM) was used. This test is described in Oil and Soap, 20, 169–171 (1943). See also Oil and Soap, 10, 106–109 (1933). According to this method, the development of rancidity in fats and oils is determined by bubbling air through test samples held at a temperature of 208° F. and measuring their peroxide contents. Values are usually reported in hours required to attain a given peroxide number. Thus, the longer the time required to reach a

certain peroxide value, the more effective is the antioxidant.

In the present tests, the test lard, when devoid of an antioxidant, had an AOM stability of 3.25 hours. The presence of 0.01 percent by weight of 4,4'-methylenebis-(2,6-di-tert-butylphenol) in this test lard provided an AOM stability of 64 hours which represents a tremendous increase in the stability of the lard. This can be readily appreciated by noting that it is generally considered that an AOM stability period of 20 hours is usually sufficient for all practical purposes, which means that the lard will be stable under the usual conditions encountered in storage or in homes for a period of 6 to 9 months. Therefore, the practice of this invention provides lard compositions which may be stored for considerably longer periods of time without danger of rancidity.

The compounds of this invention are white crystalline solids and are soluble in various organic solvents and in gasolines, diesel fuels, hydrocarbon oils and the like. These compounds are further characterized by being relatively stable, non-hygroscopic, readily crystallizable materials.

The compounds of this invention are prepared by reacting formaldehyde with a 2,6-dialkylphenol in which both alkyl groups contain from 3 to 8 carbon atoms, both of said alkyl groups being branched on their alpha carbon atoms. In conducting this process according to a preferred embodiment, approximately two moles of the above-defined phenol are condensed with each mole of formaldehyde employed, using an alkali metal hydroxide such as sodium hydroxide as catalyst. This condensation reaction is conducted in a solvent consisting essentially of a monohydric alcohol containing from 1 to about 8 carbon atoms, preferably isopropyl alcohol. The reaction temperature is in the range of from about 20 to about 100° C. and preferably in the range of from about 50 to about 60° C.

The alkali metal hydroxide catalyst is used in catalytic quantities, namely, in amount equivalent to from about 0.5 to about 3 percent by weight of the phenol used in the reaction.

The following examples, wherein all parts and percentages are by weight, illustrate the compounds of this invention and the methods by which they are prepared.

EXAMPLE 47

In a reaction vessel equipped with stirring means, condensing means, thermometer and reagent introducing means was placed a solution of 6.6 parts of potassium hydroxide dissolved in 400 parts of isopropanol. To this stirred solution maintained under nitrogen atmosphere was added 206 parts of 2,6-di-tert-butylphenol. At a temperature of 30° C. a total of 45.4 parts of 37 percent formalin solution was added dropwise. On heating to 60° C. a red color developed and a precipitation of crystalline product began. The mixture was stirred for 1½ hours at 60° C., cooled and the solid filtered off. The product was washed twice with 200 parts of isopropanol containing 10 parts of concentrated hydrochloric acid. After drying, the yield of product was 87 percent, melting point 154 to 155° C. The following chemical analysis showed the compound to be 4,4'-methylenebis(2,6-di-tert-butylphenol): Calculated for $C_{29}H_{44}O_2$, 82.2 percent carbon and 10.4 percent hydrogen. Found: 81.8 percent carbon and 10.5 percent hydrogen.

EXAMPLE 48

Using the reaction equipment of Example 47, 178 parts of 2,6-diisopropylphenol is reacted with 45.3 parts of 37 percent formalin solution in the presence of 6.6 parts of potassium hydroxide. 400 parts of isopropanol is used as the solvent. The reaction temperature is 50° C. A good yield of 4,4'-methylenebis(2,6-diisopropylphenol) is obtained by hydrolyzing the reaction mixture and extracting the product with ethyl ether. Evaporation of the ether solution gives an oil which slowly crystallizes.

EXAMPLE 49

4,4'-methylenebis[2,6 - di - (1,3,3-tetramethylbutyl) phenol] is prepared as follows: In the reaction vessel of Example 47 are placed 318 parts of 2,6-di-(1,1,3,3-tetramethylbutyl)phenol, 6.6 parts of potassium hydroxide, 45.3 parts of 37 percent aqueous formalin solution and 400 parts of isopropanol. This mixture is stirred at 60° C. for 2½ hours. On cooling, the crystalline product which is formed is filtered off.

EXAMPLE 50

In the reaction vessel of Example 47 are placed 492 parts of 2-isopropyl-6-tert-butylphenol, 4 parts of sodium hydroxide, 45.3 parts of aqueous formalin solution and 400 parts of isopropanol. This mixture is stirred at 65° C. for 3 hours. The mixture is then poured into excess cold water, extracted with ethyl ether, and the ether evaporated to give a residual oil which slowly crystallizes. This crystalline product is 4,4'-methylenebis(2-isopropyl-6-tert-butylphenol).

EXAMPLE 51

In the reaction equipment described in Example 47 and using 400 parts of isopropanol as reaction solvent and 4 parts of sodium hydroxide as condensation catalyst, 234 parts of 2,6-di-tert-amylphenol is reacted with 45.3 parts of 37 percent aqueous formalin solution. The temperature of this condensation reaction is 60° C. and the reaction time is 2½ hours. The solid material which precipitates is filtered off to give 4,4'-methylenebis(2,6-di-tert-amylphenol).

EXAMPLE 52

4,4'-methylenebis(2-sec-butyl-6-tert-butylphenol) is prepared as follows: To the reaction vessel of the apparatus described in Example 47 are added 208 parts of 2-sec-butyl-6-tert-butylphenol, 45.3 parts of 37 percent aqueous formalin solution, 4 parts of sodium hydroxide and 400 parts of n-propanol. The reactants are maintained at a temperature of 70° C. for a perod of 3 hours. The reaction mixture is then poured into cold water, extracted with ethyl ether, from which is recovered the crystalline 4,4'-methylenebis(2-sec-butyl - 6 - tert-butylphenol) by evaporating off the ether.

EXAMPLE 53

310 parts of 2,6-di-(1,1,2,2-tetramethylpropyl)phenol is reacted with 45.3 parts of 36 percent aqueous formalin solution in the reaction equipment described in Example 47. 500 parts of isopropanol is used as reaction solvent and 6.6 parts of potassium hydroxide is used as the condensation catalyst. The reaction temperature is 60° C. and the reaction time is 3 hours. 4,4'-methylene bis[2,6-di-(1,1,2,2-tetramethylpropyl)phenol] is recovered by filtration of the reaction mixture from which this compound crystallizes.

The compounds of this invention are also effective additives to the fuels and lubricants employed in engines fabricated from alloys of the lighter metals such as aluminum and magnesium. When thus employed, the fuels and lubricants of this invention effect substantial reduction in wear and corrosion caused by the chemical activity of certain fuel constituents with the metal alloys in the engine. Thus, another part of this invention is the method of operating an internal combustion engine fabricated primarily from alloys of the lighter metals on conventional fuels and lubricants which contain an additive of this invention as described above in an amount (up to about 5 percent) sufficient to reduce wear and corrosion in the engine.

This application is a continuation-in-part of applications Serial No. 536,315, filed September 23, 1955, now U.S. Patent No. 2,944,086, Serial No. 685,324, filed Sep-

tember 20, 1957, now abandoned, and Serial No. 787,327, filed January 19, 1959, now abandoned.

We claim:

1. Organic material normally subject to oxidative deterioration, containing an antioxidant quantity of a 4,4'-methylenebis(2,6-dialkylphenol) in which all the alkyl groups contain from 3–8 carbon atoms, which alkyl groups are all branched on their respective alpha carbon atoms.

2. The composition of claim 1 wherein said organic material is liquid petroleum hydrocarbon.

3. Organic material tending to deteriorate in the presence of air, oxygen or ozone, protected by an antioxidant quantity of a 4,4'-methylenebis(2,6-dialkylphenol) in which all the alkyl groups contain from 3–8 carbon atoms, which alkyl groups are all branched on their respective alpha carbon atoms, said organic material being selected from the class consisting of liquid petroleum hydrocarbon, petroleum wax, petroleum grease, rubber, fats and oils of animal and vegetable origin, tetraalkyllead antiknock fluid, synthetic diester oil, polyvinyl acetate, epoxide resins, polyester resins and alkyd polymers.

4. The composition of claim 3 wherein said 4,4'-methylenebis(2,6-dialkylphenol) is 4,4'-methylenebis(2,6-di-tert-butylphenol).

5. A fatty material normally subject to the deteriorating effect of oxidative rancidity containing from about 0.001 to about 0.1 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol).

6. An antiknock fluid composition for addition to gasoline consisting essentially of tetraalkyllead compounds and halohydrocarbon scavengers therefor protected against oxidative deterioration by small antioxidant quantity of 4,4'-methylenebis(2,6-di-tert-butylphenol).

7. Rubber normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

8. Lubricating oil normally susceptible to oxidative deterioration containing from about 0.001 to about 2 percent by weight of a 4,4'methylenebis(2,6-dialkylphenol) in which all the alkyl groups contain from 3 to 8 carbon atoms, which alkyl groups are all branched on their respective alpha carbon atoms.

9. The lubricating oil composition of claim 8 wherein said lubricating oil is a mineral lubricating oil.

10. The lubricating oil composition of claim 9 wherein said 4,4'-methylenebis(2,6-dialkylphenol) is 4,4'-methylenebis(2,6-di-tert-butylphenol).

11. The composition of claim 3 wherein said organic material is gasoline.

12. The rubber composition of claim 7 wherein the rubber is a butadiene-styrene rubbery copolymer.

13. The composition of claim 3 wherein said organic material is a wax selected from the class consisting of paraffin wax and microcrystalline petroleum wax.

14. A polybutadiene rubber normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

15. Butyl rubber normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis-(2,6-di-tert-butylphenol).

16. Corn oil normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

17. Cotton seed oil subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

18. Lard normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

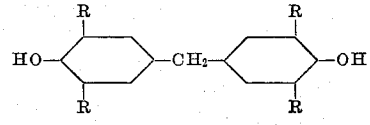
19. Liquid petroleum hydrocarbon normally subject to oxidative deterioration containing a small antioxidant quantity, sufficient to inhibit said deterioration, of 4,4'-methylenebis(2,6-di-tert-butylphenol).

20. Crankcase lubricating oil containing a viscosity index improver and normally subject to oxidative deterioration, said oil containing as an antioxidant therefor from 0.40 to 1.50 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol).

21. The composition of claim 1 wherein said organic material is an aliphatic mono-olefin hydrocarbon polymer which is substantially saturated.

22. The composition of claim 21 wherein said substantially saturated hydrocarbon polymer is polypropylene.

23. A polyethylene composition stabilized to thermal oxidation which comprises polyethylene and from 0.001 to about 2.0 percent by weight of an antioxidant material which is a member of the 4,4'-methylenebis(2,6-dialkylphenol) class of compounds having the general formula:



wherein R is an alkyl radical that is selected from the group consisting of isopropyl and tertiary butyl radicals.

24. The polyethylene composition of claim 23 wherein the antioxidant is 4,4'-methylenebis(2,6-di-tert-butylphenol).

25. The polyethylene composition of claim 23 wherein the antioxidant is 4,4'-methylenebis(2,6-diisopropylphenol).

26. Mineral oil containing a viscosity index improver, a rust preventative and an extreme pressure agent and normally subject to oxidative deterioration, said oil containing as an antioxidant therefor from 0.5 to 1.0 percent by weight of 4,4'-methylenebis(2,6-di-tert-butylphenol).

References Cited in the file of this patent

UNITED STATES PATENTS

2,570,402	Stevens et al.	Oct. 9, 1951
2,675,366	Pullman	Apr. 13, 1954
2,734,088	Knowles et al.	Feb. 7, 1956
2,745,726	Young et al.	May 15, 1956
2,796,445	Sullivan	June 18, 1957
2,816,945	Beaver et al.	Dec. 17, 1957
2,820,775	Chamberlain et al.	Jan. 21, 1958
2,822,404	Ambelang	Feb. 4, 1958
2,862,976	Dubbs et al.	Dec. 2, 1958

FOREIGN PATENTS

722,873	Great Britain	Feb. 2, 1955

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,043,775 July 10, 1962

Thomas H. Coffield et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 1 and 2, for "Thomas H. Coffield, of Heidelberg, Germany, and Allen H. Fibey, of Walled Lake, Michigan," read -- Thomas H. Coffield, of Heidelberg, Germany, and Allen H. Filbey, of Walled Lake, Michigan, assignors to Ethyl Corporation, of New York, N. Y., a corporation of Delaware, --; line 11, for "Thomas H. Coffield and Allen H. Fibey, their heirs" read -- Ethyl Corporation, its successors --; in the heading to the printed specification, lines 4 and 5, for "Thomas H. Coffield, Heidelberg, Germany, and Allen H. Filbey, 2290 Robell Drive, Walled Lake, Mich." read -- Thomas H. Coffield, Heidelberg, Germany, and Allen H. Filbey, Walled Lake, Mich., assignors to Ethyl Corporation, New York, N. Y., a corporation of Delaware --; column 20, Table VI, column 3, line 48 thereof, for "0.30-2.54" read -- 0.30-2.95 --.

Signed and sealed this 20th day of November 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents