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2,928,790

PETROLEUM HYDROCARBON OIL STABILIZED AGAINST OXIDATIVE DETERIORATION

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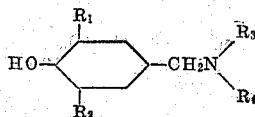
5 Claims. (Cl. 252—46.7)

This invention relates to petroleum hydrocarbon oils of improved performance characteristics, notably enhanced resistance against oxidative deterioration at elevated temperature.

Petroleum hydrocarbon oils—e.g., lubricating oils, turbine oils, transformer oils, cutting oils, etc.—undergo oxidative deterioration in service, particularly at elevated temperatures short of the cracking temperature of the particular oil. This deterioration results in the formation of gums and insoluble sludges, the corrosion of metal parts of the equipment with which the oils are used, the loss of useful properties of the oil, and the like. While some antioxidants have been developed which are somewhat effective in inhibiting this deterioration, these antioxidants had to be used at relatively high concentrations in order to provide effective prolongation of the useful life of the hydrocarbon oils. Other prior antioxidants have possessed limited solubilities in the oils. Still others are quite effective at low temperatures but are essentially ineffective when the oil is subjected to drastic oxidizing conditions, such as elevated temperatures, and the presence in the oil of metallic substances tending to catalyze the deterioration of the oil.

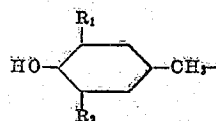
An object of this invention is to provide petroleum hydrocarbon oil characterized by enhanced resistance to oxidative deterioration, particularly at elevated temperatures below the cracking temperature of the oil. Another object of this invention is to provide additives which are capable of markedly enhancing the resistance of petroleum hydrocarbon oils to oxidative deterioration, especially at elevated temperatures. A further object is to provide synergistic combinations of additives which are particularly useful in inhibiting the oxidative deterioration of petroleum hydrocarbon oils normally tending to deteriorate in the presence of air at elevated temperatures. Other important objects of this invention will become apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing petroleum hydrocarbon oil normally tending to deteriorate in the presence of air at elevated temperatures below the cracking temperature of the oil containing from about 0.05 to about 2 percent by weight each of a P_2S_5 -terpene reaction product and a 3,5-dialkyl-4-hydroxybenzyl amine having the general formula



wherein R_1 is an alkyl group containing from 1 to 12 carbon atoms, R_2 is an alkyl group containing from 3 to 12 carbon atoms which is branched on the alpha carbon atom, R_3 is selected from the group consisting of alkyl, cycloalkyl, aralkyl, aryl, alkaryl, and

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and R_4 is selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl, aryl and alkaryl.

Such petroleum hydrocarbon oil possesses unexpectedly great resistance against oxidative deterioration, this resistance resulting from the presence therein of a combination of additives which co-act synergistically.

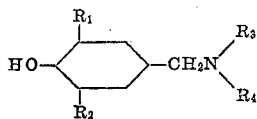
The petroleum hydrocarbon oils used in formulating the compositions of this invention include lubricating oils, turbine oils, transformer oils, cutting oils, and, in general, engine oils and industrial oils derived from crude petroleum. It is well known that such oils are susceptible to oxidative deterioration in the presence of air even when maintained at normal temperatures. Not only does this invention virtually eliminate this type of deterioration, but significantly it provides enhanced resistance to oxidative deterioration when the oils are maintained at elevated temperatures short of their cracking temperatures—about 550° to about 600° F. or higher, depending upon the particular oil. This invention is particularly applicable to the stabilization of petroleum hydrocarbon oil normally tending to deteriorate in the presence of air at elevated temperatures below the cracking temperature of the oil where the deterioration is catalyzed by the presence of iron oxide. With crankcase lubricating oils, gear oils, cutting oils, and the like, the problem of oxidative deterioration is particularly troublesome because of the combined effect of elevated temperature and the presence in the oil of iron oxides which are readily formed under these drastic conditions. Unexpectedly, the synergistic combination of additives employed pursuant to this invention is particularly effective in inhibiting this type of deterioration, while at the same time, overcoming the deterioration occurring under less stringent conditions, such as storage in the presence of air at room temperature.

The additives employed in the improved petroleum hydrocarbon oil compositions of this invention provide a remarkable synergistic effect under a wide variety of operating conditions whereby unexpected and disproportionately increased antioxidant and stabilizing effects are realized, even though the total amount of additives so employed is small. The advantages of this are many. In the first place, enhanced oxidation resistance is achieved at low cost. Secondly, when the additives are used in normal concentration levels, superlative results are achieved because of the unusually high degree of synergistic co-action which they exhibit. Third, the additives of this invention can be employed in less than normal concentration levels while, at the same time, providing effective stabilization. Moreover, the synergistic co-action of the additives of this invention obviates the necessity of employing them at high concentrations in petroleum hydrocarbon oils which are to be subjected to drastic oxidizing conditions. This, in turn, means that solubility problems with respect to the additives are not encountered.

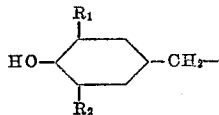
The P_2S_5 -terpene reaction product used in the compositions of this invention is obtained by reacting a terpene compound with P_2S_5 , a well-known phosphorizing agent. These reaction products are well known in the art, the literature describing their preparation. Many of them are available as articles of commerce. These reaction products can be prepared from monocyclic terpenes, such as dipentene, terpinolene, p-menthenes, α -terpineol, limonene, terpinene, sabinene, ocimene, myrcene, carene, terpenes obtained as a by-product in the manufacture of

synthetic camphor, and the like. It is preferable, however, to use P_2S_5 -reaction products formed with dicyclic terpenes since in the preparation of these reaction products, only a relatively small amount of hydrogen sulfide is evolved. Thus, reaction products formed from dicyclic terpenes contain relatively high percentages of phosphorus and sulfur in the molecule. The nature of these dicyclic terpenes is well known—they are characterized by the presence of one double bond in the molecule and are built up of two-ring systems. Thus, it is preferred, in the practice of this invention, to use P_2S_5 -reaction products of such dicyclic terpenes as α -pinene, β -pinene, turpentine (which consists chiefly of α -pinene), camphene, fenchene, pine oil, bornylene, borneol, isoborneol, and the like. Those formed from turpentine and α -pinene are particularly preferred, because the starting materials are readily available and inexpensive, and the P_2S_5 -reaction products derived therefrom are particularly effective in the practice of this invention.

The second additive used in the compositions of this invention is a 3,5-dialkyl-4-hydroxybenzyl amine having the general formula



wherein R_1 is an alkyl group containing from 1 to 12 carbon atoms, R_2 is an alkyl group containing from 3 to 12 carbon atoms which is branched on the alkyl carbon atom, R_3 is selected from the group consisting of alkyl, cycloalkyl, aralkyl, aryl, alkaryl and



and R_4 is selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl, aryl and alkaryl. In the above compounds it is preferable that the hydrocarbon radicals of the groups designated above as R_3 and R_4 contain the following ranges of carbon atoms: alkyl, 1 to 12; cycloalkyl, 5 to 6; aralkyl, 7 to 11; aryl, 6 to 10; and alkaryl, 7 to 15.

A preferred embodiment of this invention is to use as this second additive compounds of the above formula in which R_3 and R_4 are both lower alkyl groups, i.e., alkyl groups containing from 1 to 4 carbon atoms. These compounds have very good solubility characteristics in most petroleum hydrocarbon oils and produce a substantial synergistic effect when acting in concert with the P_2S_5 -terpene reaction products.

A particularly preferred embodiment of this invention is mineral oil normally tending to deteriorate in the presence of air at elevated temperature below the cracking temperature of the oil containing from about 0.05 to about 2 percent by weight each of a P_2S_5 -dicyclic terpene reaction product and N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine. Such oils possess outstanding resistance against oxidative deterioration because of the large synergistic effect caused by the particular combination of additives.

In formulating the improved petroleum hydrocarbon oils of this invention, the above synergistic additives are blended in appropriate quantity with the oil, the P_2S_5 -terpene reaction product and the amine being used either as a preformed blend or mixture, or by adding them separately in either order.

The following examples illustrate various specific embodiments of this invention. The physical characteristics of the illustrative oils used in these examples are shown in Table I.

TABLE I

Properties of representative petroleum hydrocarbon oils

Oil	A	B	C	D	E	F
Gravity at 60° A.P.I.	30.3	30.5	28.8	31.1	20.5	31.0
Viscosity, Saybolt:						
Seconds at 100° F.	178.8	373.8	309.8	169.0	249.4	335.4
Seconds at 210° F.	52.0	58.4	63.8	51.5	45.7	68.4
Viscosity Index	154.2	107.4	141.9	157.8	35.8	144.4
Pour Point	-30	+10	-20	-15		0
Flash Point	410	465			365	385
Sulfur, Percent	0.2	0.3	0.3	0.3	0.3	0.1

EXAMPLE I

To 100,000 parts of oil A is added with stirring 1000 parts (1 percent) of a P_2S_5 -turpentine reaction product prepared by heating about 4 moles of gum spirits of turpentine with 1 mole of P_2S_5 to 250° F. To this oil is then added 1000 parts (1 percent) of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.

EXAMPLE II

To 100,000 parts of oil B are added 50 parts (0.05 percent) of N-methyl-N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl) amine and 50 parts (0.05 percent) of a reaction product between 1 mole P_2S_5 and 4 moles of α -pinene formed at 300° F. The resulting oil is stirred to insure homogeneity.

EXAMPLE III

With 100,000 parts of oil C are blended 100 parts (0.1 percent) of N,N-di-methyl-N-(3,5-diisopropyl-4-hydroxybenzyl) amine and 1000 parts (1 percent) of a P_2S_5 -dipentene reaction product made from 6 moles of dipentene per mole of P_2S_5 at 280° F.

EXAMPLE IV

To 100,000 parts of oil D are added 500 parts (0.5 percent) of N-cyclohexyl-N-(3-methyl-5-isopropyl-4-hydroxybenzyl) amine and 500 parts (0.5 percent) of a P_2S_5 -fenchene reaction product made from 8 moles of fenchene per mole of P_2S_5 at 300° F.

EXAMPLE V

With 100,000 parts of oil E are blended 1000 parts (1 percent) of N,N-diethyl-N-(3-isopropyl-5-tert-butyl-4-hydroxybenzyl) amine and 200 parts (0.2 percent) of a P_2S_5 -terpinene reaction product made from 2 moles of terpinene per mole of P_2S_5 at 275° F.

EXAMPLE VI

To 100,000 parts of oil F containing 50 parts (0.05 percent) of a P_2S_5 - α -pinene reaction product (pinene: P_2S_5 , 10:1; temperature, 320° F.) is added 1500 parts (1.5 percent) of N-octyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.

EXAMPLE VII

With 100,000 parts of oil A are blended 2000 parts (2 percent) of N-butyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine and 2000 parts (2 percent) of a P_2S_5 -turpentine reaction product made at 260° F. from 4 moles of turpentine per mole of P_2S_5 .

EXAMPLE VIII

To 100,000 parts of oil B are added 250 parts (0.25 percent) of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine and 500 parts (0.5 percent) of a P_2S_5 -pinene reaction product made at 300° F. from 4 moles of pinene per mole of P_2S_5 .

EXAMPLE IX

To 100,000 parts of oil C are added 1500 parts (1.5 percent) of N-butyl-N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl) amine and 1000 parts (1 percent) of a P_2S_5 -menthene reaction product made at 280° F. from 5 moles of menthene per mole of P_2S_5 .

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EXAMPLE X

To 100,000 parts of oil D are added 1000 parts (1 percent) of N-phenyl-N,N-bis-(3,5-diisopropyl-4-hydroxybenzyl) amine and 500 parts (0.5 percent) of a P_2S_5 -borneol reaction product made at 290° F. from 8 moles of borneol per mole of P_2S_5 .

EXAMPLE XI

To 100,000 parts of oil E containing 1000 parts (1 percent) of a P_2S_5 -camphene reaction product (camphene: P_2S_5 , 6:1; temperature, 280° F.) is added 500 parts (0.5 percent) of N-benzyl-N,N-bis-(3-methyl-5-(1,1,3,3-tetramethyl-butyl)-4-hydroxybenzyl) amine.

EXAMPLE XII

With 100,000 parts of oil F are blended 200 parts (0.2 percent) of N,N-didodecyl-N-(3-methyl-5-tert-butyl-4-hydroxybenzyl) amine and 500 parts (0.5 percent) of a P_2S_5 -turpentine reaction product made at 260° F. from 4 moles of turpentine per mole of P_2S_5 .

Greatly increased resistance to oxidative deterioration resulting from substantial synergistic co-action is exhibited by each of the above illustrative compositions of this invention. Particularly striking results are achieved from those compositions containing as one of the additives P_2S_5 -turpentine and P_2S_5 -pinene reaction products, especially when these materials are used in admixture with N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine (Examples I and VIII).

To illustrate the greatly improved oxidation resistance of the compositions 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 Tests for Lubricating Oils and Its Correlation with Engine Performance," Anal. Chem., 21 737 (1949). This test effectively evaluates the performance of petroleum hydrocarbon oil antioxidants. The test equipment and procedure employed and correlation of the results with engine performance are discussed in the first paper above cited.

To demonstrate the synergistic nature and the preeminence of the additives of this invention in inhibiting oxidative deterioration of petroleum hydrocarbon oils even when catalyzed by iron oxide, tests were conducted using the Polyveriform test apparatus. In these tests, the base oil used was an initially additive-free, 95 V.I. solvent-refined SAE 10 petroleum hydrocarbon crankcase lubricating oil. A stringent oxidation catalyst, 0.05 percent by weight of ferric oxide as ferric - 2 - ethylhexoate, was placed in each oil sample together with 0.10 percent by weight of lead bromide which is used in the test oil as a part of the standard test procedure. The Polyveriform apparatus was operated under the following test conditions: The introduction of 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 300° F. The criteria used for oxidative deterioration of the oil upon completion of the above stringent oxidation tests were the acid number of the test oil and the percent by which the viscosity of the test oil had increased when measured in a Saybolt viscosimeter at 100° F. as compared with the viscosity of the oil at 100° F. before test. Intermittent baseline values on the additive-free oil were obtained and effectiveness of various additives and the additive combinations were directly related to these base line values. Thus, the smaller the acid number and the percent viscosity increase at 100° F., the more effective was the additive constituent.

In one series of tests a commercially available P_2S_5 -turpentine reaction product was used. This product was an amber, viscous liquid containing approximately 5 percent of phosphorus and 13 percent of sulfur and had a specific gravity at 60°/60° F. of 1.02. This product

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was tested in combination with an equal amount of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine. Each of the additives was tested separately in order to show the tremendous synergistic effect which was produced when the additives were used in combination. The results of these tests are shown in Table II.

TABLE II

Effect of additives on oxidation of mineral oil

Test No.	Additive	Additive Conc., percent by weight	Acid No.	Viscosity Increase at 100° F., percent
15	None	-----	7.3	117
2	P_2S_5 -Terpene reaction product	0.25	6.8	84
3	N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine	0.25	6.6	105
4	P_2S_5 -Terpene reaction product + N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.	0.25	2.0	16

The results of test 4 clearly show the outstanding synergistic effect of a typical mineral oil of this invention as compared with the use of the individual additives separately (tests 2 and 3).

In another series of tests, P_2S_5 -terpene reaction product and N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine were used at a concentration of 0.5 percent by weight. The results of these tests are shown in Table III.

TABLE III

Effect of additives on oxidation of mineral oil

Test No.	Additive	Additive Conc., percent by weight	Acid No.	Viscosity Increase at 100° F., percent
35	None	-----	7.3	117
6	P_2S_5 -Terpene reaction product	0.5	3.3	30
7	N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine	0.5	5.9	94
8	P_2S_5 -Terpene reaction product + N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.	0.5	0.6	6

Once again the enormous synergistic effect produced by the practice of this invention is made obvious by the results of test 8 as compared with those of tests 6 and 7.

In another series of tests the P_2S_5 -terpene reaction product was made from α -pinene and contained approximately 5.1 percent of phosphorus. This reaction product was used in combination with N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine. The preeminence of the compositions of this invention is shown by the results in Table IV.

TABLE IV

Effect of additives on oxidation of mineral oil

Test No.	Additive	Additive Conc., percent by weight	Acid No.	Viscosity Increase at 100° F., percent
9	None	-----	5.8	99
10	P_2S_5 -Terpene reaction product	0.4	5.5	76
11	N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine	0.4	5.0	77
12	P_2S_5 -Terpene reaction product + N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.	0.4	1.1	9

It will be seen from the above illustrative data that a truly remarkable synergistic effect is produced by employing the additives in accordance with this invention. It is interesting to note that to achieve the oxidation resistance of the compositions of this invention as obtained in tests 4, 8 and 12, it is necessary to employ a several-

fold increase of either of the anti-oxidants when they are used separately. Thus, the intensive synergistic effect achieved from this invention enables the use of much smaller quantities of the additives, obviates solubility problems and results in a considerable decrease in cost to achieve such outstanding stabilization.

The data shown in Tables II, III and IV are illustrative of the outstanding results achieved by the practice of this invention. Other compositions of this invention give uniformly excellent results, particularly when the preferred additives are used. Thus, this invention makes possible the provision of highly stable crankcase lubricating oils, turbine oils, functional fluids, transformer oils, gear oils, industrial oils, steam cylinder oils, marine engine oils, refrigeration oils, cutting oils, slushing and flushing oils, quenching and drawing oils, greases, wax compositions, and, in general, engine oils and industrial oils derived from crude petroleum.

Another feature of this invention is that the finished oils exhibit improved anti-rust properties by virtue of the additive content. In addition, the additive complement imparts surface active properties of value in various lubricant applications.

As pointed out above, a wide variety of known P_2S_5 -terpene reaction products can be used in the practice of this invention. Generally speaking, they are made by heating from 1 to 10 moles of terpene per mole of P_2S_5 to the reaction temperature of about 250 to 325° F. Particularly efficacious reaction products are those derived from dicyclic terpenes. For further details concerning such reaction products, reference may be had to U.S. Patent 2,379,453. Furthermore, complete discussions concerning the nature of dicyclic and monocyclic terpenes can be found in most standard treatises on organic chemistry.

Typical of the 3,5-dialkyl-4-hydroxybenzyl amines useful in the practice of this invention are:

N-cyclohexyl-N-(3-methyl-5-isopropyl-4-hydroxybenzyl) amine;
 N-benzyl-N-(3,5-diisopropyl-4-hydroxybenzyl) amine;
 N-benzyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-phenyl-N-(3-methyl-5-(2-octyl)-4-hydroxybenzyl) amine;
 N-(3,5-xylyl)-N-(3,5-di-tert-amyl-4-hydroxybenzyl) amine;
 N-cyclohexyl-N,N-bis(3,2-diisopropyl-4-hydroxybenzyl) amine;
 N-(p-butylbenzyl)-N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-benzyl-N,N-bis(3-methyl-5-(1,1,3,3-tetramethylbutyl)-4-hydroxybenzyl) amine;
 N-(α -naphthyl)-N,N-bis(3,5-diisopropyl-4-hydroxybenzyl) amine;
 N-(p-tolyl)-N,N-bis(3,5-di(2-dodecyl)-4-hydroxybenzyl) amine;
 N,N-di(phenyl)-N-(3,5-di(2-hexyl)-4-hydroxybenzyl) amine;
 N-phenyl-N-(p-tolyl)-N-(3,5-di(2-amyl)-4-hydroxybenzyl) amine;
 N-(p-octylphenyl)-N-(3-ethyl-5-tert-butyl-4-hydroxybenzyl) amine;
 N-octyl-N-(3-methyl-5-tert-butyl-4-hydroxybenzyl) amine;
 N-methyl-N-(3,5-diisopropyl-4-hydroxybenzyl) amine;
 N-(2-dodecyl)-N-(3,5-di(2-hexyl)-4-hydroxybenzyl) amine;
 N-sec-butyl-N-dodecyl-N-(3,5-diisopropyl-4-hydroxybenzyl) amine;
 N-propyl-N,N-bis(3-methyl-5-tert-butyl-4-hydroxybenzyl) amine;
 N-(sec-amyl)-N,N-bis(3,5-di-sec-butyl-4-hydroxybenzyl) amine;
 N-decyl-N,N-bis(3-ethyl-5-(3-decyl)-4-hydroxybenzyl) amine;

N-heptyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-isopropyl-N-(3,5-di-tert-amyl-4-hydroxybenzyl) amine;
 N-nonyl-N-(3-tert-butyl-5-tert-amyl-4-hydroxybenzyl) amine;
 N,N-diethyl-N-(3,5-di(1,1,3,3-tetramethylbutyl)-4-hydroxybenzyl) amine;
 N-propyl-N-amyl-N-(3,5-di(1,1,2,2-tetramethylpropyl)-4-hydroxybenzyl) amine;
 N-methyl-N,N-bis(3,5-di-tert-amyl-4-hydroxybenzyl) amine;
 N-heptyl-N,N-bis(3,5-di-tert-amyl-4-hydroxybenzyl) amine;
 N-undecyl-N,N-bis(3-tert-butyl-5-tert-amyl-4-hydroxybenzyl) amine;
 N-methyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-ethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-butyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-isohexyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-ethyl-N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-butyl-N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-tert-amyl-N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl) amine; and the like.

Preferred amines include the following:

N,N-diethyl-N-(3-isopropyl-5-tert-butyl-4-hydroxybenzyl) amine;
 N,N-dibutyl-N-(3,5-diisopropyl-4-hydroxybenzyl) amine;
 N-methyl-N-ethyl-N-(3,5-di(2-octyl)-4-hydroxybenzyl) amine;
 N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N,N-dipropyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 N-methyl-N-ethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine; and the like.

As pointed out above N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine is particularly preferred. These compounds can be prepared as described in U.S. patent application, Serial No. 536,316, filed September 23, 1955.

The petroleum hydrocarbon oils which are improved pursuant to this invention including lubricating oil, transformer oils, turbine oils, cutting oils, gear oils, industrial oils, mineral white oils, glass annealing oils, oils thickened with soaps or inorganic thickening agents (grease), and, in general, engine and industrial oils which are derived from crude petroleum and are normally susceptible to deterioration in the presence of air, particularly at elevated temperatures and most particularly in the presence of iron oxide.

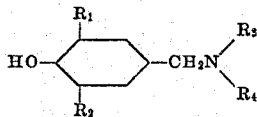
While excellent results are obtained by using each of the additives at a concentration from about 0.05 to about 2 percent by weight, it is preferable that they each be used at a concentration ranging from about 0.25 to about 1 percent by weight. Slight deviations from these concentration ranges are permissible although lower concentrations of either or both of the synergistic additives result in a diminution of the over-all effectiveness of the composition and the extent by which the additives exhibit synergy. On the other hand, concentrations much above the upper ranges described above are impracticable, expensive and may result in solubility problems. In general, it is preferable to employ the additives in substantially equal amounts by weight, although synergistic effects are uniformly achieved by following the concentration ranges set forth above.

Other additives can be successfully used in the mineral oil compositions of this invention. Thus, these oils can contain viscosity index improvers and pour point depressants (methacrylates, acrylates, etc.), extreme pressure agents, detergent-dispersants, dyes, anti-foaming

agents, and the like. For most purposes, however, it is preferable that the oils contain only the combination of additives as set forth hereinabove.

I claim:

1. Petroleum hydrocarbon oil normally tending to deteriorate in the presence of air at elevated temperatures below the cracking temperature of the oil containing from about 0.05 to about 2 percent by weight each of a P_2S_5 -dicyclic terpene reaction product and a 3,5-di-alkyl-4-hydroxybenzyl amine having the formula:



wherein R is an alkyl group containing from 1 to 12 carbon atoms and R_2 is an alkyl group containing from 3 to 12 carbon atoms which is branched on the alpha carbon atom, R_3 and R_4 are lower alkyl groups containing from 1 to 4 carbon atoms.

2. The composition of claim 1 in which R_1 and R_2 are tertiary butyl groups.

3. Petroleum hydrocarbon oil normally tending to deteriorate in the presence of air at elevated temperatures below the cracking temperature of the oil containing from about 0.05 to about 2 percent by weight each of a P_2S_5 -dicyclic terpene reaction product and N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine.

4. The composition of claim 3 in which said P_2S_5 -dicyclic terpene reaction product is a P_2S_5 - α -pinene reaction product.

5. The composition of claim 3 in which said P_2S_5 -dicyclic pinene reaction product is a P_2S_5 -turpentine reaction product.

References Cited in the file of this patent

UNITED STATES PATENTS

2,363,134	McCleary	Nov. 21, 1944
2,379,453	Noland	July 3, 1945

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,928,790

March 15, 1960

John D. Bartleson

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

Column 7, line 46, for "bis(3,2-diisopropyl" read
-- bis-(3,5-diisopropyl --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER

Acting Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,928,790

March 15, 1960

John D. Bartleson

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Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents