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[54] **LUBRICATING OIL COMPOSITION**

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[58] **Field of Search**..... 252/33.2, 33.6, 400

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[57] **ABSTRACT**

Antioxidant additives for lubricating oils and lubricating oil compositions containing said antioxidant additives. The stability of lubricating oil compositions toward oxidizing conditions is markedly improved when an antioxidant additive comprising a mixture of a metal dialkyldithiocarbamate and a Group II*a* metal sulfonate is incorporated therein. The preferred additives comprise mixtures of cadmium diamyldithiocarbamate or antimony dialkyldithiocarbamate with a barium sulfonate or a calcium sulfonate.

13 Claims, No Drawings

LUBRICATING OIL COMPOSITION

BACKGROUND OF THE INVENTION

Engine lubricating oils are used under conditions whereby they are subjected to oxidative degradation. Under oxidizing conditions, the hydrocarbon molecules of a lubricating oil may undergo a number of undesirable reactions. For example, the hydrocarbon molecules may undergo polymerization to thereby cause an increase in the viscosity of the oil. In addition, polymerization may proceed to the point where insoluble polymerizates are formed, thus resulting in sludge formation. Also, acidic oxygen-containing products may be formed. Such acidic materials tend to cause corrosion and wear.

It is taught in the prior art that oxidative degradation of hydrocarbon lubricating oils may be prevented by the addition thereto of various antioxidant additives. Examples of antioxidants used in the prior art are hindered amines, hindered phenols, and metal dialkyldithiocarbamates. However, the antioxidant additives become exhausted after a time and oxidative degradation of the hydrocarbon lubricating oil may commence. The time until an antioxidant becomes exhausted may, of course, be extended by the use of larger quantities of the additive. However, the amount of the additive used is limited by economic considerations and by its solubility in the hydrocarbon lubricating oil.

An additional advantage that may be derived from using metal dialkyldithiocarbamates as antioxidants in engine lubricating oils is that they are responsible for forming a film on the engine inlet and exhaust valves which prevents their wear. However, during the course of engine operation, the protective film is often lost and the valves wear.

SUMMARY OF THE INVENTION

It is an object of this invention to provide antioxidant additives for hydrocarbon lubricating oils that are effective at low concentrations.

It is another object of this invention to provide antioxidant additives for hydrocarbon lubricating oils that are effective for extended periods of time.

It is still another object of this invention to provide anti-oxidant additives for hydrocarbon lubricating oils which are responsible for forming lasting protective coatings on the engine valves.

It is yet another object of this invention to provide hydrocarbon lubricating oil compositions that are resistant to oxidative degradation for long periods of time.

Still another object of this invention is to provide hydrocarbon lubricating oil compositions that give protection against engine valve wear.

Other objects will be apparent to those skilled in the art in view of this disclosure.

These and other objects are obtained by the practice of my invention. In general, my invention comprises an antioxidant additive for hydrocarbon lubricating oils comprising a metal dialkyldithiocarbamate and a Group II*a* metal sulfonate; and hydrocarbon lubricating oil compositions comprising a major proportion of a hydrocarbon lubricating oil and a minor proportion of a mixture of a metal dialkyldithiocarbamate and a Group II*a* metal sulfonate.

Therefore, according to the practice of my invention, economical antioxidant additives for hydrocarbon lubricating oils are obtained that are effective at low concentrations and for extended periods of time. Lubricating oil compositions containing the anti-oxidant additives of this invention are resistant to oxidative degradation for extended periods of time as evidenced by resistance to viscosity increase, sludge formation, and increase in acid number. In addition, engine valve wear is markedly reduced in internal combustion engines lubricated by the oil compositions of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The antioxidant additives of my invention comprise mixtures of metal dialkyldithiocarbamates and Group II*a* metal sulfonates. Oil-soluble metal dialkyldithiocarbamates are known and used individually as antioxidants in lubricating oils. However, I have discovered that when a mixture of an oil-soluble metal dialkyldithiocarbamate and a Group IIa metal sulfonate is incorporated in a hydrocarbon lubricating oil there is an unexpectedly enhanced resistance of the lubricating oil to oxidative degradation. In addition, the valves of engines using hydrocarbon lubricating oil compositions of my invention have formed thereon a lasting protective coating which is not removed during the course of engine operation and which is responsible for preventing or reducing valve wear.

The metals usually associated with the oil-soluble dialkyl-dithiocarbamates are from Groups II*b*, IV*a*, and V*a* of the periodic table. The preferred metals are zinc, cadmium, lead, and antimony. Each of the alkyl groups of the metal dialkyldithiocarbamate will contain from about 3 to about 10 carbons and may be straight chain or branched. The two alkyl groups in any one metal dialkyldithiocarbamate molecule may be either the same or different. Examples of suitable metal dialkyldithiocarbamates are zinc di-n-butyldithiocarbamate, zinc diamyldithiocarbamate, lead diamyldithiocarbamate, cadmium dipropyldithiocarbamate, antimony propyloctyldithiocarbamate, cadmium hexyldecyldithiocarbamate, zinc heptylnonyldithiocarbamate, lead diheptyldithiocarbamate, zinc isopropyloctyldithiocarbamate, lead isobutylnonyldithiocarbamate, tin diisobutyldithiocarbamate, tin hexylnonyldithiocarbamate, bismuth dioctyldithiocarbamate, bismuth isoamylheptyldithiocarbamate, bismuth didecyldithiocarbamate, antimony isoamyldecyldithiocarbamate, and antimony dioctyldithiocarbamate. The preferred dialkyldithiocarbamates are cadmium diamyldithiocarbamate and a 50 weight percent solution in oil of an antimony dialkyldithiocarbamate manufactured by R. T. Vanderbilt Company Inc. under the tradename of Vanlube **73.**

The Group II*a* metal sulfonate component of my antioxidant additive is the oil-soluble Group IIa metal salt of either a synthetic sulfonic acid or a natural sulfonic acid. The so-called synthetic sulfonates are derived from the sulfonation of synthesized alkylated aromatic hydrocarbons and the so-called natural sulfonates are derived from the fuming sulfuric acid treatment of hydrocarbon oils. Chemically, the natural sulfonates are sulfonates of mixtures of alkyl aryl molecular structures of varying molecular weights. The alkyl aryl sulfonic acids from which the Group II*a* metal sulfonates are prepared have average molecular weights in the range from about 400 to about 520. The average molecular weights of the Group II*a* metal sulfonates are therefore in the range from about 840 to about 1180 and prefera-

bly from about 940 to about 1030. While Group IIa metal sulfonates in general may be used in my antioxidant additive, barium and calcium sulfonates are preferred.

The Group IIa metal sulfonate components of my antioxidant additive are surface active and have the ability to lower the surface tension of liquids in which they are incorporated. The surface activity of these sulfonates also imparts rust preventive properties to hydrocarbon oils in which they are dissolved. An outstanding characteristic of the Group IIa metal sulfonates is their capacity to hold in stable suspension dispersed salts of the Group IIa metals. Relatively high concentrations of basic Group IIa metal salts can thus be supplied for addition to lubricants to combat acidity resulting from the combustion of sulfur-containing fuel. It is therefore especially preferred that the Group IIa metal sulfonate component of my antioxidant additive have incorporated therein a basic Group IIa metal inorganic salt. Particularly preferred are a calcium sulfonate composition manufactured by Bryton Chemical Company, a division of Continental Oil Company, under the tradename Bryton Hybase C-300 and a barium sulfonate composition manufactured by Bryton Chemical Company under the tradename Bryton Hybase. Bryton Hybase C-300 comprises about 47 wt.% of hydrocarbon oil, about 30 wt.% of a calcium sulfonate having an average molecular weight of about 940, sufficient calcium carbonate to give a base number of about 300 and contains about 11.5 wt.% of calcium. Bryton Hybase comprises about 42 wt.% of hydrocarbon oil, about 47 wt.% of a barium sulfonate having an average molecular weight of about 1010, sufficient barium carbonate to give a base number of about 65 and contains about 14.6 wt.% of barium.

The antioxidant additive of my invention contains Group IIa metal sulfonate and metal dialkyldithiocarbamate at a weight ratio of about 0.3:1 to about 4:1 and preferably about 0.5:1 to about 3:1, sulfonate to carbamate. In the case where the additive is a mixture of Bryton Hybase and cadmium diamyldithiocarbamate, an especially preferred weight ratio is within the range 0.5:1 to 2.5:1 barium sulfonate to cadmium diamyldithiocarbamate. In the case where the additive is a mixture of Bryton Hybase C-300 and cadmium diamyldithiocarbamate, an especially preferred weight ratio is within the range 0.5:1 to 1.5:1. When the additive is a mixture of Bryton Hybase and Vanlube 73, the preferred weight ratio is about 1:1.

The hydrocarbon lubricating oil compositions of my invention comprise a major proportion of hydrocarbon lubricating oil and a minor proportion, usually about 0.5 to 3.0 wt.%, and preferably about 0.6 to 2.0 wt.%, of the inventive antioxidant additive. In the case where the additive is prepared from a mixture of Bryton Hybase and cadmium diamyldithiocarbamate, the lubricating oil composition comprises a major proportion of hydrocarbon oil and about 0.6 to about 1.5 wt.% of additive. When the additive is prepared from a mixture of Bryton Hybase C-300 and cadmium diamyldithiocarbamate, the lubricating oil composition comprises a major proportion of hydrocarbon oil and about 0.6 to about 1.0 wt.% of the additive. In the case where the additive is prepared from a mixture of Bryton Hybase and Vanlube 73, the lubricating oil composition comprises a major proportion of hydrocarbon oil and about 1.0 percent by weight of the additive.

Lubricating oil compositions containing the additives of my invention have unexpectedly superior resistance to oxidative degradation as evidenced by their ability to withstand long periods of use without appreciable sludge formation, viscosity increase, and acid number increase. This is of particular utility in sour gas engine operation where the additive increases engine oil life from about 400 hours to greater than about 2,500 hours. Thus oil breakdown is prevented and engine wear rate is reduced. In addition, the valves of engines lubricated by such oils have a lasting protective coating placed thereon which prevents or reduces valve wear. Furthermore, I have discovered that when lubricating oil compositions containing my antioxidant additives do begin to undergo degradation as evidenced by increase in viscosity due to exhaustion of the additive, additional additive may be added to arrest oxidative degradation and to prolong the useful life of the oil.

The efficacy of the antioxidant additives of my invention is determined by subjecting hydrocarbon lubricating oil compositions containing the additives to a catalyzed oxidation test. In the test, a sample of the hydrocarbon lubricating oil composition to be tested has added thereto 1,000 ppm of a particulate catalyst having a particle size of about 5 microns and consisting of 1 part of copper, 1 part of bronze, 1 part of babbit, and 2 parts of iron. The mixture is stirred at 300° F, and the lubricating oil composition is tested at intervals to determine several parameters, i.e., viscosity, acid number, and capacitance loss. The times in hours are recorded when the viscosity of the lubricating oil composition determined at 210° F has increased by 2.5 SUS, when the acid number has increased by 1.5, and when the capacitance loss has changed by 8.0 units on the scale of an An-Oil-Izer, an instrument manufactured by the Hopkins Manufacturing Corporation. The end point of the catalyzed oxidation test is the average, expressed in hours, of the above three times.

The following examples are presented to further illustrate my invention.

EXAMPLE I

Several oil compositions are prepared by dissolving antioxidant additives of my invention in a major proportion of a hydrocarbon gas engine oil and the oil compositions are subjected to the catalyzed oxidation test. The additives are comprised of cadmium diamyldithiocarbamate and the Group IIa metal sulfonate is the barium sulfonate containing barium carbonate which is marketed under the tradename of Bryton Hybase. For comparison, a base gas engine oil containing no antioxidant and gas engine oil compositions containing cadmium diamyldithiocarbamate alone and Bryton Hybase alone are also subjected to the catalyzed oxidation test. For each oil composition, the end point of the test is the average time, in hours, based on the above-mentioned parameters of viscosity increase, acid number increase, and capacitance loss. The difference in time to reach the end point for each composition relative to the time for the base oil to reach the end point is recorded as Δ hours. Table I contains the results of the catalyzed oxidation tests and the amount of each component of the additive. All percents are weight percents of the total oil compositions.

TABLE I

Cadmium Diamyl dithiocarbamate	Bryton Hybase	Barium Sulfonate	End Point	Δ

wt.%	wt.%	wt.%	hours	hours
—	—	—	53	—
0.4	—	—	141	88
—	1.0	0.47	36	−17
0.4	0.5	0.24	181	128
0.4	1.0	0.47	188	135
0.4	2.0	0.94	148	95
0.4	3.0	1.41	146	93
0.4	10.0	4.7	133	80

The data in Table I show that the addition of cadmium diamyldithiocarbamate alone to a hydrocarbon lubricating oil improves its resistance to oxidative degradation while the addition of a barium sulfonate alone to the lubricating oil causes a reduction in its resistance to oxidative degradation. Surprisingly, when a mixture of cadmium diamyldithiocarbamate and a barium sulfonate is incorporated in the hydrocarbon lubricating oil, there is a marked improvement in the resistance to oxidative degradation which clearly illustrates the synergistic interaction of metal dialkyldithiocarbamates and Group IIa metal sulfonates as antioxidants.

EXAMPLE II

Example I is repeated using an antioxidant additive comprising cadmium diamyldithiocarbamate and Hybase C-300. For comparison purposes, a base oil containing no antioxidant additives, an oil composition containing only cadmium diamyldithiocarbamate, and an oil composition containing only Hybase C-300 are also subjected to the catalyzed oxidation test. In Table II are shown the make-up of each oil composition, the hours elapsed for each composition to reach the end point and the Δ hours for each oil composition relative to the time to reach the end point of the base oil containing no antioxidant. All weight percents are based on the total oil compositions.

TABLE II

Cadmium Diamyldithiocarbamate, wt. %	Hybase C-300 wt.%	Calcium Sulfonate wt.%	End Point hours	Δ hours
—	—	—	53	—
0.4	—	—	141	88
—	1.0	0.30	40	−13
0.4	0.5	0.15	124	71
0.4	1.0	0.30	237	184

The data show that, similarly to the barium sulfonate, addition of a calcium sulfonate alone to a hydrocarbon lubricating oil causes a reduction in its resistance to oxidative degradation relative to a base oil containing no antioxidant. As is the case with the barium sulfonate, incorporation of a mixture of cadmium diamyldithiocarbamate and a calcium sulfonate into a hydrocarbon lubricating oil results in an unexpectedly improved resistance to oxidative degradation which again illustrates the synergistic interaction of metal dialkyldithiocarbamates and Group IIa metal sulfonates as antioxidants.

EXAMPLE III

Example I is repeated using an antioxidant additive comprising Bryton Hybase and the 50 weight percent solution in oil of an antimony dialkyldithiocarbamate manufactured by R. T. Vanderbilt Company under the tradename Vanlube 73. For comparison purposes, a base oil containing no antioxidant additives, an oil composition containing only Vanlube 73, and an oil composition containing only Bryton Hybase are also subjected to the catalyzed oxidation test. In Table III are shown the make-up of each oil composition, the

hours elapsed to reach the end point for each composition, and the Δ hours for each oil composition relative to the time to reach the end point of the base oil containing no antioxidant. All weight percents are based on the total oil compositions.

TABLE III

Vanlube 73, wt.%	Antimony Dialkyldithiocarbamate wt.%	Bryton Hybase wt.%	Barium Sulfonate wt.%	End Point hours	Δ hours
—	—	—	—	53	—
1.0	0.5	—	—	92	39
—	—	1.0	0.47	36	−17
1.0	0.5	1.0	0.47	120	67

The data in Table III illustrate the synergistic interaction of an antimony dialkyldithiocarbamate and a Group IIa metal sulfonate to produce a particularly effective antioxidant additive for hydrocarbon lubricating oils.

Similar results may be obtained when other oil-soluble metal dialkyldithiocarbamates and oil-soluble Group IIa metal sulfonates comprise the antioxidant additive. The Group IIa metal sulfonates may or may not contain a basic Group IIa metal salt. Suitable antioxidant additives may, for example, be obtained by mixing any of zinc di-n-butyldithiocarbamate, zinc diamyldithiocarbamate, or lead diamyldithiocarbamate with any of an oil-soluble barium sulfonate with or without a Group IIa metal carbonate, an oil-soluble calcium sulfonate with or without a Group IIa metal carbonate, an oil-soluble magnesium sulfonate with or without a Group IIa metal carbonate, or an oil-soluble strontium sulfonate with or without a Group IIa metal carbonate. When the oil-soluble Group IIa metal sulfonate contains a basic Group IIa metal salt such as a carbonate, the Group IIa metal of the basic salt may be the same as or different from the Group IIa metal of the sulfonate.

While the present invention has been described herein with reference to particular embodiments thereof, it will be recognized by those skilled in the art that various changes and modifications can be made therein without departing from the scope of the invention as set forth in the appended claims.

I claim:

1. An antioxidant for hydrocarbon lubricating oils consisting essentially of an oil-soluble metal dialkyldithiocarbamate wherein said metal is selected from the group consisting of metals from Groups IIb and Va of the periodic table and an oil-soluble Group IIa metal sulfonate which has incorporated therein a Group IIa metal carbonate, and wherein the weight ratio of said sulfonate to said dialkyldithiocarbamate is from about 0.3:1 to about 4:1.

2. The antioxidant of claim 1 wherein the metal associated with the dialkyldithiocarbamate is selected from the group consisting of zinc, cadmium, and antimony.

3. The antioxidant of claim 2 wherein each alkyl group of the metal dialkyldithiocarbamate contains about three to about 10 carbons.

4. The antioxidant of claim 3 wherein the Group IIa metal associated with the oil-soluble sulfonate is selected from the group consisting of barium and calcium.

5. The antioxidant of claim 4 wherein said metal dialkyldithiocarbamate consists of cadmium diamyldi-

thiocarbamate, said Group IIa metal sulfonate consists of an oil-soluble barium sulfonate containing sufficient barium carbonate to give a base number of about 65, and the weight ratio of said oil-soluble barium sulfonate to said cadmium diamyldithiocarbamate is from about 0.5:1 to about 2.5:1.

6. The antioxidant of claim **4** wherein said metal dialkyldithiocarbamate consists of cadmium diamyldithiocarbamate, said Group IIa metal sulfonate consists of an oil-soluble calcium sulfonate containing sufficient calcium carbonate to give a base number of about 300, and the weight ratio of said oil-soluble calcium sulfonate to said cadmium diamyldithiocarbamate is from about 0.5:1 to about 1.5:1.

7. The antioxidant of claim **4** wherein said metal dialkyldithiocarbamate consists of an antimony dialkyldithiocarbamate, said Group IIa metal sulfonate consists of an oil-soluble barium sulfonate containing sufficient barium carbonate to give a base number of about 65, and the weight ratio of said oil-soluble barium sulfonate to said antimony dialkyldithiocarbamate is about 1:1.

8. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and about 0.6 percent to about 1.5 percent by weight, based on said hydrocarbon lubricating oil composition, of the additive of claim **5.**

9. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and about 0.6 percent to about 1.0 percent by weight, based on said hydrocarbon lubricating oil composition, of the additive of claim **6.**

10. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil, about 0.4 percent by weight of said hydrocarbon lubricating oil composition of cadmium diamyldithiocarbamate, and about 1.0 percent by weight of said hydrocarbon lubricating oil composition of a mixture containing about 42 weight percent hydrocarbon oil, about 47 weight percent of an oil-soluble barium sulfonate, and sufficient barium carbonate to give said mixture a base number of about 65.

11. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil, about 0.4 percent by weight of said hydrocarbon lubricating oil composition of cadmium diamyldithiocarbamate, and about 1.0 percent by weight of said hydrocarbon lubricating oil composition of a mixture containing about 47 weight percent hydrocarbon oil, about 30 weight percent of an oil-soluble calcium sulfonate, and sufficient calcium carbonate to give said mixture a base number of about 300.

12. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and about 0.5 percent to about 3.0 percent by weight, based on said hydrocarbon lubricating oil composition, of the additive of claim **1.**

13. A hydrocarbon lubricating oil composition consisting essentially of a major proportion of a hydrocarbon lubricating oil and about 0.6 percent to about 2.0 percent by weight; based on said hydrocarbon lubricating oil composition, of the additive of claim **4.**

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