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LUBRICANT COMPRISING A SULFURIZED MINERAL OIL AND A POLYVALENT METAL DITHIOCARBAMATE

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This invention relates to improved lubricating compositions comprising a sulfurized mineral lubricating oil, and more particularly to extreme pressure lubricants of the lead-sulfur type, containing polyvalent metal dithiocarbamates.

Major users of industrial gear lubricants have adopted more severe specification requirements during the past few years, calling among other things for greatly improved resistance to thickening at elevated temperatures in the presence of air in long time tests. This requirement has been difficult to meet in otherwise very superior gear lubricants, particularly in the heavier grades of the better gear lubricants, wherein paraffinic residual oils are employed in order to obtain the desired viscosity characteristics and other advantages.

In accordance with this invention, very superior extreme pressure lubricants having the combination of properties required to meet the more severe requirements are obtained by employing as the base oil a stably sulfurized lubricating oil and in combination therein a minor but substantial amount of a lead soap, a minor amount of a sulfurized fatty oil and a minor amount of a polyvalent metal dithiocarbamate. We have found that a combination of superior properties is obtained in these compositions which is not obtainable in other lead-sulfur gear lubricants of the prior art. They have a considerable advantage over lead-sulfur gear lubricants of the usual type in that they contain only a very small amount of sulfur in the active form, and they thereby avoid the sludging and other difficulties associated with high contents of loosely bound, reactive sulfur. In addition, they provide the desired combination of high load bearing properties, represented by OK Timken values of at least about 45, and the very superior resistance to thickening required to give a 15 percent maximum viscosity increase by the extreme pressure oil oxidation by bubbling dry air method, hereinafter referred to as the extreme pressure oil oxidation test, specified in the United States Steel Lubricants Testing Laboratory No. 220 Lubricant Performance Requirements for Extreme Pressure Oil.

The stably sulfurized lubricating oils employed in these compositions are obtained by heating mineral lubricating oils with sulfur for a long time until the sulfurized products are substantially non-corrosive to metals. In this reaction, upon the prolonged heating, the reactive sulfur groups which are formed in the first stage of the reaction disappear and substantial thickening of the oil occurs. The product is therefore a material of very different character from the corrosive sulfurized oils ordinarily employed in lubricant compositions of this type which are obtained by heating the oils with sulfur for a short time only. The stably sulfurized mineral lubricating oil may be obtained by heating a suitable mineral lubricating oil with about 1 to 5 percent of sulfur at a temperature above about 350° F. and preferably at about 400° F. to 500° F. for several hours, so as to obtain a reaction product which is substantially non-corrosive to copper in the copper strip corrosion test at 212° F. The quantity of sulfur employed is calculated to give about 0.3 to about 1.5 percent, and preferably from about 0.5 to 1.2 percent, of sulfur in the oil. The lubricating oils employed in the sulfurization may be distillate or

residual oils obtained from paraffinic, naphthenic or mixed base crudes. For preparing various grades of a gear oil, blends of lighter and heavier oils may be conveniently employed, which may be sulfurized either separately or together.

The lead soap employed in the composition is preferably lead naphthenate, although other lead soaps such as lead oleate, lead octoate, lead linoleate, etc. may be employed if desired. The proportion of lead soap should be about 5–20 percent, and preferably about 7–15 percent by weight of the composition.

The sulfurized fatty oil may be any of the sulfurized natural or synthetically obtained fatty materials which have been employed heretofore as lubricant additives of the active sulfur type, such as may be obtained, for example, by sulfurizing lard oil, sperm oil, corn oil, or the like. A particularly suitable material of this character is sulfurized lard oil containing from about 5 to 12 percent of the sulfur, obtained by heating lard oil with about 10 to 15 percent of sulfur at a temperature about 300° F. and preferably at about 350–400° F., for a sufficient time to obtain a homogeneous product. About 0.5 to 5 percent, and preferably about 1 to 3 percent, by weight of this sulfurized oil may be employed in the lubricating composition.

The polyvalent metal dithiocarbamates employed are salts of organic substituted dithiocarbamic acids as described, for example, in U.S. 2,400,106. They are preferably polyvalent metal salts of N-aliphatic hydrocarbon substituted dithiocarbamic acids containing sufficient aliphatic carbon atoms to impart oil solubility to the molecule, and most advantageously those wherein each nitrogen is substituted by aliphatic hydrocarbon groups containing about 4 to 20 carbon atoms. Suitable polyvalent metals include, for example, the alkaline earth metals, zinc, cadmium, magnesium, tin, aluminum and iron. Metals of the group II subgroup consisting of magnesium, cadmium and zinc are especially suitable. As examples of this preferred group of compounds may be mentioned zinc dibutyl dithiocarbamate, zinc diamyl dithiocarbamate, zinc di(2-ethylhexyl) dithiocarbamate, cadmium dibutyl dithiocarbamate, cadmium dioctyl dithiocarbamate, cadmium octyl-butyl dithiocarbamate, magnesium dibutyl dithiocarbamate, magnesium dioctyl dithiocarbamate, zinc "petroleum base" dithiocarbamates and cadmium dicetyl dithiocarbamate. Especially desirable compounds of this class are zinc dibutyl dithiocarbamate, zinc diamyl dithiocarbamate, and cadmium dibutyl dithiocarbamate, which are commercially available materials. The polyvalent metal dithiocarbamate is usually employed in amounts of about 0.2–5 percent by weight, although somewhat larger or smaller amounts may be employed if desired, such as from about 0.1 to about 10 percent by weight.

The high stability against oxidative thickening in the extreme pressure oil oxidation test obtained in these compositions is surprising, since compositions comprising these stably sulfurized mineral oils have not been inhibited in this test by numerous other oxidation inhibitors of various types, including some of the most generally effective oxidation inhibitors commonly employed in lubricating compositions. In addition, the dithiocarbamates are of generally inferior oxidation inhibiting effectiveness in mineral lubricating oils of the ordinary types in the usual tests. The following table shows, for example, the effect of zinc dibutyl dithiocarbamate in an unsulfurized mineral lubricating oil in the Penn State oxidation test, as compared with the effect of a common oxidation inhibitor of a different type. The Penn State oxidation test is a well-known test employed for determining the oxidation resistance of lubricating compositions, and is carried out by circulating oxygen in a closed system through a 250

gram sample of the test oil in a glass tube at a rate of 15 liters per hour for 40 hours while the oil is maintained at 338° F. The lubricating oil employed was a refined paraffinic distillate oil having a viscosity of 328 seconds SU at 100° F. (kinematic viscosity of 71.0). The table also shows the strong pro-oxidant effect of lead naphthenate upon the same mineral lubricating oil in this test.

TABLE I

Additive	Oxygen absorption	Viscosity increase, kinematic at 100° F., percent
None	295	25.07
Zinc dibutyl dithoicarbamate (1%)	258	20.21
Diphenylamine (1%)	88	7.15
Lead naphthenate (1%)	631	127.17

As shown by the above table, the unsulfurized mineral luubricating oil containing zinc dibutyl dithiocarbamate had thickened only slightly less than the base oil alone after 40 hours at 338° F. The composition containing zinc dibutyl dithiocarbamate had a characteristic high initial oxidation resistance in this test, an oxygen absorption curve of the test showing a long induction period of about 18 hours, followed by a very rapid increase in oxygen absorption so that at the end of the 40 hour period the oxygen absorption had almost equaled that of the uninhibited oil.

In contrast with the failure of the polyvalent metal dithiocarbamates to inhibit other types of mineral lubricating oils over long periods of time, as shown by the above test, the compounds of this class are extremely effective in inhibiting the stably sulfurized mineral lubricating oils employed in the lubricating compositions of this invention even in the presence of strong pro-oxidants such as lead naphthenate.

The following examples are given for the purpose of further disclosing the invention.

Example I

A gear lubricant representative of a preferred embodiment of this invention was prepared comprising a sulfurized mineral lubricating oil containing 7.5 percent of lead naphthenate, 2.0 percent of sulfurized lard oil and zinc dibutyl dithiocarbamate in amounts of both 0.5 and 1 percent by weight. The composition also contained 50 parts per million of an antifoam compound, which was a 10 percent by weight solution of a dimethyl silicone polymer in kerosene.

The sulfurized mineral oil employed was a blend of sulfurized heavy paraffinic residual oil and a sulfurized light paraffinic distillate oil. The sulfurized heavy residual oil was obtained by heating a residual oil having a viscosity of 381 seconds Saybolt Universal at 210° F. for about 4.5 hours at 440° F. with 2.0 percent sulfur, and finally steaming in a vacuum tower to remove hydrogen sulfide. The product had a viscosity of 457 seconds Saybolt Universal at 210° F. and contained 0.92 percent sulfur. The light paraffinic distillate oil was a fraction having a viscosity of about 168 seconds Saybolt Universal at 100° F., and was sulfurized in the form of a 476 seconds viscosity blend with a minor portion of the heavy residual oil described above by heating the blend for about 8 hours at 445° F. with 2.8 percent sulfur, and finally steaming in a vacuum tower to remove hydrogen sulfide. The product had a viscosity of 591 seconds Saybolt Universal at 100° F. and contained 0.73 percent sulfur. Both oils were substantially non-corrosive to copper in the copper strip corrosion test at 212° F. The sulfurized stocks were each mixed with 2.16 percent by weight of sulfurized lard oil, based on the weight of the blend, and then blended together in about a 37.5:55 by weight ratio of heavy to light oil.

The sulfurized lard oil employed was obtained by heating a No. 1 lard oil at about 300° F. for 4 hours while

powdered sulfur was added in a proportion of 33 pounds of powdered sulfur per barrel to 170 barrels of lard oil, then heating for 8 hours longer at 300–405° F. and finally steaming in a vacuum tower to remove hydrogen sulfide. The product contained 7.09 percent of sulfur and had a viscosity of 217 seconds Saybolt Universal at 210° F.

The zinc dibutyl dithiocarbamate employed was commercial product sold by the R. T. Vanderbilt Company under the name "Butyl Zimate." Typical tests on this material show a melting point of 106° C., a sulfur content of 28.25 percent and zinc content of 14.3 percent.

The lubricant was prepared by mixing the above materials in the proportions indicated in an ordinary grease kettle for about 3 hours while the temperature was maintained at about 160–200° F., and drawing at about 150° F.

The following table shows the results obtained upon this lubricant in the extreme pressure oil oxidation test, together with comparative data upon the same composition without the zinc dibutyl dithiocarbamate and also upon the composition containing various other inhibitors of different types in place of the zinc dithiocarbamate. This test is carried out by circulating 10 liters of dry air continuously through a 300 ml. sample of the test oil in a glass tube for a period of 13 days (312 hours) while the temperature of the test oil is maintained at about 200° F.–207° F. The viscosity of the oil at 210° F. is determined both before and after the test.

TABLE II

Inhibitor	Concentration percent	Viscosity increase, SUS at 210° F., percent
None		18.6
Phenyl-alpha-naphthylamine	0.5	21.4
N,N,N',N' - tetramethyldiamino - diphenylmethane	0.5	22.0
N,N'-disalicylidene-1,2-diaminopropene	0.5	17.5
2,6-ditertiary butyl-4-methyl phenol	0.5	18.6
Diphenylamine	0.5	21.9
Diphenyl-para-phenylenediamine	0.5	21.6
Phenothiazine	0.5	21.0
Ditertiary butyl-para-cresol	0.5	17.4
Vanlube 26 [1]	1.0	17.1
Calco 2246 [1]	1.0	30.3
Zinc dibutyl dithiocarbamate	0.5	11.7
Zinc dibutyl dithiocarbamate	1.0	6.6

[1] Commercial oxidation inhibitors of unknown composition.

As shown by the above table, thickening of the composition comprising the stably sulfurized mineral lubricating oil was inhibited to well below the required 15 percent maximum in the extreme pressure oil oxidation test by means of 0.5 percent of the polyvalent metal dithiocarbamate, and a still further inhibiting effect was obtained by increasing the amount of polyvalent metal dithiocarbamate to 1.0 percent. In very striking contrast to the inhibiting effectiveness obtained by means of this compound, the other compounds of various types which are commonly employed as antioxidants in lubricating compositions were almost entirely ineffective or even increased the amount of thickening in this test.

In addition to the high stability against oxidative thickening as shown by the above table, this composition had high load bearing properties and other advantages, as shown by the following inspection tests obtained upon the composition containing 1.0 percent of zinc dibutyl dithiocarbamate:

Viscosity, SUS, at 210° F	125.7
Viscosity index	84.5
Copper strip corrosion test,	
1 hours at 212° F	Negative
Timken test:	
OK	55
Score	60
Heat stability test:	
Precipitation number, A.S.T.M. original	0.01
After extreme pressure oil oxidation test	0.01

Example II

Another lubricant was prepared of the same composition as described in Example I except that it was a heavier grade, obtained by employing the sulfurized heavy residual oil alone as the sulfurized base oil.

The following table shows the inhibiting effect of zinc dibutyl dithiocarbamate in various amounts in this composition in the extreme pressure oil oxidation test.

TABLE III

Zinc dibutyl dithiocarbamate, percent by weight	Viscosity increase, SUS, at 210° F., percent
0.0	32.8
1.0	20.7
1.5	14.3

As shown by the above table, the composition based on the sulfurized paraffinic residual oil alone was also inhibited to the required degree by employing higher proportions of the polyvalent metal dithiocarbamate.

While the combination of stably sulfurized mineral lubricating oil and polyvalent metal dithiocarbamate is employed with particular advantage in the production of superior gear lubricants of the lead-sulfur type as described above, the use of this combination of stably sulfurized mineral lubricating oil and polyvalent metal dithiocarbamate in other lubricating compositions is also contemplated, and it may be employed either alone or together with other additives of various types wherever superior resistance to oxidation and other special properties are desired. Other extreme pressure agents which may be employed in these compositions include particularly phosphorus acid esters, such as tricresyl phosphate, other heavy metal soaps, and other active sulfur compounds, such as dibenzyl disulfide, diphenol disulfide, dioctyl sulfide, dicyclohexyl disulfide, sulfurized cyclohexene, sulfurized terpinolene, sulfurized oleyl alcohol, etc. Additives of other types, including other oxidation inhibitors, particularly those of the amine type, such as diphenylamine, diphenyl-para-phenylene diamine, etc., corrosion inhibitors, anti-foam agents, etc., may also be employed.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating composition consisting essentially of a stably sulfurized mineral lubricating oil in major proportion containing about 0.3 to 1.5 percent by weight of combined stable sulfur, about 5–20 percent by weight of a lead soap selected from the group consisting of lead naphthenates and lead soaps of fatty acids containing at least 8 carbon atoms per molecule, about 0.5–5 percent by weight of a sulfurized fatty oil, and about 0.1 to 10 percent by weight of an oil soluble polyvalent metal dithiocarbamate, wherein the said polyvalent metal is chosen from the group consisting of alkaline earth metals, cadmium and zinc, said stably sulfurized mineral lubricating oil being obtained by heating a mineral lubricating oil with sulfur at a temperature above about 350° F. until a sulfurized product is obtained wherein the sulfur is present substantially entirely in a form which is nonreactive with copper in the copper strip corrosion test at 212° F.

2. The lubricating composition of claim 1 wherein the said oil-soluble polyvalent metal dithiocarbamate is chosen from the group consisting of magnesium, cadmium, and zinc salts of N-aliphatic hydrocarbon substituted dithiocarbamate acids containing from about 8 to 40 aliphatic carbon atoms.

3. A lubricating composition consisting essentially of a stably sulfurized mineral lubricating oil in major proportion containing about 0.5 to 1.5 percent by weight of combined stable sulfur, about 0.5 to 5 percent by weight of an oil-soluble zinc dithiocarbamate, about 5–20 percent by weight of a lead soap selected from the group consisting of lead naphthenates and lead soaps of fatty acids containing at least 8 carbon atoms per molecule and about 0.5 to 5 percent by weight of a sulfurized fatty oil, said stably sulfurized mineral lubricating oil being obtained by heating a mineral lubricating oil with sulfur at a temperature above about 350° F. until a sulfurized product is obtained wherein the sulfur is present substantially entirely in a form which is nonreactive with copper in the copper strip corrosion test at 212° F.

4. The lubricating composition of claim 3 wherein the said lead soap is lead naphthenate.

5. The lubricating composition of claim 3 wherein the said sulfurized fatty oil is sulfurized lard oil containing about 5–12 percent by weight of sulfur.

6. A lubricating composition consisting essentially of a stably sulfurized mineral lubricating oil containing about 0.5 to 1.5 percent of combined stable sulfur, about 0.5 to 5 percent by weight of an oil soluble zinc dialkyl dithiocarbamate wherein the said alkyl groups each contains from about 4 to 20 carbon atoms, about 7 to 15 percent by weight of lead naphthenate and about 1 to 3 percent by weight of sulfurized lard oil containing about 5 to 12 percent of sulfur, said stably sulfurized mineral lubricating oil being obtained by heating a mineral lubricating oil with sulfur at a temperature above about 350° F. until a sulfurized product is obtained wherein the sulfur is present substantially entirely in a form which is nonreactive with copper in the copper strip corrosion test at 212° F.

7. The lubricating composition of claim 6 wherein the said oil soluble zinc dithiocarbamate is zinc dibutyl dithiocarbamate.

8. The lubricating composition of claim 6 wherein the said stably sulfurized mineral lubricating oil is a sulfurized paraffinic oil.

9. The lubricating composition of claim 6 wherein the said stably sulfurized mineral lubricating oil comprises at least about 50 percent by weight of a sulfurized paraffinic residual oil.

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