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2,993,856

LUBRICANT CONTAINING A SULFURIZED TERPENE AND SULFURIZED SPERM OIL

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This invention relates to lubricating compositions having superior silver lubricating properties, and more particularly to crankcase lubricants having both superior anticorrosiveness to copper-lead and silver lubricating properties obtained by an additive combination comprising a sulfurized terpene and sulfurized sperm oil.

Because of the greatly increased use of silver for bearings and certain other engine parts during the past few years, a need has developed for a lubricant having good silver lubricating properties in addition to the other properties required of a satisfactory crankcase lubricant. Heavy duty lubricants which have been employed heretofore in internal combustion engines are generally unsuitable for use in engines containing lubricated silver parts, chiefly because of the effect upon silver lubricating properties of compounds commonly employed as corrosion inhibitors for the protection of copper-lead and other common bearing metals. The most effective of such corrosion inhibitors are compounds which are themselves corrosive to metals of the copper-lead type, their effectiveness in this respect being due to a limited chemical attack upon such metals, which results in the formation of a thin protective film upon the metal surface, but such compounds deleteriously affect the silver lubricating properties of the lubricating composition. A number of attempts which have been made heretofore to obtain a satisfactory degree of anti-corrosiveness to metals of the copper-lead type and satisfactory silver lubricating properties in a lubricating oil either by means of a single additive or by various combinations of additives have been unsuccessful, since generally opposing effects are involved. This problem is furthermore generally aggravated by the presence of detergents, since the latter tend to remove any protective coatings which are formed and are themselves frequently very corrosive to metals.

In accordance with this invention, lubricating compositions suitable for the lubrication of internal combustion engines containing both copper-lead and silver lubricated parts are obtained by employing an additive combination comprising a sulfurized terpene and sulfurized sperm oil. We have found that by employing this particular combination of different sulfur-containing additives in a suitable lubricating oil, crankcase lubricants are obtained having a high degree of anti-corrosiveness both to silver and to other metals of the copper-lead type, in addition to superior silver lubricating properties even in the presence of very effective detergents and other additives commonly employed in crankcase lubricants.

The sulfurized terpenes are a class of compounds containing sulfur in the active form, commonly employed in lubricating compositions as corrosion inhibitors for metals of the copper-lead type. The properties of the phosphorus-sulfurized compounds are modified by the presence of the phosphorus-containing groups, such compounds being less corrosive than the straight sulfurized compounds and also having anti-oxidant and other desirable properties. However, all of the compounds of this class seriously de-

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grade the silver lubricating properties of mineral lubricating oils generally, lubricating compositions of the prior art containing sulfurized terpenes being particularly deficient in the ability to maintain a lubricating film upon silver metal surfaces.

The sulfurized terpenes employed in these compositions are products obtained by treating terpenes, including monocyclic, dicyclic and acyclic terpenes, with sulfur. The terpenes may be either naturally occurring mixtures such as pine oil or turpentine, or relatively pure compounds such as pinene, dipentene, terpinolene, limonene, camphene, etc. The reaction may be carried out by any suitable method, such as, for example, by heating the terpene with sulfur at a temperature of about 250–400° F., and preferably at about 260–360° F., for about one half to about 4 hours, employing a proportion of sulfur to terpene of about 1 to 4 to about 1 to 2 by weight. An additive of this type may be employed in the lubricating composition in varying amounts, depending principally upon the amount of active sulfur which the additive contains. Preferably, a sulfurized terpene having a sulfur content of about 5–45 percent is employed, in an amount of from about 0.05 to about 3 percent by weight, based on the weight of the composition. Most advantageously, the sulfurized terpene is employed in an amount of about 0.1–1 percent by weight.

The sulfurized sperm oil, which comprises the second component of our corrosion-inhibiting additive combination, may be obtained by heating sperm oil with sulfur at about 350–400° F., and preferably at about 370–390° F., or with sulfur monochloride at about 100–200° F., according to the known methods, so as to obtain a sulfurized product containing about 5–25 percent by weight of sulfur which is corrosive to copper in the copper strip corrosion test at 212° F. Such a sulfurized product is suitably employed in the lubricating composition in amounts of from about 0.1 to about 5.0 percent by weight, advantageously in amounts from about 0.5 to about 3.0 percent by weight, and preferably in amounts of from about 1.0 to about 3.0 percent, based on the weight of the composition.

The lubricating oils employed in these compositions may be any mineral lubricating oils of suitable viscosity obtained by any of the conventional refining procedures from paraffinic, naphthenic or mixed base crudes, including straight mineral oils, distillates, and residuals, particularly those from which asphaltic constituents have been removed, as well as blends of such oils.

In addition to the corrosion inhibiting additive combination described above, the lubricating compositions of this invention may contain various other additives such as are commonly employed in crankcase lubricants as anti-oxidants, detergents, anti-corrosives, etc., in so far as no incompatibility exists. The composition preferably contains an effective detergent chosen from the class of metal salts of organic compounds, including metal fatty acid soaps, metal sulfonates, metal phenolates, metal phenolate sulfides, metal alcoholates, metal xanthates and thioxanthates, metal salicylates, metal thiocarbamates, etc. With special advantage, a compound of the class comprising metal salts of phosphorus and sulfur containing organic compounds may be employed in conjunction with these corrosion inhibiting additives. A compound of this class may be employed in amounts of from about 0.1 to about 10 percent by weight, based on the weight of the composition.

Particularly suitable phosphorus- and sulfur-containing compounds are the neutralized reaction products of hy-

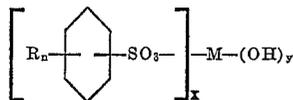
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magnesium, tin or zinc, x is 1 or 2, R_1 is hydrogen or an aliphatic group containing from about 3 to 21 carbon atoms and R_2 is an aliphatic group containing from about 3 to 21 carbon atoms. The preferred compounds are those wherein M is an alkaline earth metal and x is 1.

A compound of this preferred type is a barium alkyl phenol sulfide, which is sold in the form of a 30 percent solution in lubricating oil under the trade name of "Paranox 56," by Standard Oil Company of New Jersey.

The sulfonates which may be employed in these com-

positions are preferably alkaline earth metal salts of oil-soluble aromatic sulfonic acid, which may be represented by the following formula:



wherein the aromatic nucleus may be a single or condensed ring, R is an alkyl, alkaryl or aralkyl group, n is a number from 1 to 3, M is an alkaline earth metal, x is either 1 or 2 and y is either 1 or zero, the sum of x and y being equal to 2. Very suitable compounds of this type are the alkaline earth metal salts of petroleum or "mahogany" sulfonic acids. These compounds are derived from the sulfonic acids resulting from the treatment of heavy petroleum fractions with concentrated sulfuric acids, by either neutralizing these sulfonic acids directly with an alkaline earth metal base or by double decomposition of the alkali metal salt, preferably employing about equimolar proportions of the alkaline earth metal base and the sulfonic acid, which yields a product apparently consisting at least in part of the basic salt, represented by the above formula where y equals 1. Other oil-soluble sulfonic acids which may be employed include synthetic compounds obtained for example by alkylating a suitable aromatic compound, such as benzene, alkyl benzenes, naphthalene, anthracene, etc., with an olefin such as a propylene or butylene polymer, preferably containing 8 or more carbon atoms, in the presence of a suitable alkylation catalyst, such as aluminum chloride, sulfuric acid, phosphoric acid, etc., followed by sulfonation with sulfuric acid. While any alkaline earth metal salt of this type can be advantageously employed in the lubricating composition, the salts of barium and calcium are preferred. Also, in addition to the neutral and basic salts represented by the above formula, the CO_2 -neutralized basic salts may be employed.

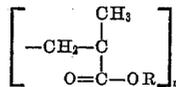
Other additives of various types such as are commonly employed in crankcase lubricants may also be employed in these compositions, such as extreme pressure agents, dyes, pour point depressants, viscosity index improvers, anti-foam agents, etc.

It is usually preferable to employ an anti-foam agent, which may very suitably be a silicone polymer of high viscosity, such as a dimethyl silicone polymer having a kinematic viscosity at 25° C. of about 1000 centistokes or above, as covered in U.S. Patent No. 2,662,055 although dimethyl silicone polymers of lower viscosity down to about 100 centistokes may be used. Dimethyl silicone polymers of this type are sold by Dow-Midland Co. under the trade name of Dow Corning Fluid. Other suitable types of liquid silicone polymers for this purpose include the dihydrocarbon silicone polymers disclosed in U.S. Patent No. 2,375,007, such as diethyl, methylethyl, diphenyl, phenylethyl and phenylmethyl silicone polymers. A material of this type may be conveniently employed in the form of a concentrate in a hydrocarbon solvent, such as kerosene. For example, a very satisfactory anti-foam agent for this purpose is prepared by diluting 10 grams of a dimethyl silicone polymer (1000 cs. at 25° C.) with

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kerosene to bring the volume up to 100 cc. A proportion of the order of 0.005–0.025 percent by weight of the foregoing concentrate is ordinarily employed, preferably sufficient to provide about 100 to 200 parts per million of the silicone polymer concentrate on the basis of the lubricating oil composition.

Particularly suitable viscosity and viscosity index improving agents for use in these compositions are methacrylate ester polymers, having the formula



wherein R is an alkyl group or a mixture of alkyl groups containing from 4 to 20 carbon atoms, and n is a number providing a molecular weight of the polymer of about 10,000 to 20,000. Various methacrylate ester polymers of this type are known which possess pour depressant and also viscosity and viscosity index increasing properties. A very satisfactory material of this type is a copolymer of the lower C_4 to C_{14} alkyl methacrylate esters. A commercial methacrylate copolymer of this type, which is primarily a viscosity index improver, is sold under the trade name of "Acryloid 710" by Rohm & Haas, this product consisting of about a 40 percent concentrate in a mineral lubricating oil of a polymer of the above formula wherein R is predominantly a mixture of lauryl and octyl groups and the molecular weight is about 10,000 to 20,000. A material of the foregoing type may be employed in the lubricating composition in a proportion of about 0.05–3.0 percent by weight based on the weight of the composition.

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

EXAMPLE 1

Lubricating compositions were prepared employing the combination of a sulfurized terpene and sulfurized sperm oil in a mineral lubricating oil, which was a blend of paraffinic and naphthenic distillate oils having Saybolt Universal viscosity at 100° F. of 1055 seconds and a viscosity index of 70. The paraffinic oils were furfural refined, lightly acid treated, clay contacted and solvent dewaxed distillate oils from paraffin base crudes, and the naphthenic oils were acid treated and neutralized distillate oils from naphthene base crudes, these oils having the following tests:

	Paraffinic Oils		Naphthenic Oils	
	A	B	C	D
Gravity, ° API.....	26.3	29.4	18.6	19.6
Flash, COC, ° F.....	500	460	450	370
Viscosity, SSU/100° F.....	1,239	330	2,381	561
Viscosity, SSU/210° F.....	94	54	91	54
VI.....	86	96.5	-18.5	0
Pour, ° F.....	+5	+5	+15	+5
Corrosion, Cu strip, 3 hrs. at 212° F.....	Neg.	Neg.	Neg.	Neg.

The blend was obtained by mixing the above oils in the following proportions by volume: 51.6 percent of A, 21.1 percent of B, 22.5 percent of C, and 4.8 percent of D.

The sulfurized terpene employed was a commercial material comprising chiefly sulfurized dipentene. It was obtained by sulfurizing a commercial dipentene by the method described in U.S. 2,445,983, which comprises essentially adding liquid terpenes to molten sulfur, employing a weight ratio of about 3:2, respectively, maintaining the temperature at about 340–400° F. for about 15 minutes, and working up the sulfurized product by treating it with aqueous sodium sulfide solution, filtering, and distilling off the light ends so as to yield a bottoms

fraction having a sulfur content of about 40 percent. The sulfurized sperm oil was a commercial material comprising chiefly sulfurized cetyl oleate. It was obtained by the method which comprises essentially heating sperm oil with about 8-15 percent its weight of sulfur at 350-400° F. for about 1-3 hours. Typical tests upon these materials are as follows:

	Sulfurized terpene	Sulfurized sperm oil
Specific gravity, 60/60° F.....	1.1728	
Gravity, ° API.....		14.4.
Viscosity:		
SSU/100° F.....		2,258.
SSU/210° F.....		241.
Pour, ° F.....		65.
Solid point, ° F.....		62.
Ash, percent.....	0.03	
Sulfated Ash, percent.....		6.01.
Neutralization number.....	2.09	0.34.
Saponification number.....		138.
Sulfur, percent (Bomb).....	37.3	10.08.
Free sulfur.....		None.
Cu strip corrosion at 212° F.....	Positive	Positive.

Lubricating compositions were prepared by incorporating the sulfurized terpene and the sulfurized sperm oil into the mineral lubricating oil in different proportions by weight. The compositions thus obtained were non-corrosive both to silver and to copper-lead bearings, as shown by the test results given in the following table.

Table I

Composition	MacCoul Corrosion Test, 350° F., 10 hrs.		EMD Silver Strip Test—Appearance
	BWL, mg.	Neut. No.	
Oil+1% Sulfurized sperm oil +0.1% Sulfurized terpene.	3	0.9	Peacock (passing).
Oil+2% Sulfurized sperm oil +0.2% Sulfurized terpene.	4	0.7	Do.

The MacCoul corrosion test is a well known test for determining the corrosiveness and oxidation stability of lubricating oils under the bearing lubrication conditions existing in internal combustion engines. In this test a copper-lead bearing specimen is rotated at high speed in a sample of the test oil maintained at 350° F. in the presence of catalytic metal surfaces and of air, and the loss in weight of the bearing specimen determined. This test is fully described in SAE Transactions, v. 50, p. 338-345 (August 1942). Oils having a bearing weight loss (BWL) after 10 hours of 10 mg. or less in this test are considered to have satisfactory anticorrosiveness to copper-lead bearings.

The EMD silver strip test is a screening test employed for determining the corrosiveness of lubricating oils to silver. It is carried out by immersing a polished silver strip in the test oil for 72 hours, the test oil being heated to approximately 285-290° F. by an oil bath maintained at 300° F. In order for the oil to pass this test the silver strip must show no flaky deposit and no etching or pitting, and there must be no excessive weight loss of the strip.

EXAMPLE 2

A lubricating composition representative of a preferred embodiment of this invention was prepared employing an additive combination comprising sulfurized terpene, sulfurized sperm oil, an organic phosphorus compound and barium alkyl phenolate sulfide. The sulfurized terpene and the sulfurized sperm oil employed were the same as those employed in Example 1. The organic phosphorus compound was a potassium salt of a P₂S₅-isobutylene polymer reaction product obtained as hereinbefore described, and sold under the trade name of "Stan-Add 47" by Standard Oil Co. (Indiana). The barium alkyl phenolate sulfide employed was "Paranox 56."

Typical tests obtained upon these two additives are as follows:

	"Stan-Add 47"	"Paranox 56"
Gravity, ° API.....	21.2	7.7
Viscosity:		
SSU/100° F.....		2,011.2
SSU/210° F.....	247	111.9
Solid point, ° F.....	5	
Ash, percent.....		14.5
Sulfated ash, percent.....	7.48	15.1
Neutralization number.....		1.25
Sulfur, percent (Bomb).....	0.72	3.49
Phosphorus, percent.....	1.54	
Potassium, percent.....	2.07	
Barium, percent.....		8.8
Cu strip corrosion.....	Neg.	Neg.

The mineral lubricating oil employed in this composition was the same as that employed in the lubricant of Example 1.

The lubricant of this example was obtained by mixing the above materials in the following proportions by weight, based on the weight of the composition:

Sulfurized terpene	0.13
Sulfurized sperm oil	1.3
"Stan-Add 47"	1.0
"Paranox 56"	1.0
Mineral lubricating oil	Remainder

EXAMPLE 3

A lubricating composition was prepared employing the same additives as those employed in the lubricant of Example 2, but with a different base oil. The base oil employed in this composition was a mineral oil blend having a Saybolt Universal viscosity at 210° F. of 80 seconds and a viscosity index of 60, comprising about 42 volume percent of a paraffinic residuum (A) obtained by dewaxing, furfural refining and clay and acid treating a residuum from a Manvel crude, and the remainder a blend of moderately refined distillate oils comprising about 28 volume percent of a heavy naphthenic distillate oil (B) about 12 volume percent of a medium viscosity naphthenic distillate oil (C) and about 18 volume percent of a light paraffinic distillate oil (D). The following tests were obtained upon these oils:

	A	B	C	D
Gravity, ° API.....	24.7	18.2	19.5	29.7
Flash, COC, ° F.....	495	435	375	395
Viscosity, SSU/100° F.....			573	179
Viscosity, SSU/130° F.....	607	713		
Viscosity, SSU/210° F.....	104	92	54	44.7
VI.....	76			92
Pour, ° F.....	0	+15	-10	+5
Corrosion, Cu strip, 3 hrs. at 212° F.....	Neg.	Neg.	Neg.	Neg.

The lubricant of this example was obtained by mixing the above materials in the following proportions by weight, based on the weight of the composition:

Sulfurized terpene	0.2
Sulfurized sperm oil	2.0
"Stan-Add 47"	1.5
"Paranox 56"	1.5
Mineral lubricating oil	Remainder

The anti-corrosive properties of the compositions of Examples 2 and 3 both to copper-lead and to silver are shown by the test data given in Table II below, together with comparative data upon similar lubricant compositions not containing the sulfurized terpene-sulfurized sperm oil combination. All of these other compositions were prepared from the same base oil as that employed in the composition of Example 3. The "Stan-Add 42" listed in the table is a commercial additive comprising the potassium neutralized P₂S₅ reaction product

of "Stan-Add 47" and in addition a sulfurized mineral oil. The "Butyl Zimate" is zinc dibutyl dithiocarbamate.

Table II

No.	Composition	MacCull Corrosion Test, 350° F., 10 hrs.		Falex Silver Pin Wear Test (Modified), Wt. Loss, mg., at—		
		BWL, mg.	Neut. No.	100° F.	200° F.	300° F.
1	Oil+2% "Paranox 56"+ 2% "Stan-Add 42".	49	2.6	12	9	17
2	Oil+2% "Paranox 56"+ 2% "Stan-Add 42"+ 0.5% "Butyl Zimate."	17	4.3	152	150	212
3	Oil+2% "Paranox 56"+ 2% "Stan-Add 42"+ 0.3% Sulfurized terpene.	5	2.7	228	337	258
4	Oil+2% "Paranox 56"+ 1.5% "Stan-Add 47"+ 0.4% Sulfurized terpene.	4	2.4	215	259	193
5	Oil+1.5% "Paranox 56"+ 1.5% "Stan-Add 47"+ 3% Sulfurized sperm oil.	24	2.2			
6	Oil+2% "Paranox 56"+ 1.5% "Stan-Add 47"+ 0.2% Sulfurized terpene +1% Sulfurized sperm oil.	8	2.4	82		109
7	Example 2	9	1.6	22		66
8	Example 3	10	2.7	33	127	131

The Falex silver pin wear test of the above table is run on a Falex machine, which is a standard tester comprising a bearing formed by two steel V blocks with a mechanism for applying load to the silver test pin held in the bearing. The test unit is immersed in a sample of the test oil and brought up to the desired temperature and the pin rotated at 290 r.p.m. for the period of the test. The amount of wear on the test pin is then determined as the difference between the original and final weights of the pin. The modified test employed was carried out for a period of 5 minutes, at temperatures of 100, 200 and 300° F., with a 15 p.s.i. load applied to the bearing and 25 minutes at 100 p.s.i. load. An oil giving a weight loss of the silver pin of less than 100 mg. at 100° F. is considered satisfactory in this test.

As shown by the data given in Table II, all of the compositions of this invention, i.e., oils No. 6, 7 and 8, containing both sulfurized terpene and sulfurized sperm oil, had the desired combination of anti-corrosiveness to copper-lead and silver lubricating properties, as shown by the satisfactorily low weight losses in both the MacCull corrosion test and the Falex silver pin test. On the other hand, all of the other oils were unsatisfactory either with respect to copper-lead corrosion or silver lubrication. Oil No. 1, containing both the barium alkyl phenolate sulfide and the potassium neutralized P₂S₅-hydrocarbon reaction product employed in oils No. 6, 7 and 8, was satisfactory with respect to silver lubrication but deficient in anti-corrosiveness to copper-lead. Oil No. 2 is representative of attempts which were made to obtain the desired combination of anti-corrosiveness to copper-lead and silver lubricating properties by means of corrosion inhibitors of the prior art, and contains in addition to the additive combination employed in oil No. 1 a small amount of zinc dibutyl dithiocarbamate, which is commonly employed as a corrosion inhibitor in lubricating oils. As shown by the data given, this oil was still unsatisfactory in copper-lead anti-corrosiveness, although improved in this respect, and it was also unsatisfactory with respect to silver lubrication. The data given for oils No. 3 and 4 show that the addition of small amounts of sulfurized terpene imparted excellent anti-corrosiveness to copper-lead, but the oils produced failed to properly lubricate the silver. The data given for oil No. 5 show that sulfurized sperm oil alone, even in an amount of 3 percent by weight, did not impart sufficient anti-corrosiveness to copper-lead to the composition.

The foregoing compositions of this invention (oils No.

6, 7 and 8) have been tested extensively in full scale engine tests, which established that they possessed the superior detergency and other lubricating properties of premium grade crankcase oils, in addition to the anti-corrosive and silver lubricating properties discussed above. Table III below gives results of CRC L-4 oxidation tests run on these oils together with comparative data for oil No. 1. The test was run at 280° F. crankcase temperature in accordance with conventional procedure.

Table III

Oil No.	1	6	7	8
CRC-L-4 Test:				
Bearing wt. loss, g. ¹	1.97	0.25	0.13	0.23
Piston Rating	8.8	9.2	9.2	9.0
Total CRC Rating	92	92	92	94
Used oil tests:				
Viscosity increase, percent, 100° F. SUS	71	65	35	50
36 hr. Neut. No.	4.3	2.9	3.2	2.9

¹ For two whole bearings.

The piston rating in the above test is on a numerical scale from 0-10, with 10 representing a perfectly clean piston and lower numbers representing progressively poorer results due to increased varnish and deposits. A piston rating above 8 in this test is satisfactory. The overall CRC rating is on a basis of 100 for perfect overall cleanliness and a value above 85 is satisfactory. A satisfactory oil should also have a bearing weight loss for two whole bearings below 0.5 gram. The foregoing tests showed that all of the compositions of this invention clearly qualified in this test. Oil No. 1, containing "Paranox 56" and "Stan-Add 42," was satisfactory from the standpoint of engine cleanliness but failed in the test because of the high bearing weight loss. Oils 6, 7 and 8, which contained in addition to the detergent-type additives of oil No. 1 small amounts of sulfurized terpene and sulfurized sperm oil, were fully equivalent to oil No. 1 from the standpoint of engine cleanliness, and in addition they gave low bearing weight losses.

Oil No. 7 (Example 3) has been employed very successfully in the lubrication of GM diesel locomotive engines. This engine contains a floating silver bushing, and it therefore requires an oil having superior silver lubricating properties in order to maintain proper lubrication of the silver bushing by splash lubrication at the temperatures of 300° F. or higher which are encountered in that area. Lubricating compositions of the prior art having sufficiently high detergency for heavy duty service and sufficient anti-corrosiveness for copper-lead bearings are incapable of lubricating silver under these conditions. The heavy duty lubricant of this invention has given outstanding performance in this service, the engines lubricated with this oil being maintained in excellent condition over long periods of time and with no difficulties encountered due to inadequate lubrication of the silver bushings.

While the additive combination comprising a sulfurized terpene and sulfurized sperm oil is employed with special advantage in crankcase oils, and has therefore been disclosed with particular reference to lubricating compositions containing detergent-type additives also, the invention is not limited to lubricating compositions of this type, since it is obvious that this additive combination may be employed in lubricating compositions generally which are required to have anti-corrosiveness to metals of the copper-lead type and good silver lubricating properties.

This application is a continuation-in-part of our application Serial No. 407,589, filed February 11, 1954, and now abandoned.

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 lubricant composition consisting essentially of a mineral lubricating oil containing about 0.05-3 percent by weight of a sulfurized terpene consisting of hydrogen, carbon and sulfur and containing about 5-45 percent of sulfur, and about 0.1-5.0 percent by weight of sulfurized sperm oil containing about 5-25 percent of sulfur, said sulfurized sperm oil imparting improved silver lubricating properties to the said composition. 5
2. A lubricant composition suitable for the lubrication of internal combustion engines having lubricated copper-lead and silver surfaces which consists essentially of a major proportion of a mineral lubricating oil containing a small amount, sufficient to impart improved anti-corrosiveness to copper-lead to the composition of a sulfurized terpene consisting of hydrogen, carbon and sulfur, and a small amount, sufficient to impart improved lubrication of silver to the composition, of sulfurized sperm oil. 15
3. A lubricant composition according to claim 2 wherein the said composition contains about 0.1-10 percent by weight of a detergent selected from the class of metal salts of organic compounds. 20
4. A lubricant composition according to claim 3 wherein the said detergent is a metal salt of an organic-substituted sulfur-containing phosphorus acid. 25
5. A lubricant composition according to claim 3 wherein the said detergent is a divalent metal salt of an alkyl phenol sulfide.
6. A lubricant composition according to claim 3 wherein the said detergent is an alkaline earth metal salt of an oil-soluble aromatic sulfonic acid. 30
7. A lubricant composition suitable for the lubrication of internal combustion engines having lubricated copper-lead and silver surfaces which consists essentially of a mineral lubricating oil having incorporated therein about 0.1-5 percent by weight of a metal salt of an organic-substituted sulfur-containing phosphorus acid, about 0.05-3 percent by weight of a sulfurized terpene consisting of hydrogen, carbon and sulfur, and about 0.1-5 percent by weight of sulfurized sperm oil. 35
8. A lubricant composition according to claim 7 wherein the said metal salt of an organic substituted sulfur-containing phosphorus acid is a phosphorus sulfide-olefin polymer reaction product neutralized with a base of a metal selected from the group consisting of alkali metals and alkaline earth metals. 40
9. A lubricant composition according to claim 7 wherein the said metal salt of an organic substituted sulfur-containing phosphorus acid is a polyvalent metal salt of a hydrocarbon substituted dithiophosphoric acid, said polyvalent metal being chosen from the group consisting of alkaline earth metals and zinc. 45

10. A lubricant composition according to claim 7 wherein the said composition contains about 0.1-5 percent by weight of an alkaline earth metal salt of an alkyl phenol sulfide.

11. A lubricant composition according to claim 7 wherein the said composition contains about 0.1-5 percent by weight of an alkaline earth metal of an oil-soluble aromatic sulfonic acid.

12. A lubricant composition suitable for the lubrication of internal combustion engines having lubricated copper-lead and silver surfaces which consists essentially of a mineral lubricating oil having incorporated therein about 0.5-3 percent by weight of a potassium neutralized phosphorus pentasulfide-olefin polymer reaction product, about 0.2-3 percent by weight of barium alkyl phenolate sulfide, about 0.1-1 percent by weight of sulfurized terpene consisting of hydrogen, carbon and sulfur and about 1-3 percent by weight of sulfurized sperm oil.

13. A method of lubricating an internal combustion engine provided with lubricated silver parts which comprises supplying to the lubricated surfaces thereof a lubricant composition consisting essentially of a mineral lubricating oil containing about 0.05-3 percent by weight of a sulfurized terpene consisting of hydrogen, carbon and sulfur, and about 0.1-5 percent by weight based on the weight of the composition of sulfurized sperm oil, said composition without the said sulfurized sperm oil being deficient in silver lubricating properties.

14. The method of claim 13 wherein the said composition contains a detergent selected from the class of metal salts of organic compounds.

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