United States Patent Office

2,820,010

Patented Jan. 14, 1958

2,820,010

LUBRICATING COMPOSITIONS

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No Drawing. Application August 11, 1955
Serial No. 527,876

3 Claims. (Cl. 252—33.4)

This invention relates to new and improved lubricating compositions. More particularly, it relates to highly detergent mineral oil lubricating compositions which are non-corrosive and wear resistant to metals such as silver and alloys of silver, copper and lead containing metal and the like.

It has been observed that one of the best additive combinations for imparting detergency to lubricants is the combination of a particular class of oil-soluble metal sulfonates and oil-soluble metal phenates. The supplemental use of conventional antioxidants, corrosion and wear inhibitors such as nitrogen-sulfur-containing compounds such as thiocarbamates or organic thiophosphates such as zinc or calcium dialkyl dithiophosphates and the like, although effective in inhibiting oxidation, corrosion and/or wear of conventional metal surfaces such as steel, steel alloys, Babbitt surfaces, cadmium and the like, have been found to be ineffective for oils which contact silver metal-wearing surfaces, such as are used in certain railroad diesel engines, for instance the silver wrist pin bushings, or in aircraft engines which have silver bearing surfaces.

It has now been discovered that these detergent lubricants containing this particular oil-soluble sulfonate-phenate additive combination can be rendered non-corrosive and wear resistant toward silver surfaces when supplemented with minor amounts of a particular class of phosphorus-sulfur-halogen-containing organic compounds.

The sulfonates are oil-soluble neutral and/or basic polyvalent metal petroleum sulfonates, of which petroleum sulfonates of the metals of group II of the periodic table having an atomic number of from 12 to 56, inclusive, are preferred, and especially of the alkaline earth metals. Suitable sulfonates include the neutral and/or basic calcium, barium and magnesium petroleum sulfonates of oil-soluble petroleum sulfonic acids. The acids can range in molecular weight from about 350 to 550 and preferably are in the range of from 400 to 500. By basic petroleum sulfonates is meant that the amount of neutralizing agent, such as calcium carbonate and/or calcium hydroxide, which is used to neutralize the petroleum sulfonic acid, is in excess of that which is normally required to neutralize the acid. The excess should be from 10 to 100 and preferably between 20 and 60 percent that normally required to neutralize the acid.

The phenates used in compositions of this invention are oil-soluble neutral and/or basic polyvalent metal polyphenates. By polyphenates is meant to include a plurality of phenolic radicals linked together through a carbon such as where a plurality of simple phenates are condensed at positions ortho and/or para to the phenolic hydroxy group through alkylidene (methylene) radicals. The cationic portion of the phenate can be the same as that in the sulfonate and usually will be, but different cations may be used. The alkaline earth metal salts of the condensation product of an alkylphenol (e. g. p-octylphenol) with formaldehyde, acetaldehyde or benzaldehyde, e. g. calcium or barium salts of octylphenol-formaldehyde condensation products ranging in molecular weight of from 500 to 1100, are particularly suitable and are preferred.

The additives which render detergent lubricants of the described class useful in the lubrication of silver and silver alloys constitute a particular class of oil-soluble phosphorus-sulfur-halogen-containing materials. One group of such materials can be prepared by reacting phosphorus sulfide with halogenated fatty materials. Reaction products of this type can be readily prepared by reacting, at temperatures of above 270° F. and preferably in the range of 285 to 325° F., halogenated fatty materials such as chlorinated sperm oil, chlorinated whale oil, chlorinated degras, or derivatives thereof such as the chlorinated free fatty acids or esters derived from said oils, with a phosphorus sulfide such as P_4S_3 and P_2S_5. The amount of phosphorus sulfide used in making reaction products of this type should be at least about equivalent to the theoretical amount required to replace the oxygen in the halogenated material. Generally the amount of phosphorus sulfide will be in the range of from 15% to 35% by weight of the halogenated fatty material. For example, a reaction product of this type was prepared by reacting chlorinated sperm oil containing 30% by weight chlorine with 20% by weight phosphorus pentasulfide at a temperature of about 300° F. for about one hour. The sludge formed was removed and the final oil-soluble product recovered contained phosphorus, sulfur and chlorine. Compounds of this type are commercially available under the trade name "Parapoid 16S" and contain 7% sulfur, 1.3% chlorine and 4.75% phosphorus. Other examples include reaction products of P_2S_5 or P_4S_3 with chlorinated degras, chlorinated castor oil, chlorinated glycerol monoleate, methyl dichlorostearate and mixtures thereof. Other chlorinated materials include chlorinated waxes, chlorinated rosins and the like and reacted with P_2S_5 or P_4S_3 as described.

Other suitable phosphorus-sulfur-halogen containing materials which can be used include additives described in U. S. Patents 2,307,183, 2,494,332 and 2,623,018. Suitable commercially available products are made by Monsanto Chemical Company and sold under the trade name of Santopoid 29, 32 and 33. Suitable materials available under these trade names have the following properties:

Property	Santopoid		
	29	32	33
Color, ASTM (diluted)	8	5½	5
Pour point, °F	−5	+5	+25
Flash point, °F. (C. O. C.)	250	250	250
Specific gravity at 60°/60° F	1.09	1.18	1.14
Viscosity:			
S. U. S. at 100° F	268	2,400	550
S. U. S. at 210° F	48	85	59
Sulfur, percent wt	8.5	8.2	8.5
Chorine, percent wt	24.0	26.0	26.0
Phosphorus, percent wt	0.56	0.56	0.55
Metals, percent wt	None	None	None

Still another phosphorus-sulfur-chlorine-containing material which is commercialy available as Anglamol 88, made by Lubrizol Corporation, and which contains 3% sulfur, 18% chlorine and 0.3% phosphorus. This product can be also used in compositions of the present invention.

The addition of minor amounts of arylamines to the above additive combination is essential. Such arylamines preferably have at least two aromatic rings. Preferred compounds are, for example, the naphthylamines: primary, secondary or tertiary alkyl, aryl or aralkyl naphthylamines in which the alkyl, aryl or aralkyl radicals are attached directly to a nuclear carbon atom of the aromatic nucleus or preferably to the nitrogen atom, such as phenyl-

alpha or beta-naphthylamine, tetralin naphthylamine, alpha alpha, alpha beta, or beta beta dinaphthylamines, various phenanthryl-, anthryl-naphthylamines, xenyl naphthylamines, benzyl phenyl naphthylamines, diphenyl naphthylamines, phenyl xenyl naphthylamines, dixenyl naphthylamines; also various phenanthryl, anthryl or picyl phenyl amines, etc. The N-aryl substituted naphthylamines are in general more useful for the present purpose.

If desired, however, other aryl amines may be used, such as diamino diaryl alkanes, e. g., diamino diphenyl methane, tetramethyl diamino diphenyl methane, tetra methyl diamino triphenyl methane, tetra ethyl diamino triphenyl methane, diamino diphenyl ethane, diamino ditolyl ethane, etc., alkylated diaryl amines, e. g., p-ethyl diphenylamine, m-ethyl diphenylamine, p-isopropyl diphenylamine, mono- and poly-amyl, hexyl, heptyl, octyl, nonyl, decyl, hexadecyl, cyclohexyl, methyl cyclohexyl and other alkyl substituted diphenylamines, etc.

The base for additives of this invention can be any natural or synthetic material having lubricating properties. Thus, the base may be a hydrocarbon oil obtained from a paraffinic, naphthenic, mid-continent or Coastal stock and/or mixtures thereof. The viscosity of these oils may vary over a wide range such as from 45 SUS at 100° F. to 100 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e. g., 2-ethyl hexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran, polyalkyl silicones, e. g., dimethyl silicone and the like. If desired, the synthetic lubricants may be used as the sole base lubricant or admixed with fixed oils and derivatives thereof.

The general formulations of compositions of this invention may be represented by:

	Broad range, percent	Limited range (percent wt.)
Oil-soluble polyvalent metal polyphenates	0.05–15	0.1–6
Oil-soluble polyvalent petroleum sulfonates	0.01–15	0.05–5
Arylamine	0.01–5	0.05–2
Base Oil (natural and/or synthetic)	Balance	Balance

The following compositions are illustrative of preferred compositions of this invention:

Composition A

	Percent weight
Oil-soluble Ca petroleum sulfonate (40% excess base)	1.5
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.2
Phenyl-α-naphthylamine	0.4
"Parapoid 16S" (P_2S_5-chlorinated sperm oil reaction product, 7% S, 1.3% Cl, 4.5% P)	0.5
Mineral lubricating oil	Balance

Composition B

Oil-soluble Ca petroleum sulfonate (40% excess base)	2.4
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.5
Phenyl-α-naphthylamine	0.2
"Santopoid 33" (8.5% S, 26% Cl, 0.55% P)	0.25
Mineral lubricating oil	Balance

Composition C

Oil-soluble Ca petroleum sulfonate (40% excess base)	1.2
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.0
Phenyl-α-naphthylamine	0.2
"Parapoid 16S"	0.5
Mineral lubricating oil	Balance

Composition D

Oil-soluble Ca petroleum sulfonate (40% excess base)	1.2
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.0
Phenyl-α-naphthylamine	0.2
"Santopoid 33"	0.25
Mineral lubricating oil	Balance

Composition E

Oil-soluble Ca petroleum sulfonate (40% excess base)	1.2
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.0
Phenyl-α-naphthylamine	0.4
"Parapoid 16S"	0.5
Mineral lubricating oil	Balance

Composition F

Oil-soluble Ca petroleum sulfonate (40% excess base)	2.4
Oil-soluble Ca salt of octyl phenolformaldehyde condensation product (av. mol wt. 1000)	1.5
Phenyl-α-naphthylamine	0.2
"Anglamol 88" (3% S, 18% Cl, 0.3% phosphorus)	0.25
Mineral lubricating oil	Balance

The mineral lubricating oil used in Compositions A–F was a solvent refined distillate blend meeting the following specification:

Gravity, ° API	min. 23
Color, ASTM	4–6
Pour point, ° F	max. 0
Flash point, ° F	min. 440
Viscosity, SUS, at 210° F	75–80
Viscosity index	min. 55

Other examples of this invention include compositions comprising a mineral lubricating oil base containing from about 1% to about 15% by weight of oil-soluble calcium and/or barium petroleum sulfonate, from about 1% to about 15% by weight calcium and/or barium salt of oil-soluble octyl phenol-formaldehyde condensation product (av. mol wt. 1000); from about 0.1% to about 0.5% by weight of a reaction product of a phosphorus sulfide, e. g., P_2S_5 or P_4S_5, with chlorinated sperm oil, chlorinated waxes, chlorinated rosin, methyl dichlorostearate and mixtures thereof.

The effectiveness of compositions of this invention in the lubrication of silver surfaces has been demonstrated by the results of comparative tests.

Compositions A through F of this invention were tested in a modified four-ball machine similar in principle to the Boerlage apparatus described in Engineering, vol. 136, July 13, 1933, using a rotating steel top ball and 3 silver discs, operated at 700 R. P. M. spindle speed, 50 pound load and 302° F. oil temperature. The results showed a reduction in scuffing and wear of the silver surfaces in the range of from 60% to 90% over similar oil compositions except that the "Parapoid 16S," "Anglamol 88" and "Santopoid 33" were replaced by various amounts ranging from 0.2% to 2% by weight of zinc dialkyl dithiophosphate, or zinc dibutyl-dithiocarbamate (Compositions 1 and 2, respectively).

Compositions A through F were also tested for a period of 100 hours in a Model 567–B diesel engine. The conditions of the silver bushings were rated on the basis of a number scale from 0 to 10, with 10 being excellent, indicating no scuffing or removal of silver from the bushing and below 6 signifying failure. Compositions A through F rated between 8 and 10, while Composition 1 rated 4 and Composition 2 rated 3; Composition 3 (mineral oil+0.2% wt. phenyl-α-naphthylamine+2.4% wt.

oil-soluble Ca petroleum sulfonate+1.5% wt. oil-soluble Ca salt of octylphenol-formaldehyde condensation product) rated 6, indicating failure of the silver bushing.

Compositions A and B were also field tested in E. M. D. F-7 freight locomotives using model 567-B engines having silver bushings. After more than 100,000 miles of operation on these compositions, the engines were in excellent condition showing no sign of wear of the silver bushings, while Composition 1 proved unsatisfactory and silver bushing failure was noted in less than 10,000 miles of operation.

In addition to the additives already described lubricating oil compositions contemplated herein may contain other agents, such as pour-point depressants, oiliness agents, blooming agents, compounds for enhancing the viscosity index of the lubricating oil, peptizing agents, etc.

This application is a continuation-in-part of our copending patent application Serial No. 278,112, filed March 22, 1952, and now abandoned.

We claim as our invention:

1. A lubricating oil composition which is non-corrosive and wear resistant toward silver consisting essentially of a major proportion of mineral lubricating oil containing from 1.2% to 2.4% of oil-soluble calcium petroleum sulfonate, from 1.0% to 1.5% of oil-soluble calcium salt of octyl phenol-formaldehyde condensation product, and from 0.2% to 0.4% each of phenyl-α-naphthylamine and 0.25% to 0.5% P_2S_5 treated chlorinated sperm oil.

2. A lubricating oil composition which is non-corrosive and wear resistant toward silver, consisting essentially of a major proportion of mineral lubricating oil containing 1.5% of oil-soluble calcium petroleum sulfonate, 1.2% of oil-soluble calcium salt of octyl phenol-formaldehyde condensation product, 0.4% of phenyl-α-naphthylamine and 0.5% of P_2S_5 treated chlorinated sperm oil.

3. A lubricating oil composition which is non-corrosive and wear resistant toward silver, consisting essentially of a major proportion of mineral lubricating oil containing 1.2% of oil-soluble calcium petroleum sulfonate, 1.0% of oil-soluble calcium salt of octyl phenyl-formaldehyde condensation product, 0.2% of phenyl-α-naphthylamine and 0.5% of P_2S_5 treated chlorinated sperm oil.

References Cited in the file of this patent

UNITED STATES PATENTS

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