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LUBRICATING COMPOSITIONS

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This invention relates to novel lubricating compositions and, particularly, those suitable for lubricating solid surfaces at high temperatures. More specifically, the present invention pertains to new and improved lubricating oil compositions which are suitable for lubricating aircraft gas turbine engines, as well as other equipment normally operated at extremely high temperatures.

In our copending application Serial No. 490,676, filed February 25, 1955, now Patent No. 2,794,981, issued June 4, 1957, of which the present application is a continuation-in-part, there are described essentially aromatic-free lubricating hydrocarbon oils containing a minor amount of a zinc, cadmium and/or lead salt of a thiocarbamic acid. Lubricants of this type are execllent for lubricating aircraft gas turbine engines and similar equipment normally operating under extremely severe conditions such as at temperatures in the range of from below minus 65° F. to about 400° F. or even higher. However, it has been observed that lubricants of this type, although effective for the lubrication and protection of metal surfaces such as of steel, steel alloys, silver, cadmium and the like, cause, or at least permit, corrosion and pitting of copper surfaces. In aircraft engines or similar equipment this may eventually result in engine failure.

The art discloses various means of preventing corrosion of copper surfaces by lubricants such as those described in U. S. Patents 2,382,781, 2,151,300 and 2,146,543 and include as the corrosion inhibitors various phosphorus-containing compounds such as organic phosphites, phosphorus-nitrogen compounds, sulfur-containing compounds, metal detergent compounds, and mixtures thereof. Under high loads and elevated temperatures the effectiveness of these materials as inhibitors of corrosion and pitting of copper surfaces has been found to be poor, particularly when in combination with a thiocarbamate.

It has now been discovered that such aromatic-free, essentially isoparaffinic, hydrocarbon oils containing a minor amount of an oil-soluble cadmium dithiocarbamate can be inhibited against corrosion or pitting of copper surfaces by the incorporation of a minor amount of an oil-soluble halogen-containing organic phosphate and/or phosphonate, without having any detrimental effect on the composition with respect to high-temperature oxidation stability.

The hydrocarbon oil should be free from aromatics and consist essentially of isoparaffins having a molecular weight of at least 350 and a pour point at least as low as —40° F. Oils of this type may be prepared by various

methods, a preferred process involving isomerization of paraffin wax such as is described in U. S. Patents 2,668,-866 and 2,668,790.

Waxes used in producing essentially aromatic-free isoparaffinic lubricating oils include commercial paraffin waxes which consist largely of n-paraffinic hydrocarbons and some naphthenic and aromatic hydrocarbons. Waxes of this type originate from distillate oil fractions such as East Texas 250 distillate, which contains about 70% straight-chain hydrocarbons covering the range from n-C_{24} to n-C_{36}, the balance being naphthenes and aromatics. On isomerizing such waxes as described in the above patents and thereafter flash-removing the light ends, solvent dewaxing, and then topping to remove volatile compounds, the topped dewaxed isomerizate contains a substantial amount of non-paraffinic material, mostly alkyl aromatics formed by dehydrogenation of naphthenes in the original wax, which must be removed by dearomatization. This may be done by suitable means, such as chemical (acid) treatment, solvent extraction, solid adsorption, or a combination of steps such as first solvent treating the oil to remove a portion of the aromatics and then treating the oil with solid adsorbents such as silica or silica-alumina gels or activated carbon to remove all of the aromatics and substantially all of the naphthenes, so that the product is essentially isoparaffinic in character. Oils of this type have a pour point of at least as low as —40° F. and preferably between —50° and —65° F., and molecular weights of at least 350 and preferably between 400 and 650.

An example of an essentially aromatic-free isoparaffinic lubricating oil (X) for use in compositions of this invention has the following properties:

°API	41.1.
Refractive index, n_n^{20}	1.4560.
Mol. weight	456.
Viscosity at 210° F	4.98.
Viscosity at 100° F	24.0.
Viscosity index, ° F	147.
Pour point, ° F	—60.
Cloud point, ° F	—60.
Flash point, ° F	460.
Volatility, percent loss in 6½ hr. at 400° F	6.4.
Monoaromatics	Less than 0.15.
Carbon, percent w	85.28.
Hydrogen, percent w	14.69.
Empirical formula	$C_{32.4}H_{66.5}$.
Naphthenicity	One ring in approximately 15% of molecules.

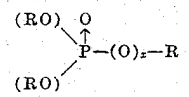
The anti-oxidant oil-soluble cadmium dithiocarbamates include the cadmium N, or N,N-hydrocarbyl substituted dithiocarbamates wherein the hydrocarbyl radicals can be alkyl, or cycloalkyl radicals. It is preferred that the hydrocarbyl radicals be alkyl radicals of from 4 to 16 carbon atoms, and preferably from 4 to 12 carbon atoms.

Illustrative examples of cadmium dithiocarbamates are cadmium dialkyldithiocarbamates such as cadmium dipropyl dithiocarbamate, dibutyl dithiocarbamate, diamyl dithiocarbamate, dihexyl dithiocarbamate, dioctyl dithiocarbamate, di-2-ethylhexyl dithiocarbamate, di-isobutyl-

dithiocarbamate, diisoamyl dithiocarbamate, N-amyl-N'-methyl dithiocarbamate, N-methyl-N'-octyl dithiocarbamate, N-octyl-N'-butyl dithiocarbamate, N-n-amyl-N'-2-methylbutyl dithiocarbamate, N-n-amyl-N'-3-methylbutyl dithiocarbamate, N'-octyl-N-2-ethylhexyl dithiocarbamate, and cadmium dicycloalkyl dithiocarbamates, such as cadmium dicyclohexyl dithiocarbamate, and the like.

The cadmium salts taken singly or in mixtures can be used in amounts varying from about 0.05% to about 5% and preferably from about 0.1% to about 2% by weight, based on the total composition.

The other essential additive, which functions as an inhibitor of pitting and corrosion of copper, is an oil-soluble halogen-containing organic phosphate or phosphonate; it can be represented by the formula:



wherein at least one of the O-linked R's is an aliphatic halohydrocarbyl radical and the other(s) R is hydrogen, an aliphatic hydrocarbyl radical, or an aliphatic halohydrocarbyl radical, all O-linked R's preferably being beta-chloro- or bromo-alkyl radicals, and wherein the R which is bonded directly to phosphorus when x is zero, is an alkenyl radical, x being an integer from zero to one.

Examples of halogen-substituted hydrocarbyl (alkyl, cycloalkyl, aralkyl) phosphates and phosphonates include haloalkyl phosphates such as tris(β-chloroethyl) phosphate, tris(β-chloro-2-ethylhexyl) phosphate, butyl di (β-chloroethyl)phosphate, butyl di(β-chloroethyl)phosphate, cresyl di(β-chloroethyl) phosphate, p-chlorophenyl di(β-chloroethyl)phosphate, β-chloroethyl diphenyl phosphate; tri(dichloropropyl) phosphate and mixtures thereof. Suitable haloalkyl alkneylphosphonates are represented by di(β-chloroethyl) vinylphosphonate, di(β-chloropropyl) vinylphosphonate and the alkyl haloalkyl vinylphosphonates, such as methyl β-chloroethyl vinylphosphate, ethyl β-chloroethyl vinylphosphonate, ethyl β-chloropropyl vinylphosphonate, and the like. Mixtures of the phosphates and phosphonates are particularly desired where oil solubility is a problem and such mixtures are exemplified by tris(β-chloroethyl) phosphate and bis(β-chloroethyl)vinyl phosphonate, or tris(β-chloropropyl)phosphate and bis(β-chloroethyl)vinyl phosphonate.

The halogen-containing phosphorus compounds are used in amounts varying from about 0.005% to about 2% and preferably from about 0.01% to about 0.5% by weight based on the total compositions.

To ensure good oxidation stability of compositions of this invention at normal engine operating temperatures, minor amounts of an organic amine antioxidant can be added. Particularly effective materials are aromatic amines such as phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine and N,N,N',N'-tetramethyldiamino-diphenylmethane. These amines, when used, are employed in amounts of from about 0.01% to about 2% by weight, based on the total composition.

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

Composition A:

	Percent
Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.25
Tris(β-chloroethyl) phosphate	0.01
Bis(β-chloroethyl) vinylphosphonate	0.015
Phenyl-α-naphthylamine	0.1
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition B:

Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.25
Tris(β-chloroethyl) phosphate	0.02
Bis(β-chloroethyl) vinylphosphonate	0.05
Phenyl-α-naphthylamine	0.2
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition C:

Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.25
Tris(β-chloroethyl) phosphate	0.01
Bis(β-chloroethyl) vinylphosphonate	0.015
Phenyl-α-naphthylamine	0.25
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition D:

Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.4
Tris(β-chloroethyl) phosphate	0.01
Bis(β-chloroethyl) vinylphosphonate	0.015
Phenyl-α-naphthylamine	0.1
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition E:

Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.25
Tris(β-chloroethyl) phosphate	0.01
Bis(β-chloroethyl) vinylphosphonate	0.015
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition F:

Cd di-2-ethylhexyldithiocarbamate	0.25
Tris(β-chloroethyl) phosphate	0.01
Bis(β-chloroethyl) vinylphosphonate	0.015
Phenyl-α-naphthylamine	0.1
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition G:

Cd diamyldithiocarbamate	0.25
Cd di-2-ethylhexyldithiocarbamate	0.25
Bis(β-chloroethyl) vinylphosphonate	0.015
Phenyl-α-naphthylamine	0.1
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

Composition H:

Cd diamyldithiocarbamate	0.50
Tris(β-chloroethyl) phosphate	0.02
Isoparaffinic lubricating oil [1] (aromatic-free)	Balance

[1] Oil (X) as described in column 2.

Other examples of this invention include compositions comprising an oil base of the type described, namely, an aromatic-free isoparaffinic lubricating oil containing from 0.1% to 1% of Cd dibutyldithiocarbamate, or Cd dihexyldithiocarbamate, or Cd dicyclohexyldithiocarbamate, or Cd diamyldithiocarbamate, and from about 0.01% to 0.5% of tris(β-chloroethyl) phosphate, or tris(β-chloropropyl) phosphate, tris(β-chloro-2 ethylhexyl) phosphate, or tris(β-bromoethyl) phosphate, bis(β-chloroethyl) vinylphosphonate, bis(β-bromoethyl) vinylphosphonate, bis(β-chlorophenyl) vinylphosphonate and mixtures thereof. To these compositions can be added from 0.1% to 1% of an amine antioxidant such as phenyl-α-naphthylamine or phenyl-β-naphthylamine.

In order to demonstrate the effectiveness of compositions of this invention in preventing pitting and corrosion of copper surfaces as well as other metal surfaces, the compositions identified below were subjected to the MIL-L-7808 oxidation-corrosion test described in Scientific Lubrication, September 1954, volume 6, No. 9, page 24, and the results are shown in Table I.

TABLE I

MIL–L–7808 oxidation-corrosion test

[347° F.]

Composition	Metal Weight Loss, mg./cm.²					Viscosity Increase, Percent at 100° F.	Acid Neut No., Mg. KOH/g.	Sludge, Percent w.
	Cu	Mg	Fe	Ag	Al			
A	0	+0.01	0	0	0	0.4	0	0.04
B	0	0	0	0.01	0	2	0.16	0.07
C	0.01	0.02	0	0.02	0.01	0	0.20	0.10
D	+0.02	0.01	0	+0.04	0	0	0.15	0.05
1*	0.18	+0.01	0.02	0	+0.01	11	1.47	0.04
2*	1.28	0	0	+0.04	0.04	−2	0.10	0.09
3*	0.07	+0.08	+0.11	+0.20	+0.07	3	0.81	0.88
4*	0.28	+0.04	+0.12	+0.16	0	−32	0.78	1.32

*(1) Oil X base containing 0.1% phenyl-α-naphthylamine + 0.1% Cd di-2-ethylhexyldithiocarbamate + 0.05% Cd diamyldithiocarbamate. (2) Oil X base containing 0.1% phenyl-α-naphthylamine + 1% Cd diamyldithiocarbamate. (3) Di-2-ethylhexyl sebacate base containing 5% tributyl phosphate + 0.5% phenyl-β-naphthylamine + 0.5% N,N'-di-sec-butyl-p-phenylene diamine + 0.5% phenothiazine. (4) Di-2-ethylhexyl sebacate base containing 5% tricresyl phosphate + 0.5% phenothiazine + 0.1% N,N'-di-sec-butyl-p-phenylenediamine.

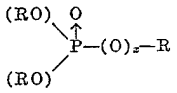
In the MIL–L–7808 bench tests, compositions A and B increased rubber swelling by only 0.3% and 1.1%, respectively, and were essentially non-corrosive to copper at 450° F. (0.62 and 0.36 mg./in.² Cu, respectively) whereas compositions 1 and 4 increased rubber swelling by 27%, and were corrosive to copper (3.2 and 2.2 mg./in.² Cu, respectively). Also compositions A and B did not pit the copper while with compositions 1 and 4 the copper surface was heavily pitted.

Other compositions of this invention which pass the MIL–L–7808 bench test include compositions B, C and D.

Compositions of this invention may contain minor amounts (0.01–1%) of extreme-pressure agents, anti-wear agents, color stabilizers, viscosity index and pour point depressants, and the like.

We claim as our invention:

1. A mineral lubricating oil comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of an oil-soluble cadmium dithiocarbamate and from about 0.05% to about 2% of an oil-soluble halogen-containing phosphorus organic compound having the general formula



wherein at least one of the O-linked R's is a chloro alkyl radical and any other O-linked R's, are selected from the group consisting of hydrogen, alkyl and chloroalkyl radical, said alkyl radicals having from 2 to 8 carbon atoms and wherein the R which is bonded directly to phosphorus when X is zero, is an alkenyl radical, X being an integer from zero to one.

2. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 2% of an oil-soluble cadmium dithiocarbamate and from about 0.05% to about 2% of a chlorine-containing C_{2-8} alkyl phosphate.

3. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of an oil-soluble cadmium dithiocarbamate and from about 0.05% to about 5% of a chlorine-containing C_{2-8} alkyl phosphonate.

4. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of cadmium di-2-ethylhexyl dithiocarbamate and from about 0.05% to about 5% of a chlorine-containing C_{2-8} alkyl phosphate.

5. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of cadmium diamyl dithiocarbamate and from about 0.05% to about 5%, of a chlorine-containing C_{2-8} alkyl phosphate.

6. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of a mixture of cadmium diamyl dithiocarbamate and cadmium di-2-ethylhexyl dithiocarbamate and from about 0.05% to about 5%, of a chlorine-containing C_{2-8} alkyl phosphate.

7. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and having incorporated therein from about 0.05% to about 5% of a mixture of oil-soluble cadmium diamyl dithiocarbamate and cadmium di-2-ethylhexyl dithiocarbamate and from about 0.05% to about 2%, of a chlorine-containing C_{2-8} alkyl phosphonate.

8. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and containing from 0.01% to 10% of a mixture of cadmium diamyl dithiocarbamate and cadmium di-2-ethylhexyl dithiocarbamate and from 0.001% to 1% of a mixture of tris(β-chloroethyl) phosphate and bis(β-chloroethyl)vinyl phosphonate.

9. A composition of claim 8 containing from 0.01 to 2% of an aromatic amine.

10. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of hydrogen and an isomerizing catalyst at a temperature between about 300° C. and 550° C. and thereafter dearomatizing the oil and containing about 0.25% each of cadmium diamyl dithiocarbamate and cadmium di-2-ethylhexyl dithiocarbamate, about 0.01% each of tris(β-chloroethyl) phosphate and bis(β-chloroethyl)-vinyl phosphonate, and about 0.1% phenyl-α-naphthylamine.

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