United States Patent Office 2,820,011 Patented Jan. 14, 1958

2,820,011

LUBRICATING COMPOSITIONS

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No Drawing. Application September 17, 1956
Serial No. 610,397

5 Claims. (Cl. 252—33.6)

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 U. S. Patent 2,794,781 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 excellent for lubricating aircraft gas turbine engines and similar equipment normally operating under extremely severe conditions such as a temperature 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 they are extremely stable at both low and moderate temperatures, lack desired high temperature stability particularly at temperatures above 400° F. and higher. In aircraft engines or similar equipment this may eventually contribute to engine failure.

The conventional anti-oxidants such as aromatic amines or alkyl phenols although relatively effective in preventing oxidation of hydrocarbon lubricating oils at low or moderate temperatures are essentially ineffective in minimizing oxidation of such oils and particularly aromatic-free lubricating hydrocarbon oils when subjected to the extremely high temperatures, namely in the neighborhood of 400° F. or higher as is encountered in gas turbine engines.

It has now been discovered that such aromatic-free essentially isoparaffinic hydrocarbon lubricating oils can be effectively inhibited against oxidation over a wide temperature range and particularly at temperatures above 400° F. and higher by addition thereto of minor but critical amounts of each of two oil-soluble polyvalent metal salts, one being an oil-soluble cadmium dithiocarbamate and the other being an oil-soluble copper salt such as an oil-soluble copper carboxylate, naphthenate, sulfonate or phenate of which the oil-soluble copper naphthenate is preferred.

The cadmium dithiocarbamate can be present in amounts varying from about 0.05% to about 5% and preferably from about 0.1% to about 2% by weight, and the copper salt can be present in amounts of from about 1 to about 200 and preferably from about 5 to 100 parts per million as copper.

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 topped to remove volatile compounds, the topped dewaxed isomerizate contains a substantial amount of non-paraffinic material, mostly alkyl aromatics formed by dearomatization. Separation of the aromatics 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 silicia-alumina gels or activated carbon to remove substantially all of the aromatics, 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° F. 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_D^{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 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-isobutyldithiocarbamate, 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 oil-soluble copper salts include copper salts of organic carboxylic acid such as aliphatic, cycloaliphatic or aromatic acids such as copper palmitate, stearate, oleate, naphthenate, benzoate, salicylate and mixtures thereof; or copper sulfonates such as copper petroleum sulfonate, copper alkyl naphthalene sulfonate, copper alkyl benzene sulfonate; or copper alkyl phenate, copper alkyl phenol sulfide and the like.

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.

To inhibit pitting and corrosion certain classes of halogen-containing organic phosphate and/or phosphonates can be added in amounts varying from about 0.005% to about 2% and preferably from about 0.01% to about 0.5% by weight.

Examples of halogen-substituted hydrocarbyl (alkyl, cycloalkyl, aralkyl) phosphates and phosphonates include haloalkyl phosphates such as tris(beta-chloroethyl) phosphate, tris(beta-chloro-2-ethylhexyl) phosphate, butyl di-(beta-chloroethyl) phosphate, butyl di(beta-chloroethyl) phosphate, cresyl di(beta-chloroethyl) phosphate, p-chlorophenyl di(beta-chloroethyl) phosphate, beta-chloroethyl diphenyl phosphate: tri-(dichloropropyl) phosphate and mixtures thereof. Suitable haloalkyl alkenylphosphonates are represented by di(beta-chloroethyl) vinylphosphonate, di(beta-chloropropyl) vinylphosphonate and the alkyl haloalkyl vinylphosphonates, such as methyl beta-chloroethyl vinylphosphate, ethyl beta-chloroethyl vinylphosphonate, ethyl beta-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(beta-chloroethyl) phosphate and bis(beta-chloroethyl) vinyl phosphonate, or tris(beta-chloropropyl) phosphate and bis(beta-chloroethyl) vinyl phosphonate.

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

Composition A

Cd diamyldithiocarbamate	0.5% wt.
Cu naphthenate	5 p. p. m. Cu.
Isoparaffinic lubricating oil * (aromatic free)	Balance.

Composition B

Cd diamyldithiocarbamate	0.5% wt.
Cu naphthenate	10 p. p. m. Cu.
Isoparaffinic lubricating oil * (aromatic free)	Balance

Composition C

Cd diamyldithiocarbamate	0.5% wt.
Cu naphthenate	10 p. p. m. Cu.
Isoparaffinic lubricating oil * (aromatic free)	Balance.

Composition D

Cd diamyldithiocarbamate	0.5% wt.
Cu naphthenate	10 p. p. m. Cu.
Phenyl-alpha-naphthylamine	0.15% wt.
Isoparaffinic lubricating oil * (aromatic free)	Balance.

Composition E

Cd diamyldithiocarbamate	0.5% wt.
Cu naphthenate	10 p. p. m. Cu.
Tris(beta-chloroethyl) phosphate	0.02% wt.
Isoparaffinic lubricating oil * (aromatic free)	Balance.

Composition F

Cd diamyldithiocarbamate	0.25%.
Cd di-2-ethylhexyldithiocarbamate	0.25%.
Phenyl-alpha-naphthylamine	0.1%.
Tris(beta-chloroethyl) phosphate	0.01%.
Bis(beta-chloroethyl) vinylphosphonate.	0.015%.
Cu naphthenate	5 p. p. m. Cu.
Isoparaffinic lubricating oil * (aromatic free)	Balance.

* Same as oil (X) identified in column 2, lines 25 to 45.

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 5 to 100 p. p. m. of Cu as copper naphthenate, petroleum sulfonate, stearate, oleate, and mixtures thereof. To these compositions can be added from 0.1% to 1% of an amine antioxidant such as phenyl-alpha-naphthylamine or phenyl-beta-naphthylamine.

The effectiveness of compositions of this invention to resist oxidation at high temperatures was determined using the High-Temperature Oxidation Test described in Industrial and Engineering Chemistry, August 1952, vol. 44, page 1834. The test temperature was maintained at 417° F. Compositions A, B, C, D, E, and F were found to be from 7 to 10 times as stable and resistant toward oxidation at 417° F. than similar compositions but in which the Cu naphthenate was omitted.

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 composition comprising a major amount of an aromatic free, essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of an isomerizing catalyst at a temperature between 300° C. and 550° C. and thereafter dearomatizing the oil and incorporating therein from about 0.05% to about 5% of an oil-soluble cadmium dithiocarbamate and an oil-soluble copper salt in an amount from about 1 to about 200 parts per million as copper.

2. A mineral lubricating oil composition comprising a major amount of an aromatic free, essentially isoparaffinic lubricating oil obtained by isomerizing a paraffin wax in the presence of an isomerizing catalyst at a temperature between 300° C. and 550° C. and thereafter dearomatizing the oil and incorporating therein from about 0.1% to about 2% of an oil-soluble cadmium dithiocarbamate and an oil-soluble copper salt in an amount from about 5 to about 100 parts per million as copper.

3. The composition of claim 2, wherein the cadmium dithiocarbamate is cadmium dialkyl dithiocarbamate and the copper salt is a copper carboxylate.

4. The composition of claim 2, wherein the cadmium dithiocarbamate is cadmium diamyl dithiocarbamate and the copper salt is copper naphthenate.

5. The compostion of claim 2, wherein the cadmium dithiocarbamate is cadmium dibutyl dithiocarbamate and the copper salt is copper naphthenate.

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