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HIGH TEMPERATURE AROMATIC-FREE MINERAL LUBRICATING OIL COMPOSITIONS

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

It is known that lubricating compositions which are effective in lubricating various equipment at normal operating temperatures, such as automotive, diesel and even certain aircraft engines, are totally ineffective when used in engines, of the type of gas turbine engines, where extremely high temperatures of the order of 400° F. or higher, are encountered. Under such high temperature conditions, known lubricating compositions deteriorate rapidly, become corrosive, volatilize and the like, thereby rendering them useless for their intended purpose.

Lubricants such as mineral oils as well as synthetic oils of the chlorinated hydrocarbon, silicone, organophosphorus, silicate ester, polyglycol, and diester types, which may or may not contain inhibiting or improving agents, have not proved to be entirely satisfactory for the protection for, example, of bearing surfaces at the temperatures encountered in aircraft gas turbine engines, or of other relatively moving solid surfaces operating at or subjected to very high temperatures and pressures. In most cases, these lubricants lack one or more of the following properties: desired load-carrying properties, good oxidation and thermal stability, resistance to hydrolysis, good pumpability properties, and low oil consumption characteristics. Thus, the silicones and silicates have the disadvantage of being poor wear inhibitors. The esters and polyglycols are deficient in regard to thermal and hydrolytic stability; while the chlorinated hydrocarbons and phosphorus compounds, in addition to these defects, are generally corrosive. Mineral oils or even synthetic hydrocarbon oils designed for high-temperature lubrication such as the 1010 and 1100 grade oils which are described in the April 1954 issue of Lubrication are also deficient because they are too viscous for engine starting at low temperatures; at high temperatures normally encountered in jet engines they are excessively volatile, provide at best marginal lubricating, tend to sludge and decompose, and are not susceptible to inhibition by known additive agents. Additionally, it has been found that at elevated temperatures the effect of oxidation inhibitors and thermal stabilizers on base lubricants cannot be predicted from results at ordinary temperatures. Thus, at elevated temperatures it has been observed that known inhibitors such as alkyl phenols, organic phosphorus compounds, organic sulfides, amines, and the like can be totally ineffective or even act as oxidation promoters. The addition of known inhibitors and additives to oils of the type discussed in order to obviate these defects has not been successful.

It has now been found that improved lubricants for jet engines and the like can be obtained having excellent thermal and oxidation stability, low-temperature pumpability, low consumption, and excellent load-carrying properties by incorporating, into a particular aromatic-free hydrocarbon base oil, minor amounts of an oil-soluble polyvalent metal salt of a thiocarbamic acid, the said cationic portion of said salt being selected from the group consisting of zinc, cadmium, and/or lead.

The hydrocarbon base oil should be aromatic-free and consist essentially or wholly of isoparaffins having a molecular weight of at least 350 and a pour point of at least —40° F. Oils of this type can be prepared by any suitable means, of which the preferred process is the production of isoparaffinic oils by isomerization of paraffin wax as described in U. S. Patents 2,668,866 and 2,668,790, as well as by any other suitable methods.

The waxes from which the aromatic-free isoparaffinic lubricating oil are prepared can be any normally solid hydrocarbon wax. The wax will usually be derived from natural mineral sources such as petroleum oil shale, oil from tar sands, gilsonite, ozokerite, or the like, but synthetic wax produced by the Fischer-Tropsch synthesis or as a by-product of other processes may also be isomerized. The process may be applied for the isomerization of crude so-called slack wax, or to so-called residue wax. While the various waxes differ somewhat in properties, e. g., melting point and hardness, they are all composed of hydrocarbons containing paraffin chains. In some paraffin waxes the chains may be slightly branched and in some the chains may be attached to naphthenic or aromatic groups. Olefinic groups are rarely present; when present they do not affect the operation of the process. In any case, the paraffin chain of the wax molecules can be isomerized to give a product having a more highly branched structure.

Essentially, the paraffin wax is isomerized in the vapor, liquid, or trickle phase in the presence of platinum, palladium, nickel, cobalt, molybdenum oxide or sulfide catalyst, or the molybdenum may be in part or even completely substituted by other group VI metals, i. e., chromium, tungsten, uranium, or by manganese or vanadium, and on suitable carriers or supports such as alumina, activated bauxite, and the like. The isomerization should be carried out at an elevated temperature of at least 300° C. and may be as high as 600° C. or higher and in the presence of a large amount of hydrogen. The mole ratio of hydrogen to hydrocarbon should be at least 1 and preferably above 5 and may be much higher such as 10, 20, 30 and 60. However, in practical operation, the ratio will rarely exceed 30. The operation may be carried out under reduced pressure, at atmospheric pressure, or at considerably elevated pressures. Pressures between about 10 and 5000 p. s. i. g. are suitable, pressures of the order of 300–1000 p. s. i. g. being generally preferred when using platinum, palladium, or nickel catalysts, while pressures of 10–50 p. s. i. g. are preferred when using molybdenum or group VI metals as catalyst.

While lubricating oils produced by the isomerization of waxes, as described above, consist largely of isoparaffinics, they also contain naphthenics and aromatic components. The aromatics must be completely removed and this can be done by any 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 in order to remove all of the aromatics and substantially the naphthenes, so that the end product is essentially isoparaffinic in character. Prior to or after the dearomatization treatment, the lubricating oil may be fractionated to remove the volatile, the low VI, and the high-pour-point fractions so that the end product is aromatic-free, essentially isoparaffinic, and has a pour point of at least —40° F. and preferably between —50° and —65°, and molecular weight of at least 350 and preferably between 400 and 650.

The following examples are illustrative of the invention.

Example I

A paraffinic wax having the following properties was isomerized:

Melting point, AMP, ° F	130/135
Average mol wt	411
Ref. ind., *n* 70/D	1.4363
Sp. gravity, *d.* 70/4	0.7849
Carbon, percent	85.50
Hydrogen, percent	14.55
Sulfur, percent	0.02
Nitrogen, percent	Less than 0.01
Aromatic carbon, percent	0
Naphthenic carbon, percent	11
Paraffinic carbon, percent	89

The isomerization was effected by vaporizing the wax with about 20 mols of hydrogen per mole of wax and passing the vapor mixture through a bed of platinum-alumina catalyst containing about 0.3% platinum under the following reaction conditions:

Temperature, ° C	420
Pressure, p. s. i. g	500
Space velocity [1]	2.5

[1] Space velocity is defined as the volume of wax processes per volume of catalyst per hour.

The product was refined by distilling off the volatile fractions, and the bottoms had the following properties:

Av. mol wt	About 420
P/p	97° F.
Ref. ind. 70° C	1.4418
Color	Light brown

The bottoms were fractionated and dewaxed using methyl isobutyl ketone in the ratio of solvent to oil of 5:1 and at a temperature of —55° C. The dewaxed oil which contained about 14% aromatics was treated with silica gel, the gel-to-oil ratio being about 8:1. The absorbent was then treated with isopentane to desorb successive fractions of the oil. The isopentane was removed and the fraction consisting essentially of isoparaffinics, as determined by ultraviolet adsorption analysis, was isolated and used as the base oil for compositions of this invention. This aromatic-free isoparaffinic oil had the following properties:

Pour point, ° F	—40
Viscosity, cs. at 210° F	5.08
Viscosity, cs. at 100° F	24.57
Viscosity index	148
Volatility, percent wt., ASTM method, 6½ hours at 400° F	7.4

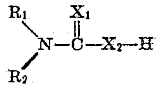
Example II

A wax having the properties shown in Example I was isomerized and refined under the same conditions but at a space velocity of 6.8 and a hydrogen-to-feed mole ratio of 30 to 1. Also, in the fractionation step, the solvent used was methyl isobutyl ketone in the ratio of solvent to oil of 10:1. The end product was an aromatic-free isoparaffinic oil having a pour point of around —55° F.

Example III

A distillate wax having a melting point of 158–160° F. and a molecular weight of about 500 was isomerized in the liquid phase at a temperature between 450 and 475° C., 500 p. s. i. g., and space velocity between 2.5 and 5.2, and the oil produced was refined as described in Example I. The end product had a pour point below —40° F., viscosity index of around 136, and less than 10% volatility loss as determined by the ASTM method.

The isoparaffinic base oils have been found to be thermally and oxidation stable, particularly at extremely high temperatures in the order of 400° F. and higher, by addition thereto of a minor amount of less than 1% and up to about 10%, and preferably between about 0.1% and about 4%, by weight of oil-soluble zinc, cadmium, and/or lead salts of a N- or N,N-hydrocarbyl substituted thiocarbamic acid, the acid portion of which can be represented by the formula:



wherein R_1 can be a hydrocarbyl radical such as alkyl, aralkyl, alkaryl, cycloalkyl; R_2 can be the same or different hydrocarbyl radical from R_1 or it can be hydrogen; X_1 and X_2 are oxygen or sulfur, at least one X being sulfur. It is desirable that both R radicals are alkyl radicals of from 4 to 16 carbon atoms in which the alkyl radicals can be of same or different chain length and structure, and it is preferred that the R's are C_4–C_{12} isoalkyl radicals of the same chain length but different structure.

These zinc, cadmium, and/or lead salts can be prepared by any suitable means such as by reacting an amine or mixtures of amines with COS or CS_2 and caustic alkali and forming the desired cadmium, zinc or lead salt therefrom by double decomposition.

Illustrative examples of zinc, cadmium, or lead thiocarbamates include zinc, cadmium, or lead dipropyl mono and dithiocarbamate, dibutyl mono and dithiocarbamate, diamyl mono and dithiocarbamate, dihexyl mono and dithiocarbamate dioctyl mono and dithiocarbamate, di-2-ethylhexyl mono and dithiocarbamate di-isobutyldithiocarbamate, diisoamyldithiocarbamate, N-amyl-N-methyl mono and dithiocarbamate, N-methyl-N-octyl mono and dithiocarbamate, N-octyl-N-butyl mono and dithiocarbamate, N-n-amyl-N'-2-methylbutyl dithiocarbamate, N-n-amyl-N'-3-methylbutyl dithiocarbamate, N-octyl-N'-2-ethylhexyl dithiocarbamate, N-ethyl-N'-phenyl mono and dithiocarbamate, dicyclohexyl mono and dithiocarbamate, diphenyl mono and dithiocarbamate, and the like.

Still further improvement can be effected by adding to the above lubricating compositions minor amounts of not more than 4% by weight of an organic amine. These amines include the aromatic, aliphatic, and heterocyclic amines, and mixtures thereof, and are represented by phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, N,N,N',N'-tetramethyldiamino-diphenyl-methane, dicyclohexylamine, N-phenyl-morpholine, octadecylamine, paraffin wax amine, cocoamine (prepared from cocoanut oil acids), and mixtures thereof. The amines which are particularly preferred are phenyl-alpha-naphthylamine and phenyl-beta-naphthylamine. These additives, when used, are used in amounts of from about 0.01% to about 2% by weight, based on the total composition.

When mixtures of the zinc, cadmium, and/or lead thiocarbamates are used, they need not exceed totally 10% and generally can be used in amounts of between 1% and 5% by weight based on the total composition.

In order to demonstrate the useful properties of lubricating compositions of this invention, the compositions identified below were subjected to (1) the MIL–L–7808 oxidation corrosion test, described in Scientific Lubrication, September 1954, vol. 6, No. 9, page 24, modified by raising the temperature to 400° F., etc.; and (2) the High-Temperature Oxidation test described in Industrial and Engineering Chemistry, August 1952, vol. 44, page 1834.

Base Oil	Additive	Amount	Modified MIL-L-7808 Test, Cu catalyst, 400° F. Induction Period, Hrs.	High-Temperature Oxidation Test, Cu catalyst, 427° F. Induction Period, min.
1010 Mineral oil	Cd diamyl dithiocarbamate	1% wt	6	
Di-2-ethylhexyl sebacate	do	do	10	
Example I	Phenyl-alpha-naphthylamine	do	6	36
Do	Neutral Ca petroleum sulfonate.	0.5% sulfate ash		0
Do	Basic Ca petroleum sulfonate	do		0
Do	Basic Ca alkyl salicylate	do		
Do	Zn alkyl salicylate	0.5% sulfate ash		32
Do	Zn petroleum sulfonate	do		28
Do	Cd petroleum sulfonate	0.77% sulfate ash		1
Do	Sn diamyl dithiocarbamate	1% wt		5
Do	Cu di-2-ethylhexyl dithiocarbamate.	do		10
Do	Ni dibutyl dithiocarbamate	do		35
Do	Zn dibutyl dithiocarbamate	do		135
Do	Cd diamyl dithiocarbamate	do	44	260
Do	Zn diamyl dithiocarbamate	do	28	115
Do	Pb diamyl dithiocarbamate	do	32	
Do	Cd diamyl dithiocarbamate	do		411
Do	Zn diamyl dithiocarbamate	do		
Do	Cd diamyl dithiocarbamate	0.5% wt		316
Do	Zn diamyl dithiocarbamate	do		

Compositions of this invention can be further improved by addition thereto of minor amounts (0.01–1%) of corrosion inhibitors, extreme pressure and anti-wear agents, and mixtures thereof.

We claim as our invention:

1. 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 incorporating therein a minor, but oxidation-stabilizing amount, of an oil-soluble cadmium salt of a thiocarbamic acid.

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 incorporating therein a minor, but oxidation-stabilizing amount, of an oil-soluble cadmium salt of an N-alkyl-substituted thiocarbamic acid.

3. A lubricating composition comprising a major amount of an aromatic-free essentially isoparaffnic 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 incorporating therein a minor, but oxidation-stabilizing amount, of an oil-soluble cadmium salt of an N,N-alkyl-substituted thiocarbamic acid.

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 incorporating therein a minor, but oxidation-stabilizing amount, of an oil-soluble cadmium salt of an N,N-alkyl-substituted thiocarbamic acid in which the two alkyl groups are dissimilar.

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 incorporating therein a minor, but oxidation-stabilizing amount, of an oil-soluble cadmium salt of an N,N-alkyl-substituted thiocarbamic acid in which the two alkyl radicals are of the same chain length but are of different structure.

6. The composition of claim 5 wherein the isomerization is carried out in the vapor phase with at least 1 mole of hydrogen per mole of wax in the presence of a platinum containing catalyst and the cadmium salt is cadmium diamyl dithiocarbamate.

7. The composition of claim 5 wherein the isomerization is carried out in the vapor phase with at least 1 mole of hydrogen per mole of wax in the presence of a platinum catalyst and the cadmium salt is cadmium di-2-ethylhexyldithiocarbamate.

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