United States Patent Office

3,309,314

Patented Mar. 14, 1967

3,309,314

LUBRICANT COMPOSITIONS

James R. Price, Robert C. Spillman, and Kenneth T. Wendler, all of Alton, Ill., assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed May 29, 1964, Ser. No. 371,184
6 Claims. (Cl. 252—32.5)

This invention relates to improved synthetic lubricating compositions which are oxidation-stable and non-corrosive, and which have excellent extreme-pressure and antiwear properties.

Recently, synthetic lubricants have gained prominence in the field of lubrication because of stringent requirements of certain new applications. These lubricants, which are frequently esters, ethers, silicones, or hydrocarbon polymers, are generally designed, and may be "tailored" for special applications where conventional mineral oils are not satisfactory. Synthetic lubricants have low pour points and desirable viscosity characteristics, and can generally be used at temperatures considerably above the decomposition temperatures of most mineral oils. Accordingly, these oils have found use in jet aircraft, missiles, automatic weapons, etc., where wide temperature ranges and extreme operating conditions are likely to be encountered. Proper lubrication of aircraft gas turbines, for example, requires ability to function at bulk oil temperatures as low as —65° F. to as high as 450° to 500° F. for some applications.

Under the extreme conditions to which these lubricants are subjected, synthetic oils are often corrosive and undergo thermal and oxidative deterioration resulting in sludge and deposit formation, viscosity change, discoloration, and other undesirable changes. Attempts to correct these deficiencies by conventional methods are often unsatisfactory because of the extreme nature of the application of the oil; for example, addition of an antioxidant to reduce deterioration may cause increased corrosion, or addition of an an antiwear agent might decrease stability. Furthermore, attempts to remedy the new deficiencies frequently compound the problem by causing increased sludging, etc. Therefore, available information regarding mineral oil formulations is of little aid in developing successful synthetic lubricants.

It has now been discovered that synthetic lubricants containing (1) 0.01 to 5% by weight of a C_8 to C_{10} oil-soluble aliphatic amine salt of a mono- to per-haloalkyl phosphonic acid, the haloalkyl radical of which contains 1 to 4 carbon atoms, and (2) 0.01 to 10% by weight of a primary to tertiary amine of which each non-hydrogen substituent is a mono- to di-nuclear unsaturated cyclic radical containing from 4 to 10 carbons and from 0 to 2 nitrogens, have excellent antiwear, oxidation and anticorrosion properties. The term "unsaturated cyclic radical" used herein includes radicals of heterocyclic groups such as pyridine, quinoline, and diazine as well as aryl radicals such as benzene and naphthalene. These amines will be referred to herein as "cyclic amines." Lubricants containing the combination of the amine-phosphonic acid salt (hereinafter also called "the salt") and the cyclic amine exhibit surprising oxidation stability, non-corrosivity, and cleanliness.

THE ADDITIVE COMBINATION

Aryl amines are, of course, well known as lubricating oil oxidation inhibitors. Although phosphonic acid-amine salts are known antiwear additives, they are not known to increase oxidation stability; indeed, these salts do not, by themselves, have antioxidant properties. It has now been found, however, that these salts cooperate with cyclic amine antioxidants to produce increased oxidation resistance. This effect is illustrated in Table I, below, which illustrates the results of an air oxidation test conducted at 400° F. Air was passed at a rate of 70 ml./min. through a 20-gram sample which contained 20 p.p.m. copper and 20 p.p.m. iron (as soluble octoates) as catalysts. The base stock, designated Oil E, consisted of about 60% C_4–C_7 alphatic-acid esters of pentaerythritol and about 40% C_5 – C_{10} aliphatic - acid esters of dipentaerythritol.

TABLE I.—RESULTS OF 400° F. AIR OXIDATION TEST

Formulation	Induction Period hr.	
	First Run	Second Run
1. Oil E plus 1% phenyl-α-naphthylamine	25	24
2. Oil E plus 0.2% salt "A" [1]	1	
3. Oil E plus 1% phenyl-α-naphthylamine plus 0.2% salt "A"	51	46

[1] Salt "A" is a mixed salt of monochloromethyl phosphonic acid and a mixture of tert-C_{18}–C_{22} alkyl primary amines.

The data in Table I illustrate the cooperative effect of an amine-phosphonic acid salt and a cyclic amine antioxidant in promoting oxidation stability of a synthetic base oil. The introduction period of the cyclic-amine-stabilized base is almost doubled by addition of the salt, which is shown to be ineffective, independent of the cyclic amine, as an oxidation inhibitor.

Further evidence of beneficial effects attributable to the presence of the cyclic amine-salt combination of the invention is evidenced in the oxidation-corrosion test results in Table II. Oil B (about 95% C_4–C_7 aliphatic acid esters of pentaerythritol, 5% C_5–C_{10} aliphatic aicd esters of dipentaerythritol), was subjected alone, and with the additives of the invention individually and in combination, to a test similar to that described in Federal Test Method Standard No. 791*a* as method 5308.4. Fluid samples (100 cc.) were heated at a temperature of 450° F. for 72 hours in the presence of 1.0 square inch of each of the metals listed in the table. Air was bubbled through the sample at the rate of 5 liters per hours. Corrosion was measured in weight loss per unit of surface area.

TABLE II.—RESULTS OF CORROSION-OXIDATION TESTS AT 450° F.

Run	Formulation	Corrosion, mg./cm.^{2}					Acid No. Increase	Viscosity (100° F.) Increase, Percent
		Mg	Al	Cu	Fe	Ag		
1	Oil B	−19.7	+0.02	−0.13	−26.9	+0.07	17.1	Solid
2	Oil B plus 1% 2,2′-dipyridylamine	−3.61	+0.08	−0.30	+0.18	+0.14	8.8	15.8
3	Oil B plus 1% salt "A" [1]	−17.35	+0.04	−1.55	+0.05	+0.14	38.9	379
4	Oil B plus 1% 2,2′-dipyridylamine plus 0.1% salt "A"	−0.45	+0.30	−0.13	+0.17	+0.27	0.1	9.9

[1] Salt "A" is a mixed salt of monochloromethyl phosphonic acid and a mixture of tert-C_{18}–C_{22} alkyl primary amines.

Several conclusions are apparent from these results. Rather severe corrosion of iron, copper, and/or magnesium is experienced in the synthetic base in the absence of any additive, or when either the cyclic amine or salt

additive is present alone. In the presence of both the cyclic amine and salt additives, however, corrosivity of all of the metals is considerably reduced. Low corrosivity to a number of different metals is essential for some applications, for instance, jet aircraft turbine lubrication, where the oil contacts parts made from a variety of metals and alloys. Also, presence of corrosion products may be detrimental to the stability of the oil, and accellerates degradation and decomposition.

As well as illustrating the excellent corrosion-inhibiting properties compositions of the invention, the data in Table II also provide further illustration of the enhanced oxidation resistance of these mixtures. The increases in acidity and viscosity, which are qualitative measures of stability, are considerably lower for the oil containing the cyclic amine-salt combination than for the oil containing no additive or only one of the additives of the combination.

Oils containing the cyclic amine-salt combination of the invention also have a particular advantage in exhibiting extremely low lead (Pb) corrosion. In the past, synthetic lubricants containing cyclic amine antioxidants have generally been corrosive to lead, in the absence of lead-corrosion inhibitors such as 2,6-di-tert-butyl-4-dimethylamine-p-cresol. Lead is corroded much more easily than other metals, such as steel, aluminum, magnesium, copper, and silver; also, lead corrosion is not predictable from corrosion results of other metals. The difference of the lead corrosion function from the normal corrosion function is apparent from a comparison of Run 3 in Table III, below, with Run 2 in Table II. These results show that in a pentaerythritol ester oil, 2,2'-dipyridylamine acts generally as a corrosion inhibitor for most metals, but promotes lead corrosion. Indeed, many other additives which are known to be corrosion inhibitors in other applications have been found to be ineffective for inhibiting lead corrosion.

The lead corrosion induced by the cyclic amines is substantially eliminated by addition of the phosphonic acid-amine salt. This is evidenced in Table III below, which shows the results of lead-corrosion tests for Oil B (the pentaerythritol ester base described before Table II) alone, Oil B with cyclic amine antioxidants, and Oil B with the amine-salt combination of the invention. These oils were subjected to the MacCoull-Ryder test and the SOD lead corrosion test. The MacCoull-Ryder test was run for five hours at 325° F; this test is described in detail SAE Journal 50, 8, p. 338 (Aug. 1942). In the SOD lead corrosion test, rapidly rotating panels of lead and copper were heated in the oil sample for one hour at 325° F. while air was bubbled through the sample; this test is described in detail in Federal Test Method Standard No. 791*a* Method 5321.1. The compositions tested and results obtained are presented in Table III below.

TABLE III.—RESULTS OF LEAD-CORROSION TESTS

Run	Formulation	MacCoull-Ryder Lead Corrosion, Weight Loss, g. (325° F., 5 hr.)	SOD Lead Corrosion, mg./in² Loss (325° F., 1 hr).
1	Oil B[1]	−0.0296	−5.70
2	Oil B plus 1% phenyl-α-naphthylamine	−2.3174	−5.94
3	Oil B plus 1% 2,2'-dipyridylamine	−1.8285	
4	Oil B plus 1% phenyl-α-naphthylamine plus 0.2% salt "A".	−0.0025	−0.06
5	Oil B plus 1% 2,2'-dipyridylamine plus 0.1% salt "A."	−0.0022	

[1] About 95% C_4–C_7 alkanoic acid esters of pentaerythritol, 5% C_5–C_{10} alkanoic acid esters of dipentaerythritol.

From these results it is apparent that the high lead corrosion induced by the cyclic amine is completely inhibited by the phosphonic acid-amine salt.

THE CYCLIC AMINE

Suitable cyclic amines to be used in the amine-salt combination of the invention are primary to tertiary amines, each non-hydrogen substituent of which is a mono- to dinuclear unsaturated cyclic radical containing from 4 to 10 carbon atoms and from 0 to 2, preferably 0 to 1 nitrogen atoms. Primary to secondary, especially secondary, amines are preferred; the cyclic radicals are preferably aromatic. Included are aryl amines and amines having nitrogen-containing heterocyclic substituents. Many of these amines are well known antioxidants for both synthetic and mineral lubricating oils. Examples of suitable aryl amines are phenyl-α-naphthylamine, phenyl-β-naphthylamine, diphenylamine, di-α-naphthylamine, di-β-naphthylamine, di-α,β-naphthylamine, triphenylamine, and diphenyl naphthylamine. Examples of suitable amines having a nitrogen-containing heterocyclic constituent are dipyridyl amines, aminopyrides, aminoquinolines, etc. Specific examples include 2,2'-dipyridylamine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2,6-diaminopyridine, 4-4' - dipyridylamine, phenyl - 2 - pyridylamine naphthyl-2-pyridylamine, 3-aminoquinoline, and phenyl-3-quinolylamine. Preferred amines are phenyl-α-naphthylamine, diphenylamine, 2-2'-dipyridylamine and the aminopyridines. The cyclic amines are used in amounts of from 0.01 to 10% by weight, preferably 0.02–5% by weight of the final lubricating composition.

THE SALT

The salt to be used in combination with the cyclic amine described above is a salt of C_8–C_{30} alkylamine and a mono- to per-haloalkyl phosphonic acid, the haloalkyl group containing 1 to 4, preferably 1 to 2 carbon atoms. The haloalkyl phosphonic acids used for preparing the salts for use in the invention generally have the formula

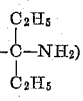
$$R-\overset{\overset{O}{\|}}{P}-(OH)_2$$

where R is mono- to per-haloalkyl containing 1 to 4, preferably 1 to 2 carbon atoms. R preferably contains 1 to 2 halogen atoms, more preferably 1 chlorine atom; it is also preferred to have at least one of the halogens substituted on the alpha carbon atom. Preferred halogens are fluorine, chlorine, and bromine, especially chlorine. Examples of suitable phosphonic acids are monochloromethylphosphonic acid, 1-monochloroethylphosphonic acid, 1,1 - dichloropropylphosphonic acid, perchloroethylphosphonic acid, dichloromethylphosphonic acid, perchloromethylphosphonic acid, monobromomethylphosphonic acid, 1,1-chlorobromopropylphosphonic acid, dibromomethylphosphonic acid, monofluoromethylphosphonic acid, and 1,1-difluoroethylphosphonic acid.

Amines which form effective salts of the phosphonic acids are primary to secondary alkyl amines having at least 8, preferably 8 to 30, and more preferably 12 to 24 carbon atoms per molecule. Branched tertiary-alkyl primary amines are preferred; "branched" in this context means having at least 2 hydrocarbon substituents attached to the main carbon chain. As the tertiary-alkyl radical, the radical of polyisobutylene and polypropylene, and mixtures of these are particularly preferred. Examples of these amines are 1,1,3,3-tetramethylbutylamine, 1,1,3,3,5,5 - hexamethylhexylamine, 1,1,3,3,5,5,7,7-octamethyloctylamine, and 1,1,3,3,5,5,7,7,9,9-decamethyldecylamine.

Tertiary alkyl methyl primary amines, such as 2,2,4,4-tetramethylpentylamine and 2,2,4,4,6,6-hexamethyl hexylamine are also suitable.

Other primary amines having 8 to 30 carbons which are appropriate for forming the salts of the invention are described in Bortnick, U.S. 2,606,923, issued Aug. 12, 1952, and Bortnick, U.S. 2,611,782, issued Sept. 23, 1952. These include tert-tridecylamine,



as well as isoheptyl diethyl carbinylamine, isooctylethyl propylcarbinylamine, etc. Primary amines of this type are commercially available from Rohm and Haas Company under the trade name of "Primenes." The amine may also be a polyamine, such as a diamine or triamine, and may contain other non-reactive groups, such as amide or ether groups, in the carbon chain.

Some specific examples of secondary amines for making the phosphonic acid salts are diamylamine, dihexylamine, di(2-ethylhexyl)-amine, dioctylamine, didecylamine, didodecylamine, ditetradecylamine, dihexadecylamine, dioctadecylamine, dibromodioctadecylamine, isopropyloleylamine, diricinoelylamine, butylricinoleylamine, butyl-2-ethylhexylamine, dilaurylamine, methyloleylamine, ethyloctaylamine, isoamylhexylamine, dicyclohexylamine, dicyclopentylamine, cyclohexyloctylamine, cyclohexylbenzylamine, benzyloctylamine, benzyl-2-ethylhexylamine, allyloctylamine, dodecyl-2-ethylhexylamine, (1-isobutyl-3-methylbutyl)-3,3,3-methylcyclohexylamine, di(1-isobutyl-3-methylbutyl)-amine; N-n-dodecyldiethylenetriamine, N-n-tetradecyldiethylenetriamine, octylethylene diamine, N-2-ethylhexyl N-hexadecyl triethylene tetramine, heptyl trimethylene diamine, N-tetradecyl tripropylene tetramine, N,N'-diallyl trimethylene diamine, 3-hexyl-morpholine, and the like.

The phosphonic acid-amine salts for use in the invention can be prepared by direct neutralization of haloalkylphosphonic acid with a substantially stoichiometric amount of amine. The reaction occurs at normal or moderately elevated temperatures and may be carried out in the presence of an inert diluent or solvent, such as a hydrocarbon, alcohol, ether, ketone, etc. Preparation of these salts is described in Watson et al., U.S. 2,858,332, issued Oct. 28, 1958.

The phosphonic acid-amine salts useful in the invention may also be modified with an alkali metal as described in Price et al., U.S. 3,112,267, issued Nov. 26, 1963. The full amine salt of the phosphonic acid is prepared and is then treated in a low-boiling solvent with an alkali metal hydroxide, carbonate, or alcoholate such that one of the amine groups is replaced with an alkali metal. Preferred alkali metals are sodium, potassium, and lithium.

The amine-phosphonic acid salts are used in amounts of from about 0.005 to 5% by weight, preferably about 0.01 to 5% by weight of the lubricating composition. Weight ratios of the amount of salt to the amount of cyclic amine used in the combination of the invention are from about 0.01/1 to about 10/1, preferably from about 0.1/1 to about 5/1. The combination may be added as a package to lubricating oils.

THE BASE OIL

The additive combination of the invention is appropriate in mineral as well as synthetic lubricating oils, but is particularly useful in synthetic oils which are used under more extreme conditions where the particular advantages of the additives of the invention become more pronounced. Synthetic lubricants suitable for the invention are of various types, such as aliphatic esters, silicones, polyalkylene oxides, polyphenyl ethers, fluorinated hydrocarbons, polyolefins, and phosphate esters. Examples of silicones include methyl silicone, methylphenyl silicone, methylchlorophenyl silicone, etc. Examples of polyalkylene oxides are polyisopropylene oxide, polyisopropylene oxide diether, and polyisopropylene oxide diester. Fluorinated hydrocarbons include fluorinated oils and perfluorinated hydrocarbons.

Preferred synthetic lubricant base stocks are esters of alcohols having 1 to 20, especially 4 to 12, carbon atoms and aliphatic carboxylic acids having from 3 to 20, especially 4 to 12, carbon atoms. The ester base may be a simple ester (reaction product of a monohydroxy alcohol and a monocarboxylic acid), a polyester (reaction product of an alcohol and an acid, one of which has more than one functional group), or a complex ester (reaction product of a polyfunctional acid with more than one alcohol, or of a polyfunctional alcohol with more than one acid). Also, excellent synthetic lubricants may be formulated from mixtures of esters, such as major proportions of complex esters and minor amounts of diesters.

Monohydric alcohols suitable for making ester base stocks include methyl, butyl, isooctyl, dodecyl and octadecyl alcohols. "Oxo" alcohols prepared by the reaction of olefins with carbon monoxide and hydrogen are suitable. Neo alcohols, i.e., alcohols having no hydrogens on the beta carbon atom are preferred. Examples of such alcohols are 2,2,4-trimethylpentanol-1 and 2,2-dimethyl propanol.

Polyalcohols used for the production of base oil esters preferably contain 1 to 12 carbons. Examples of dialcohols are 2-ethyl-1,3-hexanediol, 2-propyl-3,3-heptanediol, 2-butyl-1,3-butanediol, 2,4-dimesityl-1,3-butanediol, and polypropylene glycols having molecular weights of from about 100 to 300. Alcohols having 3, 4, 5 or more hydroxyl groups per molecule are also suitable and are preferred; examples of these polyols are pentaerythritol, dipentaerythritol, and trimethylolpropane. Mixtures of alcohols may also be used.

Suitable carboxylic acids for making the ester base oils include mono- and di-basic aliphatic carboxylic acids. Examples of appropriate acids are butyric, valeric, sebacic, azelaic, suberic, succinic, caproic, adipic, ethyl suberic, diethyl adipic, oxalic, malonic, glutaric, pentadecanedicarboxylic, diglycolic, thiodiglycolic, acetic, propionic, caprylic, lauric, palmitic, pimelic, and mixtures thereof. Preferred acids are sebacic, azelaic, glutaric, adipic, and their mixtures.

Examples of suitable ester base oils are ethyl palmitate, ethyl laurate, butyl stearate, di(2-ethylhexyl) sebacate, di-(2-ethylhexyl) azelate, ethyl glycol dilaurate, di-(2-ethylhexyl) phthalate, di-(1,3-methylbutyl) adipate, di-(1-ethylpropyl) azelate, diisopropyloxylate, dicyclohexyl sebacate, glycerol tri-n-heptoate, di(undecyl) azelate, and tetraethylene glycol di-(2-ethylene caproate), and mixtures thereof. An especially preferred mixture of esters consists of about 50 to 80% wt. bis(2,2,4-trimethylpentyl) azelate and 20 to 50% wt. 1,1,1-trimethylyl propane triheptanoate.

Especially preferred esters for use as base stocks in the present invention are esters of monocarboxylic acids having 3 to 12 carbons and polyalcohols such as pentaerythritol, dipentaerythritol, and trimethylolpropane. Examples of these esters are pentaerythrityl butyrate, pentaerythrityl tetrabutyrate, pentaerythrityl tetravalerate, pentaerythrityl tetracaproate, pentaerythrityl dibutyratedicaproate, pentaerythrityl butyratecaproate divalerate, pentaerythrityl butyrate trivalerate, pentaerythrityl butyrate tricaproate, pentaerythrityl tributyratecaproate, mixed C_{4-10} saturated fatty acid esters of pentaerythritol, dipentaerythrityl hexavalerate, dipentaerythrityl hexacaproate, dipentaerythrityl hexaheptoate, dipentaerythrityl hexacaprylate, dipentaerythrityl tributyratecaproate, dipentaerythrityl trivalerate trinonylate, dipentaerythrityl mixed hexaesters of C_{4-10} fatty acids and trimethylolpropane heptylate. Pentaerythritol esters of mixtures of C_4–C_{12} acids are excellent base oils, and are commercially available from Hercules Chemical Company.

Ester oils may be prepared by simple reaction of the

alcoholic and acidic reactants in proportions suitable for producing the desired product; preparation preferably takes place in a solvent such as an aromatic hydrocarbon, and in the presence of a catalyst, such as HCl, HF, HBr, H_2SO_4, H_3PO_4, $SOCl_2$, BF_3, etc. Preparation of suitable esters is described in Eichemeyer, U.S. 3,038,859, issued June 12, 1962, and Young, U.S. 3,121,109, issued Feb. 11, 1964.

Some specific embodiments of the compositions of the invention are as follows:

Composition 1

Base A:
60% w. bis(2,2,4-trimethylpentyl)azelate
40% w. 1,1,1-trimethylyl propane triheptanoate
+1% w. phenyl α-naphthylamine
+0.2% w. salt of mixed C_{18}–C_{24} primary amines and monochloromethyl phosphoric acid

Composition 2

Base B:
60% w. C_4–C_7 acid esters of pentaerythritol
40% w. C_5–C_{10} acid esters of dipentaerythritol
+1% w. diphenylamine
+0.2% w. salt of mixed C_{18}–C_{24} primary amines and monochloromethyl phosphonic acid

Composition 3

Base B+1% w. 2,2′-diphyridylamine+0.2% w. salt of mixed C_{18}–C_{24} primary amines and monochloromethyl-phosphonic acid

Composition 4

Base A+1% 4-aminopyridine+0.2% w. salt of C_{18}–C_{24} mixed primary amines and 1,1-dichloroethylphosphonic acid

Composition 5

Base B+1% diphenylamine+0.2% w. salt of C_{18}–C_{24} mixed primary amines and monochloromethylphosphonic acid

We claim as our invention:

1. A lubricant composition comprising a major amount of a synthetic ester lubricating oil and
(1) 0.01 to 5% by weight of a salt of an alkyl amine selected from the group consisting of alkyl primary and alkyl secondary amines having from 8 to 30 carbon atoms and a mono- to per-haloalkyl phosphonic acid, wherein the haloalkyl radical contains 1 to 2 carbon atoms, and
(2) 0.01 to 10% by weight of 2,2′-dipyridylamine.

2. The composition of claim 1 wherein the salt is a mixed salt of an alkyl primary amine having 8 to 30 carbon atoms and moonchloromethylphosphonic acid.

3. The composition of claim 1 wherein the phosphonic acid is monochloromethylphosphonic acid.

4. The composition of claim 1 wherein the synthetic ester lubricating oil comprises esters of monocarboxylic acids having from 4 to 12 carbon atoms and pentaerythritol.

5. The composition of claim 1 wherein the synthetic ester lubricating oil comprises a mixture of from 50 to 80% by weight bis(2,2,4-trimethylpentyl)azelate and 20 to 50% by weight 1,1,1-trimethyl propane triheptanoate.

6. A lubricant additive composition consisting essentially of
(1) a salt of an alkyl amine selected from the group consisting of alkyl primary and alkyl secondary amines having from 8 to 30 carbon atoms and a mono- to per-haloalkyl phosphonic acid, wherein the haloalkyl radical contains 1 to 2 carbon atoms, and
(2) 2,2′-dipyridylamine, the weight ratio of (1) to (2) being from about 0.01/1 to about 10/1.

References Cited by the Examiner

UNITED STATES PATENTS

2,559,754	7/1951	Bittles et al.	252—32.5 X
2,683,691	7/1954	Thorpe et al.	252—32.5
2,777,819	1/1957	Williams et al.	252—32.5
3,121,691	2/1964	Eickemeyer	252—50 X
3,126,344	3/1964	Matuszak et al.	252—56 X

OTHER REFERENCES

Barnes et al.: "Synthetic Ester Lubricants," Lubrication Engineering, Aug. 1957, pages 454–458.

DANIEL E. WYMAN, *Primary Examiner.*

P. P. GARVIN, *Assistant Examiner.*