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3,483,129

PERFLUORINATED SUBSTITUTED PHENYL PHOSPHINE LUBRICANT ADDITIVES

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20 Claims

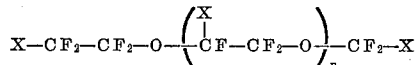
ABSTRACT OF THE DISCLOSURE

Perfluorinated substituted phosphines; for example, tris[4-(pentafluorophenoxy)tetrafluorophenyl] phosphine and tris(4-heptafluorotolyl) phosphine are used as additives to perfluorinated aliphatic polyethers. A minor percentage, up to 5 percent but preferably 0.01–0.2 percent, of the additives are used. The resulting compositions are useful as lubricants and hydraulic fluids at temperatures as high as 650° F.

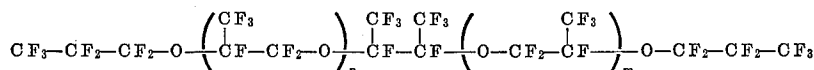
The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without payment to use of any royalty thereon.

BACKGROUND

It has been taught in the art that prefluorinated aliphatic polyethers are useful as lubricants at high temperatures. Among the compounds which can be used are, for example, compounds of the general formula:



where n is a positive integer including zero and X is a member of the class consisting of fluorine and the perfluoromethyl radical. The preparation of these compounds (hereinafter referred to as base fluid I) is disclosed by Miller in U.S. Patent No. 3,242,218. Also among the compounds which are particularly useful are compounds of the type (hereinafter referred to as base fluid II):



where n' and m are integers greater than 2. The preparation of these latter compounds is disclosed by Milian in U.S. Patent No. 3,214,478.

Developments in aerospace technology have placed a severe demand on lubricants, particularly where the lubricants are to function in oxidizing atmospheres and at temperatures up to 650° F. Such conditions test not only the oxidative stability of the lubricant but also its high temperature stability in the presence of metals such as steel, titanium and the like. The above described perfluorinated aliphatic polyethers, without additives, have failed under such exacting conditions. Specifically, such polyethers corrode ferrous and titanium alloys above 500° F. to a significant degree.

In our copending application (Ser. No. 581,419 filed Sept. 21, 1966, now U.S. Patent 3,393,151 dated July 16, 1968) we suggested the use of lubricant compositions comprising a perfluorinated aliphatic polyether and a compound such as tris(pentafluorophenyl)phosphine or tris(pentafluorophenyl)phosphine oxide. We found that the latter compositions were highly effective in reducing corrosion and fluid degradation at temperatures of 550–600° F., but their usefulness is somewhat limited by their volatility at these and, particularly, higher temperatures.

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OBJECTS

It is therefore an object of this invention to provide new and useful compositions of matter.

It is a further object to permit more latitude in the choice of metals for future aerospace systems for operation at 650° F. in the presence of a lubricant.

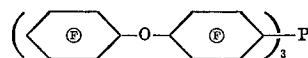
It is a further object to provide compositions which can withstand severe oxidative stress at temperatures of 650° F. without appreciable degradation.

It is a further object of the invention to provide such compositions for use as lubricants, hydraulic fluids, and the like, for contact with metal bearings and other metal surfaces in gas turbine engines and in aerospace systems at temperatures in some cases as high as 650° F.

It is a specific object of the invention to provide compositions comprising a perfluorinated aliphatic polyether and substituted perfluorinated phenyl phosphines.

DESCRIPTION OF THE INVENTION

We have now found that the foregoing and related objects can be attained in a composition comprising a perfluorinated aliphatic ether and a minor proportion of a perfluorinated phenoxyphenyl phosphine having the structure:



Particularly useful compositions comprise, as the phosphine, tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine; and comprise as the ether, base fluid I or base fluid II.

The perfluorinated phenoxyphenyl phosphine additive is preferably used in proportions of about 0.01–0.2 percent by weight partly for the reason that optimum performance is attained and partly for the reason that the additive is more readily dissolved in the base fluid. Tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine is soluble in the base fluids at room temperature at concentrations of about 0.02 weight percent or less. Between 0.02 and 0.2 weight percent, the phosphine is not soluble at room temperature but is soluble at elevated temperatures. However, concentrations above 0.2 weight per-

cent, and up to about 5 percent, are not believed to be detrimental and can be used if additive solubility is not required at room temperature. It is recommended that at least 0.1 percent additive be used for operations at 650° F.

The compositions can be prepared by adding the desired proportion of the additive to the base fluid and heating with agitation until the composition is homogeneous and solution has taken place.

Another example of a substituted perfluorinated phenyl phosphine that can be used is, tris(4-heptafluorotolyl) phosphine.

Tris(4-heptafluorotolyl)phosphine, having the structure



is highly effective in reducing corrosion of ferrous and titanium alloys in the perfluorinated aliphatic polyether fluids and inhibits the degradation of the fluids themselves. This new additive is effective in concentrations as low as 0.10 wt. percent and optimum concentrations appear to be near 0.25 wt. percent. The optimum concentrations of previous perfluoroarylphosphine additives, set forth in patent application Ser. No. 581,419, filed Sept. 21,

1966, were as high as 0.5 to 1.0 wt. percent. Thus optimum effectiveness of tris(4-heptafluorotolyl)phosphine is obtained at lower concentrations than with former additives as evidenced in 600° F. oxidation-corrosion tests.

Tris(4-heptafluorotolyl)phosphine is soluble in the perfluorinated aliphatic polyether fluids in 0.25 wt. percent for several days at room temperature. Concentrations of the additive less than 0.25 wt. percent remain soluble for longer periods of time below room temperature. Concentrations of the additive as high as 5 wt. percent are not believed to be seriously detrimental and can be used if additive solubility is not required at room temperature.

EXAMPLE 1

Compositions consisting of base fluid I with 0.05 and 0.20 percent tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine were formulated and compared with base fluid I with no additives in an oxidation-corrosion test in contact with various metal washers. The test procedure involves the total immersion of the metal specimen in the test composition and, for a period of 24 hours, the bubbling of one liter per hour of dry air through the composition and over the metal specimens at a temperature of 600° F. The weight change (mg. per cm.²) of the metal washers is used as the measure of corrosion. The metal specimens chosen represent a variety of ferrous alloys likely to be encountered in the commercial use of the compositions of the invention. Results are shown in Table 1, weight changes of less than 0.10 mg. per cm.² being considered negligible and weight changes less than 0.20 mg. per cm.² being minor.

EXAMPLE 2

The test procedure of Example 1 was carried out using 0.05 percent of the additive with base fluid II. Results are shown in Table 2.

EXAMPLE 3

The test procedure of Example 1 was carried out using 0.01, 0.02, 0.05, and 0.1 percent of the additive with base fluid I. The metal specimens used included commercially pure titanium and two titanium alloys likely to be encountered in the commercial use of the compositions of the invention. Fluid evaporation losses and percent viscosity changes during the experiment were also measured. Results are shown in Table 3.

EXAMPLE 4

The test procedure of Example 1 was carried out using

0.05 and 0.10 percent of the additive with base fluid II and the various titanium specimens. Results are shown in Table 4.

EXAMPLE 5

The test procedure of Example 1 was carried out using 0.10 and 0.20 percent of the additive with base fluid I. The composition was maintained at a temperature of 650° F., at which temperature kinematic viscosity changes became significant. Results are shown in Table 5.

EXAMPLE 6

Compositions consisting of base fluid I and 0.10, 0.25 and 0.50 wt. percent tris(4-heptafluorotolyl)phosphine were formulated and compared with base fluid I with no additives at 600° F. according to the test procedure of Example 1 using various ferrous alloys. Results are shown in Table 6.

EXAMPLE 7

Composition of base fluid II and 0.25 wt percent tris (4-heptafluorotolyl)phosphine was formulated and compared with base fluid II without an additive at 600° F. according to the test procedure of Example 1 using various ferrous alloys. Results are shown in Table 7.

EXAMPLE 8

Compositions consisting of base fluid I and 0.25 and 0.50 wt. percent tris(4-heptafluorotolyl)phosphine were formulated and compared with the uninhibited base fluid I at 600° F. according to the test procedure of Example 1 using commercially pure titanium and two titanium alloys. Results are shown in Table 8.

The previous examples were repeated using various proportions of the phosphine additives to base fluid I and to base fluid II. Additive additions of about 0.01–0.2 percent performed best for overall use, with proportions above about 0.2 percent being best for use at 650° F. Concentrations of up to 5 percent were useful.

The compositions are useful as completely non-flammable hydraulic fluids in the temperature range of about –20° to +700° F., as gas turbine engine lubricants in the range of about 0° F. to 650° F., in greases to be used at –30° F. to 600° F., and as liquid coolants and general purpose lubricants up to 650° F.

It is to be understood that the foregoing examples and description are for the purpose of illustration only, and that various changes may be made therein without departing from the spirit and scope of the invention.

TABLE 1

Wt. percent (C ₆ F ₅ OC ₆ F ₄) ₃ P additive	Weight change in mg. per cm. ²					
	4140 Steel	52100 Bearing steel	M-2 Tool steel	M-50 Tool steel	410 Stain- less steel	440C Stainless steel
None.....	+0.73	+0.24	+1.07	+0.66	+0.23	+0.35
0.05.....	+0.10	+0.06	+0.13	+0.08	+0.05	+0.02
0.2.....	+0.02	+0.07	+0.30	+0.08	+0.05	+0.04

TABLE 2

Wt. percent (C ₆ F ₅ OC ₆ F ₄) ₃ P additive	Weight change in mg. per cm. ²					
	4140 Steel	52100 Bearing steel	M-2 Tool steel	M-50 Tool steel	410 Stain- less steel	440C Stainless steel
None.....	+0.88	+0.29	+0.86	+0.98	+0.21	+0.57
0.05.....	+0.14	+0.09	+0.08	+0.10	+0.04	+0.05

TABLE 3

Wt. percent (C ₆ F ₅ OC ₆ F ₄) ₃ P additive	Fluid evap. loss, percent	Kinematic viscosity change at 100° F., percent	Weight change in mg. per cm. ²		
			Titanium (commer- cially pure)	Titanium alloy (4% Al, 4% Mn)	Titanium alloy (6% Al, 4% V)
None.....	7.8	-7.4	-0.09	-0.32	+0.16
0.01.....	3.3	-0.4	+0.06	+0.04	+0.08
0.02.....	0.7	+1.1	-0.01	+0.03	-0.01
0.05.....	0.2	+1.4	+0.02	+0.02	0.00
0.1.....	0.3	+1.9	0.00	+0.01	0.00

TABLE 4

Wt. percent (C ₆ F ₅ OC ₆ F ₄) ₃ P additive	Fluid evap. loss, percent	Kinematic viscosity change at 100° F., percent	Weight change in mg. per cm. ²		
			Titanium (commer- cially pure)	Titanium alloy (4% Al, 4% Mn)	Titanium alloy (6% Al, 4% V)
None.....	4.7	-6.1	-0.07	-0.13	+0.12
0.05.....	1.0	+1.6	+0.02	+0.04	+0.04
0.1.....	0.9	+1.6	+0.03	+0.01	+0.01

TABLE 5

Wt. percent (C ₆ F ₅ OC ₆ F ₄) ₃ P additive	Fluid evap. loss, percent	Kinematic viscosity change at 100° F., percent	Weight change in mg. per cm. ²		
			Titanium (commer- cially pure)	Titanium alloy (4% Al, 4% Mn)	Titanium alloy (6% Al, 4% V)
None.....	50.0	-91.8	-0.60	-2.60	¹ +0.01
0.1.....	2.3	+1.4	+0.13	+0.07	² +0.09
0.2.....	0.2	+1.8	+0.08	+0.12	³ +0.06

¹ Gray-black surface.² Blue-violet discoloration with slight graying.³ Blue-violet discoloration; no graying.

TABLE 6

Wt. percent (CF ₃ C ₆ F ₄) ₃ P additive	Weight change in mg. per cm. ²					
	4140 Steel	52100 Bearing steel	M-2 Tool steel	M-50 Tool steel	410 Stain- less steel	440C Stainless steel
None.....	+0.73	+0.24	+1.07	+0.66	+0.23	+0.35
0.1.....	+0.15	+0.11	+0.11	+0.04	-0.01	0.00
0.25.....	+0.10	+0.09	0.00	+0.01	+0.01	0.00
0.5.....	+0.09	+0.05	+0.21	+0.10	+0.01	+0.03

TABLE 7

Wt. percent (CF ₃ C ₆ F ₄) ₃ P additive	Weight change in mg. per cm. ²					
	4140 Steel	52100 Bearing steel	M-2 Tool steel	M-50 Tool steel	410 Stain- less steel	440C Stainless steel
None.....	+0.88	+0.29	+0.86	+0.98	+0.21	+0.57
0.25.....	+0.16	+0.08	+0.24	+0.08	+0.04	+0.03

TABLE 8

Wt. percent (CF ₃ C ₆ F ₄) ₃ P additive	Fluid evap. loss, percent	Kinematic viscosity change at 100° F., percent	Weight change in mg. per cm. ²		
			Titanium (commer- cially pure)	Titanium alloy (4% Al, 4% Mn)	Titanium alloy (6% Al, 4% V)
None.....	7.8	-7.4	-0.09	-0.32	+0.16
0.25.....	0.3	+1.8	0.00	0.00	+0.01
0.5.....	0.3	+1.8	+0.02	+0.01	+0.02

We claim:

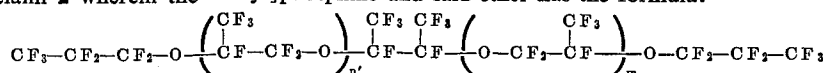
1. A composition suitable for use as a lubricant at high temperatures, said composition comprising a major amount of a perfluorinated aliphatic polyether and a minor stabilizing proportion of a perfluorinated phenoxyphenyl phosphine.

2. The composition according to claim 1 wherein said phosphine is tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine.

3. The composition according to claim 1 wherein said proportion is about 0.01-5 percent by weight of the composition.

4. The composition according to claim 1 wherein said proportion is about 0.01-0.2 percent by weight of the composition.

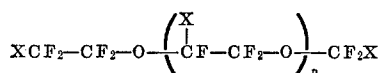
5. The composition according to claim 2 wherein the



phosphine is present in a proportion of about 0.01-5 percent by weight of the composition.

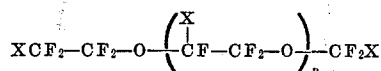
6. The composition according to claim 2 wherein the phosphine is present in a proportion of about 0.01-0.2 percent by weight of the composition.

7. The composition according to claim 1 wherein said ether has the formula:



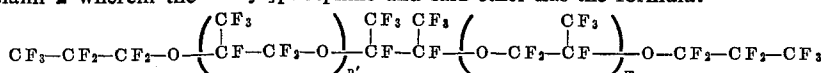
where n is a positive integer including zero and X is a member of the group consisting of fluorine and the perfluoromethyl radical.

8. The composition according to claim 1 wherein said phosphine is tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine and said ether has the formula:



where n is an integer including zero and X is a member of the group consisting of fluorine and the perfluoromethyl radical.

9. The composition according to claim 1 wherein said phosphine is tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine and said ether has the formula:



where n' and m are integers greater than 2.

10. The composition according to claim 9 wherein the proportion of said phosphine is about 0.01-5 percent by weight of the composition.

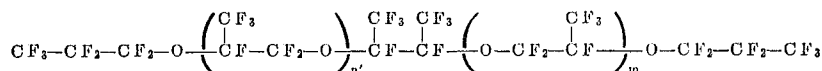
11. A composition suitable for use as a lubricant at high temperatures, said composition comprising a major proportion of a perfluorinated aliphatic polyether and a minor stabilizing proportion of a perfluorinated tolyl phosphine.

12. The composition according to claim 1 wherein said phosphine is tris[4-heptafluorotolyl]phosphine.

13. The composition according to claim 11 wherein said proportion is about 0.10-5 percent by weight of the composition.

14. The composition according to claim 11 wherein said proportion is about 0.25 percent by weight of the composition.

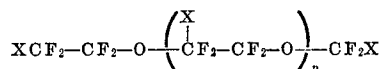
15. The composition according to claim 12 wherein



the phosphine is present in a proportion of about 0.10-5 percent by weight of the composition.

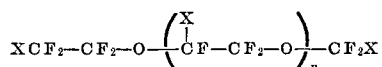
16. The composition according to claim 12 wherein the phosphine is present in a proportion of about 0.25 percent by weight of the composition.

17. The composition according to claim 11 wherein said ether has the formula:



where n is a positive integer including zero and X is a member of the group consisting of fluorine and the perfluoromethyl radical.

18. The composition according to claim 11 wherein said phosphine is tris(4-heptafluorotolyl)phosphine and said ether has the formula:



wherein n is an integer including zero and X is a member of the group consisting of fluorine and the perfluoromethyl radical.

19. The composition according to claim 11 wherein said phosphine is tris(4-heptafluorotolyl)phosphine and said ether has the formula:

where n' and m are integers greater than 2.

20. A composition according to claim 19 wherein the proportion of said phosphine is about 0.10-5 percent by weight of composition.

References Cited

UNITED STATES PATENTS

3,115,466	12/1963	Orloff et al.	252-49.9
3,214,478	10/1965	Milian	260-615
3,367,870	2/1968	Spivack	252-49.8
3,393,151	7/1968	Dolle et al.	252-49.9
2,888,481	5/1959	Wilson	252-49.9 X

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