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3,306,855 CORROSION AND RUST INHIBITED POLY (HEXA-FLUOROPROPYLENE OXIDE) OIL COMPOSI-TIONS

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a corporation of Delaware No Drawing. Filed Mar. 24, 1966, Ser. No. 537,012 5 Claims. (Cl. 252-49.9)

10This invention relates to poly(hexafluoropropylene oxide) oils and more particularly to poly(hexafluoropropylene oxide) oil compositions containing perfluoroalkylether phosphate esters as corrosion and rust inhibitors.

There is a definite present need for lubricants which will operate at temperatures above 500° F. for long periods. To date, the only lubricants which even remotely approach serviceability under such conditions are certain polymers of hexafluoropropylene-1,2-epoxide, 20 hereinafter referred to as hexafluoropropylene oxide.

The useful poly(hexafluoropropylene oxide) oils are those of the formulae

$R_{f}O\{CF(CF_{3})CF_{2}O\}_{n}CF_{2}CF_{3}$

and

 $R_{f}O{CF(CF_{3})CF_{2}O}_{p}CF(CF_{3})$ CF(CF₃){OCF₂CF(CF₃)}rOR_f

in which R_f is a perfluoroalkyl group having 1 to about 30 6 carbon atoms. These oils may be tailored, if desired, to operate at temperatures as high as 800° F. They are not affected by either oxygen or moisture at these temperatures.

At operating temperatures up to about 400° F., these oils have no apparent adverse effect on metals. However, 35 when operating at temperatures of 500° to 700° F., corrosion has been found to occur especially with metals such as steels, stainless steels, magnesium, aluminum, silver, titanium, copper and bronze. Rusting of ferrous 40metals has also been encountered. Accordingly, it is desirable to provide inhibitors which prevent corrosion and rusting of metals in contact with these oils at extreme temperatures.

Poly(hexafluoropropylene oxide) oils are also used to 45 prevent rusting of metal parts at ambient temperatures. Many parts or sub-assemblies of devices, after being manufactured, are filled with these oils and stored until needed, often a considerable period of time. Although poly(hexafluoropropylene oxide) oils are superior to hydrocarbon 50 oils for this use, complete rust prevention is not obtained with these oils alone. Accordingly there is a need for corrosion and rust inhibitors for these oils.

In order to be useful with these oils, a corrosion or rust inhibitor must possess a number of specific properties. 55 First of all, it must inhibit corrosion or rust. Furthermore, it must be soluble in and compatible with the oil. The solubility must be sufficient to provide an effective amount of inhibitor in the oil, both at operating temperatures and at ambient temperatures. There must be no 60 separation of the inhibitor from the oil even while the device containing the oil is not in use. The inhibitor itself must also possess a high degree of thermal stability at the temperatures at which the oils are used. An inhibitor which decomposes under operating conditions will 65 lose its effectiveness rapidly. Moreover, the inhibitor should not seriously affect lubricant properties, particularly lubricity, oil viscosity and oil viscosity index. These and other requirements eliminate most, if not all, known corrosion and rust inhibitors.

70It is an object of this invention to provide poly(hexafluoropropylene oxide) oil compositions containing cor-

rosion and rust inhibitors which considerably reduce or prevent corrosion and rusting of metals even at extremely high temperatures. Other objects will become apparent from the following description of this invention.

It has now been discovered that reduced corrosion and rusting of metals in the presence of poly(hexafluoropropylene oxide) oils can be obtained by using a poly(hexafluoropropylene oxide) oil composition which comprises poly(hexafluoropropylene oxide) oil of the formula

$R_fOFCF(CF_3)CF_2O_nCF_2CF_3$

or

$R_{f}O{-CF(CF_{3})CF_{2}O_{p}CF(CF_{3})}$ $CF(CF_3)$ $+ OCF_2CF(CF_3)$ $+ OR_f$

where n, p and r are integers indicating the degree of polymerization and R_f is a perfluoroalkyl group having 1 to about 6 carbon atoms, said oil having an average molecular weight of at least about 3,000 and a pour point not in excess of about 50° F. and, as corrosion and rust inhibitor, an effective amount of perfluoroalkylether phosphate ester of the formula

 $[R_1OFCF(CF_3)CF_2OF_mCF(CF_3)CH_2O]_wP(O)(OH)_{3-w}$

in which m is 0 to about 12, w is 1 to 2 and R_f is as 25previously stated.

Poly(hexafluoropropylene oxide) oils of the above formulae are extremely stable to elevated temperatures. Those polymers having average molecular weights of at least about 3,000 and pour points not in excess of about 50° F. are quite useful as lubricating oils. Polymers of the type $R_fO{CF(CF_3)CF_2O}_nCF_2CF_3$ having an average molecular weight of about 5,500 to 7,000 are preferred. These molecular weight designations are based upon number average molecular weights obtained by the spectroscopic method. The pour point designation is based upon Federal Test Method Standard 791, method 351.

These poly(hexafluoropropylene oxide) oils may be prepared in several ways. Hexafluoropropylene oxide is readily homopolymerized to products of the structure

$$CF_3CF_2CF_2O\{CF(CF_3)CF_2O\}_nCF(CF_3)COF$$

where n is 0 or an integer indicating the degree of polymerization, as described in Canadian Patent No. 725,740, issued January 11, 1966. Polymers of the structure

$$F(CF_{2})_{x} CFO - \frac{\Gamma}{L}CF(CF_{3})CF_{2}O - \frac{\Gamma}{L}CF(CF_{3})COF$$

where x and y are each 1 to about 4, are prepared by polymerizing hexafluoropropylene oxide in the presence of a ketone of the structure

$$\begin{array}{c} F(C F_2)_x \\ C=0 \\ F(C F_2)_y \end{array}$$

as described in Canadian Patent No. 707,363, issued April 6, 1965. Polymers of the structure

$F(CF_2)_2CF_2O(CF(CF_3)CF_2O)_nCF(CF_3)COF$

where z is 0 to 1 are prepared by polymerizing hexafluoropropylene oxide in the presence of an acid fluoride of the formula $F(CF_2)_zCOF$ as described in French Patent No. 1,362,548.

All of the above polymers are readily hydrolyzed in the presence of water to the corresponding acids of the formula $R_fOfCF(CF_3)CF_2Of_nCF(CF_3)COOH$ where R_f is a perfluoroalkyl group having 1 to 6 carbon atoms. The acids derived from these products react with elemental fluorine according to the method of British Patent No. 1,000,802 to form $R_fOFCF(CF_3)CF_2OF_nCF_2CF_3$. These polymers also dimerize under the influence of

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ultraviolet light, as described in U.S. Patent No. 3,214,478, to form oils of the formula

 $R_{f}OFCF(CF_{3})CF_{2}OF_{p}CF(CF_{3})$

$$CF(CF_3) \pm 0CF_2CF(CF_3) \pm_r 0R_f$$

The corrosion and rust inhibitors used in the compositions of this invention are the perfluoroalkyl ether phosphate esters of the formula

$$[R_{f}O\{CF(CF_{3})CF_{2}O\}_{m}CF(CF_{3})CH_{2}O]_{w}P(O)(OH)_{3-w}$$

in which m is 0 to about 12, w is 1, 2 or mixtures thereof, and R_f is a perfluoroalkyl group having 1 to about 6 carbon atoms. These esters are prepared by reacting phosphoric acid with an alcohol of the formula

$$R_{fO}$$
 (CF₃) CF₂O₂ CF(CF₃) CH₂OH

These alcohols can be prepared by reduction of the corresponding acid fluorides of the formula

$$R_{f}O \in CF(CF_{3})CF_{2}O = CF(CF_{3})COF$$

as described by Le Bleu and Fassnacht in U.S. application Serial No. 287,777, filed June 14, 1963.

The poly(hexafluoropropylene oxide) oil composition should contain an effective amount of the phosphate ester as corrosion and rust inhibitor. By "effective amount" is meant the amount required to produce a useful inhibitor effect for the required service life of the device containing the oil at the opearting temperature. The various metals differ considerably in the amount of corrosion and rust which will occur and the amount of inhibitor required to prevent it. Furthermore, inhibitor is probably consumed while doing its job, hence increased service life or higher use temperatures will require larger amounts of inhibitor.

In general, the amount of phosphate ester in the oil composition will be in the range of about 0.1 to 2% by weight. So long as at least about 0.1% of inhibitor is present, a significant amount of corrosion and rust inhibition is obtained. As the amount of inhibitor is increased, a quantitative reduction in corrosion and rusting is obtained up to a point. At about 1% by weight concentration, corrosion inhibition reaches a maximum, higher concentrations seldom producing any significant increase in effect.

To prevent rusting over long periods, about 1 to 2%by weight and preferably about 1.5% of the phosphate ester is recommended. Thus, if both inhibition of rusting on storage and corrosion at high temperatures is desired, from 1 to 1.5% of phosphate ester of the structure

$[R_{f}OFCF(CF_{3})CF_{2}O]_{m}CF(CF_{3})CH_{2}O]_{w}P(O)(OH)_{3-w}$

and particularly monoester where w equals 1 is recommended.

The following examples, illustrating the novel oil compositions of this invention and their utility, are given without any intention that the invention be limited thereto. All percentages are by weight.

Examples 1 to 5

The compositions of this invention are tested using a modified form of the apparatus specified in the WADD Microoxidation-Corrosion Test of High Temperature Fluids, Fluids and Greases Section, Aeronautical Systems 65 Division, Wright-Patterson Air Force Base, replacing the specified Pyrex tube with an Inconel tube. Basically the apparatus consists of a $\frac{1}{2}$ in. nickel tube adapted for mounting three washers outside the lower end of the tube. The $\frac{1}{2}$ in tube is inserted inside a $\frac{13}{16}$ in. vertical nickel 70 tube so that the washers are immersed in a body of oil contained in the larger tube. The larger tube, which is adapted with a condenser for recovering any oil which may be stripped from the tube, is inserted in an aluminum heating block. 75

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Various steel washers having the following compositions are used.

	TABLE 1		
5	Steel	Composition	
	QQ-S-636 Steel 301 Stainless 316 Stainless	3% Cr, 0.9% Mn, balance Fc. 18% Cr, 8% Ni, 2% Mn, 1% Si, balance Fe. 18% Cr, 14% Ni, 3% Mo, 2% Mn, 1% Si, balance	
10	440C Stainless	18% Cr, 1% Mn, 1% Si, 0.8% Mo, balance Fe.	

The test consists of placing weighed and measured test washers of the metals to be tested in the apparatus, adding sufficient oil composition to insure the washers are covered, assembling the remaining apparatus and inserting it in the heating block. The fluid is then heated to 650° F. and air is passed down through the smaller nickel tube into the body of oil containing the washers 20 for 72 hours.

Corrosion is determined by weighing the test washers before and after the test. The corrosion rate is calculated from the weight change and the known surface area of the washer. Before weighing, both before and after
the test, the test washers are metallurgically cleaned, i.e., scrubbed with scouring powder and water, rinsed with water, degreased and dried with acetone.

The oil is a hexafluoropropylene oxide polymer of the formula

having an average molecular weight of 6,200. The inhibited oil compositions contain 1% of a phosphate ester of the formula

$n-C_3F_7$ (CF(CF₃)CF₂O) (CF₃)CF₂O) (OH)₂

For comparison, control experiments in which no inhibitor is added to the polymer oil are carried out for each Example.

40 The following table summarizes the test conditions and results for these examples

TABLE	п
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45	Example	Metal		t change, m.²/day	
50			Control	With Inhibitor	
55	1 2 3 4 5	QQ-S-636 Steel 301 Stainless 316 Stainless 440C Stainless Titanium (8% Mn)	$\begin{array}{r} -2.24 \\ -0.81 \\ -0.63 \\ -2.61 \\ -1.35 \end{array}$	$\begin{array}{r} -0.24 \\ -0.63 \\ -0.45 \\ -0.73 \\ +0.56 \end{array}$	

Examples 6 to 8

Oil compositions containing poly(hexafluoropropylene oxide) of the formula

$C_3F_7OFCF(CF_3)CF_2O_nC_2F_5$

having an average molecular weight of 4,300 and a phosphate ester of the formula

$n-C_3F_7O+CF(CF_3)CF_2O+CF(CF_3)CH_2OP(O)(OH_2)$

in the amount indicated in the table below are tested for rust preventing qualities using test method D-665 of the American Society for Testing Materials. Procedure B is followed using synthetic sea water. Briefly, the test consists of immersing an iron billet in a mixture of the oil composition and the sea water for 48 hours and then examining the surface of the billet for rusting.

For comparison, a control experiment in which no inhibitor is present is carried out. The following results 75 are obtained.

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Example	Inhibitor Conc., Percent	Percent of Surface Rusted	
	0.5	0	
	0.2	8	
	0.1	10	
Control	0.0	45	

Examples 9 to 11

Examples 6 to 8 are repeated except that a phosphate ester of the formula

$[n-C_3F_7O+CF(CF_3)CF_2O+2CF(CF_3)CH_2C]_2P(O)OH$

is used as inhibitor. Substantially the same results are 15obtained.

Examples 12 to 14

Examples 6 to 8 are repeated except that a phosphate ester of the formula

$n-C_3F_7O_1CF(CF_3)CF_2O_{18}CF(CF_3)CH_2OP(O)(OH)_2$

is used as inhibitor. Substantially the same results are obtained.

Although the invention has been described and exempli-25fied by way of specific embodiments, it is to be understood that it is not limited thereto. As will be apparent to those skilled in the art, numerous modifications and variations of these embodiments may be made without departing from the spirit of the invention or the scope of the follow-30 ing claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A poly(hexafluoropropylene oxide) oil composition 35 which comprises a major amount of base oil selected from the group consisting of poly(hexafluoropropylene oxide), oils of the formula

$R_{f}OFCF(CF_{3})CF_{2}OF_{n}CF_{2}CF_{3}$

and

$R_{f}OFCF(CF_{3})CF_{2}OF_{p}CF(CF_{3})CF(CF_{3})$

fOCF2CF(CF3)frORf

where n, p and r are integers indicating the degree of polymerization and R_f is a perfluoroalkyl group having 1

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to 6 carbon atoms, said oil having an average molecular weight of at least 3,000 and a pour point not in excess of 50° F. and, as corrosion and rust inhibitor, an effective amount of perfluoroalkylether phosphate ester of the formula

$[R_{f}O\{CF(CF_{3})CF_{2}O\}_{m}CF(CF_{3})CH_{2}O]_{w}P_{1}O)(OH)_{3-w}$

in which m is 0 to 12, w is 1 to 2 and R_f is as previously stated.

2. The composition of claim 1 in which the poly-10 (hexafluoropropylene oxide) oil is of the formula

$R_{f}OFCF(CF_{3})CF_{2}OF_{n}CF_{2}CF_{3}$

and 0.1 to 2% by weight of perfluoroalkylether phosphate ester is present.

3. The composition of claim 2 in which R_f is $CF_2CF_2CF_2$, the poly (hexafluoropropylene oxide) oil has an average molecular weight of 5,500 to 7,000 and 1.0 to 1.5% of perfluoroalkylether phosphate ester is 20 present.

4. The composition of claim 1 in which the poly-(hexafluoropropylene oxide) oil is of the formula

 $R_{f}OFCF(CF_{3})CF_{2}OF_{p}CF(CF_{3})CF(CF_{3})$

 $\frac{1}{10} OCF_2 CF(CF_3) \frac{1}{1} OR_f$

and 0.1 to 2% by weight of perfluoroalkylether phosphate ester is present.

5. The composition of claim 4 in which R_f is $CR_3CF_2CF_2$, the poly(hexafluoropropylene oxide) oil has an average molecular weight of 5,500 to 7,000 and 1.0 to 1.5% of perfluoroalkylether phosphate ester is present.

References Cited by the Examiner UNITED STATES PATENTS

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