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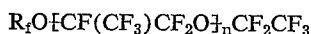
CORROSION INHIBITED POLY(HEXAFLUOROPROPYLENE OXIDE) OIL COMPOSITIONS

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5 Claims. (Cl. 252-48.4)

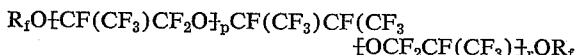
This invention relates to poly(hexafluoropropylene oxide) oils and more particularly to poly(hexafluoropropylene oxide) oil compositions containing polychlorotrifluoroethylene oils as corrosion inhibitors.

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, hereinafter referred to as hexafluoropropylene oxide.

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



and



in which R_1 is a perfluoroalkyl group having 1 to about 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.

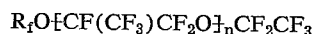
At operating temperatures up to about 400° F., these oils have no apparent adverse effect on metals. However, when operating at temperatures of 500° to 700° F., corrosion has been found to occur especially with metals such as steels, stainless steels, magnesium, aluminum, silver, titanium, copper and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

To be useful in this situation, a corrosion inhibitor must possess a number of specific properties. First of all, it must inhibit corrosion. 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 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 loses 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 inhibitors.

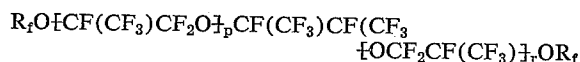
It is an object of this invention to provide poly(hexafluoropropylene oxide) oil compositions containing corrosion inhibitors which considerably reduce or prevent corrosion of metals even at extremely high temperatures. Other objects will become apparent from the following description of this invention.

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It has now been discovered that reduced corrosion 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 structure



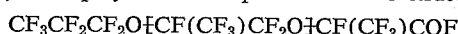
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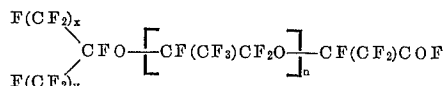
where n , p and r are integers indicating the degree of polymerization and R_1 is a perfluoroalkyl group having 1 to about 6 carbon atoms, said poly(hexafluoropropylene oxide) oil having an average molecular weight of at least about 3,000 and a pour point not in excess of about 50° F. and, as corrosion inhibitor, an effective amount of a high boiling polychlorotrifluoroethylene oil of the formula $Cl\{CF_2CFCl\}_sCl$, where s indicates the degree of polymerization, said polychlorotrifluoroethylene oil having an average molecular weight of 500 to 1,000.

Poly(hexafluoropropylene oxide) oils of the above structures 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 $R_1O\{CF(CF_3)CF_2O\}_nCF_2CF_3$ 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.

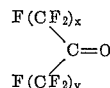
These poly(hexafluoropropylene oxide) oils may be prepared in several ways. Hexafluoropropylene oxide is readily homopolymerized to products of the structure



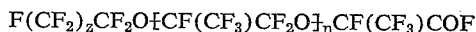
where n is 0 or an integer indicating the degree of polymerization, as described in Canadian Patent No. 725,740, issued January 11, 1966. Polymers of the structure



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

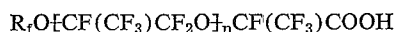


as described in Canadian Patent No. 707,363, issued April 6, 1965. Polymers of the structure

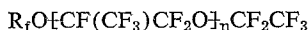


where z is 0 to 1, are prepared by polymerizing hexafluoropropylene oxide in the presence of an acid fluoride of the structure $F(CF_2)_zCOF$ as described in French Patent No. 1,326,548.

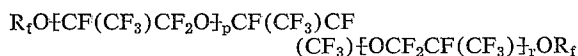
All of the above polymers are readily hydrolized in the presence of water to the corresponding acids of the structure



where R_f is a perfluoroalkyl group having 1 to about 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



These polymers also dimerize under the influence of ultra-violet light, as described in U.S. Patent No. 3,214,478, to form oils of the structure



The polychlorotrifluoroethylene oils used as corrosion inhibitors in the compositions of this invention are high boiling liquid polymers of chlorotrifluoroethylene of the structure $Cl\{CF_2CFCH_2Cl\}_s$, wherein s indicates the degree of polymerization. These polymers should have average molecular weights of about 500 to 1,000. It has been found that the addition of a small amount of a perfluoroalkanesulfonic acid to the chlorotrifluoroethylene polymer oil used as inhibitor aids rust prevention. Perfluoroalkanesulfonic acids having 1 to about 18 carbons may be used. These acids are described by Brice and Trott in U.S. Patent No. 2,732,398.

The poly(hexafluoropropylene oxide) oil composition should contain an effective amount of polychlorotrifluoroethylene oil as corrosion inhibitors. 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 operating temperature. Various metals differ considerably in the amount of corrosion which will occur and the amount of inhibitor required to prevent high temperature corrosion. 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 polychlorotrifluoroethylene inhibitor 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 inhibition is obtained. As the amount of inhibitor is increased, a quantitative reduction in corrosion is obtained up to a point. At about 1% by weight concentration the effect reaches a maximum, higher concentration seldom producing any significant increase in effect. For a general purpose, high temperature oil, it is usually preferable to add about 0.5 to 1.5% by weight of inhibitor. This amount is sufficient to meet the requirement of the vast majority of needs for the oils.

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 11

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 Division, Wright-Patterson Air Force Base, replacing the specified Pyrex tube with an Inconel tube. Basically the apparatus consists of a $\frac{1}{8}$ in. nickel tube adapted for mounting three washers outside the lower end. The $\frac{1}{8}$ in. tube is inserted inside a $\frac{1}{16}$ in. vertical nickel 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.

Various steel washers having the following compositions are used.

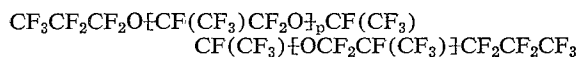
TABLE I

Steel	Composition
5 QQ-S-636 Steel.....	3% Cr, 0.9% Mn, balance Fe.
M-50 Steel.....	4.3% Mo, 4.1% Cr, 1% V, 0.4% Ni, 0.3% Mn, balance Fe.
52100 Steel.....	1.6% Cr, 0.5% Mn, 0.4% Si, balance Fe.
301 Stainless.....	18% Cr, 8% Ni, 2% Mn, 1% Si, balance Fe.
304 Stainless.....	20% Cr, 12% Ni, 2% Mn, 1% Si, balance Fe.
310 Stainless.....	20% Cr, 22% Ni, 2% Mn, 1.5% Si, balance Fe.
316 Stainless.....	18% Cr, 14% Ni, 3% Mo, 2% Mn, 1% Si, balance Fe.
321 Stainless.....	19% Cr, 12% Ni, 2% Mn, 1% Si, balance Fe.
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 the test temperature and air is passed down through the smaller nickel tube into the body of oil containing the washers for 72 hours. Test temperatures of 650° and 700° F. are used.

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 structure



having an average molecular weight of 6,200. The inhibited oil compositions contain 1% of a polychlorotrifluoroethylene oil of the structure $Cl\{CF_2CFCH_2Cl\}_s$ having an average molecular weight of about 940 and sold commercially under the trade name "Kel-F-40."

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

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

TABLE II

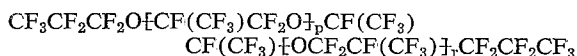
Example	Temp., °F.	Metal	Weight change, mg./cm. ² /day	
			Control	With Inhibitor
1.....	650	QQ-S-636 Steel.....	-1.66	-0.71
2.....	650	52100 Steel.....	-1.53	-0.83
3.....	650	M-50 Steel.....	-5.47	-1.06
4.....	650	301 Stainless.....	-0.81	-0.47
5.....	650	304 Stainless.....	-2.87	-1.55
6.....	650	310 Stainless.....	-0.63	-0.64
7.....	650	316 Stainless.....	-2.61	-1.62
8.....	650	440C Stainless.....	-2.61	-0.87
9.....	650	Titanium (8% Mn)....	-1.35	-0.50
10.....	700	QQ-S-636 Steel.....	-3.50	-1.54
11.....	700	316 Stainless.....	-1.95	-1.66

Examples 12 to 22

The procedure of Examples 1 to 11 above is repeated using a poly(hexafluoropropylene oxide) oil of the formula $n-C_3F_7O\{CF_2CF_2(CF_3)CF_2O\}_pCF_2CF_3$ having an average molecular weight of 6,000. Results essentially identical with those shown in Table II above are obtained.

Examples 23-29

The procedure of Examples 1 to 11 is repeated using an oil composition containing hexafluoropropylene oxide polymer of the structure



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having an average molecular weight of 6,100 which has been heat treated to remove less stable components and 1% of "Kel-F-40" polychlorotrifluoroethylene oil which itself contains 2% of perfluorooctanesulfonic acid. The resulting oil composition is evaluated at 650° F. using washers of various metals. The following results are obtained.

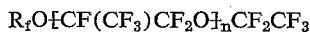
TABLE III

Example	Metal	Weight Change, mg./cm. ² /day	
		Control	With Inhibitor
23.-----	301 Stainless-----	-0.81	-0.37
24.-----	316 Stainless-----	-0.63	-0.48
25.-----	440C Stainless-----	-2.61	-1.93
26.-----	52100 Steel-----	-1.53	-0.31
27.-----	QQ-S-636-Steel-----	-1.66	-0.36
28.-----	M-50 Steel-----	-2.24	-1.25
29.-----	Titanium (8% Mn)-----	-1.35	-0.76

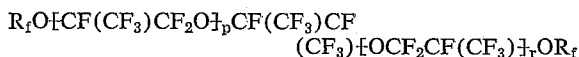
Although the invention has been described and exemplified by way of specific embodiments, it is to be understood that it is not limited thereto. As will be apparent to those skilled in the art, numerous modifications and variations of these embodiments may be made without departing from the spirit of the invention or the scope of the following 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 which comprises a major amount of base oil selected from the group consisting of poly(hexafluoropropylene oxide) oils of the structure



and

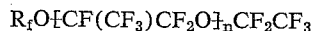


where n , p and r are integers indicating the degree of polymerization and R_f is a perfluoroalkyl group having 1 to 6 carbon atoms, said poly(hexafluoropropylene oxide) oil having an average molecular weight of at least 3,000 and a pour point not in excess of 50° F. and, as corrosion inhibitor, an effective amount of a polychloro-

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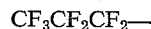
trifluoroethylene oil of the structure $Cl\{CF_2CFCl\}_sCl$, where s indicates the degree of polymerization, said polychlorotrifluoroethylene oil having an average molecular weight of 500 to 1,000.

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



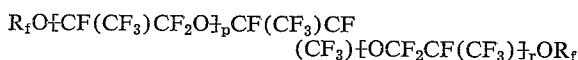
and 0.1 to 2% by weight of polychlorotrifluoroethylene oil and a rust inhibiting amount of a perfluoroalkanesulfonic acid in which the alkyl group has 1 to 18 carbon atoms is present.

3. The composition of claim 2 in which R_f is



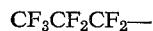
the poly(hexafluoropropylene oxide) oil has an average molecular weight of 5,500 to 7,000 and 0.5 to 1.5% of polychlorotrifluoroethylene oil is present.

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



and 0.1 to 2% by weight of polychlorotrifluoroethylene oil and a rust inhibiting amount of a perfluoroalkanesulfonic acid in which the alkyl group has 1 to 18 carbon atoms is present.

5. The composition of claim 4 in which R_f is



the poly(hexafluoropropylene oxide) oil has an average molecular weight of 5,500 to 7,000 and 0.5 to 1.5% of polychlorotrifluoroethylene oil is present.

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