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**PERFLUORINATED ALIPHATIC POLYETHER  
LUBRICANT WITH A PERFLUORINATED  
PHENYL COMPOUND ADDITIVE**

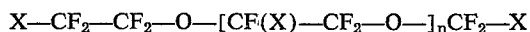
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No Drawing. Continuation-in-part of application Ser. No. 475,608, July 28, 1965. This application Sept. 21, 1966, Ser. No. 581,419

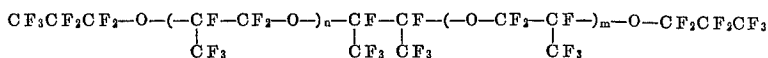
10 Claims. (Cl. 252—49.9)

**ABSTRACT OF THE DISCLOSURE**

A lubricant comprising (1) a major amount of a base fluid of a perfluorinated aliphatic polyether selected from the group consisting of compounds having the following structures:



where  $n$  is a positive integer including zero and represents the number of  $-CF(X)-CF_2-O-$  units in the molecule and where  $X$  is a member of the class consisting of fluorine and the perfluoromethyl radical; and



wherein  $n$  and  $m$  are positive integers of at least 2; and (2) a perfluorophenyl phosphorus compound selected from the group consisting of  $(C_6F_5)_3P$  and  $(C_6F_5)_3PO$  in an amount of about 0.05 to 5.0 percent by weight of the base fluid.

This application is a continuation-in-part of application Ser. No. 475,608, filed July 28, 1965, now abandoned, by the inventors of the present application.

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

The present invention relates to lubricants composed of perfluorinated aliphatic polyethers having a perfluoroaryl-type additive admixed therewith.

In the advancing technology of lubrication, particularly as it has been motivated by the sophistication of aerospace exploration and travel encountering ever-increasing speeds and wide ranges in temperatures, myriad new lubricant compositions have been required to replace the traditional petroleum-based oils and greases. Particularly significant improvements in these areas have been achieved by the use of perfluorinated aliphatic polyethers.

While these polyethers have, in and of themselves, demonstrated improved lubricity over a broad range of environmental extremes of temperature and other degrading influences, their use has been seriously limited by the interaction between them and the mechanical components with which they are used. At temperatures on the order of 500 degrees Fahrenheit and above for example, the perfluorinated aliphatic polyethers have a pronounced tendency to attack most metals in such a way that the metal parts become pitted or corroded to the detriment of their proper functioning. The reverse action of the metals on the fluids on the other hand is such that they undergo deleterious changes in viscosity and other important properties. While these problems could be successfully avoided in certain limited applications, for example by metallurgical refinements such as forming the parts to be lubricated of metals with a high nickel or cobalt content, these expedients would be extremely costly and difficult to maintain within reasonable tolerances.

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By way of illustration of the problems encountered in the prior art where perfluorinated aliphatic polyether fluids have been employed as lubricants for mechanical components composed of mild steels, serious corrosion has occurred at temperatures of from 550 to 600 degrees Fahrenheit; and even the stainless steels and the hitherto highly regarded titanium alloys have been attacked at temperatures of 600 degrees Fahrenheit. In use with the titanium alloys, moreover, the perfluorinated aliphatic polyether lubricating fluids themselves have undergone negative viscosity changes to the detriment of continued lubricating capacity. As temperatures of this order and even higher to 700 degrees Fahrenheit and above are encountered with increasing frequency in highly oxidative or otherwise degrading environments, such problems have represented a serious deterrent to the use of these otherwise desirable lubricating fluids.

It is accordingly an object of this invention to provide improved lubricants based upon perfluorinated aliphatic polyether neat fluids.

Still another object of the invention is to provide such lubricants which will not attack conventional ferrous metals and titanium alloys thereof at elevated temperatures and will not themselves be subject to deleterious change in response thereto.

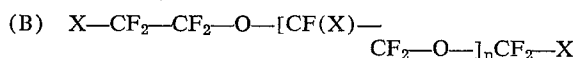
Yet another object of the invention is to provide an improved additive for perfluorinated aliphatic polyether lubricating fluids.

Still another object of the invention is to render perfluorinated aliphatic ether lubricating fluids available for use in mechanisms without the need for complex and critical metallurgical modifications.

These and other object and advantages which will appear from the following disclosure are achieved by the incorporation with the perfluorinated aliphatic polyether neat fluids of minor proportions by weight of perfluoroaryl-type additives and particularly of those perfluoroaryl compounds containing at least one perfluoroaryl group and a Group IV or Group V element of the Mendeleevian Periodic Table of Elements. Although particularly outstanding results have been achieved in the case of phosphorus perfluoroaryl compounds, the corresponding tin, germanium and silicon compounds are useable. While tests have indicated that the effectiveness of such additives is significant when they are present in weight ratios of as low as 0.05 percent of the total lubricant composition and that they do not impair the performance capabilities of the lubricant when they are present in a weight ratio of as high as 5.0 percent, an additive-to-total composition weight ratio within the range of from 0.2 percent to 0.5 percent by weight has demonstrated optimum properties. Although the perfluoroaryls are not readily soluble at room temperatures in the perfluorinated aliphatic polyethers and the relatively low molecular weight compounds are somewhat volatile, it appears that they are nonetheless capable of inhibiting the corrosion of high-iron-containing steels as well as titanium alloys to which they are exposed, even at temperatures on the order of 600 degrees Fahrenheit and in oxidizing atmospheres. Moreover, the use of some of the higher molecular weight analogs of these perfluoroaryl compounds, and particularly of those containing phosphorus, improves corrosion resistance at elevated temperatures, as a primary result in all probability, of the decrease in the volatility or sublimation tendencies of the higher molecular weight materials.

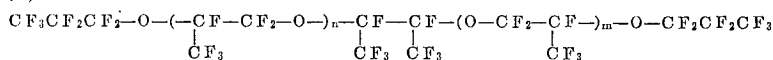
More specifically the perfluorinated aliphatic polyethers employed in the present invention as the base or neat

fluid are selected from the group consisting of polyethers of the following structure:



where  $n$  is a positive integer including zero and represents the number of  $-CF(X)-CF_2-O-$  units in the molecule and where  $X$  is a member of the class consisting of fluorine and the perfluoromethyl radical; and

(A)



wherein  $n$  and  $m$  are positive integers of at least 2.

The polyethers constituting base fluid B above are pre-

which formulation was bubbled one liter of air per hour for a specified period of time at a constant temperature, namely, 550° F. or 600° F. The 550° F. tests were conducted for 48 hours while the 600° F. tests were for 24 hours. The apparatus employed for the tests consisted of an oxidation test tube and take-off adapter coupled to an air entry tube with the metal specimens to be tested. An aluminum block bath was the heating means and an "overboard" test (no reflux condenser) was used. The re-

sults of this testing procedure are summarized in Tables I-V below.

TABLE 1.—NOMINAL COMPOSITION OF METAL SPECIMENS

| Specimen                                   | Percent C  | Percent Mn | Percent P  | Percent S | Percent Cr  | Percent Mo | Percent Si |
|--------------------------------------------|------------|------------|------------|-----------|-------------|------------|------------|
| (1) 1006 steel <sup>1</sup>                | .08 max.   | .25-.40    | .040 max.  | .050 max. |             |            |            |
| (2) 1020 steel <sup>1</sup>                | .18-.23    | .30-.60    | .040 max.  | .050 max. |             |            |            |
| (3) 1040 steel <sup>1</sup>                | .37-.44    | .60-.90    | .040 max.  | .050 max. |             |            |            |
| (4) 4130 steel <sup>1</sup>                | .28-.33    | .40-.60    | .040 max.  | .040 max. | .80-1.10    | .15-.25    | .20-.35    |
| (5) 4140 steel <sup>1</sup>                | .38-.43    | .75-1.00   | .040 max.  | .040 max. | .80-1.10    | .15-.25    | .20-.35    |
| (6) 410 stainless steel <sup>1</sup>       | .15 max.   | 1.00 max.  |            | 1.00 max. | 11.50-13.50 |            |            |
| (7) 52100 bearing steel <sup>1</sup>       | .95-1.10   | .25-.45    | .025 max.  | .025 max. | 1.30-1.60   |            | .20-.35    |
|                                            | Percent C  |            | Percent Cr | Percent V | Percent W   | Percent Mo |            |
| (8) M-1 tool steel <sup>1 2</sup>          | .80        |            | 4.00       | 1.00      | 1.50        | 8.50       |            |
| (9) M-2 tool steel <sup>1 2</sup>          | .85        |            | 4.00       | 2.00      | 6.25        | 5.00       |            |
|                                            | Percent Al | Percent V  | Percent Mn | Percent N | Percent C   | Percent H  | Percent Fe |
| (10) Titanium, 6 Al-4 V alloy<br>(3-4911)  | 5.5-6.75   | 3.5-4.5    |            | .07 max.  | .10 max.    | .015 max.  | .40 max.   |
| (11) Titanium, 4 Al-4 Mn alloy<br>(3-4925) | 3.0-5.0    |            | 3.0-5.0    | .07 max.  | .15 max.    |            | .50 max.   |

<sup>1</sup> AISI—American Iron and Steel Institute.

<sup>2</sup> SAE—Society of Automotive Engineers.

<sup>3</sup> AMS—Aeronautical Material Specifications.

Reference for Specimens 1-5 and 7: "ASME Handbook, Metals Properties," 1st ed., McGraw, Hill, New York 1954.

Reference for Specimens 6 and 8-11: "Metals Handbook, Vol. 1, Properties and Selection of Metals," 8th ed., American Society for Metals, Metals Park, Ohio, 1961.

pared by the polymerization of a perfluorooolefin epoxide, such as hexafluoropropylene epoxide and tetrafluoroethylene epoxide, by hydrolysis of the resulting polymerization product and the simultaneous fluorination and decarboxylation of the hydrolyzed product. A more detailed description of the manner in which the polyethers of base fluid B are prepared is set forth in U.S. Patent No. 3,242,218. Similarly a complete description of the manner in which the polyethers constituting the base fluid A are prepared is given in U.S. Patent No. 3,214,478 as amended by the Certificate of Correction, appended thereto, dated 5 July 1966.

The effectiveness of the perfluorinated aliphatic polyether base fluids A and B above plus a perfluoroaryl-type additive, such as a perfluorinated phenyl compound, for reducing and inhibiting corrosion in certain steels and titanium alloys is well illustrated by the following oxidation tests. In each instance the specimen of steel or alloy was immersed in a formulation consisting of (1) either base fluid A or B and (2) about .5 percent by weight of a perfluoroaryl-type additive such as triperfluorophenylphosphine and triperfluorophenylphosphine oxide through

TABLE 2.—COMPATIBILITY OF POLYMERIC PERFLUORINATED ALIPHATIC POLYETHER FORMULATIONS WITH 410 STAINLESS STEEL (SS)

| [Fluid A]           |                                                                            |
|---------------------|----------------------------------------------------------------------------|
| Additive in Fluid A | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of 410 SS Specimen |
| 0.5 wt. percent  P  | +0.01                                                                      |
| 0.5 wt. percent  PO | +0.02                                                                      |
| None                | +0.49                                                                      |
|                     |                                                                            |
| [Fluid B]           |                                                                            |
| Additive in Fluid B | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of 410 SS Specimen |
| 0.5 wt. percent  P  | 0.00                                                                       |
| None                | -0.56                                                                      |

Summary of Oxidation-Corrosion Test Conditions: 600° F., 20 ml. sample, one liter/hr. air rate, 24-hour duration, overboard, one metal specimen.

TABLE 3.—COMPATIBILITY OF POLYMERIC PERFLUORINATED ALIPHATIC POLYETHER FORMULATIONS WITH 1006, 1020, 1040, 4130 AND 4140 STEELS

| [Fluid A]           |  | Test temp. (° F.) | Test duration (hrs.) | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of steel specimens |       |       |       |       |
|---------------------|--|-------------------|----------------------|----------------------------------------------------------------------------|-------|-------|-------|-------|
| Additive in Fluid A |  |                   |                      | 1006                                                                       | 1020  | 1040  | 4130  | 4140  |
| 0.25 wt. percent  P |  | 550               | 48                   | +0.04                                                                      | +0.32 | +0.05 | +0.02 | +0.02 |
| None                |  | 550               | 48                   | +0.19                                                                      | +0.55 | +0.49 | +0.45 | +0.27 |
| 1.0 wt. percent  P  |  | 600               | 24                   | -0.02                                                                      | +0.04 | +0.22 | -0.17 | +0.37 |
| 0.5 wt. percent  PO |  | 600               | 24                   | +0.09                                                                      | +0.12 | +0.12 | +0.30 | +0.06 |
| None                |  | 600               | 24                   | +0.63                                                                      | +0.24 | +0.98 | +1.06 | +2.18 |

See footnote at end of table.

TABLE 3—Continued  
[Fluid B]

| Additive in Fluid B                                                   | Test temp.<br>(° F.) | Test duration<br>(hrs.) | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of steel specimens |       |       |       |       |
|-----------------------------------------------------------------------|----------------------|-------------------------|----------------------------------------------------------------------------|-------|-------|-------|-------|
|                                                                       |                      |                         | 1006                                                                       | 1020  | 1040  | 4130  | 4140  |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P   | 600                  | 24                      | +0.07                                                                      | +0.21 | +0.05 | +0.07 | +0.10 |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{PO}\right)_3$ -PO | 600                  | 24                      | -0.08                                                                      | -0.01 | +0.03 | +0.03 | -0.15 |
| None.....                                                             | 600                  | 24                      | +0.21                                                                      | +0.37 | +1.62 | +1.00 | +2.44 |

Summary of Oxidation-Corrosion Test Conditions: 20 ml. sample, one-liter/hr. air rate, overboard, 5 metal specimens.

TABLE 4.—COMPATIBILITY OF POLYMERIC PERFLUORINATED ALIPHATIC POLYETHER FORMULATIONS WITH M-1 AND M-2 TOOL STEELS AND 52100 BEARING STEEL

| [Fluid A]                                                             |                                                                                                   |       |       |
|-----------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|-------|-------|
| Additive in Fluid A                                                   | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of tool steel and bearing steel specimens |       |       |
|                                                                       | M-1                                                                                               | M-2   | 52100 |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{PO}\right)_3$ -PO | +0.22                                                                                             | +0.54 | +0.14 |
| None.....                                                             | +0.89                                                                                             | +2.18 | +1.34 |

| [Fluid B]                                                           |                                                                                                   |       |       |
|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|-------|-------|
| Additive in Fluid B                                                 | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of tool steel and bearing steel specimens |       |       |
|                                                                     | M-1                                                                                               | M-2   | 52100 |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P | +0.22                                                                                             | +0.08 | +0.14 |
| None.....                                                           | +0.84                                                                                             | +3.10 | +1.00 |

Summary of Oxidation-Corrosion Test Conditions: 600° F., 20 ml. sample, one-liter/hr. air rate, 24-hour duration, overboard, three specimens.

TABLE 5.—COMPATIBILITY OF POLYMERIC PERFLUORINATED ALIPHATIC POLYETHER FORMULATIONS WITH TITANIUM ALLOYS

| [Fluid A]                                                             |                      |                                                 |                                                                            |            |
|-----------------------------------------------------------------------|----------------------|-------------------------------------------------|----------------------------------------------------------------------------|------------|
| Additive in Fluid A                                                   | Fluid loss (percent) | Kinematic viscosity change at 100° F. (percent) | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of titanium alloys |            |
|                                                                       |                      |                                                 | 4% Al-4% Mn                                                                | 6% Al-4% V |
| 0.05 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P  | 1.8                  | -3.5                                            | +0.07                                                                      | +0.09      |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P   | 1.0                  | +1.0                                            | +0.07                                                                      | +0.06      |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{PO}\right)_3$ -PO | 0.5                  | 0                                               | +0.06                                                                      | +0.06      |
| None.....                                                             | 7.1                  | -14.7                                           | -0.35                                                                      | +0.17      |
| [Fluid B]                                                             |                      |                                                 |                                                                            |            |
| Additive in Fluid B                                                   | Fluid loss (percent) | Kinematic viscosity change at 100° F. (percent) | Corrosion Effect, weight change (mg./cm. <sup>2</sup> ) of titanium alloys |            |
|                                                                       |                      |                                                 | 4% Al-4% Mn                                                                | 6% Al-4% V |
| 0.5 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P   | 0.8                  | +1.8                                            | +0.06                                                                      | +0.04      |
| 5.0 wt. percent $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P   | 0.2                  | (*)                                             | +0.03                                                                      | +0.02      |
| None.....                                                             | 17.8                 | -36.7                                           | -0.70                                                                      | -0.13      |

\*Not measured due to insolubility of 5.0 wt. percent  $\left(\text{C}_6\text{F}_{11}\text{P}\right)_3$ -P in Fluid B at 100° F.

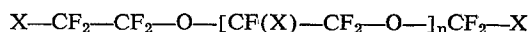
Summary of Oxidation-Corrosion Test Conditions: 600° F., 20 ml. sample, one-liter/hr. air rate, 24-hour duration, overboard, two metal specimens.

From the above test data it will be apparent that there was only nominal or no evidence of corrosion on those specimens in which the neat or base fluid A or B contained the perfluoroaryl phosphorus compounds as an additive. On the other hand the specimens immersed in the neat fluid A or B without any additive were significantly corroded.

While the within invention has been described above in connection with certain specific embodiments and examples thereof, it is to be understood that the foregoing particularization has been for the purpose of illustration only and does not limit the scope of the invention as it is more precisely defined in the subjoined claims.

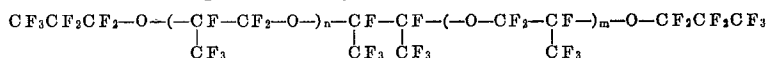
We claim:

1. A lubricant comprising (1) a major amount of a base fluid of a perfluorinated aliphatic polyether selected from the group consisting of compounds having the following structures:

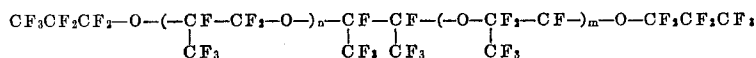


where  $n$  is a positive integer including zero and represents the number of  $-\text{CF}(\text{X})-\text{CF}_2-\text{O}-$  units in the

molecule and where X is a member of the class consisting of fluorine and the perfluoromethyl radical; and



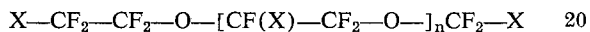
wherein  $n$  and  $m$  are positive integers of at least 2; and  
(2) a perfluorophenyl phosphorus compound selected



from the group consisting of  $(\text{C}_6\text{F}_5)_3\text{P}$  and  $(\text{C}_6\text{F}_5)_3\text{PO}$  in an amount of about 0.05 to 5.0 percent by weight of the base fluid.

2. The lubricant of claim 1 in which the phosphorus compound is present in the amount of 0.2 to 0.5 percent by weight of the base fluid.

3. The lubricant of claim 1 in which the polyether base fluid has the following structure:



where  $n$  is a positive integer including zero and represents the number of  $-\text{CF}(\text{X})-\text{CF}_2-\text{O}-$  units in the molecule and where X is a member of the class consisting of fluorine and the perfluoromethyl radical.

4. The lubricant of claim 1 in which the polyether base fluid has the following structure:

wherein  $n$  and  $m$  are positive integers of at least 2.

5. The lubricant of claim 1 in which the phosphorus compound is  $(\text{C}_6\text{F}_5)_3\text{P}$ .

6. The lubricant of claim 1 in which the phosphorus compound is  $(\text{C}_6\text{F}_5)_3\text{PO}$ .

7. The lubricant of claim 3 in which the phosphorus compound is  $(\text{C}_6\text{F}_5)_3\text{P}$ .

8. The lubricant of claim 4 in which the phosphorus compound is  $(\text{C}_6\text{F}_5)_3\text{PO}$ .

9. The lubricant of claim 7 in which the phosphorus compound is present in the amount of about 0.2 to 0.5 percent by weight of the base fluid.

10. The lubricant of claim 8 in which the phosphorus compound is present in the amount of about 0.2 to 0.5 percent by weight of the base fluid.

#### References Cited

##### UNITED STATES PATENTS

|           |        |        |       |          |    |
|-----------|--------|--------|-------|----------|----|
| 2,888,481 | 5/1959 | Wilson | ----- | 252-49.9 | XR |
| 3,245,907 | 4/1966 | Stark  | ----- | 252-46.4 |    |

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