

1

3,313,731

POLYFLUOROALKOXY-SUBSTITUTED HETEROCYCLIC LUBRICANT STABILIZED WITH A FLUOROARYL TIN COMPOUND

Roland E. Dolle, Jr., and Christ Tamborski, both of Dayton, Ohio, assignors to the United States of America as represented by the Secretary of the Air Force
No Drawing. Filed Jan. 7, 1966, Ser. No. 519,397
4 Claims. (Cl. 252—49.7)

ABSTRACT OF THE DISCLOSURE

Lubricant formulations composed of either polyfluoroalkoxy triazine or polyfluoroalkoxy phosphonitrile base fluids stabilized against high-temperature oxidation and corrosion with perfluoroaryl organometallic compounds.

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 a novel lubricant formulation and specifically to lubricants embodying polyfluoroalkoxy-substituted heterocyclic base fluids.

With the advent of new high performance gas turbine engines and other technological advances particularly in aerospace applications, there is an ever-increasing demand for lubricating materials which are capable of withstanding severe oxidative stress and degrading influences at high temperatures on the order of 500 degrees Fahrenheit and above for prolonged periods of time without appreciable deterioration. At the same time, the high temperature oxidative stability must be achieved without a sacrifice of low temperature fluid properties and lubricating characteristics. While a variety of new lubricating compositions such as polyphenylethers and polyperfluoroalkylethers have been developed to meet the demands of the newly encountered operational parameters and have been capable of withstanding high temperatures on the one hand or of resisting oxidative degradation on the other, the presently available materials lack one or more of the important properties required.

At the same time the known synthetic hydrocarbon oils possess good low temperature fluid properties and exceptional lubricity but do not have sufficient oxidative stability at temperatures above 400 degrees Fahrenheit, even when they are compounded and formulated with the best additive systems known for their particular class of neat fluids. The trimethylolpropane esters which are inhibited with the best antioxidant systems presently known for them also deteriorate rapidly above 425 degrees Fahrenheit. On the other hand, while the polyphenylether-based lubricants appear to have excellent oxidative stability at temperatures as high as 500 degrees Fahrenheit, they have high pour points on the order of 40 degrees Fahrenheit and relatively poor lubricating characteristics.

Upon this state of the art has entered a new class of lubricating fluids, namely the polyfluorinated alkoxy-substituted heterocyclic compositions such as polyfluoroalkoxy-substituted triazine derivatives and polyfluoroalkoxy-substituted cyclic triphosphonitriles. While the polyfluorinated alkoxy-substituted triazine derivatives as a class

2

demonstrate good low temperature viscosity characteristics and adequate lubricating potential, they degrade severely upon exposure to oxidative degrading environments at temperatures of 475 degrees Fahrenheit and above. Similarly, the substituted phosphonitrile neat fluids degrade significantly at temperatures on the order of 500 degrees Fahrenheit.

It is accordingly an object of the present invention to provide an improved lubricant composition which will be characterized by adequate lubricity over a broad temperature range and which will not succumb to oxidative degradation at temperatures of 475 degrees Fahrenheit and above.

Yet another object of the present invention is to provide a high-temperature oxidative resistant lubricant formulation comprising a polyfluoroalkoxy-substituted heterocyclic neat fluid.

Yet another object of the present invention is to provide such a lubricant composition embodying the polyfluorinated alkoxy-substituted triazines and the polyfluorinated alkoxy-substituted phosphonitriles.

These and other objects and advantages which will appear from a reading of the following disclosure are achieved according to the present invention by the incorporation with the above-named based fluids of minor proportions of a series of perfluorinated aryltin compounds. In spite of the fact that such aryltin additives were known to have no improving effect upon the high temperature oxidative degradation of the non-fluorinated alkoxy-substituted triazine compounds, it was found that, when these additives were incorporated with the fluorinated variety, they substantially reduced to the point of practically eliminating oxidative degradation at temperatures of 500 degrees Fahrenheit and above. It has been found for example that very little, if any, bulk property changes occur in the polyfluoroalkoxy-substituted triazine formulations embodying the aryltin additives after oxidation exposure at 475 and 500 degrees Fahrenheit as compared with the immobile residue which remained after similar exposure of these neat fluids without the additive combined therewith.

While both the perfluorinated aryltin additives and their hydrogen analogs result in substantial improvements in the high temperature oxidation resistance of the neat fluids in question, the perfluorinated additives have been found to be capable of more advantageous use in a variety of situations, probably because they are more soluble in the fluorinated alkoxy-triazines at room temperature whereas the non-fluorinated additives are soluble only at elevated temperatures. The unobviousness of the improvements gained by the practice of the within invention is corroborated by the fact that perfluorinated arylphosphorus and perfluorinated arylgermanium compounds are not effective in reducing oxidation of the polyfluoroalkoxy-substituted triazines at temperature of 475 degrees Fahrenheit and the fact that the non-fluorinated aryltin additives have not improved the performance of lubricants based upon other neat fluids such as the aliphatic hydrocarbon types at temperatures substantially above the 400 degree Fahrenheit level. Similarly, the use of a perfluorinated arylphosphorus additive was not as effective as a perfluorinated aryltin compound in substantially reducing the oxidation of phosphonitrile neat fluids at elevated temperatures.

In specific embodiments of the present invention involving polyfluorinated alkoxy-substituted triazines, 2-(1,1,7-trihydro-perfluoroheptyloxy)-4,6-bis(1,1,5-trihydro-perfluoropentylloxy)-s-triazine, 2-(1,1,9-trihydro-perfluorononyloxy)-4,6-bis(1,1,5-trihydro-perfluoropentylloxy)-s-triazine and 2,4,6-tris(1,1-dihydro-perfluorobutylloxy)-s-triazine were employed as a neat fluid with which a minor proportion on the order of 0.5 weight percent of the total composition was represented by a perfluorinated aryltin additive such as tetra(pentafluorophenyl)tin. While the precise weight percent of the aryltin additive is not critical, it is preferably and most advantageously employed in the range of from 0.1 to 5.0 weight percent of the total lubricant formulation.

As a demonstration of the improvements provided by this invention, the above-specified polyfluorinated alkoxy-substituted triazines with which 0.5 weight percent (based upon the weight of the total composition) of tetra(pentafluorophenyl)tin admixed by stirring at elevated temperatures, were tested by bubbling dry air at the rate of twenty liters per hour through a twenty milliliter sample of the lubricant formulations for twenty-four hours at temperatures of 475 degrees Fahrenheit and 500 degrees Fahrenheit. At the conclusion of the tests the formulation had little or no bulk property changes and only yellowed. By way of comparison, the same neat fluids without the aryltin additives severely decomposed resulting in much fluid loss and a residue which did not flow at room temperature. More specifically, the aryltin additive-containing formulations after twenty-four hours exposure to the above test conditions underwent a fluid loss of within the range of from 11.0 to 15.4 percent and a viscosity increase within the range of from 0 to 33.1 percent at 100 degrees Fahrenheit. The same fluids without the additives on the other hand suffered fluid losses of from 72.9 to as high as 85.5 percent at the 475 degree exposure and the fluids were not mobile at room temperature and only a glassy solid remained after the test.

By way of further specific example of the improvement gained, where the 2,4,6-tris(1,1-dihydro-perfluorobutylloxy)-s-triazine with a melting point of from 226 to 232 degrees Fahrenheit was exposed to the micro-oxidation tests involving the bubbling of dry air at the rate of twenty liters per hour through the sample for four hours at 475 degrees Fahrenheit, the base fluid without any additive underwent a fluid loss of 28.9 percent, a viscosity increase at 247 degrees Fahrenheit of 124 percent and a neutralization number increase in milligrams of KOH per gram of sample of 13.6, whereas the same fluid with 0.5 weight percent of tetra(pentafluorophenyl)tin admixed therewith and exposed to the same test conditions, demonstrated a fluid loss of only 1.4 percent, a viscosity change at 247 degrees Fahrenheit of -4.0 percent and a neutralization number increase in milligrams of KOH per gram of sample of 0.1. Still another facet of the improvements and advantages gained by the use of the aryltin additives with the polyfluoroalkoxy-substituted triazine derivatives has been demonstrated by micro-oxidation-corrosion tests wherein the lubricant formulation, in which five different metal specimens were immersed, was exposed to twenty liters per hour of dry air, bubbled through the fluid and over the metal specimens at 500 degrees Fahrenheit for twenty-four hours. Where a lubricant formulation comprising 2-(1,1,7-trihydro-perfluoroheptyloxy)-4,6-bis(1,1,5-trihydro-perfluoropentylloxy)-s-triazine and a tetra(pentafluorophenyl)tin additive, the latter representing 0.5 weight percent of the total formulation, was subjected to this test, the fluid loss was only 8.1 percent, the viscosity increase at 100 degrees Fahrenheit was only 2.7 percent, there was no neutralization number change in milligrams of KOH per gram of sample, and there were no insolubles formed. Moreover, the metal weight loss at the conclusion of the test was found to be only 0.03 milligram per square centi-

meter on the 301 stainless steel, only 0.01 milligram per square centimeter in the use of either an aluminum alloy or M-10 tool steel specimen, only 0.03 milligram per square centimeter in the case of a titanium alloy specimen and only 0.13 milligram per square centimeter in the case of a silver specimen. Beyond this, at the end of the tests the aluminum alloy and silver showed no stains, whereas the stainless steel, titanium alloy and tool steel showed only a very slight to moderate stain. The lubricant formulation slightly browned in some instances during the test but in all cases remained clear. Thus it can be seen that the triazine-aryltin formulations undergo only negligible viscosity changes and there are no serious effects upon the metals of the type in connection with which such lubricants are likely to be used even after the prolonged exposures at 500 degrees Fahrenheit.

In similar tests, the antioxidant capability of the perfluorinated aryltin additives was dramatically illustrated when they were combined with a polyfluorinated alkoxy-substituted cyclic triphosphonitrile such as trimeric bis(1,1,5-trihydro-perfluoropentylloxy)phosphonitrile. While the substituted phosphonitrile neat fluid degraded significantly at 500 degrees Fahrenheit, the formulated fluid containing the aryltin additive in the approximate weight proportion of 0.5 percent based upon the total composition had only about one-half the viscosity increase after exposure to the oxidative degrading conditions at 500 degrees Fahrenheit. By way of specific example, this particular polyfluorinated alkoxy-substituted cyclic triphosphonitrile containing the 0.5 weight percent of tetra(pentafluorophenyl)tin was exposed for twenty-four hours to the bubbling therethrough of dry air at the rate of twenty liters per hour at a temperature of 500 degrees Fahrenheit. While the base fluid with no aryltin additive demonstrated a fluid loss at the end of the test period of 25.9 percent, a viscosity increase at 100 degrees Fahrenheit of 138 percent and a neutralization number increase in milligrams of KOH per gram of sample of 0.1, the same base fluid with 0.5 weight percent (based upon the weight of the total formulation) of the tetra(pentafluorophenyl)tin admixed therewith demonstrated a fluid loss of only 11.1 percent and a viscosity increase at 100 degrees Fahrenheit of only 62.4. By way of comparison, this same neat fluid when admixed with 0.5 weight percent of tri(pentafluorophenyl)phosphine and exposed to the same test conditions for the same length of time had a fluid loss of 20.1 percent and a viscosity increase at 100 degrees Fahrenheit of 104 percent.

Thus it has been demonstrated that the oxidative stability of the polyfluoroalkoxy-substituted triazines and the polyfluoroalkoxy-substituted cyclic triphosphonitriles at temperatures of 475 degrees Fahrenheit and 500 degrees Fahrenheit is greatly enhanced by the incorporation therewith of minor amounts of perfluorinated aryltin additives.

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

We claim:

1. An improved high-temperature, oxidation-resistant lubricant formulation comprising a major weight proportion of a polyfluoroalkoxy-substituted heterocyclic base fluid selected from the group consisting of polyfluoroalkoxy-substituted triazines and polyfluoroalkoxy-substituted cyclic triphosphonitriles and a minor weight proportion of a perfluorinated aryltin compound admixed therewith.

2. A lubricant formulation according to claim 1 wherein said polyfluoroalkoxy-substituted heterocyclic neat fluid is one of that class which consists of 2-(1,1,7-trihy-

5

dro - perfluoroheptyloxy) - 4,6-bis(1,1,5-trihydro-perfluoropentyloxy) - s-triazine, 2-(1,1,9-trihydro-perfluorononyloxy) - 4,6 - bis(1,1,5 - trihydroperfluoropentyloxy)-s-triazine and 2,4,6 - tris(1,1 - dihydro-perfluorobutyloxy)-s-triazine.

3. A lubricant formulation according to claim 1 wherein said polyfluoroalkoxy-substituted heterocyclic neat fluid is trimeric bis(1,1,5-trihydro-perfluoropentyloxy) phosphonitrile.

4. A lubricant according to claim 1 wherein said perfluorinated aryltin compound is tetra(pentafluorophenyl) tin.

5

10

6

References Cited by the Examiner

UNITED STATES PATENTS

2,165,324	7/1939	Wiezerich et al.	252—49.7 X
2,272,133	2/1942	Shappiro	252—49.7
3,038,900	6/1962	Dess	252—51 X
3,234,304	2/1966	Nichols	252—49.9 X
3,245,907	4/1966	Stark et al.	252—49.7 X

DANIEL E. WYMAN, *Primary Examiner*.

W. H. CANNON, *Assistant Examiner*.