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HIGH TEMPERATURE LUBRICATING OILS

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This invention relates to synthetic hydrocarbon fluid compositions. It is more particularly concerned with such compositions having improved thermal and viscosity characteristics.

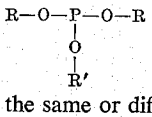
As is well recognized in the art, developments in modern aircraft brought about ever-increasing speeds and operation at continually higher altitudes. With these advances, greater demands are being made on functional elements, including lubricants, hydraulic fluids and the like. With jet engines, operating at supersonic speeds, the high temperatures encountered require use of lubricants which function and remain stable at temperatures in the order of 700° F. and sometimes even higher, without being cracked. At the same time, operation in all climates and at the high altitudes reached, extremely low temperatures are frequently met up with so that functional fluids used under these conditions must have relatively low pour points and high viscosity indices. As a typical case, the specifications for a hydraulic fluid to be used on the proposed supersonic aircraft include a −40° F. viscosity of less than 3000 cs. accompanied by thermal stability at 650° F. Thermal stability and freedom from spontaneous ignition under operating conditions are also among the severe requirements of such fluids. Even relatively slight improvements are frequently significant, particularly in border-line cases.

Because of such requirements, mineral oils are generally not suitable for use and resort is therefore had to synthetic hydrocarbon lubricants, i.e., hydrocarbon fluids synthesized from various hydrocarbon and non-hydrocarbon materials. Although these synthetic hydrocarbon fluids possess many desirable properties, in order to employ them advantageously under extremely high temperature operating conditions, it may be desirable to further improve their thermal and viscosity characteristics.

It is therefore an object of this invention to improve the high temperature properties of synthetic hydrocarbon lubricating oils. It is a further object to produce such lubricants which are stable at temperatures even higher than the maxima previously attained. Another object is to increase the autogenous ignition temperatures of these synthetic hydrocarbon oils. Other objects and advantages of this invention will become apparent to those skilled in the art, from the following more detailed description of the invention.

In accordance with the present invention, synthetic hydrocarbon oils can be still further improved to make them more suitable for the present-day requirements with respect to high temperature stability and the like. Such improvement may be made by mixing these fluids with certain specific phosphite esters.

The phosphites used in the compositions of the present invention are organic esters of phosphorous acid and have the following formula:



wherein R represents the same or different aryl or aralkyl (alkyl-substituted aryl) group and R′ is an alkyl group. R contains from 6 to about 18 carbon atoms while R′ may contain from 1 to about 18, preferably from about 8 to about 12 carbons. Some examples of the R substituents include the phenyl, naphthyl, tolyl, xylyl etc. and

higher alkyl substituted phenyl and naphthyls containing a total of up to 18 carbons. The straight or branched chain alkyls including methyl, ethyl, propyl, butyl, isobutyl, pentyl, decyl, dodecyl, pentadecyl, octadecyl etc. are exemplary of suitable R′ substituents.

The amount of phosphite used in the oil is in the range of from about 0.5 to about 20% by weight, preferably from about 2.0% to about 15%, for maximum effectiveness at 700° F. Improved stability at temperatures less than 700° F. may be obtained, however, with even lesser amounts. In practice, it is merely necessary to mix the phosphite with the oil with slight agitation to obtain adequate dispersion. Instead of a single ester, mixtures of two or more esters may be used.

The selected phosphites of the present invention may be employed to improve the thermal stability and viscosity characteristics of a variety of synthetic hydrocarbon lubricating oils. They are particularly advantageous for further improving the superior thermal and viscosity characteristics already possessed by synthetic hydrocarbon oils. Typical synthetic hydrocarbon oils include those prepared using the Grignard and Friedel-Crafts reactions, polymerization, alkylation etc. Good quality synthetic oils are prepared using aromatic alkylation reactions wherein aromatic extracts such as those in the 160 to 270° C. range are reacted with cracked wax or C_8–C_{18} olefinic polymers. The alkylation of napthalene or naphthalene mixtures with olefins or olefin polymers such as amylene or diisobutylene also results in the production of interesting synthetic oils.

The present invention is particularly directed to improving the characteristics of alpha-olefin polymer fluids possessing desirable high and low temperature characteristics. Polymer fluids of this type are prepared by polymerizing alpha-monoolefins by heating them in the presence of suitable polymerization catalysts, and then fractionating the polymer product to obtain the desired polymer. These liquid polymers may be further improved as a lubricant by hydrogenation and by heat treatment.

Exemplary of such liquid alpha-olefin polymers are the dimer-free polymers of normal alpha-monoolefins, which polymers have been completely saturated by hydrogenation, described in the patent of Seger and Hamilton, U.S. Patent No. 3,149,178. More particularly, these polymers are produced by the polymerization of 1-decene or a mixture of normal alpha-monoolefins having from about 6 carbon atoms to about 12 carbon atoms and having a mean chain length of about 10 carbon atoms.

Polymers of this type are largely trimer or higher and possess excellent properties as lubricants at extreme temperatures. Thus, as described in U.S. Patent No. 3,149,178, they may, for example, possess pour points less than about −50° F. and a V.I. of about 125 or above.

In order to illustrate the present invention more specifically, lubricant compositions were prepared by mixing various amounts of the above-described phosphite esters with a hydrogenated polymer of decene (largely trimer and free of dimer) prepared according to the procedure of U.S. Patent No. 3,149,178 and possessing the following characteristics:

Molecular weight	420
Pour point	<—65
K.V. at:	
400° F.	1.05
210° F.	3.75
100° F.	16.8
Viscosity index	128

To determine the improved results obtained by adding the esters to the polymer oil, these mixtures were sub-

jected to the following tests for thermal stability and autogenous ignition temperature (AIT).

Thermal stability test M–839

Twenty grams of sample (of known viscosity) in a glass ampule is purged with nitrogen for two minutes. The container, including the free space, is submerged in a bath at the specified test temperature and held there for 90 minutes. During the test a stream of nitrogen is passed over the tip of the container. The evaporation loss, the neutralization number and the viscosities at 210° F. and 100° F. are measured at the completion of the test. The percentage loss in kinematic viscosity at 100° F. after the test is taken as a measure of the thermal stability of the sample.

Autogenous ignition temperature test (AIT)

An Erlenmeyer flask is immersed in a liquid, metal or salt bath and heated at a constant rate. At every 20° F. rise in temperature several drops of the sample are introduced to the hot flask until a temperature is attained where the sample will spontaneously ignite. Once this temperature has been established the autogenous ignition temperature is found by lowering and raising the temperature until the minimum temperature which will cause 1–2 drops of sample to ignite is ascertained.

The test results obtained with the indicated compositions are set forth in Table I. Comparison of Test 1 (synthetic hydrocarbon oil without ester additive) with Tests 2 and 3 shows that the AIT of the synthetic oil was raised from 705° F. in Test 1 to 735° F., respectively. In Test 1, the loss in ginematic viscosity (K.V.) at 100° F. after heating for 90 minutes at 700° F., was 21.5%, while in Test 3, it was only 3.1% and in Test 4, it was only 4.5%. Even in Test 2 with the smaller amounts of phosphite, the improvement in K.V. loss was quite appreciable. Retention of excellent low temperature (—40° F.) viscosity is also evident from the table. Furthermore, it will be noted from Tests 5 and 6 and that phosphite esters such as tridecyl phosphite and phenyl didecyl phosphite, which are not within scope of the general formula given hereinabove, not only fail to improve the AIT, but cause a significant reduction in the AIT of the synthetic hydrocarbon oil.

All of these results indicate that significant improvements are obtained by the present invention.

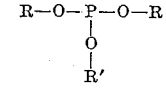
The compositions of the present invention may be advantageously employed as lubricants including hydraulic fluids, per se, or as blending stocks for lubricants. These compositions have such outstanding properties at extremes of temperatures (e.g., —65° F. to 770° F.) that they are extremely valuable as jet aircraft lubricants, hydraulic fluids and the like.

Other additives typically used in lubricants in order to improve them in other respects may be added to the extent that they are compatible with the instant compositions without interfering with the improvements attained.

Various modifications and changes may be made in the described embodiments without departing from the spirit and scope of the present invention.

Having described the invention, that we desire to secure and claim by Letters Patent is:

1. A lubricating composition comprising a major proportion of a synthetic hydrocarbon fluid consisting of a liquid polymer of an alpha-olefin and a minor proportion sufficient to impart thermal stability thereto of an organic ester of phosphorous acid having the formula,



wherein R is selected from the class consisting of aryl and aralkyl groups containing from 6 to about 18 carbon atoms and R′ represents an alkyl group containing from 1 to 18 carbon atoms.

2. The composition of claim 1 wherein said ester is present in an amount from about 0.5 to about 20% by weight.

3. The composition of claim 1 wherein said ester is present in an amount from about 2.0 to about 15% by weight.

4. The composition of claim 1 wherein said ester is diphenylmethyl phosphite.

5. The composition of claim 1 wherein said ester is diphenyl-decyl phosphite.

6. The composition of claim 1 wherein the synthetic hydrocarbon fluid is a liquid polymer of decene.

7. The compositon of claim 1 wherein the synthetic hydrocarbon fluid is a dimer-free decene trimer.

TABLE I

Test No.	Sample	Kinematic Viscosity			AIT,	Thermal Stability at 700° F.		
		210° F.	100° F.	—40° F.	° F.	K.V. 100° F.	Percent loss evap.	Percent Loss K.V. 100° F.
1	Hydrogenated Decene Trimer	3.70	16.54	2,072	705	12.98	8.1	21.5
2	1+5% Diphenylmethyl Phosphite	3.44	14.67	1,588	735	12.08	13	17.7
3	1+10% Diphenylmethyl Phosphite	3.19	12.93	1,416	770	12.53	13.3	3.1
4	1+10% Diphenyl-decyl Phosphite	3.45	14.91	1,779	700	14.24	9.3	4.5
5	1+10% Tridecyl Phosphite				690		51	
6	1+10% Phenyl didecyl Phosphite				675		65	

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