

[54] **FLAME RESISTANT HYDRAULIC FLUID**
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[22] Filed: **Feb. 3, 1972**
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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 102,252, Dec. 28,
1970, abandoned.
[52] U.S. Cl. **252/78, 252/49.9**
[51] Int. Cl. **C09k 3/00**
[58] Field of Search **252/78, 49.8, 49.9, 75**

References Cited

UNITED STATES PATENTS

2,420,953 5/1947 Hunt 252/49.9
2,509,620 5/1950 Watson et al. 252/78

2,707,176 4/1955 Gamrath et al. 252/78
2,909,489 10/1959 Fields 252/78
3,136,726 6/1964 Moreton 252/78 X
3,211,652 10/1965 Hinkamp 252/78 X
3,280,031 10/1966 Brennan et al. 252/78 X
3,282,847 11/1966 Schneider 252/78
3,352,780 11/1967 Gros Lambert 252/78 X
3,496,107 2/1970 Lima et al. 252/78 X
3,657,128 4/1972 Street 252/78 X

Primary Examiner—Leon D. Rosdol
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ABSTRACT

A flame resistant fluid useful in hydraulic systems, the fluid comprising a major amount of a synthetic hydrocarbon oil having at least 30 carbon atoms in each molecule, and a small amount of a mixture comprising chlorinated polyphenyls and a trihydrocarbon phosphate.

12 Claims, No Drawings

FLAME RESISTANT HYDRAULIC FLUID

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 102,252, filed Dec. 28, 1970 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to flame resistant fluids. It more particularly relates to fluids to which have been added minor amounts of an additive mixture having the ability to impart flame resistance and other desirable characteristics thereto.

2. Discussion of the Prior Art

Lubricants, useful as hydraulic fluids, and especially as such in aircraft, must have a high degree of flame resistance. This includes resistance to flaming from frictional heat, or, in the case of military aircraft, from incendiary projectiles. There are several fire resistant functional fluids known, but there are none which involve the use of synthetic hydrocarbon fluids and small amounts of trihydrocarbon phosphates and chlorinated polyphenyls.

U.S. Pat. No. 3,280,031 discloses the use of certain synthetic hydrocarbons, including decene trimers, with an organic ester of phosphorous acid as hydraulic fluids.

U.S. Pat. No. 3,136,726 relates to a flame resistant and explosion resistant fluid comprising a mixture of a chlorinated biphenyl and a triaryl or monoalkyl diaryl phosphate. In the mixture, each component is present in about equal weight percents. It is well-known in the art, however (see for examples U.S. Pat. Nos. 3,432,436 and 3,432,437), that such mixtures, while they provide excellent flame and explosion resistant fluids, have limited application at temperatures of 0°F and below. This is due in large measure to their relatively high viscosity characteristics and their tendency to crystallize out or form solids at such low temperatures.

Many efforts have been made to overcome the defects of the chlorinated hydrocarbon-phosphate fluids. For example, U.S. Pat. No. 2,707,176 discloses the use of small amounts of alkylated polystyrene with such fluids. Also, U.S. Pat. No. 2,432,436 teaches blends of chlorinated diphenyl ether with a chlorinated biphenyl, which blend may contain as much as 50 percent of a triaryl phosphate. U.S. Pat. No. 2,432,437 likewise discloses blends of chlorinated diphenyl ether, a chlorinated biphenyl and a triaryl phosphate. It will be noted that these two references teach blends having from 20 to 80 percent of the phosphate ester and from 80 to 20 percent of the two chlorinated components. Each specific blend contains at least 40 percent of the phosphate, the remainder being the chlorinated components.

U.S. Pat. No. 3,496,107 discloses the same chlorinated biphenylphosphate blend with from 20 to 30 parts by weight of a petroleum-base oil. The compositions disclosed must have at least 35 parts by weight of the chlorinated member.

In view of the large amounts of chlorinated polyphenyl and phosphate required to give fluids with the desired properties, as taught by the above references, it was surprising that additive amounts of each, when

combined with a synthetic hydrocarbon, would give the same desirable properties.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a liquid flame resistant fluid composition comprising a major proportion of a synthetic hydrocarbon fluid containing at least 30 carbon atoms in each molecule, and minor amounts of a chlorinated polyphenyl and a trihydrocarbon phosphate.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The synthetic hydrocarbons which may be used are of the type normally made by polymerizing olefins in the presence of a suitable catalyst, such as BF_3 or AlCl_3 . Those necessary in the practice of this invention must contain at least 30 carbon atoms. The preferred member is one made by trimerizing decene. The synthetic hydrocarbon, or polyolefin, suitable for use in this invention may have an upper limit of about 100 carbon atoms. Such hydrocarbon fluids retain their fluidity at the lower temperatures and are enhanced in their resistance to flame and explosion hazards.

Synthetic hydrocarbons having the requisite number of carbon atoms per molecule may be prepared from a variety of monoolefins. The lower olefins may be used, as for example ethylene, propylene, butylene and the like, provided the degree of polymerization is sufficient.

The chlorinated polyphenyls suitable for use in the fluid composition of the invention are those containing from 1 to about 5 chlorine atoms per molecule. The respective chloro derivatives consist primarily or substantially entirely of chlorine substituted on the aromatic rings, and in each case the chlorinated polyphenyl can be either a particular selected isomer or compound, or it can be a mixture of isomers, an unresolved mixture of isomers or a mixture of chlorinated polyphenyls of varying numbers in the molecule.

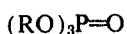
Although higher polyphenyls may be used, the biphenyls and triphenyls are preferred. The preferred chlorinated biphenyl is one having substantially 2 chlorine atoms in the molecule, with the total thereof being about 30 percent by weight of such molecule. Such chlorinated biphenyl can be either the specific dichloro biphenyl derivative or a mixture of chlorinated biphenyls averaging about 2 chlorine atoms per molecule.

The combined chlorine content of those biphenyls having from 1 to about 5 chlorine atoms will range from about 18 to about 55 percent. Suitable chlorinated biphenyls are available in the trade under the trade-name designation of Arochlor. In such terms Arochlor 1221, 1232, 1242, 1248 and 1254 refer to those biphenyls having about 21, 32, 42, 48 and 54 percent of chlorine, respectively. If one desires to prepare his own chlorinated biphenyl, it may be made in a manner well known to the art, i.e., by chlorinating a biphenyl.

The preferred terphenyl is also available under the tradename Arochlor 5442, which is a terphenyl containing about 42 percent of chlorine.

The proportion of chlorinated biphenyl or terphenyl will generally be from about 2 to about 7 percent by weight of the composition. Preferably, the composition should contain no more than about 5 percent of either member.

The trihydrocarbon phosphates suitable for use in this invention are those conforming to the formula



wherein all of the R groups may be the same or different substituted or unsubstituted hydrocarbon radicals. R more specifically may be aromatic in character and be selected from phenyl, naphthyl, cresyl, xylyl and the like. Among the compounds which may be derived from such groups may be mentioned triphenyl phosphate, trinaphthyl phosphate, tricresyl phosphate, trixylyl phosphate, diphenyl cresyl or dicresyl phenyl phosphate, cresyl dixylyl or xylyl dicresyl phosphate, naphthyl diphenyl phosphate, and the like. Among these, the tricresyl phosphate is preferred. R likewise may be aliphatic and selected from methyl, ethyl, propyl, butyl, amyl, hexyl and higher members up to about 12 carbon atoms. The preferred aliphatic member is tributyl phosphate. Such phosphates may be used in concentrations ranging from about 0.20 to about 5 percent by weight of the composition. Preferred in this range is a weight percent of from about 0.25 to about 3.

It will be understood that this invention contemplates the use of mixtures of the chlorinated polyphenyls as well as mixtures of the trihydrocarbon phosphates. When mixtures of polyphenyls are employed, the total amount of both need not exceed about 10 percent by weight of the total composition. The phosphates, when in combination, preferably will constitute no more than the stated 5 percent by weight.

The composition may also contain additives to impart other desirable properties to the fluid, such as for example antioxidants. One such antioxidant which may be mentioned is 4,4'-methylenebis(2,6-ditert-butylphenol).

The following examples are given by way of illustration only and they are not intended to limit the invention.

EXAMPLE 1

91.5 percent by weight polydecene lubricant, made from a fluid which is about 85 percent decene trimer, the remainder being mostly the decene tetramer. The fluid typically has a KV at 100°F of about 21 cs and a KV at 210°F of about 4 cs;

5 percent by weight chlorinated biphenyl containing about 2 chlorine atoms per molecule corresponding to about 30 percent chlorine;

3 percent by weight tricresyl phosphate; and
0.5 percent by weight 4,4'-methylenebis(2,6-ditert-butylphenol).

EXAMPLE 2

88.75 percent by weight of a polydecene lubricant, made from a fluid which is substantially decene trimer. The fluid has a KV of 2406 cs at -40°F, 18.11 cs at 100°F and 3.93 cs at 210°F;

3 percent by weight tributyl phosphate;
0.25 percent by weight tricresyl phosphate;
2.5 percent by weight chlorinated biphenyl containing about 1 chlorine atom per molecule corresponding to about 20 percent chlorine;

5 percent by weight chlorinated terphenyl containing about 4 chlorine atoms per molecule corresponding to about 40 percent chlorine;

0.5 percent by weight alkyl phenol antioxidant.
This composition had a KV of 2,568 cs at -40°F, 16.98cs at 100°F and 3.72 cs at 210°F. The pour point

of both the composition and the base fluid was below -65°F. After 10 days storage at -40°F, the composition remained clear.

EVALUATION OF PRODUCT

The above blends were subjected to several flame tests to determine their ability to resist flaming under a variety of conditions.

Manifold Ignition Test

This method is used for determining the relative flammability of a liquid in contact with a hot surface and is run in accordance with Federal Test Method Standard No. 791B, Method 6053 (1/15/69). Essentially, the procedure involves heating a tube to about 1,300°F and dropping 10 ml portions of the test liquid at a rate of 10 ml in 40 to 60 seconds from various heights onto various points on the tube. In this test, the blend of Example 1 ignites on contact with the tube, but is self-extinguishing after dripping from the tube.

High Temperature Spray Ignition

This test determines the relative flammability of liquids as described in Federal Test Method Standard 791B, Method 6052 (1/15/69), it consists of forcing the sample through an orifice at 1,000 psi and attempting to ignite the liquid with an acetylene torch. In this test the blend of Example 1 ignites upon passing through the acetylene flame, but is self-extinguishing after leaving it and before reaching the wall of the hood in which the test is run.

Low Temperature Spray Ignition

The low temperature test is run in a manner similar to the one immediately above, but with a "cooler" flame. In this test, the blend of Example 1 is ignited and is carried toward the hood wall in a continuous sheet of flame, but is extinguished before reaching it.

Wick Flammability Test

A device similar to the one described in Federal Test Method Standard No. 791B, Method 352 (1/15/69) was set up. The device comprised an electric wind-shield wiper and a bunsen burner. Wicks (pipe cleaners) were soaked in the test blend and were inserted in the wiper, which was set up so that this cleaner passed through the center of the flame at the reversing point of the cycle. It was found that 12 passes and 10 passes through the flame were required to obtain continuous burn for the blends of Example 1 and Example 2, respectively.

Navy Wick Test

In this test, 3 liters of the blend were placed in a trough and allowed to come to equilibrium at about 60°F. The wicks, made from 2 inch asbestos glassblowers tape and immersed in the liquid so that about one-half inch of it is above the liquid, are lighted. The object is to determine (1) how long it takes for the flame to leave the wick and begin its movement down the liquid in the trough and (2) the flame speed. To determine the flame speed in the liquid two filaments are spaced in the trough and tied to a clock. As the flame moves along the liquid, the first thread is burned, starting the clock. The second thread stops the clock when burned. The following results were obtained with the blend of Example 1:

Time to leave wick	>3600 seconds
Flame speed	Nil

Not covered in the above tests, but of extreme importance, especially in military aircraft, is the ability of a fluid to resist flaming from incendiary devices. It has been found by means of the following test that the functional fluids of this invention are remarkably resistant to such things as incendiary bullets.

Gun Fire Test

Three quarters of a gallon of fluid was placed in aluminum reservoirs pressurized to 30 psig with air and 50-caliber armon-piercing incendiary ammunition were fired into these. The test procedures outline in AFML TR 67-4 Sup. I Sect. II were followed with the exception that a more rigid specimen holding fixture was used.

In the test ten incendiary bullets were fired into the fluid. With the blend of Example 1 seven of these produced no fires; three produced only minor fires.

Rubber Swell Test

In addition to the required flame properties, fluids in a hydraulic system must have the ability to swell rubber in in acceptable amount. Too little swelling might result in system leaks, whereas too much might not only deteriorate the rubber itself but also damage parts of such system or cause system failure by clogging or otherwise.

The fluids of this invention possess excellent rubber swell characteristics, as determined by standard rubber-swell tests, as, for example, outlined in Federal Test Method Standard 791, Method 3603. Using such method with the blend of Example 1, results showed that a sample of rubber swelled 19.7 percent at 158°F in 168 hours and 11.7 percent at 275°F in 72 hours. With the blend of Example 2, the rubber swelled 18.2 percent at 156°F in 168 hours.

Using the same method, a slightly different composition was tested. The composition was similar to the one described in Example 1, the difference being that the decene fluid was present to the extent of 91.45 percent, and 0.05 percent by weight of benzotriazole was added. When samples of "L" rubber (a standard Buna type rubber) were subjected to this composition for 168 hours at 158°F, results showed swelling of 16.4 and 16.5 percent, respectively.

Although the present invention has been described with certain specific embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this

invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the appended claims.

I claim:

1. A liquid flame resistant composition comprising from about 0.20 to about 5 percent by weight of a triaryl or trialkyl phosphate, from 2 to about 10 percent by weight of a chlorinated polyphenyl, the remainder being a polymerized olefin fluid containing at least 30 carbon atoms.

2. The composition of claim 1 wherein the said polymeric olefin has from about 30 to about 100 carbon atoms.

3. The composition of claim 1 wherein the polymeric olefin is a decene trimer.

4. The composition of claim 1 wherein said chlorinated polyphenyl is chlorinated biphenyl containing from 1 to about 5 chlorine atoms per molecule.

5. The composition of claim 4 wherein the chlorinated biphenyl contains about 2 chlorine atoms per molecule.

6. The composition of claim 1 wherein the aryl group is a cresyl group.

7. The composition of claim 4 wherein the alkyl group is butyl.

8. The composition of claim 1 wherein said chlorinated polyphenyl is present to the extent of from about 2 to about 7 percent by weight thereof.

9. The composition of claim 1 wherein said triaryl or trialkyl phosphate is present to the extent of from about 0.5 to about 5 percent by weight thereof.

10. The composition of claim 1 wherein said polymeric olefin is a mixture of decene trimers and tetramers, said chlorinated polyphenyl is a biphenyl containing about 30 percent chlorine and said triaryl phosphate is trisresyl phosphate.

11. The composition of claim 1 wherein said polymeric olefin is a substantially decene trimer, said chlorinated polyphenyl is a mixture thereof and said phosphate is a mixture thereof.

12. The composition of claim 11 wherein the mixture of chlorinated polyphenyls is a mixture of a chlorinated biphenyl and a chlorinated terphenyl and the mixture of phosphates is a mixture of trisresyl phosphate and tributyl phosphate.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,873,464
DATED : March 25, 1975
INVENTOR(S) : HENRY E. BIEBER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 50

"were" should be --are--

Column 6, line 25
(claim 7)

"4" should be --1--

Signed and Sealed this
fourteenth Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks