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ORGANOPOLYSILOXANE-HALOFLUOROCARBON HYDRAULIC FLUID

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3 Claims. (Cl. 252—78)

The present invention relates to organopolysiloxane compositions having relatively non-flammable or combustion retarding properties which are useful as hydraulic fluids and lubricants.

The organopolysiloxane oils and their many uses are now well known. Although such oils have relatively high flash points and flame points, they are not actually combustion retardant materials, and will continue to burn once they have been ignited. The conventional oils have also left much to be desired in regard to their lubricating qualities when used with certain metals, and have been deficient in imparting corrosion resistance to many metals.

It is an object of the present invention to provide organopolysiloxane compositions having improved lubricating and combustion retarding properties, and having an improved ability to render metals corrosion resistant. It is a further object of the invention to provide improved hydraulic fluids. Other objects and advantages will be apparent from the following specification.

The composition of the present invention comprises a mixture of (1) from 30 to 60 percent by weight of an aliphatic halofluorocarbon having the empirical formula $C_aH_bX_cF_d$, where a is an integer from 4 to 5 inclusive, b is an integer from 0 to 1 inclusive, c is an integer from 4 to 7 inclusive, d is an integer from 2 to 6 inclusive, the sum of $b+c+d$ having a minimum value of 8 and a maximum value of $2a+2$, and X represents an atom of the group consisting of Cl and Br atoms, said halofluorocarbon having a boiling point of at least 150° C. at atmospheric pressure, (2) from 0 to 15 percent by weight inclusive of an alkyl diester of an aliphatic dicarboxylic acid having from 4 to 10 inclusive carbon atoms in the chain exclusive of the carboxylic groups, the alkyl ester groups containing from 2 to 10 carbon atoms inclusive, (3) from 25 to 70 percent by weight of a liquid organopolysiloxane containing repeating units of the formula (RR'SiO) where R and R' are selected from the group consisting of monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive and halogenated monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive, said radicals being free of acetylenic linkages, at least 80 molar percent of the organic radicals in the polymer being methyl, and said siloxane having an average degree of substitution of from 1.9 to 2.3 organic radicals attached to silicon per silicon atom, (4) from 0.043 to 0.86 percent by weight of an acid anhydride selected from the group consisting of alkyl succinic-, alkenyl succinic-, alkyl glutaric-, and alkenyl glutaric anhydrides and mixtures thereof, the alkyl and alkenyl radicals in said acid anhydride containing from 8 to 23 inclusive carbon atoms, (5) from 0.043 to 0.86 percent by weight of an alkyl diester of the aforesaid acid anhydrides in which the alcoholic residual radical contains from 1 to 4 inclusive carbon atoms, and (6) from 0.014 to 0.28 percent by weight of benzotriazole.

In the defined halofluorocarbons, the X atoms can be either the same or different, and mixtures of the defined

halofluorocarbons can be used if desired. The halofluorocarbon should have a boiling point of at least 150° C. at atmospheric pressure. Thus, the halofluorocarbons within the scope of this invention are the chlorofluoro-, bromofluoro-, and chlorobromofluoro substituted butanes, butenes, pentanes, pentenes, and pentadienes. Such compounds can be prepared by the methods disclosed in the Ruh and Gordon Patents 2,634,301, issued April 7, 1953, and 2,681,940, –1, –2 issued, on June 22, 1954, and assigned to the assignee of the present invention, and by other methods known to the art.

The most preferred halofluorocarbons are the various isomers having the empirical formulae $C_5HCl_5F_4$, $C_5Cl_5F_3$, $C_5Cl_6F_2$, $C_4F_6Br_4$, $C_4Cl_4F_4Br_2$, and $C_4Cl_6F_4$. Examples of specific isomers which can be used are:

$CCl_2{=}CClCF_2CHClCClF_2$

$CCl_2{=}CClCF_2CCl{=}CClF$

$CCl_2{=}CClCF_2CCl{=}CCl_2$

$CBrF_2CBrFCBrFCBrF_2$

$CCl_2FCClFCClFCCl_2F$

$CCl_2FCBrFCBrFCCl_2$

In many cases pure forms of the various isomers are not available, and they are employed as mixtures of a given empirical formula. Furthermore, in many cases the exact structures of the materials obtained by a given process are not at present known to the art, and hence it is often impossible even to determine which isomers are present in a given mixture.

Among the compounds with four carbon atoms employed in accordance with this invention, best results have been obtained with the butanes of the general formula $C_4Cl_eBr_gF_{10-e-g}$, where e is an integer from 0 to 6 inclusive, g is an integer from 0 to 4 inclusive, and $e+g$ has a value from 4 to 7 inclusive.

The liquid organopolysiloxanes employed in accordance herewith contain repeating polymeric units of the formula (RR'SiO) where R and R' are monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive or halogenated monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive, said radicals being free of acetylenic unsaturation. Examples of suitable radicals are alkyl radicals, e. g. methyl, ethyl, t-butyl, and heptyl; cycloalkyl radicals, e. g. cyclobutyl; aryl radicals, e. g. phenyl, benzyl, and tolyl; halogenated aryl radicals, e. g. mono- and dichlorophenyl, trifluorotolyl ($F_3CC_6H_4$—), and bromophenyl; halogenated alkyl, e. g. tetrafluoroethyl, chlorotrifluoroethyl, and octafluorobutyl; alkenyl, e. g. vinyl and allyl; and halogenated alkenyl, e. g. trifluorovinyl.

Polymers containing the above radicals are well known, and many such are commercially available. These polymers can be prepared, for example, by the hydrolysis or cohydrolysis of the appropriate organohalo- or organoalkoxysilanes, or by the catalyzed condensation or copolymerization of the appropriate organosilanols or organosiloxanes. The halogenated radicals are preferably those in which the halogen has an atomic weight of less than 100, i. e. Cl, Br, and F.

Polymers containing halogenated alkyl or halogenated alkenyl radicals can be prepared, for example, by the methods shown in the copending applications of Loren A. Haluska, No. 374,449 (filed August 14, 1953, now abandoned) and No. 464,181 (filed October 22, 1954, now Patent No. 2,800,494), both assigned to the assignee of this invention.

In the polymeric and copolymeric organosiloxanes employed in this invention, at least about 80 molar percent of the organic radicals present should be methyl radicals.

This limitation insures a minimum of viscosity change with changes in temperature. The most preferred polymers are those in which the organic substitution is in the form of methyl, phenyl, chlorophenyl or dichlorophenyl radicals, at least 80 molar percent of the organic radicals in the polymer being methyl. It is preferred that at least 70 molar percent of the polymeric units be of the defined RR'SiO type. Of course, mixtures of the defined polymers can be employed if desired.

The organosiloxane employed can contain, along with the defined RR'SiO units, units of the formula $R_3SiO_{.5}$ and $RSiO_{1.5}$ where R is as above defined and can be the same or different radicals on each silicon. The amount of mono- and/or triorgano substituted units present, however, should be limited to an amount such that the average degree of substitution of the polymer lies within the range of from 1.9 to 2.3 organic radicals attached to silicon per silicon atom.

Preferably the siloxane is composed essentially of repeating units of the formula Me_2SiO, along with PhMeSiO, Ph_2SiO, or ClC_6H_4MeSiO units as preferred optional units, and is preferably end-blocked with $Me_3SiO_{.5}$, or $Me_2PhSiO_{.5}$ units. The symbols Me and Ph are used herein to designate methyl and phenyl radicals respectively. Any $MeSiO_{1.5}$, $PhSiO_{1.5}$, $ClC_6H_4SiO_{1.5}$ or $Cl_2C_6H_3SiO_{1.5}$ units present should not exceed 15 molar percent of the total units. As is common in organosiloxanes, the polymer can contain other substituents (such as hydroxy and alkoxy radicals) attached to the Si atoms. Such extraneous substituents are preferably kept to a minimum, however.

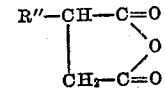
The incorporation of small amounts of phenyl-containing units in the siloxane is advantageous in improving the compatibility of those halofluorocarbons which tend to separate from an all methyl substituted siloxane at low temperatures. Chlorophenyl or dichlorophenyl substituted units can be incorporated to improve the lubricity of the siloxane. All facts considered, however, the most preferred material is a trimethylsiloxy end-blocked dimethylpolysiloxane. The above described siloxanes are well known commercially available materials. When the composition of this invention is used as a hydraulic fluid, preferably the siloxane employed has a viscosity of from 5 to 500 centistokes as measured at 25° C.

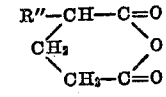
The defined alkyl diesters of aliphatic dicarboxylic acids are optional ingredients of the present invention. They can be omitted entirely, or employed in an amount up to 15% by weight of the total composition. Preferably the esters are employed in an amount of from 1 to 10% by weight.

In the esters used herein, the acid chain has from 4 to 10 inclusive carbon atoms exclusive of the carboxylic groups, and the alkyl ester groups can contain from 2 to 10 carbon atoms inclusive, the latter groups being either straight or branched-chain. Examples of suitable compounds are: diethyl adipate, dioctyl adipate, dibutyl pimelate, dihexyl suberate, didecyl azelate, di(2-ethylhexyl) sebacate, and the diethyl ester of dodecanedioic acid. Mixtures of any such esters can be employed if desired.

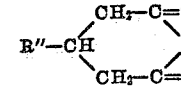
The presence of the defined esters has a tendency to improve the compatibility of some of the halofluorocarbons with the siloxanes, and to improve the lubricity of the mixture. They can also impart rubber swelling properties to the mixture. Such rubber swelling characteristics are sometimes desirable in a hydraulic fluid in order to improve the seal obtained in various parts of the hydraulic system. It has been found, however, that certain of the halofluorocarbons, particularly the various isomers having the general empirical formulae $C_5Cl_5F_3$, $C_5HCl_5F_4$, and $C_4F_4Cl_6$, themselves impart the desired degree of rubber swelling to the mixture.

In the defined alkyl- or alkenyl succinic or glutaric anhydrides, the alkyl and alkenyl groups can contain from 8 to 23 inclusive carbon atoms, and can be either a normal or branched-chain group. The position of the double bond in the alkenyl group is immaterial, as is the position of either group on the cyclic anhydride molecule. These materials can be represented by the formulas:





and

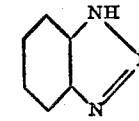


where R'' is the defined alkyl or alkenyl radical, e. g., octyl, octenyl, 2-ethylhexyl, dodecenyl, octadecyl, octadecenyl, and tricosenyl radicals. Preferably about 0.1% by weight of the anhydride is employed, although the range from 0.043 to 0.86% has been found suitable. Mixtures of the anhydrides can be used when desired. In fact mixed isomers of the glutaric anhydrides are often employed.

The alkyl diesters of the above defined acid anhydrides which are employed herein are those in which the alkyl ester group contains from 1 to 4 inclusive carbon atoms. The esters can be derived from either straight or branched chain, primary, secondary, or tertiary alcohols. To avoid confusion from the repetition of the term "alkyl," these particular ester groups are referred to in the claims as the "alcoholic residual radical." Examples of preferred esters of this type are: diethyl dodecenyl succinate, dibutyl 2-ethylhexyl succinate, diisopropyl octadecenyl succinate, di-t-butyl tricosenyl succinate, diethyl dodecyl succinate, and the comparable glutarates.

As with the anhydrides themselves, the esters thereof are employed in the range of from 0.043 to 0.86% by weight, preferably in an amount of about 0.1% by weight. Mixtures of these esters can, of course, also be used.

The benzotriazole employed herein is a well known article of commerce. It has the structural formula:



Although any amount from 0.014 to 0.28% of this material can be used, the preferred amount for economy and performance is in the region of 0.03 percent. It can be seen that the total amount of acid anhydride, ester thereof, and benzotriazole ranges from 0.1 to 2.0% of the total composition.

The compositions of this invention can be prepared by merely mixing the defined materials in any conventional manner. Other materials, e. g. oxidation inhibitors, stabilizers, rust inhibitors, and additives to improve lubricity, can be added to the composition to impart particular properties. The ingredients employed in accordance with this invention should, of course, be chosen to give a mixture which is compatible at temperatures at which it will be employed. Greases can be prepared from the present compositions by the addition of soaps such as lithium stearate, or thickeners such as carbon black or silica.

The present compositions are useful in the same applications as those in which the organopolysiloxane liquids have been used alone, e. g. as lubricants, dielectrics, damping fluids, and hydraulic fluids. They are of special interest, of course, in those applications in which combustion retarding properties are desired. Although the compositions of this invention can be made to swell

rubber if desired, they do not have the deleterious effects upon the rubber which have been common in former hydraulic fluids of the relatively non-flammable type. Furthermore, the incorporation of the defined halofluorocarbons has been found to have very little, if any, effect upon the known superior viscosity-temperature slope properties of the siloxane fluids.

The following examples are illustrative only. All parts given are parts by weight.

Example 1

A mixture was prepared containing 56.77 parts of trimethylsiloxy end-blocked dimethylpolysiloxane having a viscosity of 10 cs .at 25° C., 38 parts of tetrafluorohexachlorobutane (largely the $CFCl_2CFClCFClCFCl_2$ isomer), 5 parts of di-(2 ethylhexyl) sebacate, 0.1 part of dodecenyl succinic anhydride, 0.1 part of diethyl dodecenyl succinate, and 0.03 part of benzotriazole. The dodecenyl radicals in both the anhydride and the ester were mixtures of various branched-chain 12 carbon radicals. The mixture was prepared by warming the benzotriazole in the anhydride and ester until solution was attained, then this solution was added with mixing to the remainder of the ingredients.

The resulting mixture was found to be an excellent hydraulic fluid. It remained a compatible mixture even after one week at temperatures of —65° F. (—54° C.) and had the desired properties of lubricity, hydrolytic stability, thermal stability and low viscosity-temperature slope. It would not support combustion, and was not corrosive to steel or copper in the presence of moisture. The freezing point of the mixture was less than —75° C., and the following viscosities were found at the indicated temperatures: 99° C.=2.28 cs., 54.5° C.=4.14 cs., —17.7° C.=19.1 cs., —54° C.=102.2 cs.

Example 2

When mixtures are prepared in accordance with Example 1, but using n-octyl succinic-, n-dodecenyl succinic-, octadecenyl succinic- (branched chain), or tricosenyl succinic anhydrides, or octenyl glutaric-, dodecenyl glutaric- (branched chain) or ocetadecyl glutaric anhydrides in place of the dodecenyl succinic anhydride of that example, suitable hydraulic fluids are produced.

Example 3

When mixtures are prepared in accordance with Example 1, but using dibutyl dodecenyl succinate, diisopropyl octadecyl glutarate, or diethyl dodecyl (branched chain) succinate in place of the diethyl dodecenyl succinate of that example, hydraulic fluids of comparable desirable properties are obtained.

Example 4

Mixtures prepared from 50 parts of one of the various aliphatic halofluorocarbons hereinafter defined, 30 parts of a dimethylpolysiloxane having a viscosity of 100 cs. at 25° C., 19.77 parts of a trimethylsiloxy end-blocked copolymer of dimethyl- and phenylmethylsiloxane units containing 10 mol percent of the phenylmethylsiloxane, 0.1 part of dodecenyl succinic anhydride, 0.1 part of diethyl dodecenyl succinate, and 0.03 part of benzotriazole are all highly desirable hydraulic fluids, although they lack the degree of rubber-swelling properties exhibited by the mixture of Example 1. The halofluorocarbons referred to above are: $C_5HCl_5F_4$, $C_5Cl_5F_3$, $C_5Cl_6F_2$, $C_4F_6Br_4$, and $C_4Cl_4F_4Br_2$, each of these being a mixture of the various isomers of the given empirical formula.

Example 5

A trimethylsiloxy end-blocked dimethylsiloxane copolymer containing 5 molar percent $Cl_2C_6H_3SiO_{1.5}$ units and 5 molar percent ClC_6H_4MeSiO units was prepared by cohydrolyzing Me_3SiCl, Me_2SiCl_2, $ClC_6H_4MeSiCl_2$, and $Cl_2C_6H_3SiCl_3$. When this copolymer is substituted for the dimethylpolysiloxane in the formulation of Example 1, a suitable hydraulic fluid of improved lubricating properties is obtained.

Example 6

A copolymer of 80 molar percent $(CH_3)_2SiO$ units, 10 molar percent $CH_3C_{18}H_{37}SiO$ units, 5 molar percent $C_2F_4CH_2SiO$ units, and 5 molar percent $(CH_3)_3SiO_{.5}$ units was prepared by cohydrolyzing the corresponding organochlorosilanes in the conventional manner. When 57.31 parts of this copolymer are mixed with 32 parts tetrafluorohexachlorobutane, 10 parts dibutyl adipate, and 0.69 part of a mixture consisting of 0.3 part dodecenyl succinic anhydride, 0.3 part diethyl dodecenyl succinate, and 0.09 part benzotriazole, a good hydraulic fluid is obtained.

The hydraulic fluids described in the above examples are of particular importance because of their high degree of hydrolytic stability. This property is tested by heating a strip of copper or steel (approximately 1 x 5 x 0.076 cm., and about 3.6 g. in weight) in an enclosed test mixture of 25 g. water and 75 g. fluid for 48 hours at 93° C., the mixture being rotated throughout the test. To be satisfactory, the weight change in the metal must be less than 0.5 mg. per $cm.^2$, and there should be little or no appearance of corrosion. The mixtures of the present invention have superior qualities in regard to this test as well as in regard to the previously described desirable properties of hydraulic fluids.

That which is claimed is:

1. A liquid composition consisting essentially of a mixture of (1) from 30 to 60 percent by weight of an aliphatic halofluorocarbon having the empirical formula $C_aH_bX_cF_d$, where a is an integer from 4 to 5 inclusive, b is an integer from 0 to 1 inclusive, c is an integer from 4 to 7 inclusive, d is an integer from 2 to 6 inclusive, the sum of $b+c+d$ having a minimum value of 8 and a maximum value of 2_a+2, and X represents an atom of the group consisting of Cl and Br atoms, said halofluorocarbon having a boiling point of at least 150° C. at atmospheric pressure, (2) from 0 to 15 percent by weight inclusive of an alkyl diester of an aliphatic dicarboxylic acid having from 4 to 10 inclusive carbon atoms in the chain exclusive of the carboxylic groups, the alkyl ester groups containing from 2 to 10 carbon atoms inclusive, (3) from 25 to 70 percent by weight of a liquid organopolysiloxane containing repeating units of the formula (RR'SiO) where R and R' are selected from the group consisting of monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive and halogenated monovalent hydrocarbon radicals of from 1 to 7 carbon atoms inclusive, said radicals being free of acetylenic linkages, from 80 to 100 inclusive molar percent of the organic radicals in the polymer being methyl, and said siloxane having an average degree of substitution of from 1.9 to 2.3 organic radicals attached to silicon per silicon atom, (4) from 0.043 to 0.86 percent by weight of an acid anhydride selected from the group consisting of alkyl succinic-, alkenyl succinic-, alkyl glutaric-, and alkenyl glutaric anhydrides, the alkyl and alkenyl radicals in said acid anhydride containing from 8 to 23 inclusive carbon atoms, (5) from 0.043 to 0.86 percent by weight of an alkyl diester of the aforesaid acid anhydrides in which the alcoholic residual radical contains from 1 to 4 inclusive carbon atoms, and (6) from 0.14 to 0.28 percent by weight of benzotriazole.

2. A liquid composition consisting essentially of a mixture of (1) from 30 to 60 percent by weight of an aliphatic halofluorocarbon selected from the group consisting of halofluorocarbons having the general empirical formulas $C_5HCl_5F_4$, $C_5Cl_5F_3$, $C_5Cl_6F_2$, $C_4F_6Br_4$, $C_4Cl_4F_4Br_2$, and $C_4Cl_6F_4$, (2) from 1 to 15 percent by weight of di(2-ethylhexyl) sebacate, (3) from 25 to 70 percent by weight of a trimethylsiloxy end-blocked dimethylpolysiloxane having a viscosity of from 5 to 500 cs. at 25° C., (4)

from 0.043 to 0.86 percent by weight of an acid anhydride selected from the group consisting of alkyl succinic-, alkenyl succinic-, alkyl glutaric-, and alkenyl glutaric anhydrides, the alkyl and alkenyl radicals in said acid anhydride containing from 8 to 23 inclusive carbon atoms, (5) from 0.043 to 0.86 percent by weight of an alkyl diester of the aforesaid acid anhydrides in which the alcoholic residual radical contains from 1 to 4 inclusive carbon atoms, and (6) from 0.014 to 0.28 percent by weight of benzotriazole.

3. The composition of claim 2 in which (4) is dodecenyl succinic anhydride and (5) is diethyldodecenyl succinate.

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UNITED STATES PATENT OFFICE

Certificate of Correction

Patent No. 2,877,184 March 10, 1959

William H. Ragborg

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 42, for "ocetadecyl" read —octadecyl—; column 6, line 34, for "$C_aH_bX_dF_d$" read —$C_aH_bX_cF_d$—; line 65, for "0.14" read —0.014—.

Signed and sealed this 14th day of July 1959.

[SEAL]

Attest:
KARL H. AXLINE,
Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.