

[54] FIRE-RESISTANT HYDRAULIC FLUID

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[51] Int. Cl. C09k 3/02

[58] Field of Search 252/78, 75, 49.6, 73

[56] References Cited

UNITED STATES PATENTS

2,550,760	5/1951	Bishop	252/79
2,691,633	10/1954	Benoit	252/49.6
2,960,474	11/1960	Furby et al.	252/78
3,296,138	1/1967	Cupper et al.	252/78 X
3,478,113	11/1969	Bray et al.	252/73 X
3,513,097	5/1970	Langenfeld	252/78

3,538,001	11/1970	Gothel et al.	252/78 X
3,637,507	1/1972	Gentit	252/78
2,509,620	5/1950	Watson et al.	252/78
2,746,926	5/1956	Barry	252/78
3,074,889	1/1963	Attwood	252/78
3,657,128	4/1972	Street	252/78 X

OTHER PUBLICATIONS

"Synthetic Lubricant Fluids from Branched Chain Diesters," Industrial Engineering Chemistry, Vol. 39 (1947) pp. 484, 489.

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[57] ABSTRACT

Fire-resistant hydraulic fluids having improved low temperature characteristics, e.g., viscosity, pour point, and cloud point, consist mainly of a mixture of a synthetic hydrocarbon, a dialkyl carboxylate ester and an orthosilicate.

7 Claims, No Drawings

FIRE-RESISTANT HYDRAULIC FLUID

BACKGROUND OF THE INVENTION

1. Field of the Invention

A hydraulic fluid should be fire-resistant; it should not adversely affect the materials of construction of the system in which it is used; it must possess adequate lubricity and mechanical stability; it must be chemically stable; it must possess good low temperature properties such as viscosity, pour point and cloud point; and, finally, it must be low foaming. These characteristics have been summarized in specification MIL-H-83282.

2. Description of the Prior Art

Aryl and alkyl phosphates are widely used in fire-resistant hydraulic fluids to provide both flame resistance and lubricity. Petroleum-base oils, though good lubricants and economically desirable, are not often used in high proportions in fire-resistant hydraulic fluids because of their flammability. Chlorinated hydrocarbons are often used as good flame retardants for petroleum-base oils. A typical fire-resistant hydraulic fluid would be a phosphate ester, a chlorinated hydrocarbon or a mixture of these with or without a minor amount of mineral oil.

SUMMARY OF THE INVENTION

We have discovered that a fire-resistant functional fluid can be prepared from a synthetic hydrocarbon oil, 20-30 percent by weight of an ester of a dicarboxylic acid and 10-15 percent of an alkyl silicate, with small percentages of other functional additives. Such functional additives include antiwear agents, such as tricresyl phosphate, antioxidants such as dialkyl paracresol, hydrolysis suppressants such as cycloaliphatic epoxides, and antifoamants.

The synthetic hydrocarbon oil of the present invention comprises substantially a dialkyl aromatic hydrocarbon oil having a viscosity of from 8,500 to 10,000 cs at -40°F., 25-35 cs at 100°F., and 4-8 cs at 210°F. The preferred ester of a dicarboxylic acid is a dialkyl adipate ester of a C₆-C₁₀ alcohol. This fluid is hydrolytically stable, has excellent low temperature properties such as viscosity, pour point and cloud point, and has a high flash point, fire point, and autogenous ignition temperature.

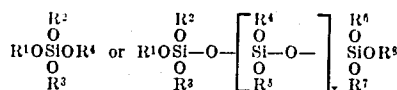
DESCRIPTION OF THE INVENTION

The hydrocarbon oils suitable for purposes of the present invention comprises hydrocarbons and mixtures of hydrocarbons which are alkyl, alkenyl, aryl and aralkyl hydrocarbons. Individual hydrocarbons will contain from about 8 to about 50 carbon atoms and be chosen from the classes of aromatic, alkyl aromatic, alkane, alkene, paraffinic and naphthenic molecules. The hydrocarbon oil is present in the hydraulic fluid composition to the extent of 30-80 percent by weight of the total composition. An important characteristic of the hydrocarbon oil is its viscosity, especially at low temperatures. The viscosity should range from 8,000 to 10,000 cs at -40°F., 20 to 40 cs at 100°F., and 2-10 cs at 212°F. A preferred oil is substantially a dialkyl aromatic hydrocarbon such as di(tridecyl)benzene, tridecyl-(tetradecyl)benzene, di(tetradecyl)benzene, or mixtures of same. The hydrocarbon oil may be a dewaxed mineral oil, or preferably a synthetic hydrocar-

bon oil. A synthetic hydrocarbon oil is preferred over a mineral oil because of its lower pour point. The most stable mineral oils are paraffinic in nature and characterized by their high pour points. The pour point is the lowest temperature at which the oil is observed to flow when cooled and examined under prescribed conditions, ASTM D 97-66. However, in choosing a synthetic hydrocarbon oil for its pour point, the viscosity of the oil, its flammability, and other properties, must be balanced by the discovery of additional components to form the base fluid meeting the severe specifications of the present invention.

The second important component of the hydraulic fluid is an ester of a C₂-C₂₀ dicarboxylic acid, i.e., a dialkyl carboxylate. Such acids include oxalic, succinic, malonic, glutaric, adipic, pimelic, suberic, azelaic acid, and substituted acids of the same names. The alcoholic portion of the ester is derived from a C₁-C₁₈ aliphatic alcohol such as methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, and undecyl alcohol. These terms include all geometrical isomers, e.g., the term "butyl alcohol" includes isobutyl alcohol. For best over-all performance in low temperature viscosity, rubber swell, cost, stability and flash point, a dialkyl ester of adipic acid is preferred. The ester will usually be present in 10-40 percent by weight and preferably 15-35 percent by weight.

The third important component of the hydraulic fluid is an alkyl silicate ester of the general formulae



wherein Rⁱ (where i = 1-8) is an alkyl group of from 3-12 carbon atoms and preferably from 6-10 carbon atoms, and x has the value of 0 or 1. Examples of the alkylsilicates include isopropyl orthosilicate, butyl orthosilicate, hexyl orthosilicate, 2-ethyl hexyl orthosilicate, 2-ethylbutoxy disiloxane, 3-propyl heptyl orthosilicate, and 2-methyl hexyl orthosilicate. The alkylsilicate esters will usually be present in 2-25 percent by weight and preferably 5-20 percent by weight.

The hydrocarbon oil, dicarboxylate ester and alkylsilicate ester form the fire-resistant base stock of the present hydraulic fluid. Specific additives are combined with this base stock to impart particular properties. For example, antiwear agents, antioxidants, hydrolysis suppressants, rust inhibitors, antifoamants, and additional viscosity index improvers may be added in small percentages. Specifically, a triaryl phosphate, and preferably tricresyl phosphate is present in the amount of 0.5-3 percent by weight, as is a dialkyl paracresol, such as dipropyl paracresol, dibutyl paracresol, or dihexyl paracresol. A very small amount (0.05-0.5 weight percent) of a diepoxide as described in U.S. application Ser. No. 865,471, filed Oct. 10, 1969 and now abandoned, is usually present as a hydrolysis suppressant. Usually an antifoamant will be present in percentages below 0.01 percent by weight.

The hydrolytic stability of the composition is excellent. It undergoes little change in acid number, viscosity, or flash point when subjected to 275°F. for one week even in the presence of added water.

The following are typical examples of base fluid formulations which are in accord with this invention. They

are given by way of illustration and not by limitation. The ingredients are known and commercially available chemicals. The fluids are prepared by simply mixing together the components of Table I with small amounts (0.5 percent or less) of specific additives discussed hereinbefore, such as antifoamant and hydrolysis sup-

TABLE I

Ingredient	Weight Percent Composition					
	A	B	C	D	E	F
Hydrocarbon	62	60	62	62	65	72
Di-2-ethylhexyl adipate	24	—	—	—	—	—
Isooctyl Adipate	—	24	24	24	—	—
Di-2-ethylhexyl sebacate	—	—	—	—	16	—
2-ethylhexyl orthosilicate	—	12	—	—	—	—
2-ethylbutyl orthosilicate	10	—	10	—	15	24
Tricresyl phosphate	2	2	2	2	2	2
2-ethylbutoxy disiloxane	—	—	—	10	—	—
Dibutyl paracresol	1	1	1	1	1	1

The properties of the fire-resistant hydraulic fluid of Table I are summarized in Table II. This fluid meets or exceeds MIL-H-83282 specifications in these categories; oxidation-corrosion inhibition, low temperature stability, lack of rubber swelling, low foaming tendency, water content below 100 ppm, lack of solid contamination, lubricity, resistance to flame propagation, and compatibility with other fluids

TABLE II

Property	MIL-H-83282 ¹	Fluid ²
Viscosity, cs		
100°F	16.5 minimum	17.0
210°F	3.5 minimum	3.74
-40°F	3,000 ± 60	2,996
Flash point, °F ASTM D 92	400 minimum	420
Fire Point, °F ASTM D 92,	475 minimum	475
Acid No., mg KOH/g ASTM D 974	0.10 maximum	0.01
Pour Point, °F	-65 maximum	-80
Lubricity, 4-Ball Wear Test		
40 kg, Scar diameter, mm	0.65 maximum	0.52, 0.53

¹This specification describes a hydraulic fluid which is fire-resistant and has a synthetic hydrocarbon base.
²Hydraulic Fluid B of Table I.

In addition, this fluid has been subjected to additional tests which are not within the scope of MIL-H-83282 specifications. These results are summarized in Table III.

TABLE III

Property	Fluid ¹
Copper Strip Test ASTM D 130 3 days at 212°F	1b
Thermal Stability 48 hours at 520°F Percent change in viscosity at 100°F	-9
Final acid number Appearance	1.1 Slight haze
Shear Stability	

TABLE III-Continued

Property	Fluid ¹
Percent viscosity loss after 2 hours in sonic oscillator 210°F -40°F	0.8 3
Oxidation Hours to absorb 1 liter of O ₂ /100 ml of fluid at 340°F	14.4
Hydrolytic Stability ² Percent change in viscosity Final acid number	-2.0 0.10
Metal weight change, mg/cm ² Copper Magnesium Aluminum Iron Cadmium	-0.02 +0.06 +0.00 +0.08 -0.01

¹Hydraulic Fluid B of Table I.
²In this test, 125 ml of fluid, 0.15 percent by weight of H₂O and 5 metal specimens are sealed in a 250 ml jar under air. The jar is rotated end over end at 5 rpm for 1 week at 275°F.

The fire resistance of the fluids of the present invention is demonstrated by the flash point and fire point of Table II and by the following test comparisons with a petroleum-base hydraulic fluid meeting Specification MIL-H-5606B (see Table IV).

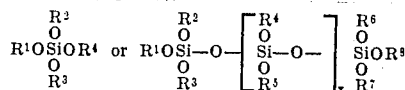
TABLE IV

	Fluid B in Table I	MIL-H-5606B Hydraulic Fluid, Petroleum Base
Flash Point, °F., ASTM D 92	420	200
Fire Point, °F., ASTM D 92	475	225
Autoignition Temp, °F., ASTM D 286	775	575
Pipewick Flammability, number of passes	48	5
Flame Propagation MIL-H-83282, Sec. 4.4.3.1.1	No propagation after 2 hours	Propagation after 36 seconds
High Temperature-High Pressure Spray Ignition, Fed. Std. 791-6052	Ignites with difficulty. Does not continue to burn after source of ignition is removed.	Ignites when any portion of flame touches any portion of stream. Continues to burn vigorously when ignition source is removed.

As will be evident to those skilled in the art, numerous modifications and variations of the invention illustrated above may be made without departing from the spirit of the invention, or the scope of the following claims.

I claim:

1. A fire-resistant hydraulic fluid comprising a base stock consisting essentially of;
- 30-80 percent by weight of a hydrocarbon oil having a maximum viscosity of 10,000 cs at -40°F. and a minimum viscosity of 4 cs at 210°F.,
- 15-35 percent by weight of a dialkyl carboxylate ester of a C₆-C₁₀ alkanol and a C₂-C₁₀ dicarboxylic acid, and
- 5-20 percent by weight of an alkyl silicate ester of the general formulae:



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wherein the R^i , i being an integer of from 1–8, are alkyl groups of from 3 to 12 carbon atoms and x has the value of 0 or 1.

2. The fire-resistant hydraulic fluid of claim 1, in which the hydrocarbon oil is a dialkyl aromatic hydrocarbon oil, wherein the alkyl contains 12–14 carbon atoms.

3. The fire-resistant hydraulic fluid of claim 1, in which the alkyl of the alkyl silicate contains from 6–10 carbon atoms.

4. The fire-resistant hydraulic fluid of claim 1, in which the carboxylic acid is of the form $\text{HOOC}(\text{CH}_2)_x$.

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COOH , where $x = 2$ to 10.

5. The fire-resistant hydraulic fluid of claim 1, in which the dialkyl carboxylate ester is diisooctyl adipate.

6. The fire-resistant hydraulic fluid of claim 4, in which the alkyl silicate is 2-ethylhexyl orthosilicate.

7. The fire-resistant hydraulic fluid of claim 1, additionally containing 1–3 percent by weight of tricresyl phosphate, 0.5–2 percent by weight of dialkyl paracresol, and 0.05–0.5 percent by weight of a diepoxide hydrolysis suppressant.

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