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FIRE-RESISTANT HYDRAULIC FLUID

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This application is a continuation-in-part of application Serial No. 164,386, filed January 4, 1962 and now abandoned.

This invention relates to hydraulic fluids comprising stable water-in-oil emulsions of mineral oils. These emulsions are characterized by fire resistance, low pour point, low temperature pumpability, antirust properties, wear-reducing properties and emulsion stability.

There has been a need, particularly in the mining and metallurgical industries, for a hydraulic fluid for hydraulically operated equipment that will not present a fire hazard when leakage or line rupture exposes the fluid to high temperatures. Fire-resistant fluids are desirable in such locations as die-casting plants, glass-molding plants, steel mills and coal mines.

Among the types of fire-resistant fluids that are available are included: phosphate esters, mixtures of water and glycols such as ethylene glycol, oil-in-water, and water-in-oil emulsions. The water-in-oil emulsion-type fluids are particularly desirable because of their lower cost and because of the ease of conversion from the use of conventional mineral oil hydraulic fluids to the emulsion-type fluids. There are a number of problems that arise, however, in the use of emulsion-type hydraulic fluids. One of these is that the emulsion tends to separate or migrate in storage. Migration is a phenomenon in which the emulsion tends to stratify into layers of different density and water content on standing. This of course is an undesirable property. Another problem is that emulsion-type fluids tend to promote greater wear of pump parts than is experienced with fluids in which the base is entirely mineral oil.

It is an object of the present invention to provide improved hydraulic fluids of the water-in-oil type that are fire resistant, that have a minimum tendency to undergo water migration in storage, that resist separation in freezing-thawing cycles, that have desirably low pour points, that exhibit low temperature pumpability, and that reduce wear-promoting tendencies.

In accordance with the present invention, it has been found that a fire-resistant water-in-oil emulsion hydraulic fluid that possesses the above-recited properties can be prepared from a mixture of about 35 to 67 wt. percent of a low cold test mineral oil, from about 3 to about 10 wt. percent of an emulsifier package which is more explicitly defined hereinafter, and from about 30 to about 55% water, and preferably with smaller concentrations of auxiliary agents. Preferably for proper fire resistance, the emulsion should contain at least 40% water and the preferred range is 40 to 45 wt. percent of water.

The base oil may be any natural or synthetic mineral oil having a pour point no higher than 0° F., preferably −20° F. or lower. Coastal naphthenic oils or properly dewaxed paraffinic oils may be used, for example. Preferably, the oil has a viscosity in the range of 75 to 200 SSU at 100° F.

The emulsifier package is made up of several (i.e. more than two) ingredients. The first of these is a metal, organo sulfonate having a molecular weight in the range of from about 300 to about 1200. These sulfonates are the alkali metal and alkaline earth metal sulfonates, e.g. Ca, Na, Ba, Li, Mg. etc. The sulfonate functions not only as an emulsifier but also as an antirust agent. The sulfonates are preferably the sodium and/or calcium salts of sulfonic acids obtained by sulfonating alkylated aromatic hydrocarbons such as those naturally occurring in naphthenic lubricating oils of 500–1200 SSU viscosity at 100° F. Specific sulfonates include the salts of acids obtained in the manufacture of USP white oil, or synthetic sulfonates obtained from alkylated or cycloalkylated benzene or naphthalene of suitable molecular weight.

Sodium sulfonates used as water/oil emulsifiers tend to make emulsions most stable as oil-in-water emulsions. Increasing the molecular weight of the sodium sulfonate tends to make the water-in-oil emulsions more stable. Unfortunately, when the sodium sulfonate molecular weight increases, a tendency of gelation is sometimes noted in the water-free portion of the emulsion hydraulic fluid system. This gelation would not permit shipment of a water-free "concentrate" to a fluid user to save freight charges. (The fluid user then adds water to make the emulsion.)

Calcium sulfonates used as water/oil emulsifiers tend to make emulsions most stable as water-in-oil emulsions. However, freeze-thaw stability (cycling emulsions from room temperature to freezing conditions) of emulsions containing calcium sulfonate as a major emulsifier is poor. In accordance with the present invention it has been unexpectedly found that a combination of calcium sulfonate and sodium sulfonate produces a superior emulsifier system. In such a system the weight ratio of sodium sulfonate to calcium sulfonate will be from about 1/1 to about 10/1 with a preferred ratio of about 5/1.

The second component of the emulsifier package is an alkoxylated aliphatic alcohol obtained by treating an aliphatic alcohol of 12 to 20 carbon atoms with from less than 1 mole to up to 4 moles of ethylene oxide or propylene oxide per mole of alcohol. Among the alkoxylated alcohols that may be used are a partially saturated alkoxylated tallow alcohol, an alkoxylated lauryl alcohol, an unsaturated alkoxylated oleyl alcohol, and an alkoxylated tridecyl alcohol. Several methods for carrying out the oxyalkylation are illustrated in U.S. Patents 1,970,578 and 2,174,761.

Tallow alcohol is a mixed alcohol obtained by the hydrogenation of tallow. It is principally C_{16}–C_{18} alcohols with minor amounts of C_{12}, C_{14} and C_{20} alcohols. The tridecyl alcohol may be a C_{13} oxo alcohol prepared by the well-known oxo process wherein an olefin is reacted with carbon monoxide and hydrogen in the presence of a suitable catalyst, usually cobalt. The reaction products are primarily aldehydes of one more carbon atom than the starting olefins. The aldehydes are converted to the corresponding alcohols in a separate hydrogenation step.

The lauryl alcohol may be the commercial mixture of saturated aliphatic alcohols known as Lorol, consisting mostly of C_{12} and C_{14} alcohols but having small proportions of C_{10} and C_{16}–C_{18} alcohols.

A third ingredient of the emulsifier package is a "coupling agent," which is actually a supplementary emulsifier, selected on the two bases of creating a favorable hydrophilelipophile balance and of disordering the emulsifier monolayer. Thus, if the other emulsifiers are excessively oil soluble, a highly water-soluble ingredient is selected; and the shape of the molecule of the "coupling agent" is chosen so as to prevent close packing of the molecules of the main emulsifiers. Usually the choice is made empirically, as emulsifier theory is not yet adequate for detailed mathematical predictions.

The "coupling agent" is preferably a hydroxy compound selected from the group consisting of glycols and glycol ethers of from 3 to 8 carbon atoms and aliphatic alcohols of from 3 to 20 carbon atoms. Specific coupling agents include diethylene glycol, propylene glycol, butyl carbitol, ethylene glycol monomethyl ether, tetramethyl-

ene glycol, ethylene glycol monobutyl ether, isopropanol, tridecyl alcohol, oleyl alcohol, and C_8 oxo alcohol.

The composition of a two-component or three-component emulsifier package may range from about 35 to 90 wt. percent of sulfonate, 10 to 65 wt. percent of the alkoxylated alcohol, and from 0 to 30% of the "coupling agent."

A particularly useful four-component emulsifier package employs, in addition to the three above-described ingredients, about 0.2 to 1.0 wt. percent oleic acid. Oleic acid is well known as an antiwear agent and emulsifier. However, its elastomer swelling properties, especially on widely used elastomers such as Buna N (butadiene/acrylonitrile rubber) usually precludes its use as a hydraulic fluid additive.

While it may be omitted, it is preferred to include as an ingredient of the emulsion an antiwear agent, preferably one that is stable in the presence of water at 190° F. for at least 1000 hours. Depending on the potency of the antiwear agent it may be present from 0.1 to about 10 wt. percent. A satisfactory antiwear agent is an ester of a C_1 to C_4 monohydric alcohol and a C_8 to C_{20} fatty acid, such as methyl oleate which is employed in about 5 wt. percent concentration in the finished emulsion. Related antiwear agents that may be used include isopropyl oleate or other esters of low molecular weight monohydric alcohols and high molecular weight monobasic aliphatic acids. Specific alcohols include methyl, ethyl, isopropyl, secondary and tertiary butyl. Acids include oleic, lauric, ricinoleic, myristic and decanoic.

Other deirable ingredients include an antioxidant, preferably a phenolic material in concentrations of from about 0.05 to about 2 weight percent, a bactericide in concentrations of from about 0.01 to about 0.5 wt. percent and a vapor phase rust inhibitor in concentrations between about 0.01 and about 2 wt. percent. A particularly effective antioxidant is 2,6 di-tert. butyl-4-methyl phenol, which may be used in a concentration of about 0.5 wt. percent. Bis phenols such as 4,4'- methylene bis (2,6-di-tert.-butyl phenol) are also useful antioxidants. Other suitable antioxidants include, for example, phenyl-α-naphthylamine, phenyl- β-naphthylamine and butylated hydroxy anisole. A suitable bactericide is the sodium salt of dichlorophene, which may be obtained commercially under the name of Sindar G–4. Tris nitro, 2-nitro-2-methyl propane diol, and similar bactericides may also be used.

While the sulfonate component of the emulsifier does function as a rust-preventing agent, there is need for an additional rust inhibitor to prevent rusting in the vapor space of the pumps of the hydraulic system; hence, a vapor phase rust inhibitor is needed. Morpholine is a preferred inhibitor for this purpose, and can be used at about 0.03 to 0.13 wt. percent concentration. Cyclohexyl amine is also an effective vapor phase rust inhibitor. Other effective vapor phase rust inhibitors include ethylene diamine, amyl amine or similar volatile amine. Any volatile amine-type compound having a vapor pressure close to that of water may be used.

The nature of the invention, the manner in which it may be practiced, and the benefits derivable from the invention will be more fully understood when reference is made to the following examples.

EXAMPLE 1

The following is a general description of the method for manufacturing a concentrate which can later be converted to a water-in-oil emulsion suitable for use as a fire-resistant hydraulic fluid.

A kettle is charged with a suitable base oil together with emulsifiers and antioxidants. The mixture is heated to about 150° F. and blended for a period of 1 to 2 hours. After one hour the bactericide and rust inhibitor and any other minor ingredients employed are added. A sample of the blend is then taken and to it is added slowly the amount of water required to make a finished emulsion. Then, viscosity and centrifuge stability tests are run. Should the concentrate require rebalancing, either 0.5 wt. percent of sulfonate or 0.5 wt. percent of ethoxylated alcohol may be added. If neither of the above materials provides a good test emulsion the concentrate may be balanced by adding up to 0.5 wt. percent of diethylene glycol or other "coupling agent" as previously disclosed.

If the concentrate is to be converted into a finished emulsion in the plant, the desired amount of water is added to the finished concentrate with good mixing during a period of 40 minutes and the mixture is stirred for an additional 30 minutes with maximum agitation. Care should be taken to avoid "water stratification"; an excellent method is to use a bottom-drain "pump-around" circuit.

EXAMPLE 2

Using the general procedure of Example 1, three different emulsifiable concentrates and the corresponding finished emulsions were prepared with ingredients set forth in Table I.

TABLE I

Ingredients, wt. percent	Concentrate			Emulsion Hydraulic Fluid [1]		
	I	II	III	I	II	III
Naphthenic Oil [2]	79.6	79.6	88.4	45.4	45.4	50.4
Water				43.0	43.0	43.0
Methyl Oleate	8.8	8.8		5.0	5.0	
Oleic Acid			1.4			0.8
Na Sulfonate [3]	4.0	5.3	3.7	2.3	3.0	2.1
Ca Sulfonate [4]			0.88			0.5
Ethoxylated Alcohol	[5] 4.5	[6] 3.2	[7] 2.3	[5] 2.6	[6] 1.8	[7] 1.3
Diethylene Glycol	2.1	2.1	2.1	1.2	1.2	1.2
Antioxidant [8]	0.9	0.9	0.88	0.5	0.5	0.5
Bactericide [9]	0.2	0.2	0.17	0.1	0.1	0.1
Vapor Phase Rust Inhibitor [10]	0.07	0.07	0.17	0.04	0.04	0.1

[1] In each case consists of 57 wt. % (60 vol. %) of the concentrate and 43 wt. % (40 vol. %) of water.
[2] Coastal naphthenic distillate oil. Viscosity at 100° F. is 100 SUS. V.I. is about 26.
[3] Concentrate in mineral oil containing 63 wt. % sulfonate of 400–500 mol. wt. (avg. 450) obtained in manufacture of white oil.
[4] Concentrate in mineral oil containing 43–46 wt. % sulfonate of 880 avg. mol. wt.
[5] Product of treating 1 mole of tallow alcohol with 3 moles of ethylene oxide.
[6] Product of treating 1 mole of C_{13} Oxo alcohol with 1.5 moles of ethylene oxide.
[7] Product of treating 1 mole of oleyl alcohol with 2 moles of ethylene oxide.
[8] 2,6-di-tert. butyl p-cresol.
[9] 40% aqueous solution of the sodium salt of dichlorophen.
[10] 90% morpholine, 10% water.

EXAMPLE 3

Emulsions of Example 2 were subjected to a number of tests including centrifuge stability, flame resistance, freeze-thaw separation, and antiwear performance. The tests are described as follows:

Centrifuge stability test

A 100 ml. sample of finished emulsion is centrifuged 70 minutes at 1500 r.p.m. in an ASTM D–91 apparatus. The bottom 9±0.3 grams are distilled in the ASTM D–95 apparatus. Good performance is shown by similarity between water content of bottom sample and bulk water content.

Flame resistance tests

A fire-resistant hydraulic fluid must meet the requirements of Schedule 30, Subpart B, Bureau of Mines, United States Department of the Interior, published in the Federal Register, Sept. 25, 1959, page 7728. To simplify the work in comparing the competitive samples, only the room temperature pipe cleaner test, subparagraph 3 of paragraph (c) of Section 35.22 was run here. However, this is considered to be the most difficult of the tests to pass, and normally a fluid will pass all of the other fire resistance tests if it will pass this one.

Freeze-thaw separation test

A 100 ml. sample of the test emulsion is placed in a graduate, cooled to −10° F. and then warmed to +77° F. six times. After these six cycles, the graduate is stored on a shelf for 2 days, at which time separated oil and/or water is noted.

Antiwear performance

The fluid under test may be run in any or all of the following pumps. For the present comparative tests the first of those listed was used.

(*a*) *Vickers—single stage vane.*—8 g.p.m. pump, 1150 r.p.m., 1000 p.s.i., 160° F. Cartridge is weighed before and after testing for component and total wear loss.

(*b*) *Vickers—two stage vane.*—13.4 g.p.m. pump, 1150 r.p.m. 400 p.s.i. to 2000 p.s.i., 120° F. Pressure is regulated to run 5 seconds at 400 p.s.i.g., then 5 seconds at 2000 p.s.i.g. for duration of test. Cartridges are evaluated as above.

(*c*) *Denison—multi-piston.*—7.3 g.p.m. pump, 1150 r.p.m., 3000 p.s.i., 160° F. Parts are evaluated as above.

(*d*) *Commercial shearing and stamping company.*—Gear type 14 g.p.m. pump, 1150 r.p.m., 1500 p.s.i., 160° F. Visual examination only.

Emulsions I and II were also compared in the above tests with a number of commercially available emulsion-type hydraulic fluids. The results of these tests are set forth in Table II. It will be seen from the results that the emulsions of the present invention were superior to all of the commercially available materials in many of their properties, particularly in flame resistance, prevention of wear, and separation on standing.

Emulsion III was compared to Emulsions I and II and was found to be superior to the latter in low temperature pumpability, pour point and pump wear.

TABLE II

	Emulsions of Invention		Competitive Commercial Emulsions						
	I	II	A	B	C	D	E	F	G
Inspections:									
Gravity, ° API	17.3	17.3	17.4	21.6	19.6	----------	----------	24.9	----------
Pour Point, ° F	+25	−10	−5	0	−25	----------	----------	----------	−5
Viscosity, SSU at 100° F	518	450	1,110	411	669	325	----------	232	952
Weight Percent Water	43.0	43.0	41.7	43.0	43.0	32.5	----------	----------	----------
Neut No., mg. KOH/gm., ASTM D974	0.05	0.05	0.53	Basic	0.13	----------	----------	0.11	----------
Test Results:									
Centrifuge Stability, Percent H_2O in Bottom 10%	52.2	44.0	67.0	57.7	62.2	32.5	88	----------	77.2
ASTM D130 Copper Strip Corrosion, 3 hrs. at 212° F.[1]	0+	0	----------	1B	1A	----------	----------	1A	----------
Flame Resistance, Cycles to Burn at 77° F	44.2	44.2	42.4	41.4	----------	24.8	32.2	----------	----------
Freeze-Thaw Separation at 6 Cycles	None	None	None	None	None	None	[2] >19	[2] 7	[3] 43
Fluid Condition After 48 Hours at 185° F.:									
Free Oil, Percent	5	0	30	40	50	----------	----------	20	----------
Free H_2O, Percent	0	0	0	30	0	----------	----------	----------	----------
Relative Wear at 250 Hours in Vickers Single Stage Vane Pump	1.10	1.00	3.90	1.22	1.92	4.08	2.00	1.22	2.08

[1] Zero rating is equal to freshly polished strip; zero plus represents trace of tarnish.
[2] Percent H_2O.
[3] Percent oil.

As shown in the examples, the hydraulic fluid of the invention can be prepared as a concentrate for later mixing with water when the fluid is to be used. If the concentrate contains no antiwear agent it will range in composition from about 77 to about 96% oil and from about 4 to about 23 weight percent of emulsifier. If, as is preferred, it also contains the antiwear agent it will range in composition from about 56 to about 96% oil, from about 4 to about 23 weight percent of emulsifier and from about 0.2 to about 22 weight percent of antiwear agent.

The examples herein presented are merely illustrative of the invention. There is no intent to limit the scope of the invention to those examples, nor is it to be limited by any theory regarding its mode of operation. Variations within the purview of the appended claims are contemplated.

What is claimed is:

1. A water-in-oil emulsion adapted for use as a hydraulic fluid which comprises from about 30 to about 55 weight percent of water, about 35 to about 67 weight percent of a mineral lubricating oil, having a pour point no higher than 0° F. and about 3 to about 10 weight percent of an emulsifier, said emulsifier consisting of a mixture of (a) about 35 to 90 weight percent of a metal organo sulfonate, wherein said sulfonate has a molecular weight of from about 300 to 1200 and is selected from the group consisting of alkali metal and alkaline earth metal sulfonates of alkylated aromatic hydrocarbons, (b) about 10 to 65 weight percent of a condensate of a C_{12}–C_{20} aliphatic alcohol with about 1 to 4 moles of a C_2–C_3 alkylene oxide per mole of alcohol and (c) 0 to about 30 weight percent of a hydroxy compound selected from the group consisting of glycols and glycol ethers of from 3 to 8 carbon atoms and aliphatic alcohols of from 3 to 20 carbon atoms.

2. The water-in-oil emulsion of claim **1** wherein said fluid contains as an additional ingredient, about 0.2 to 1.0 wt. percent oleic acid.

3. The water-in-oil emulsion of claim **1** wherein said water concentration is in the range of 40 to 45 weight percent.

4. The water-in-oil emulsion of claim **1** including as an additional ingredient from about 0.1 to about 10 weight percent of an antiwear agent consisting of an ester of a C_1 to C_4 monohydric alcohol and a C_8 to C_{20} fatty acid.

5. The water-in-oil emulsion of claim **1** containing as an additional ingredient from about 0.05 to about 2 weight percent of an antioxidant selected from the group consisting of 2,6-di-tert. butyl-4-methyl phenol, 4,4′ methylene bis (2,6-di-tert.-butyl phenol), phenyl-α-naphthylamine, phenyl-β-naphthylamine and butylated hydroxy anisole.

6. The water-in-oil emulsion of claim **1** containing as an additional ingredient from about 0.01 to about 2 weight percent of a vapor phase rust inhibitor wherein said inhibitor is a volatile amine having a vapor pressure close to that of water.

7. The water-in-oil emulsion of claim **1** wherein (a) is a mixture of sodium sulfonate and calcium sulfonate in a weight ratio of from about 1/1 to about 10/1.

8. A concentrate, capable of dispersion in water to form a fire-resistant hydraulic fluid, which comprises from about 56 to about 96 weight percent of a mineral lubricating oil, having a pour point no higher than 0° F., from about 4 ot about 23 weight percent of an emulsifier and from about 0.2 to about 22 weight percent of an antiwear agent, said emulsifier consisting of a mixture of

(a) about 35 to about 90 weight percent of a metal organo sulfonate wherein said sulfonate has a molecular weight of from about 300 to about 1200 and is selected from the group consisting of alkali metal and alkaline earth metal sulfonates of alkylted aromatic hydrocarbons, from about 10 to 65 weight percent of a condensate of a C_{12}–C_{20} aliphatic alcohol with about 1 to 4 moles of a C_2–C_3 alkylene oxide per mole of alcohol and from 0 to 30 weight percent of a hydroxy compound selected from the group consisting of glycols and glycol ethers of from 3 to 8 carbon atoms and aliphatic alcohols of from 3 to 20 carbon atoms, said antiwear agent consisting of an ester of a C_1 to C_4 weight monohydric alcohol and a C_8 to C_{20} fatty acid.

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