3,346,501

NON-INFLAMMABLE HYDRAULIC FLUID

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This invention relates to hydraulic fluid compositions for use in devices and systems for the transmission of mechanical energy by fluid pressure.

Certain fluids, known as hydraulic fluids, are used by certain technologies as mechanical power or pressure transmitting media. In the prior art it was recognized that hydraulic fluids in general should be noncorrosive, nonfoaming, stable liquids which do not congeal at the low temperatures encountered in their use and do not separate or gasify at the elevated temperatures to which they may be subjected. It was also considered important that they should have sufficient viscosity over a wide temperature range to permit efficient operation of the mechanism.

Water is historically the oldest fluid used for this purpose and is still widely employed. However, at atmospheric pressure water freezes at 32° F. and for many applications the fluid may be subjected to temperatures below this point. Since the advent of petroleum oils of suitable quality, such oils have also been extensively utilized in this application. Petroleum oils are very suitable materials for this purpose and much hydraulic equipment has been designed and manufactured for use with these oils. Petroleum oils have the advantages over water of having a more suitable viscosity, lubricating properties, and they are relatively noncorrosive. Petroleum oils, however, have the major disadvantage of being flammable and may thereby create fire hazards. For example, in industrial operations, such as the die casting of metals, the heavy casting machinery or the controls therefor are operated largely by hydraulic means. The hydraulic fluids used in such apparatus have frequently been a source of fire and danger since a leak or ruptured fluid line may spray fluid onto a surface having a sufficiently high temperature to ignite the fluid.

In recent years, new types of hydraulic fluids, which are less flammable, have been developed to operate in the machinery designed for petroleum hydraulic oils. One of the major generic types of these fluids is the so-called water-glycol or Hydrolube fire-resistant hydraulic fluid. These fluids contain the major components of glycol, water and a polymeric viscosity control agent. They have, as lesser components, additives to impart special properties such as lubricity and corrosion resistance to the fluid. A hydraulic fluid of this type is disclosed in the Zisman et al. patent, U.S. 2,602,780, wherein the glycols employed are any of the common glycols or glycol ethers having 2 to about 14 carbon atoms. These water-glycol fluids are considerably less hazardous from a flammability standpoint than petroleum hydraulic oils, and they are particularly fire resistant when a substantial portion of the water is present. However, they possess certain inherent disadvantages due to the fact that in certain applications, the water will evaporate from these water-glycol fluids leaving a flammable residue with a relatively low flash point of 230–280° F. These flash points are lower than the flash points of many petroleum hydraulic oils. Such fluids can be a fire hazard due to the possibility of a pinhole leak spraying fluid onto hot surfaces causing the evaporation of a sufficient water to leave a residue with a relatively low flash point. In many applications where hydraulic fluids are employed, hot surfaces in the temperature range of 200–400° F. are common, being encountered on steam lines, ovens, exteriors of furnaces, etc. as compared to hot surfaces above 450° F.

Accordingly, it is a purpose of this invention to provide a novel water base, fire-resistant hydraulic fluid which may be employed in application where hot surfaces present a possible hazard, and which possesses the other characteristics, as described above, which are desirable in hydraulic fluids.

These and other objects are accomplished in accordance with this invention by providing a hydraulic fluid base composition characterized by a residue flash point of at least 450° F. containing by weight from about 20 to 70 percent water and from about 30 to 80 percent of at least one polyhydric alcohol ether containing more than 14 carbon atoms and having a molecular weight of 400 to about 6000. The expression "polyhydric alcohol ether" includes the derivatives such as esters thereof. The expression "residue flash point" as used herein refers to the flash point of the hydraulic fluid residue after the water had evaporated. The method for determining the residue flash point is set forth in Example 1 below. For application where high viscosity is desired, from about 1 to 50 weight percent of at least one conventional soluble organic polymeric thickener is also included in the hydraulic fluid base. The expression "soluble organic polymeric thickener" as used herein refers to those thickeners which are soluble in water-polyhydric alcohol ether mixtures. The hydraulic fluid base may include solvents with sufficiently high flash points such as formamide. For most applications requiring hydraulic fluids, this hydraulic fluid base is formulated with conventional additives such as buffering agents, antifoaming agents, antiwear agents, and corrosion inhibitors.

The polyhydric alcohol ether may be any of the common water-soluble polyhydric alcohol ethers having a molecular weight of 400 to about 6000. These include polyalkylene glycols or polyols, particularly polyethylene glycols, and glycols incorporating heteric and/or block polyethylene and polypropylene groups. These ethers also include ethylene oxide and heteric or block ethylene oxide-propylene oxide polyols on various starting base polyols to give alkoxyols, diols, triols, tetrols, etc. or mixtures thereof. A particularly useful class of compounds for this purpose is the water-soluble polyalkylene ether glycols which have the general formula $H(OR)_nOH$ where R is an alkylene radical and *n* is an integer which, in a preferred embodiment, is sufficiently large that the compound as a whole has a molecular weight of 400 to about 6000. Not all of the alkylene radicals present need to be the same. Glycols containing a mixture of radicals as in the compound $HO(CH_2OC_2H_4O)_nH$, or

$$HO(C_2H_4O)_n(C_3H_6O)_m(C_2H_4O)_nH$$

wherein *n* and *m* are together sufficient for attainment of the desired molecular weight can be used. Polyethylene ether-polypropylene ether glycols, having the above-indicated formula, are among the preferred glycols. Ethylene oxide or heteric ethylene oxide-propylene oxide adducts or an alkyl alcohol such as disclosed in U.S. Patents 2,425,755 and 2,425,845 may be employed. By way of example, butoxy heteric polyethylene-polypropylene glycols which have the general formula

$$C_4H_9O(C_2H_4O)_x(C_3H_6O)_yH$$

and methoxy polyethylene glycols having the general formula $CH_3O(C_2H_4O)_nH$ may be employed.

Soluble thickeners for hydraulic fluids are well known to those skilled in the art as can be seen by reference to U.S. Patent No. 2,462,694 which discloses a large number of such soluble thickeners in columns 2, 3 and 4 thereof. For the hydraulic fluids of the instant invention, soluble thickeners with molecular weights in excess of 6000 which may range up to 100,000 may be employed. However, soluble thickeners of a molecular weight of about 10,000 to 25,000 are preferred.

An excellent soluble organic polymeric thickener for use with the hydraulic fluid of this invention comprises a copolymer of ethylene oxide and 1,2-propylene oxide or 1,3-propylene oxide, preferably one containing more than 50 mol percent of ethylene oxide and less than 50 mol percent of the propylene oxide, copolymerized to a thick fluid polymer. A thickener having the optimum water solubility, viscosity, shear strength, and other properties desirable in a hydraulic fluid composition, may be made by copolymerizing about 75 mol percent of ethylene oxide and about 25 mol percent of isopropylene oxide to a molecular weight of about 10,000 to 25,000. The polymer thus formed thickens the aqueous base to the desired viscosity when added in only a small proportion. The higher molecular weight polymers are the more effective thickening agents. The polymers have a composition which can be indicated as follows:

$$HO-[CH_2CH_2-O]_n[-\underset{|}{\overset{CH_3}{C}}H-CH_2-O]_q-H$$

in which n and q are whole numbers, and n/q is greater than 1, which, it is clear, is characterized by the frequent random recurrence of methyl group branches.

It is preferred that hydraulic fluids incorporating the above described hydraulic fluid bases contain at least one corrosion inhibitor known to be effective by those skilled in the art. Suitable corrosion inhibitors include the alkali metal benzoates, pelargonates, nitrates, nitrites, organophosphates and fatty acid salts; the mercaptobenzothiazoles and the like benzotriazole amines such as morpholine, dimethylaminoethanol, diethylaminoethanol, triethanolamine, diethanolamine, monoethanolamine, dibutylamine, etc.; phosphates and other salts of the said amines. Conventional vapor phase corrosion inhibitors, such as morpholine, dibutylamine and cyclohexylamine, are also desirable. Combinations of these inhibitors may be employed if desired.

In addition, it is desirable for such hydraulic fluids to include at least one of the conventional antifoaming agents, such as silicon antifoam agents along with at least one of the conventional buffering agents, such as the alkali metal hydroxides, alkali metal salts of straight chain fatty acids, such as alkali metal acetates etc., to maintain reserve alkalinity. Also, certain long-chain fatty acids and derivatives thereof may be employed as antiwear agents and rust preventatives, such as, for example, oleic acid, stearic acid, lauric acid, capric acid, and corresponding fatty oils or glycerides and the like along with alkali metal soaps of fatty acids. It is preferred to maintain the pH of these hydraulic fluids in a range of from about 7 to 11.

It should be noted that some additives can serve a dual function. For example, morpholine can serve as both a liquid and a vapor phase corrosion inhibitor, and lauric acid amine salts can serve as wear-resisting agents and corrosion inhibitors.

The range of proportions of the additives may vary widely. Good results are obtained with a hydraulic fluid containing as additives to the above described hydraulic fluid base composition by weight about 0.02 to 2.5 percent of at least one corrosion inhibitor, about 0.0005 to 0.1 percent of at least one antifoaming agent, about 0.2 to 1.0 percent of at least one antiwear agent, and about 0.2 to 3.0 percent of at least one buffering agent.

A preferred hydraulic fluid composition contains by weight about 35 to 40 percent of water, about 40 to 60 percent of at least one polyhydric alcohol ether having a molecular weight of 400 to about 6000, about 5 to 15 percent of a soluble organic polymeric thickener, about 0.5 to 2.5 percent of at least one corrosion inhibitor, about 0.001 to 0.1 percent of at least one antifoaming agent, about 0.25 to 1.0 percent of at least one antiwear agent, and about 0.2 to 3.0 percent of at least one buffering agent.

The practice of this invention will be more completely understood by reference to the following examples.

EXAMPLE 1

A series of six hydraulic fluid bases were prepared by blending water with polyethylene glycol, having a molecular weight of 600 to produce fluids containing 30, 50, 55, 60, 65 and 70 weight percent of the polyethylene glycol. A similar series of hydraulic fluid bases was prepared wherein a polyethylene glycol having a molecular weight of 1000 was employed in lieu of the glycol having a molecular weight of 600. All fluids were clear, nonfoaming liquids. The separation temperatures of the fluids were then determined by placing 10 grams of the fluid in a 13 x 120 millimeter test tube. A 220° F. thermometer was inserted and the test tube was rapidly heated on a Bunsen flame while stirring until clouding occurred. The fluid was allowed to cool while stirring until the fluid became clear again, at which time the temperature was taken as the separation temperature. In all cases the separation temperatures were above 210° F. A 10-gram sample of each fluid in a 6-dram vial containing a pour point thermometer was kept at +30° F. for 16 hours. It was then reduced in temperature at the rate of 5° F. every 30 minutes. The temperature at which the fluid will no longer flow, as tested in the ASTM D97 pour point procedure, was then determined. This temperature is referred to herein as the "low temperature crystallization point." These points were all 10° F. or below.

Residues for testing purposes were obtained from these hydraulic fluids by maintaining 200 cc. samples of each fluid in an open 16-ounce jar for one week at 210° F. and the flash points of the residues were determined by ASTM Method D92. The residues were liquids with flash points of 480° F. for the fluids incorporating the 600 molecular weight glycol. For the fluids incorporating the 1000 molecular weight glycol the residues were soft waxes with flash points of 490° F.

EXAMPLE 2

A series of five hydraulic fluid bases were prepared by first blending water with polyethylene glycol, having a molecular weight of 600, to produce fluids which contain 55 weight percent of the polyethylene glycol, balance water. As a thickener, a copolymer of about 75 mol percent of ethylene oxide and about 25 mol percent of 1,2-propylene oxide copolymerized to a thick fluid polymer, having an average molecular weight of about 17,000, was then blended with each polyethylene glycol water mixture. The amounts of the thickener were sufficient to produce hydraulic fluids containing, respectively, 0, 2, 4, 8 and 16 weight percent thickener based on the total mixture. These fluids were all clear liquids with separation temperatures of greater than 210° F. and low temperature crystallization points of —35° F., as determined by the method of Example 1. Residues were obtained and the flash points determined as set forth in Example 1. The residues were found to be liquids with flash points greater than 450° F.

EXAMPLE 3

A series of four hydraulic fluid bases were prepared by blending components to obtain mixtures consisting of by weight: 42 percent of the respective polyhydric alcohol ether indicated in Table I below, 8 percent of the 75 mol percent ethylene oxide-25 mol percent propylene oxide copolymer thickener, described in Example 2, balance water. The resulting hydraulic fluids were clear liquids having fluid and residue properties as given in Table I below. The separation temperatures and low temperature crystallization points were determined, the residues were obtained and the flash points determined, all as set forth in Example 1.

TABLE I

Polyhydric alcohol ether	Base fluid properties			Residue properties	
	Foaming tendency	Low temp. Crystallization point, ° F.	Separation temp., ° F.	Appearance	Flash point, ° F.
I	Low	−30	198	Viscous liquid.	475
II	Slight	−35	202	do	470
III	do	−45	210	do	485
IV	do	<−45	>210	do	455
V	do	−45	180	do	500
VI	Low	−30	200	Soft wax	470

The material indicated by numerals I through VI under Polyhydric Alcohol Ether in Table I are as follows:

(I) The polyoxyethylene adduct of a polyoxypropylene hydrophobic base, having an average molecular weight of 950, wherein the oxyethylene content is about 50 weight percent of the molecule.

(II) The 50% ethylene oxide-50% propylene oxide heteric adduct of glycerine having a theoretical molecular weight of approximately 1000.

(III) Polyethylene glycol having a molecular weight of 600.

(IV) The methoxypolyethylene alcohol having the general formula

$$CH_3OCH_2(CH_2OCH_2)_nCH_2OH$$

wherein n has an average value of 11 or 12 and the molecular weight is 525 to 575.

(V) The acetic acid ester of a 600 molecular weight polyethylene glycol.

(VI) A solution of 30 percent formamide and 70 percent 4000 molecular weight polyethylene glycol.

EXAMPLE 4

Nine hydraulic fluid bases were prepared by blending components to obtain mixtures consisting of by weight 50 percent of the polyhydric alcohol ether indicated in Table II below, 8 percent of the 75 mol percent ethylene oxide-25 mol percent propylene oxide copolymer thickener described in Example 2, balance water. The resulting hydraulic fluid bases were clear, nonfoaming liquids. The separation temperatures and low temperature crystallization points were determined, the residues were obtained and the flash points determined, all as set forth in Example I. The fluids were all viscous liquids with properties as shown in Table II below.

TABLE II

Fluid No.	Polyhydric alcohol ether		Low temp. Crystallization point, ° F.	Separation temp., ° F.	Residue flash point, ° F.
	Type	Molecular weight			
1	Polyethylene glycol	200	−40	>210	340
2	do	400	−25	>210	460
3	do	600	−20	>210	480
4	do	1,000	−10	>210	490
5	do	1,500	+10	195	490
6	do	Equal parts 400 4,000	<+20	185	480
7	do	Equal parts 400 6,000	<+20	175	480
8	50% Ethylene oxide 50% Propylene oxide Glycerine adducts	1,000	−30	190	510
9	75% Ethylene oxide 25% Propylene oxide	2,000	−30	205	475

The polyhydric alcohol ethers employed in fluids Nos. 6 and 7 were 50 percent by weight mixtures of polyethylene glycols having average molecular weights of 40° with polyethylene glycols, having an average molecular weight of 4000 in fluid No. 6 and 6000 in fluid No. 7.

The polyhydric alcohol ether employed in fluid No. 8 is the 50% ethylene, oxide, 50% propylene oxide heteric adduct of glycerine having a theoretical molecular weight of 1000.

The polyhydric alcohol ether employed in fluid No. 9 was a copolymer of about 75 mol percent ethylene oxide and about 25 mol percent propylene oxide copolymerized to a fluid polymer having an average molecular weight of approximately 2000.

It can be seen from Table II that suitable hydraulic fluids can be prepared from water, water-soluble polyhydric alcohol ethers within the molecular weight range of 400 to 6000, and water-soluble thickeners to give fluid residues having a flash point above 450° F. and separation temperatures of 175° F. and above. Where a polyhydric alcohol ether having a molecular weight below 400 is employed, it can be seen that the flash point of the residue is well below 450° F.

EXAMPLE 5

A hydraulic fluid base having a separation temperature greater than 210° F. and a residue flash point greater than 450° F. prepared by blending water with a copolymer of ethylene oxide and 1,2-propylene oxide containing about 75 mol percent of ethylene oxide and about 25 mol percent of the propylene oxide copolymerized to a fluid polymer having an average molecular weight of 2000 to provide a mixture containing 60 percent of the polymer, balance water.

EXAMPLE 6

A hydraulic fluid base having a separation temperature greater than 210° F. and a residue flash point greater than 450° F. prepared by blending components to obtain a mixture consisting of 50 percent polyethylene glycol of a molecular weight of 600, 8 percent of the 50% ethylene oxide-50% propylene oxide heteric adduct of glycerine having a theoretical molecular weight of approximately 17,000, balance water.

EXAMPLE 7

A hydraulic fluid having a separation temperature greater than 210° F. and a residue flash point greater than 450° F. prepared by blending components of the following formulation, all percentages being by weight of the total mixture:

	Percent
Polyethylene glycol (molecular weight 600)	50.000
Water	38.895
Thickener [1]	9.000
Dibutylamine caprate	1.000
Benzotriazole	0.050
Sodium nitrite	0.050
Silicone antifoam agent	0.005
Potassium acetate	1.000

[1] 50% ethylene oxide-50% propylene oxide heteric adduct of glycerine having a theoretical molecular weight of approximately 17,000.

While there has been shown and described hereinabove the present preferred embodiments of this invention, it is to be understood that various changes, alterations and modifications can be made thereto without departing from the spirit and scope thereof as defined in the appended claims.

What is claimed is:

1. A hydraulic fluid base characterized by a residue flash point of at least 450° F., containing by weight from about 20 to 70 percent water and from about 30 to 80 percent of at least one water-soluble polyhydric alcohol ether having a molecular weight of 400 to 6000.

2. A hydraulic fluid base characterized by a residue flash point of at least 450° F., containing by weight about 20 to 70 percent water, about 30 to 80 percent of at least one water-soluble polyhydric alcohol ether having a molecular weight of 400 to 6000, and about to 1 to 50 percent of at least one soluble polyoxyalkylene polymeric thickener having a molecular weight in excess of 6,000 and up to 100,000.

3. The hydraulic fluid base of claim **2** wherein the polyhydric alcohol ether is a polyalkylene ether polyol.

4. A hydraulic fluid characterized by a residue flash point of at least 450° F., containing by weight about 20 to 70 percent water, about 30 to 80 percent of at least one water-soluble polyhydric alcohol ether having a molecular weight of 400 to 6000, 0 to about 50 percent of at least one soluble polyoxyalkylene polymeric thickener having a molecular weight in excess of 6,000 and up to 100,000, and about 0.02 to 2.5 percent of at least one corrosion inhibitor.

5. A hydraulic fluid in accordance with claim **4** which contains from about 0.2 to 1.0 percent by weight of at least one antiwear agent selected from the group consisting of fatty acids and alkali metal soaps of fatty acids.

6. A hydraulic fluid in accordance with claim **5** which contains from about 0.0005 to 0.1 percent by weight of at least one silicone antifoaming agent.

7. A hydraulic fluid in accordance with claim **5** which contains from about 0.2 to 3.0 percent by weight of at least one buffering agent to maintain reserve alkalinity.

8. A hydraulic fluid in accordance with claim **7** which contains from about 0.2 to 1.0 percent by weight of at least one silicone antifoaming agent.

9. A hydraulic fluid characterized by a residue flash point of at least 450° F., consisting essentially of by weight about 35 to 40 percent of water, about 40 to 60 percent of at least one water-soluble polyhydric alcohol ether having a molecular weight of 400 to 6000, about 5 to 15 percent of a soluble polyoxyalkylene polymeric thickener having a molecular weight in excess of 6,000 and up to 100,000, about 0.5 to 2.5 percent of at least one corrosion inhibitor, about 0.001 to 0.1 percent of at least one silicone antifoaming agent, about 0.25 to 1.0 percent of at least one antiwear agent selected from the group consisting of fatty acids and alkali metal soaps of fatty acids, and about 0.2 to 3.0 percent of at least one buffering agent to maintain reserve alkalinity.

References Cited

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