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# WATER-IN-OIL EMULSION HYDRAULIC FLUIDS

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This invention relates to improved fire-resistant hydraulic fluids. More particularly, it pertains to water-in-oil colliery hydraulic fluids and lubricants which are fire and wear-resistant, stable and non-corrosive and to oil concentrates which are readily emulsifiable with large amounts of water.

Although it is known in the art that certain emulsions are useful as coolants and lubricants in metal working operations, the use of emulsions in hydraulic systems has been limited because of their inability to resist wear, their poor stability and their inability to pass fire-resistant requirements for which such fluids are primarily used.

In colliery equipment such as various hydraulic machinery, e.g., winder brake mechanism and wagon tipper to hydraulic jacks, pit props and roof bar straighteners, mechanical loaders and various other fluid drive mechanisms which are subjected to load, shock and vibration, it is essential that the hydraulic fluid employed therein function properly and efficiently without the danger of being flammable or toxic.

A variety of so-called fire-resistant fluids are commercially available such as phosphate ester base fluids, but these have been found to possess poor low temperature viscosity-temperature properties, and they are toxic. Water-glycol solution or various water-oil emulsions have been found to have a tendency to form deposits under high pressures and are costly.

It is an object of this invention to provide a composition which can be emulsified readily on the job to yield a fire resistant hydraulic fluid having good lubricating properties. Another object is to provide a fluid which after emulsification is a satisfactory lubricant for colliery hydraulic equipment, which is stable, non-toxic, fire-resistant, resistant to deterioration, inhibits corrosion and not cause wear. Still another object of this invention is to provide a water-mineral oil emulsion usable as lubricants and fire-resistant hydraulic fluids for various equipment used in colliery hydraulic equipment.

These and other objects are accomplished in accordance with this invention by providing a particular mineral oil base containing two particular types of dissimilar non-ionic surface active agents in critical amounts so that the oil compensation is readily emulsified with large amounts of water to form a stable, fire-resistant water-in-oil emulsion, particularly useful in colliery hydraulic equipment.

The mineral oil base should be one having a viscosity index (Dean-Davis) of at least 80, preferably between 90 and 100. Mineral oil fractions of this type are derived from paraffinic, naphthenic or mixed base crudes. They should also be in the lubricating oil range and have a viscosity, as determined at 100° F., of from 75 to 250 SUS, preferably between 100 and 150. A typical mineral oil base of this kind is a high viscosiy index refined mineral lubricating oil having the following properties:

| | |
|---|---|
| Gr., API°, 60° C | 32.2 |
| Color, ASTM | 1 |
| Pour point, ° F | 5 |
| Flash, ° F., COC | 370 |
| Fire, ° F | 435 |
| Viscosity, SUS, at 100° F | 103 |
| Viscosity index | 93 |
| Neutralization No | 0.01 |

The two non-ionic surface agents which are added to



the mineral oil are (1) a monoester of a long chain fatty acid having at least 8 carbon atoms and an alkitan and (2) a polyalkylenoxy phenoxy alkanol. Each of these additives must be present in critical amounts of which the monoester (1) is used in amounts ranging from 1% to 4%, preferably from 1.5% to 3% and the polyalkylenoxy phenoxy alkanol (2) is used in amounts ranging from 0.5% to 3%, preferably from 1% to 2%.

In the monoester non-ionic surface agent by alkitans is meant partially dehydrated polyhydric alcohols which results in the conversion of the polyhydric alcohol to inner ether polyhydric compounds having 1 or 2 ethers and 4 to 6 hydroxyl groups in the molecule. Compounds of this type are exemplified by sorbitan, mannitan, xylitan, dulcitan, etc. Fatty acids which are used to form the monoesters of alkitans are saturated and unsaturated fatty acids having at least 8 carbon atoms, preferably from 12 to 18 carbon atoms, such as lauric, stearic, oleic, linoleic, ricinoleic acids and the like. Monoesters of this type include sorbitan monolaurate, sorbitan monostearate, sorbitan monooleate, sorbitan monoricinoleate, mannitan monolaurate, mannitan monooleate, and mixtures thereof.

The second essential additive is an oil-soluble alkyl phenoxy polyalkylene glycol having the formula R-phenyl $\text{-}(\text{OR}')_n\text{OR}''\text{—OH}$, where $n$ is an integer of from 2 to 6, preferably 3 to 4, R is an alkyl radical of 4 to 20 carbon atoms, preferably 4 to 12, and R′ and R″ are the same or different alkylene groups such as ethylene or propylene groups, they are preferably the same, and preferably ethylene. Compounds of this type are $C_{4-12}$ alkyl phenoxy-$(\text{alkoxy})_{4-6}$ alkanols exemplified by isobutylphenoxy tetraethyleneoxy ethanol, diisobutylphenoxy tetraethyleneoxy ethanol, nonylphenoxy tetraethyleneoxy ethanol, octylphenoxy hexaethyleneoxy ethanol, diisobutylphenoxy tripropyleneoxy propanol, and mixtures thereof.

In addition to the above two essential additives it is preferred to use in such compositions small amounts of from about 0.01% to about 2%, preferably from about 0.2% to about 1% of oil-soluble antioxidants. The antioxidants include phenolic and aromatic amine comuounds. The phenolic compounds are illustrated by the alkyl phenols, e.g., di- and trialkyl phenols, for instance 2,4-, 2,3- 3,4-, 2,6- and 3,5-diamyl phenol, 2,4-dimethyl-6-tert. butylphenol, 2,6-ditert. butyl-4-methylphenol, as well as bisphenols such as 4,4′-methylene-bis(2,6-dietert.-butylphenol). The amines are illustrated by arylamines such as phenyl-alpha-naphthylamine or phenyl-beta-naphthylamine.

Illustrative examples of mineral oil bases of this invention which are emulsified with from about 20% to about 45%, preferably from about 30% to about 40% of water to form a stable fire-resistant hydraulic fluid are presented below.

| | | |
|---|---|---|
| Composition A: | | |
| Sorbitan monooleate | percent wt | 2 |
| Diisobutylphenoxy(ethoxy)$_4$ethanol | do | 1 |
| Mineral lubricating oil (V.I. 93, visc. at 100° F., SUS=103) | | Balance |
| Composition B: | | |
| Sorbitan monooleate | percent wt | 2 |
| Diisobutylphenoxy(ethoxy)$_4$ethanol | do | 1 |
| 2,6-ditert.butyl-4-methylphenol | do | 0.2 |
| Phenyl-alpha-naphthylamine | do | 0.1 |
| Mineral lubricating oil (same as A) | do | 0.1 |
| Properties: | | |
| Gr., API°, 60° | | 31.3 |
| Color, ASTM | | 1 |
| Pour point, ° F | | 10 |
| Flash, ° F., COC | | 380 |
| Visc., SUS, at 100° F | | 112 |
| Neut. No | | 0.25 |

Composition C:

| | |
|---|---|
| Sorbitan monooleate—percent wt— | 1.5 |
| Nonylphenoxy(ethoxy)$_2$ethanol—do— | 1 |
| 4,4'-methylene(2,6-ditert.butylphenol)—do— | 0.2 |
| Phenyl-alpha-naphthylamine—do— | 0.1 |
| Mineral lubricating oil (V.I.=80, visc., SUS, at 100° F.=150)— | Balance |

Composition D:

| | |
|---|---|
| Mannitan monostearate—percent wt— | 2 |
| Diisobutylphenoxy(ethoxy)$_4$ethanol—do— | 1 |
| 2,6-ditert.butyl-4-methylphenol—do— | 0.2 |
| Phenyl-alpha-naphthylamine—do— | 0.1 |
| Mineral lubricating oil (same as A)— | Balance |

Composition E:

| | |
|---|---|
| Mannitan monostearate—percent wt— | 2 |
| Diisobutylphenoxy(propoxy)$_2$propanol—do— | 1 |
| 2,6-ditert.butyl-4-methylphenol—do— | 0.2 |
| Phenyl-alpha-naphthylamine—do— | 0.1 |
| Mineral lubricating oil (same as A)— | Balance |

The finished emulsion fluid is prepared by slowly adding to the oil base composition such as A, B, C, D or E, from 20% to 45% based on the total composition, an aqueous base, such as water which may or may not contain 0.1% to 1% of a corrosion or wear inhibitor such as water-soluble inorganic nitrites, nitrates, chromates, phosphates or water-soluble low molecular weight salts such as alkali metal or alkaline earth metal (Na, K, Ca, Ba) acetate or propionate. The water-in-oil emulsion can be mixed by any suitable means such as by air agitation, propeller agitation or by passing through a colloid mill until a homogeneous stable water-in-oil emulsion is formed. For economical reasons, the water is added to the oil in desired amounts at the time the emulsion is to be used, although a stable water-in-oil emulsion can be prepared and stored for a moderate period.

A finished water-in-oil emulsion (Composition I) was prepared by admixing 60% of Composition B with 40% water and the mixture was passed through a colloid mill until a stable homogeneous water-in-oil emulsion was formed.

The properties of Composition I were as follows:

| | |
|---|---|
| Sp. gr— | 0.9165 |
| Color— | White |
| Neut. No— | 0.12 |
| Visc. at 100° F., SUS— | 367 |
| Visc. index— | 144 |

Other finished compositions include:

| Composition II: | Percent |
|---|---|
| Water— | 30 |
| Composition A— | 70 |

Composition III:

| | |
|---|---|
| Water containing 0.1% Ca acetate— | 40 |
| Composition B— | 60 |

Composition IV:

| | |
|---|---|
| Water containing 0.1% $NaNO_2$— | 35 |
| Composition C— | 65 |

Composition V:

| | |
|---|---|
| Water— | 40 |
| Composition D— | 60 |

The outstanding properties of compositions of this invention as compared to other emulsions are shown in Table I. The stability of the test compositions were determined by measuring separation of water and oil from 100° C. sample of the final water-in-oil emulsion composition at 140° F. The wear-resistant properties were determined by the Vickers' hydraulic pump test as described in "Lubrication Engineering," February 1949, pages 16 and 17. The fire resistance was determined by the pipe cleaner test described in "Lubrication Engineering," March-April 1955, pages 86–87.

*Table I*

| Composition Stability Test | I | | II | | X[a] | | Y[b] | | Z[c] |
|---|---|---|---|---|---|---|---|---|---|
| | Free Oil, Percent v. | Free Water, Percent v. | Free Oil, Percent v. | Free Water, Percent v. | Free Oil, Percent v. | Free Water, Percent v. | Free Oil, Percent v. | Free Water, Percent v. | |
| 1 day | 1 | slight | 1 | slight | unstable | | slight | 2 | |
| 6 days | | | | | | | 6 | | |
| 10 days | 9 | slight | 9 | slight | unstable | | 50 | 20 | |
| 17 days | 21 | slight | 20 | slight | unstable | | | 20 | |
| 27 days | 42 | slight | 40 | slight | unstable | | | | |
| Vickers' Hydraulic Pump Test[d] | 0.32 (1000 hrs.) | | | | | | 1.44 (200 hrs.) | | 6.6 (120 hrs). |

[a] Composition X (water-in-oil emulsion) = 40% water + 60% mineral oil containing 0.75% sorbitan monooleate and 2.25% polyethylene substituted sorbitan monooleate (Tween 81) having the following properties: Av. M. W., 471; visc. (cp. at 25° C.), 350–550; sp. gr., 1–1.05; flash point, °F., 550; fire point, ° F., 600.

[b] Composition Y (water-in-oil emulsion) = 40% water + 60% mineral oil + 5% polyethylene substituted sorbitan monooleate (Tween 81) + 0.51% glycerol monooleate + 0.12% sulfurized oleic acid.

[c] Composition Z = oil-in-water emulsion comprising 50% water + 50% mineral oil composition containing 20% Na petroleum sulfonate, 1% ricinoleic acid, 1% hexylene glycol, 1% lard oil, 2% water, 0.3% Dowicide-O, 0.1% sodium hydroxide and the balance mineral oil.

[d] Fluid circulated at 150° F. and 1000–1500 p.s.i., and combined wear (wt. loss gm.) of cam rings and vanes after 1000 hours determined.

In the pipe cleaner test, Compositions I through V passed over 50 cycles while mineral oil or mineral oil containing 4% of Ca petroleum sulfonates and/or $CaC_{12-22}$ alkyl salicylate ignited after about 5 cycles.

From the results presented in Table I, it can be seen that Compositions I and II of the present invention are superior to Compositions X, Y and Z with respect to stability and wear, although these compositions are also water-in-oil emulsions, but which contain different nonionic surface active agents from those used in compositions of the present invention.

I claim as my invention:

1. A hydraulic fluid for colliery equipment consisting essentially of a water-in-oil emulsion in which the water phase is from about 20% to about 45% of the emulsion and the oil phase is from about 55% to about 80% of the emulsion, the oil phase being essentially an 80–100 V.I. mineral oil having a viscosity in the range of from 75 to 250 SUS at 100° F. containing from about 1% to about 4% of a monoester of a long chain fatty acid having from 8 to 18 carbon atoms and an alkitan selected from the group consisting of sorbitan and mannitan and from about 0.5% to about 3% of an oil-soluble $C_{4-20}$ alkyl phenoxy(ethoxy)$_{4-6}$ethanol based on the oil.

2. A hydraulic fluid for colliery equipment consisting essentially of a water-in-oil emulsion in which the water phase is from about 20% to about 45% of the emulsion and the oil phase is from about 55% to about 80% of the emulsion, the oil phase being essentially a 80–100 V.I. mineral oil having a viscosity in the range of from 75 to 250 SUS at 100° F. containing from about 1.5% to about 3% of a monoester of a fatty acid having from

12 to 18 carbon atoms and an alkitan selected from the group consisting of sorbitan and mannitan, and from about 1% to about 2% of an oil-soluble $C_{4-20}$ alkyl phenoxy(ethoxy)$_{4-6}$ethanol based on the oil.

3. A hydraulic fluid for colliery equipment consisting essentially of a water-in-oil emulsion in which the water phase is from about 20% to about 45% of the emulsion and the oil phase is from about 55% to about 80% of the emulsion, the oil phase being essentially a 80–100 V.I. mineral lubricating oil having a visosity in the range of from 100 to 150 SUS at 100° F. containing from about 1.5% to about 3% of sorbitan monooleate and from about 1% to about 2% of a $C_{4-20}$ alkyl phenoxy (ethoxy)$_{4-6}$ethanol based on the oil.

4. A hydraulic fluid for colliery equipment consisting essentially of a water-in-oil emulsion in which the water phase is from about 30% to about 40% of the emulsion and the oil phase is from about 70% to about 60% of the emulsion, the oil phase being essentially a 80–100 V.I. mineral lubricating oil having a viscosity in the range of from 100 to 150 SUS at 100° F. containing from about 1.5% to about 3% of sorbitan monooleate, and from about 1% to about 2% of an oil-soluble diisobutyl phenoxy(ethoxy)$_4$ethanol based on the oil.

5. The hydraulic fluid composition of claim 4 containing in the emulsion from about 0.01% to about 1% each of 2,6-ditert.butyl-4-methylphenol and phenyl-alpha-naphthylamine.

6. A water-in-oil emulsifiable mineral oil composition for use as a lubricant and hydraulic fluid, said mneral oil base composition comprising major amount of an 80–100 V.I. mineral oil having a viscosity in the range of from 75 to 250 SUS at 100° F. containing from about 1% to about 4% of a monoester of a long chain fatty acid having from 8 to 18 carbon atoms and an alkitan selected from the group consisting of sorbitan and mannitan and from about 0.5% to about 3% of an oil-soluble $C_{4-20}$ alkyl phenoxy(ethoxy)$_{4-6}$ethanol.

7. A water-in-oil emulsifiable mineral oil composition for use as a lubricant and hydraulic fluid, said mineral oil base composition comprising a major amount of an 80–100 V.I. mineral oil having a viscosity in the range of from 75 to 250 SUS at 100° F. containing from about 1.5% to about 3% of a monoester of a fatty acid having from 12 to 18 carbon atoms and an alkitan selected from the group consisting of sorbitan and mannitan and from about 1% to about 2% based on the oil of an oil-soluble $C_{4-20}$ alkyl phenoxy(ethoxy)$_{4-6}$ethanol.

8. A water-in-oil emulsifiable mineral oil composition for use as a lubricant and hydraulic fluid said mineral oil base composition comprising a major amount of an 80–100 V.I. mineral lubricating oil having a viscosity in the range of from 100 to 150 SUS at 100 F. containing 2% sorbitan monooleate and 1% diisobutyl phenoxy (ethoxy)$_{4-6}$ethanol.

9. The composition of claim 8 containing from about 0.01% to about 1% each of 2,6-ditert.butyl-4-methylphenol and phenyl-alpha-naphthylamine.

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