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2,961,404

## EMULSION LUBRICANT AND HYDRAULIC FLUID

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This invention relates to improved emulsion lubricants and hydraulic fluids. More particularly, it pertains to water-in-oil emulsion lubricants especially useful for slow speed diesel engines and as fire-resistant hydraulic fluids which possess good lubricating properties and which are stable, non-corrosive and wear-resistant.

Although it is known in the art that certain emulsions are useful as coolants and lubricants in metal working operations and as rust and corrosion inhibitors, their use as engine lubricants and as hydraulic fluids has been limited. Under engine operating conditions emulsions generally lack desired lubricity and cause wear and corrosion.

Fluid compositions for use in many hydraulic systems should be fire-resistant and non-corrosive. They should be capable of preventing wear and be thermally stable and resistant to oxidation. Various compositions have been proposed for use as hydraulic fluids, but none of them are entirely satisfactory. Thus, mineral oils are highly flammable, castor oil results in sludge and gum formation, esters of carboxylic acids cause swelling of rubber, the organic phosphates and the glycols are corrosive, the halogen-containing materials tend to hydrolyze to produce corrosive materials, conventional emulsions lack adequate wear resistant properties, while the silicone compounds lack lubricity and present a health hazard.

It is an object of this invention to provide an emulsion lubricant and fire-resistant hydraulic fluid having good lubricating properties. Another object is to provide a fluid which is a satisfactory lubricant for low speed diesel engines and hydraulic equipment, which is stable, fire-resistant, resistant to deterioration, inhibits corrosion and does not cause wear. Still another object of this invention is to provide an emulsion lubricant and fire-resistant hydraulic fluid of good lubricating quality even when subjected to various adverse conditions of temperature, loads and speeds as encountered in various diesel engines operating on high sulfur fuels or when used in hydraulic systems.

These and other objects are accomplished in accordance with this invention by providing a water-in-oil emulsion which is (a) from about 20% to about 45% water phase and (b) from about 55% to about 80% oil phase, in which the emulsion contains a combination of minor amounts of three essential additives, namely (1) from about 0.5% to about 6% of an oil-soluble basic polyvalent metal aromatic carboxylate, (2) from about 0.5% to about 6% of an oil-soluble basic polyvalent metal organic sulfonate, the metals of both being selected from

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group II metals of the periodic table and having an atomic number of from 12 to 56 and (3) from about 0.01% to about 2% of a water-soluble polymeric amide having a molecular weight of at least 1000.

The oil-soluble basic polyvalent metal aromatic carboxylates, and preferably the alkaline earth metals salts, include such compounds as basic calcium, barium, magnesium, strontium and zinc salts of hydrocarbon substituted benzoic, salicylic, resorcylic, anthranilic and naphthoic acids such as the basic calcium, barium, magnesium and/or zinc salts of  $C_3$ - $C_{22}$ -alkylbenzoic,  $C_8$ - $C_{22}$ -alkylsalicylic,  $C_3$ - $C_{22}$ -alkylnaphthoic acids and mixtures thereof.

The preferred salts are the basic barium, calcium, magnesium, and zinc salts of laurylsalicylic acid, or of stearylsalicylic acid or of a mixture of alkylsalicylic acids in which the alkyl groups contain from 8 to 30, preferably 14 to 22, carbon atoms. The basic calcium salts of these alkylsalicylic acids are particularly preferred. The highly basic salts may be prepared, for example, by the processes described in U.S. Patent 2,409,687 or 2,616,910.

The oil-soluble basic polyvalent metal organic sulfonates, of which petroleum sulfonates are preferred, are preferably the alkaline earth metal sulfonates. Especially suitable sulfonates include the basic calcium, barium, magnesium and zinc petroleum sulfonates of oil-soluble petroleum sulfonic acids. The acid should range in molecular weight from about 350 to 550 and preferably are in the range of from 400 to 500. Other sulfonates include the oil-soluble basic calcium, barium, magnesium and zinc tetra-tertiarybutylphenyl sulfonate, dinonyl naphthalene sulfonate, diwaxbenzene sulfonate, wax-phenol sulfonate and mixtures thereof.

By a basic salt as used with reference to the aromatic carboxylates and the sulfonates is meant that the amount of metal neutralizing agent, e.g. metal oxide, metal hydroxide, or metal carbonate in the product is in excess of that stoichiometrically required to neutralize the carboxylic or sulfonic acid to produce the normal salt. The excess basicity of the salts used in compositions of this invention should be from 25% to 1200%, preferably from about 40% to 800%.

The water-soluble polymeric amides, derived from ethylenically unsaturated polymerizable amides, include homopolymeric amides such as polyacrylamides, polymethacrylamide and (N-polyvinylpyrrolidone) and copolymers thereof as used as their copolymers with other ethylenically unsaturated polymerizable polar monomers such as vinyl compounds, allyl compounds and other acryl compounds, including vinyl ethers, vinyl esters, vinyl alcohol, allyl alcohol, acrylic acids, acrylic esters, acrylonitrile, etc. in the ratio of the amide to the other homopolymer of at least 2:1, preferably between 4:1 to 10:1, respectively, said homo or copolymer having a molecular weight of at least 1000 and preferably from 2000 to 200,000. Water-soluble polymers of this type include polyacrylamide, polymethacrylamide, N,N'-dimethylacrylamide, N,N'-diethylacrylamides, poly(vinylpyrrolidone), copolymer of acrylamide/vinyl acetate (10:1) copolymer of methacrylamide/methylmethacrylate (5:1), copolymer of acrylamide/vinyl alcohol (10:1), copolymer of N-vinyl pyrrolidone/vinyl acetate (10:1) and mixtures thereof. The molecular weight

the homopolymers can vary from 10,000 to 100,000 and that of the copolymers varied from 20,000 to 250,000. Water-soluble polyacrylamides having a molecular weight of from 20,000 to 50,000 are preferred.

In addition to the above three 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% optional additives which include antioxidants and antiwear agents. The antioxidants include phenolic, amine and/or metal thiophosphate compounds. 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-diamylphenol, 2,4-dimethyl-6-tert.butylphenol, 2,6 - di-tert.butyl - 4 - methylphenol. The amines are illustrated in arylamines such as phenyl-alpha-naphthylamine or phenyl-beta-naphthylamine. The metal thiophosphates are illustrated by alkaline earth metal thiophosphates, e.g., calcium or zinc dimethyl cyclohexyldithiophosphate. The anti-wear agents are sulfur-containing compounds such as oil-soluble polychloro hydrocarbyl thiocarbonate esters, e.g., polychloronaphtha methyl xanthate marketed by Monsanto Chemical Co. under the name "Santopoid S" and characterized by sp. gr. 1.19 at 60°/60° F., flash point 250° F., viscosity 63 cs. at 100° F., sulfur 11%, chlorine 31%. Thiocarbonates of this type are prepared by reacting a chlorinated petroleum naphtha with an alkali metal (potassium) amyl dithiocarbonate; organic sulfides such as dibenzyl disulfide or dichlorodibenzyl disulfide. Dyes and anti-foaming agent can be added to composition of this invention. Oil-soluble dyes include naphthol yellow, Sandoz yellow, methylene blue, alizarin compounds, etc. while anti-foaming agents include silicone polymer (DC-200 fluids ranging in viscosity in centistokes from 100 to 1000 at 250° C.) or silicone type A fluid made by Dow-Corning Co. and described in U.S. Patents 2,563,588 and 2,662,055 and mixtures thereof.

Although the aqueous phase of the water-in-oil emulsion containing the polyamide should range from about 20% to about 45%, it can vary, preferably from about 30% to about 40% by weight of the emulsion. The oil phase containing the oil-soluble additives comprises the balance of the emulsion.

The oil may be entirely a hydrocarbon oil of wide viscosity range, e.g., from less than 50 SUS at 100° F. to 150 SUS at 210° F. Oils of this type can be obtained from various crudes such as paraffinic, naphthenic or mixed base crudes; refined oils in the lubricating oil viscosity range are preferred. On the other hand, the hydrocarbon oil may be blended with fixed oils such as castor oil, lard oil and the like and/or with synthetic lubricants such as polymerized olefins, organic esters of organic and inorganic acids, e.g., di-2-ethylhexyl sebacate, dioctyl phthalate, trioctyl phosphate; polymeric tetrahydrofuran, polyalkyl silicone polymer, e.g., dimethyl silicone polymer and the like. Where mixtures or blends are used the hydrocarbon oil such as a mineral lubricating oil is always present in the predominant amount such as from about 60% to about 95% of the oil blend.

A straight mineral lubricating oil, having a viscosity index of at least 50 and ranging in viscosity at 100° F. of from 75 to 400 SUS, is usually preferred. When it is derived from a lubricating oil stock of low viscosity index it is readily provided as raffinate in a selective solvent extraction process as is well understood in the art. The emulsion can be prepared by adding the required amount of water containing the polymeric amide to an oil containing the other two essential additives, while constantly stirring the mixture. Heating the emulsion during or after it is prepared is not necessary. If desired, the emulsion can be put through a homogenizer to insure a more stable emulsion. Instead of making the finished emulsion, the oil concentrate composition can be prepared and the required amount of water containing a polymeric amide

added when the emulsion lubricant is ready for use. In this way storage and shipping costs can be reduced.

A finished emulsion fluid [composition (A)] of the invention was prepared by slowly adding 39.9% water containing 0.1% of polyacrylamide (mol. wt. 38,000-48,500) to a vessel containing 2% each of oil-soluble basic calcium petroleum sulfonate (180% excess base) and oil-soluble basic calcium C<sub>18</sub>-C<sub>22</sub> alkyl salicylate (200% excess base) dispersed in 56% mineral oil of 100 SUS at 100° F. The entire mixture was passed through a colloid mill until a homogeneous water-in-oil emulsion was formed. A similar composition (A') was prepared but to which was added 0.5% 2,6-di-tert.butyl-4-methylphenol and 0.1% phenyl-alpha-naphthylamine.

Other illustrative compositions of the invention, wherein the proportions are all in percentage by weight, are as follows:

#### Composition B

|                                                                                          | Percent |
|------------------------------------------------------------------------------------------|---------|
| Basic calcium petroleum sulfonate (180% excess base) -----                               | 1.2     |
| Basic calcium C <sub>18</sub> -C <sub>22</sub> alkyl salicylate (200% excess base) ----- | 1.2     |
| "Santopoid S" (chloronaphtha methyl xanthate) -----                                      | 3.0     |
| Polyacrylamide (M.W. 38,000-48,500) -----                                                | 0.4     |
| 2,6-di-tert.butyl-4-methylphenol -----                                                   | 0.3     |
| Phenyl-alpha-naphthylamine -----                                                         | 0.06    |
| Yellow dye (Sandoz Chem. Co.) -----                                                      | 0.018   |
| Mineral oil (100 SUS at 100° F.) -----                                                   | 54.0    |
| Water -----                                                                              | Balance |

#### Composition C

|                                                                                        | Percent |
|----------------------------------------------------------------------------------------|---------|
| Basic barium petroleum sulfonate (50% excess base) -----                               | 1.2     |
| Basic barium C <sub>12</sub> -C <sub>22</sub> alkyl salicylate (50% excess base) ----- | 1.2     |
| "Santopoid S" (chloronaphtha methyl xanthate) -----                                    | 0.3     |
| Polyacrylamide -----                                                                   | 0.4     |
| 2,6-di-tert.butyl-4-methylphenol -----                                                 | 0.3     |
| Phenyl-alpha-naphthylamine -----                                                       | 0.06    |
| Yellow dye (Sandoz Chem. Co.) -----                                                    | 0.018   |
| Mineral oil (100 SUS at 100° F.) -----                                                 | 57.0    |
| Water -----                                                                            | Balance |

#### Composition D

|                                                                     | Percent |
|---------------------------------------------------------------------|---------|
| Basic calcium dinonyl naphthalene sulfonate (50% excess base) ----- | 2       |
| Basic calcium cetyl salicylate (25% excess base) -----              | 2       |
| Polyvinylpyrrolidone -----                                          | 0.6     |
| Mineral oil -----                                                   | 56      |
| Water -----                                                         | 39.4    |

#### Composition E

|                                                                     | Percent |
|---------------------------------------------------------------------|---------|
| Basic calcium dinonyl naphthalene sulfonate (50% excess base) ----- | 2       |
| Basic calcium diwaxbenzoate (25% excess base) -----                 | 2       |
| Copolymer of acrylamide/methylmethacrylate -----                    | 0.6     |
| Mineral oil -----                                                   | 56      |
| Water -----                                                         | 39.4    |

The outstanding properties of compositions of this invention are shown in Table I. The stability of the test composition was determined by measuring separation of water and oil from the emulsion by cycling the composition at 0° F. to room temperature each cycle lasts approximately four days. The fire resistance was determined by the Pipe Cleaner Test described in "Lubrication Engineering," March-April 1955, pages 86-87.

TABLE I

| Composition..... | A'                   |                        | B                    |                        | X <sup>a</sup>       |                        | Y <sup>b</sup>       |                        |
|------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|
| Stability Test I | 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 cycle.....     | slight....           | slight....             | slight....           | slight....             | slight....           | 3.....                 | slight....           | 1.                     |
| 2 cycles.....    | do.....              | 1.....                 | do.....              | 1.....                 | do.....              | 6.....                 | do.....              | 2.                     |
| 3 cycles.....    | do.....              | 1.....                 | do.....              | 2.....                 | do.....              | 8.....                 | do.....              | 9.                     |
| 4 cycles.....    | do.....              | 1.....                 | do.....              | 3.....                 | do.....              | 12.....                | do.....              | 15.                    |
| 5 cycles.....    | do.....              | 3.....                 | do.....              | 8.....                 | do.....              | 14.....                | do.....              | 19.                    |

<sup>a</sup> Composition X same as composition A', but polyacrylamide omitted.

<sup>b</sup> Composition Y same as composition B, but polyacrylamide omitted.

The substitution in Composition A' of other water-soluble wear inhibitors for the water-soluble polyamides, such as vinylacetate, vinyl alcohol, methylmethacrylate and acrylonitrile resulted in compositions having poor emulsion stability and viscosity.

In the Pipe Cleaner Test, Composition A through E passed over 50 cycles while mineral oil or mineral oil containing 4% of Ca petroleum sulfonates and/or Ca C<sub>12-22</sub> alkyl salicylate ignited after about 5 cycles.

Compositions of this invention are particularly suitable for use in diesel engines, in die casting machines, in permanent mold machines in steel mill equipment such as coke pushers, pipe coupling tighteners, combustion control mechanisms, plastic molding presses and glass blowing machines and the like.

We claim as our invention:

1. A water-in-oil emulsion lubricant and hydraulic fluid which is from about 20% to about 45% water phase and from about 55% to about 80% oil phase, the oil phase being essentially a mineral oil having incorporated therein from about 0.5% to about 6% each, based on the oil, of an oil-soluble basic alkaline earth metal organic sulfonate selected from the group consisting of alkaline earth metal petroleum sulfonate and alkaline earth metal naphthalene sulfonate and an oil-soluble basic alkaline earth metal C<sub>8-30</sub> alkyl salicylate and from about 0.1% to 2% of a water-soluble polymeric amide selected from the group consisting of polyacrylamide and polyvinyl pyrrolidone having a molecular weight of from 38,000 to 48,500.

2. A water-in-oil emulsion lubricant and hydraulic fluid which is from about 20% to about 45% water phase and from about 55% to about 80% oil phase, the oil phase being essentially a mineral oil having incorporated therein from about 2% to about 4% each, based on the oil, of an oil-soluble basic alkaline earth metal petroleum sulfonate and an oil-soluble basic alkaline earth metal C<sub>8-30</sub> alkyl salicylate and from about 0.1% to about 2% of a water-soluble polyacrylamide having a molecular weight of from 38,000 to 48,500.

3. A water-in-oil emulsion lubricant and hydraulic fluid

which is from about 20% to about 45% water phase and from about 55% to about 80% oil phase, the oil phase being essentially a mineral oil having incorporated therein from about 2% to about 4% each, based on the oil, of an oil-soluble basic alkaline earth metal petroleum sulfonate and an oil-soluble basic alkaline earth metal C<sub>8-30</sub> alkyl salicylate, from about 0.1% to about 5% of an oil-soluble chloro naphtha methyl xanthate and from about 0.1% to about 2% of a water-soluble polyacrylamide having a molecular weight from 38,000 to 48,500.

4. A water-in-oil emulsion lubricant and hydraulic fluid which is from about 30% to about 40% water phase and from about 70% to about 60% oil phase, the oil phase being essentially a mineral oil having incorporated therein from about 2% to about 4% each, based on the oil, of oil-soluble basic calcium petroleum sulfonate, and oil-soluble basic calcium C<sub>18-22</sub> alkyl salicylate, from about 0.1% to about 5% of oil-soluble chloronaphtha methyl xanthate and from about 0.1% to 1% of water-soluble polyacrylamide having a molecular weight from 38,000 to 48,000.

5. A water-in-oil emulsion lubricant and hydraulic fluid which is from about 40% water phase and about 60% oil phase, the oil-phase being essentially a mineral oil having incorporated therein from about 1% to about 2% each of oil-soluble basic calcium petroleum sulfonate and oil-soluble basic calcium C<sub>18-22</sub> alkyl salicylate and from about 0.1% to 1% of water-soluble polyacrylamide having a molecular weight of from 38,000 to 48,500.

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

#### References Cited in the file of this patent

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