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WATER-IN-OIL EMULSIONS

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This application is a continuation-in-part of application Ser. No. 138,292, filed Sept. 15, 1961, and now abandoned.

Water-in-oil emulsions have found wide acceptance as fire-resistant hydraulic fluids. However, a problem with such fluids is their tendency to cause wear of metallic pump parts and other equipment with which they come in contact. The water phase, though dispersed in the oil, creates a wear problem that is not encountered with straight petroleum oil compositions.

Water-in-oil emulsion hydraulic fluids frequently require a water-phase additive in order to reduce wear of metal parts with which the fluid comes in contact. Water-phase additives which have been employed previously for such purpose have had the disadvantage that they tend to precipitate from the emulsion, particularly when the water content of the emulsion becomes reduced during use. The omission of water-phase additives, on the other hand, is undesirable since it is frequently impossible to obtain satisfactory wear-resistance by the use of additives which are dissolved only in the oil phase.

In order to overcome these problems, the present invention provides water-in-oil emulsions which contain a wear-reducing additive in the water phase, which additive, in addition to being very effective in reducing wear, is soluble in the oil phase and consequently does not precipitate from the emulsion upon reduction of the water content of the latter. The wear-reducing additives according to the invention are the alkanolamine salts of organic monocarboxylic acids.

In one embodiment, the fluid according to the invention contains, in addition to the alkanolamine carboxylates, an additive for reduction of loss of copper from copper-containing equipment with which the fluid is contacted during use. Such loss may occur through electrolytic action, though the invention is not restricted to any theory of the cause of the loss. The copper lost from portions of the equipment may be plated out upon other metallic portions of the equipment.

In this embodiment of the invention, the beneficial wear-reducing action of the alkanolamine carboxylates is obtained, while also reducing or eliminating copper transfer which would otherwise occur. These beneficial results are obtained by employing, in combination with the alkanolamine carboxylates, an alkaline earth metal salt of alkyl aromatic sulfonic acids.

The alkanolamine salts which are employed in the composition according to the invention are salts of organic monocarboxylic acids having 12 to 26 carbons atoms per molecule. Suitable acids include fatty acids, petroleum naphthenic acids, abietic acid and its hydrogenated and dehydrogenated derivatives, and acids produced by liquid phase partial oxidation of hydrocarbon mixtures such as de-aromatized petroleum lubricating oils, petroleum waxes, etc. Pure fatty acids such as oleic, palmitic and stearic acid, can be employed, or mixtures derived from the known natural glycerides such as lard oil, palm oil, coconut oil, tallow, etc. Specific examples of suitable alkanolamines for the salts have the formula, NRR'R'', wherein R, R' and R'' are selected from the group consisting of hydroxyalkyl containing 2 to 4 carbon atoms, hydrogen, alkyl, aminoethyl and phenyl provided that at least one of the radicals R, R' and R'' is hydroxyalkyl include ethanolamine, diethanolamine, triethanolamine, isopropanolamine, diisopropanolamine, triisopropanolamine, isobutanolamines, N-aminoethyl ethanolamine, N-phenyl ethanolamine, dimethyl ethanolamine, isobutyl ethanolamine, etc.

Generally, the alkanolamine salts of organic monocarboxylic acids, which salts are soluble both in water and in petroleum oil, such salts constituting a recognized class of compounds, are suitable for use according to the invention. Such salts will be sometimes referred to hereafter as "amine salts" or "amine carboxylates."

Since the amine salts are soluble in either the water or oil phases, they can be dissolved initially either in the oil phase or in the water phase. This makes it possible, by dissolving the salts in the oil phase initially, to prepare, store and transport a concentrate comprising oil and additives, from which the emulsion containing all necessary ingredients can be prepared by adding water alone at the point of use.

The oil solubility of the amine salts is further advantageous in that, if water loss from the emulsion occurs during service, there is no precipitation of the salts from the composition. The salts are, however, preferentially soluble in the water, and the salts dissolved in the aqueous phase provide important wear-resisting characteristics, in the absence of which the aqueous phase would cause undesirable wear of metal parts.

The composition according to one embodiment of the invention contains, as additional additive, alkaline earth metal salts of alkyl aromatic sulfonic acids, hereafter sometimes referred to as "sulfonate salts." Suitable metals include calcium, magnesium, zinc, barium, strontium, etc. Suitable sulfonic acid include synthetic alkyl benzene sulfonic acids having for example 8 to 16 carbon atoms in the alkyl group, oil-soluble petroleum sulfonic acids produced by conventional sulfonation procedures, etc. Complex salts having excess alkalinity, as known in the art of detergent additives for lubricating oils, can be employed. Simple salts lacking such excess alkalinity can alternatively be employed.

The sulfonate salts are effective to reduce the loss of copper from parts such as copper-containing thrust plates in a vane pump. When used in combination with the amine carboxylates according to the invention, the alkaline earth sulfonates provide particularly good reduction in loss of metal from thrust plates and other parts of a vane pump.

The composition of the invention is an emulsion of water in petroleum oil, which emulsion contains certain amine salts as wear-reducing agents, and contains in one embodiment certain sulfonate salts as copper-transfer-reducing agents. Emulsions of water in petroleum oil are well known in the art, and the invention involves the addition of the amine salts, and in one embodiment the sulfonate salts, to such emulsions.

In one particularly advantageous embodiment, the amine sats, and preferably the sulfonate salts also, are employed in combination with non-ionic water-in-oil emulsifying agents. Combinations of relatively hydrophobic emulsifying agents, tending to act as water-in-oil emulsifying agents, and of relatively hydrophilic emulsifying agents, tending to act as oil-in-water emulsifying agents, are preferably employed, the combination acting to produce particularly stable water-in-oil emulsions. An example of such combination is a mixture of glycerol monooleate as relatively hydrophobic agent and polyoxyethylene sorbitan trioleate (Atlas Powder Co.'s "Tween 85") as relatively hydrophilic agent.

Suitable emulsifying agents for use according to the invention include the carboxylic acid partial esters of polyhydric alcohols, and the polyalkoxylated derivatives of such esters, as disclosed for example in "Atlas Surface Active Agents," Atlas Powder Co., Wilmington, Del.

(1950); in Patent No. 2,965,574, issued Dec. 20, 1960, to Raymond B. Tierney et al.; and elsewhere in the art. The esters having relatively low HLB (hydrophile-lipophile balance) are generally suitable for use as water-in-oil emulsifying agents, and are advantageously employed in combination with those esters, frequently the polyoxyalkylated ones, which have relatively high HLB and have oil-in-water emulsifying tendencies.

Preferred hydrophobic esters are the glycerol monoesters of fatty acids having 16 to 20 carbon atoms, and preferred hydrophilic esters are the polyoxyethylene sorbitan esters of fatty acids having 16 to 20 carbon atoms, which esters are the reaction product of 1 to 3 fatty acid molecules and 3 to 20 ethylene oxide molecules per molecule of sorbitan.

Although non-ionic emulsifiers are preferred, other known types of water-in-oil emulsifying agents, or combinations of agents, can be employed.

Preferably, the emulsion contains 1.0 to 5.0 volume percent of water-in-oil emulsifier. Where both hydrophobic and hydrophilic emulsifier are used, the amount of hydrophilic emulsifier is preferably in the above range and the total amount of emulsifier is preferably in the range from 2.0 to 8.0 volume percent.

In addition to the alkanolamine salts and alkaline earth metal sulfonates disclosed previously, various known additives for water-in-oil emulsion fluids can be employed in the composition according to the invention. Such additives include oil-soluble wear-reducing additives such as the alkaline earth metal dialkyl dithiophosphates, the chlorohydrocarbon xanthates, etc.; anti-static agents; anti-oxidants; corrosion inhibitors for aqueous systems; etc. However, in many cases, it is preferable to use the alkanolamine carboxylate salts and alkaline earth metal sulfonate salts without other wear-reducing additives.

In one embodiment, the composition according to the invention contains alkali metal, ammonium or amine salts of alkyl aromatic sulfonic acids as previously described. Suitable alkali metals for such salts include sodium, potassium, lithium, etc., and suitable amines include alkylamines having for example 1 to 10 carbon atoms, alkanolamines as previously disclosed herein, etc.

The compositions according to the invention contain, in one embodiment, a water-soluble salt of an aromatic carboxylic acid, a water-soluble salt of nitrous acid, or both. Alkali metal, alkaline earth metal or nitrogen base salts of the respective acids can be employed; e.g. sodium, potassium, calcium, magnesium, ammonium, methylamine, ethylenediamine, ethanolamine etc. salts, of nitrous acid, benzoic acid, salicylic acid, etc. The salts provide, in some instances at least, a beneficial reduction in the loss of metal from equipment with which the composition is contacted. Other corrosion inhibitors for aqueous systems can be employed.

The alkanolamine salts of carboxylic acids which are employed in the emulsions according to the invention are used in amount effective to improve the wear-reducing properties of the emulsion. This amount varies with the circumstances, but is usually in the range from 0.1 to 5.0 volume percent based on emulsion. Frequently, less than 1.0 volume percent, or even less than 0.5 volume percent, is sufficient. The amount of alkaline earth sulfonates which are employed in one embodiment is usually in the range from 0.1 to 5.0 volume percent. The amount of the alkali metal or nitrogen base salts of sulfonic acids which are employed in one embodiment is usually in the range from 0.1 to 5.0 volume percent. The amount of water-soluble salt of aromatic carboxylic acid, or of nitrous acid, employed in one embodiment, is usually in the range from 0.0 to 1.0 volume percent. Other amounts of the various additives can be employed in some cases.

The composition of the invention contains, in one embodiment, free alkanolamine in addition to alkanolamine salt of carboxylic acid. The amount of such free amine is usually in the range from 0.05 to 2.5 volume percent based on emulsion. Frequently, less than 0.5 volume percent, or even less than 0.25 volume percent, is sufficient to obtain beneficial reduction in wear from the presence of the free amine.

Preferred ranges of the various components of the fluid based on oil phase are generally 1.6 times the preferred ranges based on emulsion, as given previously.

Preferably, the emulsion according to the invention contains 25 to 45 volume percent of water, but any amount of water greater than 20 volume percent and insufficient to cause formation of an oil-in-water emulsion can be used.

The following examples illustrate the invention:

Example 1

The following compositions, which are water-in-oil emulsions, are prepared; the amounts shown being volume percents in the oil phase and water phase respectively:

	A	B	C	D	E	F
Oil Phase:						
Petroleum oil	92	92	96	92	92.7	89
Emulsifier A	4	4	2	4	2	4
Emulsifier B	4	4	2	4	2	4
Zn-Ba dithiophosphate	----	----	----	----	3.3	----
Basic barium sulfonates	----	----	----	----	----	3
Water Phase:						
Water	97	97	95	95	95	95
Amine salts	3	3	----	----	----	----
Amine salt-Na sulfonate composition	----	----	5	5	5	5
Volume ratio, oil phase to water phase	62:38 in all compositions					

The petroleum oil is a solvent-refined and dewaxed petroleum distillate having viscosity of 100 SUS at 100° F. The emulsifier A is polyoxyethylene sorbitan trioleate (Atlas Powder Co.'s "Tween 85"). The emulsifier B is glycerol monooleate. The zinc-barium dithiophosphate is a complex metal dihydrocarbon dithiophosphate containing about 11.3 wt. percent barium, 1.8% zinc, 4.3% sulfur and 2.1% phosphorus. The basic barium sulfonate indicated in the above table has average molecular weight of 1010 and base number of 65 mg. of KOH per gram, and contains 47 wt. percent neutral barium sulfonates, 42% petroleum lubricating oil and 0.4 wt. percent water.

The amine salts are isopropanolamine salts of tall oil acids and are prepared by admixing at room temperature 477 grams of mixed isopropanolamines and 876 grams of tall oil acids, the latter having the following properties: acid number 190 mg. of KOH per gram, saponification number 192 mg. of KOH per gram, iodine number 150, refractive index 1.484, specific gravity 0.936, viscosity 265 Saybolt Universal seconds at 100° F., fatty acid acid content 73%, rosin acid content 25%, unsaponifiables content 2%; the fatty acid content is composed of 45–52% oleic, 35–42% linoleic, 4–11% conjugated linoleic and 2–6% saturated fatty acids. The amine and the tall acids are used in stoichiometric amounts, so that compositions A and B contain substantially no free amine.

The amine salt-sodium sulfonate composition contains 48.25% water, 17.5% sodium salts of oil-soluble petroleum sulfonic acids, 11.0% of naphthenic petroleum lubricating oil having viscosity of about 100 SUS at 100° F., 9.25% of triethanolamine and 7.4% of tall oil fatty acids, which acids contain 4% of rosin acid. The composition also contains 3.75% propylene glycol as coupling agent, 1% of a bactericide containing 10 parts of phenylmercuric acetate, 50 parts of potassium orthophenylphenate and 40 parts of inert material, 0.10% of a silicone fluid anti-foaming agent, and 1.0% of sodium benzoate and 0.75% of sodium nitrite as corrosion inhibitors. The triethanolamine is present in excess, so that compositions C, D, E and F contain free triethanolamine.

Compositions A and B differ only in that B contains 10 p.p.m. of a conventional anti-static additive, whereas

A contains no such additive. The anti-static additive contains chromium salts of mixed mono- and dialkyl salicylic acids having 14 to 18 carbon atoms in each alkyl group, and calcium salts of di(2-ethylhexyl) sulfosuccinate. Composition B contains the anti-static additive in addition to the components shown in the table. The other compositions contain only the components shown in the table.

Each composition is prepared by dissolving the indicated additives in the oil and water phases respectively, then passing the water phase as fine droplets through a sparger into the oil phase.

Composition C shows some formation of globules of water, indicating less than optimum emulsion stability. Composition D is free of such tendency to form water globules and has highly satisfactory emulsion stability.

The anti-wear properties of the compositions are determined by circulating the emulsion through a Vickers vane pump (Model V 105 C 10) for 200 hours at 8 gallons per minute flow rate through the pump, 1000 p.s.i. and fluid temperature of 150° F. The weight loss in grams undergone by the ring, vanes, rotor and thrust plates during the run is measured; the total weight of the pump is about 900 grams. The following results are obtained:

Composition	Weight Loss in Grams					Total Weight Loss, Percent
	Ring	Vanes	Rotor	Thrust Plates	Total	
A	0.3261	0.0793	0.048	0.2604–0.2345	0.9483	0.105
B	0.1335	0.0574	0.065	0.3068–0.2996	0.8623	0.096
C	0.0588	0.0368	0.016	0.0771–0.0777	0.2664	0.030
D	0.0538	0.0395	0.007	0.1217–0.1203	0.3423	0.038
E	0.2617	0.0206	0.030	0.0432–0.0186	0.3741	0.042
F	0.0698	0.067	0.026	0.0485–0.0515	0.2628	0.029

Comparison of compositions C, D, E and F with compositions A and B shows the beneficial effect of the free alkanolamine on the reduction of weight loss. Compositions A and B, which contain substantially no free alkanolamine, have improved wear-resisting properties resulting from the presence of the alkanolamine salts, but the inclusion of the free alkanolamine in compositions C, D, E and F, in addition to the alkanolamine salts, provides a very substantial further improvement in wear-resisting properties.

Composition F contains barium sulfonates in addition to the alkanolamine salt-sodium sulfonate composition. Comparison of this composition with composition D, which is the same but without the barium sulfonates, shows the beneficial effect of the barium sulfonates. With composition D, there is considerable loss of copper from the thrust plates and plating of copper on the ring for example. With composition F, the undesirable copper plating is substantially eliminated, while maintaining a highly satisfactory low rate of wear generally.

Example 2

A composition is prepared containing oil, water, emulsifiers A and B, the amine salt-sodium sulfonate composition, and barium sulfonates, all as defined in Example 1, and in the same proportions as in composition F of Example 1. The amine salt-sodium sulfonate composition is dissolved initially in the oil phase, rather than in the water phase as in Example 1. The emulsion gives, in the pump test of Example 1, substantially similar results to those obtained with composition F in Example 1, indicating that the wear-resisting properties of the emulsions are not widely different, whether the amine salt-sodium sulfonate composition is dissolved initially in the oil phase or the water phase. Both methods of preparing the emulsion are applicable generally to the various amine salts disclosed herein.

Example 3

An emulsion having the oil-phase composition of composition F of Example 1 and the water-phase composition of composition A of Example 1 is prepared in a 62:38 volume ratio of oil phase to water phase. The barium sulfonates in the emulsion provide superior results, as compared with composition A which lacks barium sulfonates, in a manner generally similar to composition F of Example 1 as compared with composition D of Example 1.

Generally similar results to those obtained in the preceding examples are obtained using other alkanolamine salts and other alkaline earth metal sulfonates, such as those disclosed previously.

Example 4

The following additional compositions, both water-in-oil emulsions, are prepared; the amounts shown being volume percents in the oil phase and water phase respectively:

	G	H
Oil Phase:		
Petroleum oil	92.7	88.9
Emulsifier A	2	4.0
Emulsifier B	2	3.0
Zn-Ba dithiophosphate	3.3	
Ba sulfonates		1.8
Amine salts		0.5
Dye concentrate		1.5
2,6-ditertiarybutyl p-cresol		0.3
Water Phase:		
Water	100	100.0
Volume ratio, oil phase to water phase	62.38	63.38

The emulsions are prepared by mixing the oil phase, containing the indicated additives, with water, using the technique disclosed in Example 1.

In composition H, the amine salts are triethanolamine salts of tall oil fatty acids obtained by admixing at room temperature triethanolamine and tall oil acids in a volume ratio of 1.25 to 1. An excess of triethanolamine is present, so that composition H contains free triethanolamine. The tall oil acids have the same properties as those used in composition A of Example 1. The barium sulfonates are a 30% solution of neutral barium sulfonates in petroleum oil. In composition H, the amine salts are initially dissolved in the oil phase, but upon admixture of the latter with water, the amine salts become incorporated in the water phase to a large extent.

The following results are obtained in 200 hours in the 8 gallon per minute Vickers pump under the Example 1 conditions:

Composition	Weight Loss in Grams					Total Weight Loss, Percent
	Ring	Vanes	Rotor	Thrust Plates	Total	
G	0.8282	0.0387	0.107	0.0679–0.0218	0.9673	0.1075
H	0.058	0.055	0.0	0.053–0.048	0.214	0.024

These data show the superiority of composition H, a composition according to the invention, to composition G, a prior art composition lacking the amine salts of the invention.

The invention claimed is:

1. An emulsion of water in petroleum oil suitable for use as a fire-resistant hydraulic fluid which consists essentially of 20 to 45 volumes of water and 55 to 80 volumes of petroleum oil containing 1.6 to 8 volume percent of glycerol moonester of fatty acid having 16 to 20 carbon atoms, 1.6 to 8 volume percent of polyoxyethylene sorbitan ester of fatty acid having 16 to 20 carbon atoms, said ester being the reaction product of 1 to 3 fatty acid molecules and 3 to 20 ethylene oxide molecules per mole-

cule of sorbitan 0.08 to 4 volume percent of alkanolamine having the formula NRR'R'' wherein R, R' and R'' are selected from the group consisting of hydroxyalkyl containing 2 to 4 carbon atoms, hydrogen, lower alkyl, aminoethyl and phenyl provided that at least one of the radicals R, R' and R'' is hydroxyalkyl, 0.16 to 8 volume percent of a salt of alkanolamine as defined above and an organic monocarboxylic acid having 12 to 26 carbon atoms and 0.16 to 8 volume percent of alkaline earth metal salt of sulfonic acid selected from the group consisting of alkyl benzene sulfonic acids having 8 to 16 carbon atoms in the alkyl group and oil-soluble petroleum sulfonic acids.

2. Emulsion according to claim **1** wherein said salt of alkanolamine is a triethanolamine salt of tall oil acids.

3. Emulsion according to claim **1** wherein the alkaline earth metal is barium.

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