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FIRE-RESISTANT HYDRAULIC FLUIDS

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This invention relates to an improved composition and method of its preparation and is particularly concerned with improved water-in-oil emulsions useful as fire-resistant hydraulic oils and metalworking oils and their method of preparation.

Hydraulic systems are being employed more and more extensively in industry to operate machinery from remote locations and with comparative ease. Various types of liquids have been employed as the operative fluid in these hydraulic systems; however, for one reason or another, these liquids have been found to lack required properties. Various oils, such as mineral oils, have found much favor in the past; however, many applications of hydraulic systems cannot tolerate leaks with such a pressure transmitting medium since the oil, under high pressure, may then find its way to heat and flame where explosion or combustion occurs. Hydraulic systems are used in metalworking and treating plants and leaks in the system have caused serious accidents in the past.

Water-in-oil emulsions have been tried in the prior art to provide a useful hydraulic oil that had the benefit of low flammability. As long as these emulsions remain unbroken with the water uniformly dispersed throughout the oil in the form of fine particles, the fire resistance remains high. However, adequate stability in this respect of the emulsion has not been present in prior formulations. The water particles tend to agglomerate in clusters and to settle to the lower part of the reservoir, hereby impairing the fire resistance of the fluid remaining in the upper part. In some cases, an upper layer of clear oil possessing no fire resistance whatsoever will result. In more severe cases, the water may coalesce into larger droplets which eventually will settle out and form a layer of free water on the bottom. In addition to impairment of fire resistance, the latter condition is objectionable in that free water may enter the circulating system and may cause corrosion of lines and working parts and rapid wear of pump parts due to lack of lubrication. It is essential, therefore, that the water particles be dispersed in the oil so that good lubricity is obtained. It is further essential that the water particles be small and uniformly distributed throughout the oil to keep corrosion tendency to a minimum and provide the minimal amount of wear.

Several water-in-oil emulsions have met with some success in that they have eliminated or mitigated fire hazards present in such operations. They have further met with some success in that they have controlled wear of moving parts to a considerable degree although they do not

possess the antiwear properties of compounded mineral oils containing no water. It has been desired to improve the wear resistance of these water-in-oil emulsions up to the level of mineral oil and intensive investigations have been made to find a satisfactory additive system capable of maintaining highly stable water-in-oil emulsions with high wear resistance. Furthermore, in many instances, prior emulsion lubricants have been limited to operating hydraulic systems at low to moderate temperatures, e.g., at temperatures below 150° F. There are, however, many occasions where operating temperatures exceed 150° F. by a considerable margin. An example is the coal mining industry where mining machinery must operate in close quarters. In order to hold dimensions of hydraulic equipment to a minimum, capacity of the cooling system is restricted with the result that operating temperatures often exceed 150° F. In many cases, the system operates at 175° F. and in some cases even higher. While stability is important at these temperatures, it is even more important to prevent wear from being excessive at these elevated temperatures.

An object of this invention is to provide an improved composition for use as an hydraulic oil.

A further object of this invention is to provide an improved composition having fire-resisting properties for use as an hydraulic oil.

A further object of this invention is to provide an improved stable water-in-oil emulsion having fire-resisting properties for use as an hydraulic oil.

A further object of this invention is to provide an improved stable water-in-oil emulsion having fire-resisting properties for use as an hydraulic oil and having stability under high temperature use conditions.

A further object of this invention is to provide an improved water-in-oil emulsion which causes minimum wear of moving parts even at elevated temperatures above 150° F.

A further object of this invention is to provide an improved water-in-oil emulsion which is free from deposit-forming tendency.

These and other important objects will be made apparent in the ensuing detailed discussion of this invention.

It has been found that a stable, fire-resistant water-in-oil emulsion with good lubricating properties can be obtained by emulsifying up to 50 percent by volume of water with an oil of specified properties using an oil-soluble calcium petroleum sulphonate emulsifier in conjunction with critical amounts of potassium salts of low molecular weight aliphatic acids. It has also been found that certain advantages can be obtained when critical amounts of potassium salts of low and high molecular weight aliphatic acids are used in combination.

Several criteria are useful in evaluation of water-in-oil emulsions, particularly those intended for use as hydraulic fluids. Of first importance is the lubricating ability of the product. Also of importance is stability of emulsion, par-

ticularly in use at high temperature. Likewise of importance is the ability of the emulsion to remain homogeneous throughout the test and not to form deposits which may tend to clog ports or screens.

A recognized test for lubricating capabilities, the so-called Vickers Pump Test, may be achieved by circulating the fluid by means of a Vickers pump, such as Vickers Vane Type Pump, Model V–111–E10 (rated at 2 gal. per min.), manufactured by Vickers Incorporated, of Detroit, Michigan. This is a positive displacement, vane-type hydraulic pump. The rotor, with twelve steel vanes in contact with a steel ring, turns at 1200 r.p.m. The twelve vanes and the ring are weighed before and after the test, and the weight of metal worn off during the test is determined by difference. The pump test stand has a five gallon fluid reservoir and the fluid is circulated at 1000 p.s.i. pressure. A convenient duration of test is 100 hours, preferably run at a temperature of 175° F. to simulate the severe operating conditions which hydraulic oils very frequently encounter in service. Wear in the Vickers pump occurs both on the vanes and on the ring. Vane wear is highly important and critical in the operation of the pump. Ring wear, although less important, still is of significance. Since pumps of this general type are widely used in hydraulic systems, capability of a hydraulic fluid, as a lubricant, to minimize such wear, is a necessity.

In order to evaluate deposit forming tendencies, strainers may be inserted in the system. These can be examined at the end of the test run when the system is dismantled for inspection. At the same time, the reservoir can be examined for deposits since they tend to agglomerate at the walls or bottom due to decreased velocity of flow, as compared to the velocity of flow through the pump and piping.

It has been found that a hydraulic fluid which is a stable emulsion when used in such a pump and which possesses to a high degree the lubricating qualities desirable in such fluids may be provided by compounding together an oil of a viscosity of about 100–400 seconds Saybolt Universal at 100° F. and a viscosity index of at least 80, a calcium petroleum sulphonate emulsifier having a molecular weight of at least about 975, in sufficient quantity and of such nature that a "reserve" alkalinity or free alkalinity exists in the composition, an oxidation inhibitor, and the potassium salt of a low molecular weight fatty acid, either alone or in conjunction with the potassium salt of a high molecular weight fatty acid. The water phase of these emulsions when prepared for use amounts to broadly 10–50 percent of the water-in-oil emulsion or preferably about 25–45 percent of the water-in-oil emulsion.

The oil to be used should be paraffinic in nature, as measured by its viscosity index, which is generally considered to be indicative of the "paraffinicity" of a lubricating oil. The viscosity index of the oil to be used should be at least about 80.

The emulsifier to be used is a basic calcium oil soluble petroleum sulphonate of high molecular weight, of at least about 975. A commercial product useful for the purpose is "Basic Calcium Petronate HMW" supplied by L. Sonneborn Company, having a molecular weight of the order of 1000. It has been noted that free or "reserve" alkalinity is essential. The above invert emulsifier contains about 40 percent active ingredient and has an alkalinity equivalent to about 20–25 mg. of KOH per gram of sulphonate as supplied. This is sufficient to provide the reserve alkalinity found essential in the compounded product. The calcium petroleum sulphonate may be present in the blend in the amount of about .25–6.00 percent by weight of the total blend but preferably about 1–4 percent by weight can be used to provide entirely satisfactory results.

An oxidation inhibitor may be provided to prevent oxidative degeneration of the product in use which would otherwise bring about the formation of acid oxidation products. While many compatible oxidation inhibitors may be used, such as amine types, aminophenol types, and some phenolic inhibitor types, a preferred and convenient inhibitor, commercially available, is the "Agerite Stalite" of R. H. Vanderbilt Company (p,p'-dioctyldiphenylamine). The oxidation inhibitor may be added in the amount of 0.1–5.0 percent by weight of the total composition or preferably about 0.25–1.5 percent by weight of the total composition.

A substantial improvement in antiwear properties is found to occur when a limited amount of the potassium salt of a low molecular weight fatty acid such as potassium acetate is added to the formulation. This is particularly true when the operation occurs at high temperatures, such as above 150° F. The reduction in wear increases with increased addition of this antiwear agent up to a critical level and then further increase of the agent causes increased wear instead of reduction. Hence the broad range for this agent is about 0.01 to 1.0 percent by weight of the total but the preferred range for this agent is about 0.025 to 0.25 percent by weight. The preferred acid ingredients of the soaps of this invention are those of saturated short chain fatty acids such as formic, acetic, propionic and butyric acids. Particularly preferred is acetic acid. The broad range of useful amounts of blends of soaps of short chain fatty acids and long chain fatty acids is .03–1.50 percent by weight total and the preferred range is .05–0.5 percent by weight. The ratio of long chain acid soaps to short chain acid soaps may vary from 5:95 to 95:5.

The emulsions described herein are preferably prepared in the following manner. Two-thirds of the mineral oil is charged to a steam heated kettle equipped with mechanical agitation. The oil is heated to 140–150° F. and the short chain fatty acid or mixture of short and long chain fatty acids are added followed by an equivalent amount of alkali, e.g., potassium hydroxide, dissolved in an equal quantity of water. The materials are mixed for an additional 15 minutes to neutralize the acids; the temperature is then raised to 190° F. When the temperature reaches 190° F., the calcium petroleum sulphonate is added and the temperature is raised to 260° F. The batch is maintained at this temperature for 5–10 minutes and the batch is then quenched immediately by adding the remainder of the mineral oil. The oxidation inhibitor is added and the temperature adjusted to 175–185° F. In a separate kettle, the required amount of water is heated to 175–185° F. and slowly added to the oil mixture in the first kettle with vigorous agitation. Finally, the emulsion is passed through a colloid mill or homogenizer to obtain the finished emulsion of uniform, small particle size.

It has been found that when small amounts of potassium soaps of long chain fatty acids are included in the formulation the wear decreases. However, when the amounts of these agents are increased, the viscosity of the formulation increases to an undesirable degree above a certain critical limit. Also, soaps prepared from long chain fatty acids have a tendency to form undesirable deposits on screens and strainers as well as internal reservoir surfaces. We have now found that these shortcomings can be eliminated by substituting potassium soaps of short chain fatty acids in place of potassium soaps of long chain fatty acids, without causing undesirable side effects. Therefore, potassium soaps of short chain fatty acids may be used to replace potassium soaps of long chain fatty acids wholly or in part without adversely affecting wear reduction, but with the important benefits indicated above. The improvements indicated are illustrated in Table I hereinbelow.

TABLE I

Results of Vickers Pump Tests

[100 hours (±15) at 170–175° F. and 1,000 p.s.i.]

	Percent by Weight							
Example No.	1	2	3	4	5	6	7	8
Basic Calcium Petronate HMW	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Agerite Stalite	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4
Base Oil, 108 S.U.S. @100° F., Viscosity Index 95	57.0	56.8	56.91	56.82	56.82	56.51	56.86	56.69
Potassium Stearate[1]		0.2						0.13
Potassium Acetate			0.09	[2] 0.18	[2] 0.18	.49		0.18
Ca Acetate (Anhydrous)							[2] 0.14	
Water	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Total Wear, mg	308	50	50	70	86	217	267	43
Vane Wear, mg	19	23	9	10	13	5	70	7
Ring Wear, mg	289	27	41	60	73	212	197	36
Roughness Rating Vanes[3]	1	1	1	1	1	1	3	1–2
Roughness Rating Ring[3]	1	1	1–2	2–3	1–2	1–2	1	1–2
Reservoir Deposits	None	[4]	None	None	None	None	None	None

[1] Prepared from HFA 405 (Hydrogenated Animal Fatty Acid), essentially a commercial stearic acid.
[2] Equivalent to 0.11 Glacial Acetic Acid.
[3] Ratings: 1=Excellent; 2=Good; 3=Fair; 4=Poor.
[4] Moderately Heavy.

Example No. 1 of Table I shows the high wear characteristic of compositions not containing the antiwear agents. Example No. 2 illustrates previous findings, namely, the effectiveness of potassium stearate in reducing total wear from 308 mg. to 50 mg. Example No. 3 demonstrates that an equal wear reduction can be accomplished by the use of potassium acetate. It will be noted, however, that less than one-half the amount of additive is needed to obtain the same wear reduction. In other words, potassium acetate is at least twice as effective as potassium stearate. It will also be noted that in Example No. 2, when using potassium stearate, wear is about evenly divided between vanes and ring (23 and 27 mg. respectively). In contrast, the use of potassium acetate has shifted a large portion of the wear from the critical vanes to the much less critical ring. Moreover, potassium acetate provides a further important improvement over potassium stearate in that it eliminates the reservoir deposits characteristic of the latter.

Examples No. 3 and No. 4 are identical in composition, both employing twice the amount of potassium acetate shown in No. 2. Total wear figures for No. 3 and No. 4, which are in fairly good agreement (70 and 86 mg., respectively) demonstarte that an increase in concentration does not result in further reduction of wear but instead causes a slight increase in wear, in the particular composition employed. This is shown also in Example 6. Increase in concentration of potassium acetate to 0.49% by weight causes a drastic increase in ring wear (212 mg.), although vane wear remains remarkably low.

While it is thus possible to replace all of the potassium stearate by potassium acetate, it may be desirable to use the latter as a partial replacement only. One of the advantages that can be gained by the latter technique is that the formulator is enabled to balance the composition so as to distribute the total wear between the two rubbing surfaces in accordance with the design of the pump while retaining low over-all wear. Combinations of soaps of short and long chain fatty acids also have been found useful as a means of controlling emulsion viscosity since long chain fatty acid soaps tend to increase viscosity whereas short chain acids tend to decrease it. Thus important advantages accrue from the use of such combinations which cannot be gained when either type of antiwear agent is used alone.

In Example No. 7, shown in Table I, calcium acetate is used as the antiwear agent. It will be noted that total wear is but slightly less than that shown in Example 1 containing no antiwear agent. Moreover, wear has again shifted to the more critical vanes, with a weight loss of 70 mg. as compared to 19 mg. in No. 1. Although the amount of calcium acetate is equivalent to the amount of potassium acetate used in Example 4, its effect on wear characteristics of the fluid is in no way comparable to the latter. Example No. 8 shows the synergistic action of potassium stearate and potassium acetate.

The radical difference in antiwear effects between the calcium and potassium soaps of short chain fatty acids is surprising. Calcium acetate is widely used in lubricating compositions of various kinds as an antiwear agent. However, it was found totally ineffective in the system under consideration when used in the concentration range here contemplated. On the other hand, we have found quite unexpectedly that potassium acetate, when used in relatively low concentrations, produces a drastic reduction of wear. This difference could not have been predicted from prior knowledge, running quite contrary to what the prior art indicated.

The invention has been amply illustrated in the detailed discussion of the invention. These examples are given, however, only to illustrate the invention and are not intended as limitations. The only limitations intended are found in the following claims.

We claim:

1. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion, the water content of said emulsion, being about 10–50 percent by weight, the oil having a viscosity of about 100–400 Saybolt Universal seconds at 100° F. and a viscosity index of at least 80, about .25–6.00 percent by weight of oil-soluble calcium petroleum sulphonate having a molecular weight of at least 975, the calcium petroleum sulphonate having a minimum alkalinity equivalent to about 20–25 mg. of potassium hydroxide per gram of sulphonate as supplied, and about 0.01 to 1.0 percent by weight of a potassium salt of a saturated straight-chain fatty acid having a carbon chain length of C_2–C_4, whereby a stable emulson is provided which effects minimum wear.

2. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulson, the water content of said emulsion being about 10–50 percent by weight, the oil having a viscosity of about 100–400 Saybolt Universal seconds at 100° F. and a viscosity index of at least 80, about 0.25–6.00 percent by weight of oil-soluble calcium petroleum sulphonate having a molecular weight of at least 975, the calcium petroleum sulphonate having a minimum alkalinity equivalent to about 20–25 mg. of potassium hydroxide per gram of sulphonate as supplied, and about 0.01 to 1.0 percent by weight of potassium acetate, whereby a stable emulsion is provided which effects minimum year.

3. A composition for use as hydraulic fluid consisting

essentially of a water-in-oil emulsion, the water content of said emulsion being about 10–50 percent by weight, the oil having a viscosity of about 100–400 Saybolt Universal seconds at 100° F. and a viscosity index of at least 80, about 0.25–6.00 percent by weight of oil-soluble calcium petroleum sulphonate having a molecular weight of at least 975, the calcium petroleum sulphonate having a minimum alkalinity equivalent to about 20–25 mg. of potassium hydroxide per gram of sulphonate as supplied, about 0.01 to 1.0 percent by weight of a potassium salt of a saturated straight-chain fatty acid having a carbon chain length of C_2–C_4, and about 0.02–1.49 by weight of potassium stearate, the ratio of the potassium salt of the C_2–C_4 saturated straight-chain fatty acid to potassium stearate being from 5:95 to 95:5, whereby a stable emulsion is provided which effects minimum wear.

4. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion, the water content of said emulsion being about 25–45 percent by weight,

the oil having a viscosity of about 100–400 Saybolt Universal seconds at 100° F. and a viscosity index of at least 80, about 1–4 percent by weight of oil-soluble calcium petroleum sulphonate having a minimum alkalinity equivalent to about 20–25 mg. of potassium hydroxide per gram of sulphonate as supplied, about .025–0.25 percent by weight of potassium acetate and about .025–0.25 percent by weight potassium stearate, the ratio of potassium acetate to potassium stearate being from 5:95 to 95:5, whereby a stable emulsion is provided which effects minimum wear.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,159,580 December 1, 1964

Irving P. Hammer et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 5 and 6, TABLE I, "Example No. 8", opposite "Agerite Stalite", for "0.4" read -- 0.5 --; column 5, line 48, for "demonstarte" read -- demonstrate --.

Signed and sealed this 4th day of May 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents