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NON-INFLAMMABLE HYDRAULIC FLUID

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5 Claims. (Cl. 252-76)

The present invention relates to an improved non-in-15 flammable hydraulic fluid of the glycol-fluid base type. It relates further to a hydraulic fluid of the type mentioned above having an improved viscosity index and a superior lubricating or wear preventing quality. It has improved resistance to rust of ferrous metals in ad-20 dition to its property of non-inflammability.

In the prior art numerous hydraulic fluids have been proposed. Some of these are of the hydrocarbon type which are advantageous for many applications but which are rather highly inflammable and unsuitable for certain 25 uses. In industrial operation, such as the die casting of metals, for example, the control of the heavy casting machinery are operated largely by hydraulic means. The hydraulic fluids used in such controls have frequently been a source of fire and danger. For this reason there is a growing demand for noninflammable, hydraulic fluids. Glycolwater base type fluids have been investigated to a considerable extent for this application. These fluids are not absolutely noninflammable but their resistance to 35 flame is so much greater than that of the hydrocarbon oils that they may be considered substantially noninflammable.

On the other hand, although the flame resistant properties of the glycol-water base fluids have long been recognized, these fluids have left much to be desired in several important respects. They are usually too thin or non-viscous for hydraulic use and consequently must be thickened by addition of a more viscous material. The choice of thickeners compatible with these glycolwater bases has been limited and it has been rather dif-45 ficult to find thickeners which are entirely suitable for use with the glycol-water base. Unless the thickener is compatible, the solution is unstable, the thickener tending to settle out and to interfere with proper operation of the 50 fluid or the mechanism in which it is used.

Furthermore, as suggested above, water base hydraulic fluids have relatively very poor lubricating characteristics. While hydraulic fluids are used primarily to transmit forces through hydraulic means, they must provide lubrication for hydraulic pumps and associated mechanical parts in order to prevent excessive wear. The prior art hydraulic fluids of this type have been poor lubricants, on the whole. Many of them have permitted rusting of ferrous metals which obviously is highly objectionable. Aside from the damage done by the rust itself, the parts 60 frequently stick, or freeze, so that the operation is uncertain and erratic. In vital hydraulic controls, such erratic operation cannot be tolerated at all and it is always objectionable in any hydraulic mechanism.

It is known that certain of the long chain fatty acids and derivatives thereof have useful anti-wear and rust preventive properties when used in hydrocarbon base oils. Thus, the use of oleic acid, stearic acid, lauric acid, the

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corresponding fatty oils or glycerides and the like, in mineral base oils to reduce wear and also to help inhibit rust is well known. These materials, however, are substantially insoluble in water base hydraulic oils or fluids and are, therefore, unsuitable for use in the compositions of the present invention.

According to the present invention it has been discovered that a combination of glycol-water base fluid may be blended with a polyglycol or polyglycolether type 10 polymeric thickener to improve viscosity and viscosity index, and a water soluble soap of an organic aliphatic acid may be used to impart the other required properties. In particular a water soluble soap, preferably an alkali metal soap of a moderately long chain aliphatic acid, shows exceptional utility as an anti-wear and anti-rust agent.

The alkali metal soaps of straight chain fatty acids of C₁₂ chain length or longer are substantially insoluble in water. The branched chain soaps, however, of acids having from at least 7 carbon atoms up to about 14 carbon atoms are soluble in water, and soaps of highly branched acids up to about C_{18} are soluble in the compositions of this invention. They may be used to form stable blends having good wear preventing properties,

or lubrication properties, and giving good rust resistance. Especially preferred and contemplated in the preferred embodiment of this invention are the alkali metal soaps of the C₉ to C_{13} Oxo acids. These Oxo acids are highly branched chain acids and are obtained by subjecting an 30 olefin to the well known Oxo process.

In one preparation of these acids, an olefinic hydrocarbon is carbonylated with carbon monoxide and hydrogen in the presence of a carbonylation catalyst at elevated temperatures and pressures. Operable catalysts include the well known cobalt containing catalysts, for example, cobalt, stearate, cobalt carbonyl, and the like. Pressures ranging from about 100 to about 300 atmospheres are used and a temperature in the range of about 200 to about 400° F. The ratio of hydrogen to carbon monoxide employed may vary between about 0.5 volume to 2.0 volumes of hydrogen per volume of carbon monoxide.

The olefinic starting material preferably comprises olefins having from 8 to 12 carbon atoms per molecule, however, olefins having from 6 to 24 carbon atoms may be used. The olefin is carbonylated in the process and the resulting aldehyde has one more carbon atom than the starting olefin. The process proceeds in accordance with the following equation:

 $\mathbf{RCH} = \mathbf{CH}_2 + \mathbf{CO} + \mathbf{H}_2 \xrightarrow{} \mathbf{RCH}_2 - \mathbf{CH}_2 - \mathbf{CH}_2$

RCH-CH. сно

The aldehyde resulting from the carbonylation of the olefin is then oxidized to obtain the desired branched chain acid. This reaction is brought about by subjecting the aldehyde in basic solution to the action of an oxygenating substance such as a mixture of nitrogen and oxygen (air), a material releasing nascent oxygen $(KMnO_4)$ or the like. The oxidation reaction, one which is well known in the art, proceeds in accordance with 65 the following equation:

 $\begin{array}{c} \operatorname{RCH}_{2}-\operatorname{CH}_{2}-\operatorname{CH}_{0}+[0] \xrightarrow[(Base)]{} \operatorname{RCH}_{2}-\operatorname{CH}_{2}-\operatorname{CH}_{2}-\operatorname{CH}_{2} \xrightarrow[(Base)]{} \operatorname{RCH}_{2}-\operatorname{CH}_{2$

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or

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If desired, the Oxo reaction may be carried out in the presence of water in the form of vapor instead of hydrogen. The desired branched chain acid is thus obtained directly from the Oxo process. The same conditions of temperature and pressure are necessary for 5 this reaction as for the carbonylation reaction resulting in the aldehyde as described above.

Regardless of the manner of preparing the acid for the concept of this invention it is essential only that material be a branched chain acid and that it contain from 10 9 to 13 carbon atoms.

The soaps of these branched chain acids are prepared by reaction of the acid with the desired alkali metal hydroxide. Especially preferred are the sodium or potassium soaps which have excellent water solubility and 15 thus provide clear stable solutions.

A preferred composition consists of about 40 to 65%by weight of water, about 9 to 34% of ethylene glycol, 20 to 30% of a polyglycol or polyglycolether thickener of sufficiently high molecular weight to increase the viscosity substantially, and 0.5 to 2% of the sodium soap of Oxo or other branched chain acids of the C₉ to C₁₃ range. The potassium soaps may be substituted for the sodium soaps and the proportion of water to ethylene glycol may be varied considerably depending upon the viscosity, pour point, freezing point, or other requirements.

EXAMPLE I

A fluid containing 62.9% by weight of water, 11.1% of ethylene glycol, 25% of a polymeric glycolether having a viscosity of about 90,000 S.U.S. at 100° F., sold by Union Carbide and Carbon Chemical Corp., under the trade name "Ucon 75 H–90,000"¹ was modified by addition of 1% of the sodium soap of a C_{13} Oxo acid. This product had a viscosity of 290 S.U.S. at 100° F. and a viscosity index of 162.

EXAMPLE II

A composition was prepared exactly as above except that 1% of sodium soap of C₉ Oxo acid was used as the modifier. Comparative lubrication tests were made using the 4-ball wear tester wherein three ball bearings, onehalf inch in diameter, are clamped in a holding device and a fourth ball is rotated so as to bear on the first three under an applied load. This test of steel on steel was conducted at 167° F. under a 10 kg. load for one hour. In this test a glycol-water base fluid containing only the polymer (no soap present) showed a wear scar diameter of 1.5 mm. after the one hour test. This is considered excessive wear. The same product containing 1% of 55 sodium soap of C_{13} Oxo acid (Example I) showed a wear scar diameter of only 0.54 mm. which is fully equivalent to results obtained with mineral oils. The product of Example II showed only slightly higher wear, 0.67 mm. scar diameter. The blends containing the soaps also prevented rusting of steel specimens stored in the fluids for periods up to a month.

From the foregoing it is evident that the soaps are highly effective for imparting anti-wear and anti-rust properties to the blends. Results are tabulated as follows:

A Table I

5	Fluid	Wear Scar, mm. in 4- Ball Test	Rust Test Result
	Example I Example II Fluid Without Soap	0. 54 0. 67 1. 50	No Rust. No Rust. Heavy Rust in less than 24 bours
	and the second sec		nours.

The quantity of soap which may be used may varyfrom as little as 0.1 to as much as 5% by weight, based on the total composition. Preferred compositions are about 0.5 to 2%. The quantity of thickener employed will depend upon its type, but in general about 20 to 30% of a polyglycol ether type thickener is preferred. These are highly suitable because of their excellent compatibility with the glycols. In some cases as little as 5% up to as much as 40% of the thickener may be employed. A preferred thickener is the material mentioned above with a viscosity of about 90,000 S.U.S. at 100° F. However, polymeric glycol ether products with S.U.S. viscosities substantially lower than 90,000, e.g., 400 and up to as much as 200,000 S.U.S. at 100° F., may also be used. Some of the commercial products in this class in-clude "Ucon 75 H-490," "Ucon 75 H-1400," and "Ucon 75 H-9150" sold by the Carbide and Carbon Chemical Corp.

30 It will be understood that additional conventional modifiers such as rust inhibitors, anti-foaming agents and the like may be incorporated as will be obvious to those skilled in the art.

This application is a continuation-in-part of Serial No. 35 263,972, and now abandoned, filed December 28, 1951, for the same inventors.

What is claimed is:

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 A composition consisting essentially of about 40 to 65% by weight of water, about 9 to 34% by weight of ethylene glycol, about 20 to 30% by weight of a polyalkylene glycol having a viscosity at 100° F. of between 400 and 200,000 S.U.S. and 0.5 to 2.0% by weight of an alkali metal soap of a branched chain acid containing from 9 to 13 carbon atoms, said acid being prepared by the carbonylation of an olefinic hydrocarbon having from 8 to 12 carbon atoms with carbon monoxide and hydrogen in the presence of a cobalt carbonylation catalyst at a temperature of about 200 to about 400° F. and at a pressure of about 100 to about 300 atmospheres and the subsequent oxidation of the carbonylated olefins thus obtained.

2. A composition according to claim 1 wherein said polyalkylene glycol has a viscosity at 100° F. of about 90,000 S.U.S.

3. A composition according to claim 2 wherein said alkali metal soap is a sodium soap.

4. A composition according to claim 2 wherein said branched chain acid contains 13 carbon atoms.

5. A composition according to claim 2 wherein said 60 branched chain acid contains 9 carbon atoms.

References Cited in the file of this patent UNITED STATES PATENTS

1,928,956	Tatter Oct. 3, 1933
2,553,364	Fasce May 15, 1951
2,558,030	Zisman June 26, 1951
2,602,780	Zisman et al July 8, 1952
2,737,497	Wasson et al Mar 6 1956
2,768,141	Langer Oct. 23, 1956

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¹A commercially available polyalkylene glycol prepared by copolymerizing about 75 mol percent of ethylene oxide with about 25 mol percent of propylene oxide. This material has a pour point of 40° F., a flash point of 485° F., and a specific gravity at 20/20° C. of 1.095.