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HYDRAULIC FLUIDS CONTAINING NONIONIC SURFACE ACTION AGENTS AND PHOSPHATE ESTERS OF NONIONIC SURFACE ACTIVE AGENTS

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ABSTRACT OF THE DISCLOSURE

A water-in-oil emulsion hydraulic fluid comprising about a 20 to 60% by weight water phase and about a 40 to 80% by weight oil phase, wherein said emulsion also contains (I) about 0.5 to 10% by weight based on the weight of the oil, of a mixture of mono- and diphosphate esters and salts thereof and (II) about 0.5 to 10% by weight based on the weight of the oil, of a polyoxyethylene ether of an aliphatic alcohol surface active agent.

BACKGROUND OF THE INVENTION

This invention relates to new and useful invert (water-in-oil) emulsions and more particularly to invert mineral oil emulsions which are outstanding lubricating and hydraulic fluids. This invention is especially concerned with fire resistant hydraulic fluids which have outstanding lubricity and stability characteristics.

The conventional hydraulic fluid is a petroleum oil which is an excellent fluid for this function when properly formulated with suitable corrosion inhibitors, antioxidants, extreme pressure additives, etc., but it suffers from the one major deficiency of flammability. Recently, considerable efforts have been directed toward the development of hydraulic fluids to replace such oils by developing fluids which retain the beneficial properties of the oil, but which would be essentially fire resistant and have good stability. An acceptable hydraulic fluid should have the following characteristics:

(1) Optimum hydraulic efficiency
(2) Excellent lubrication
(3) Corrosion protection
(4) No effect on seals in hydraulic systems
(5) Stability
(6) Low flammability
(7) Low cost

Properly formulated petroleum oils are excellent hydraulic fluids, however, they have the distinct drawback of being etxremely flammable. Serious fires have been caused by hydraulic lines rupturing and the subsequent release, under high pressure, of the oil onto molten metal in die casting operations or the oil coming into contact with heated parts or sparks from electrical equipment, causing ignition of the oil. This serious hazard has led industry to initiate programs in changing over to fire resistant hydraulic fluids particularly in coal mines as well as in various other obvious industrial applications.

Three types of fire resistant hydraulic fluids have been reported. They are:

(1) Straight synthetic liquids of the organic phosphate ester type (e.g., tricresyl phosphate).

(2) Water-glycol fluids generally based on polyethylene glycols.

(3) Water-in-oil (invert) emulsions.

While the first two types normally exhibit good lubricity and wear properties, they are quite expensive and vary in their fire resistant and stability properties. The

third type has opened up a new horizon in this field. The use of water-in-oil (invert) emulsions allows the oil to remain in a continuous phase so that the hydraulic fluid may retain and exhibit the beneficial anti-corrosion and lubricating properties of the oil while also being resistant to flammability as well. However, merely emulsifying a petroleum oil with water fails to yield an emulsion of adequate lubricating qualities or stability, especially at high pressures.

It has now been discovered that stable, water-in-oil emulsions can be prepared having outstanding fire-resistant, lubricity and wear properties by the employment of the instant invention.

It is therefore an object of the present invention to provide new and useful water-in-oil emulsions. It is another object of this invention to provide new and useful water-in-oil emulsions which are outstanding hydraulic fluids. It is still another object of the present invention to provide new and useful water-in-oil emulsions which have outstanding lubricating characteristics. It is a further object of this invention to provide new and useful water-in-oil emulsions which are stable and fire resistant under heat and pressure. Other objects, advantages and applications of the instant new and unobvious water-in-oil emulsions of the instant invention will be readily apparent from the following detailed description as well as the appended claims.

SUMMARY OF THE INVENTION

The disadvantages of the prior art are overcome and the forementioned as well as other objects of the instant invention are accomplished according to the present invention by providing water-in-oil emulsions which comprise from about 20–60% by weight water and from about 40–80% by weight oil, to which has been added (I) from about 0.5% to about 10% by weight based on the weight of the oil, of a mixture of phosphate esters and salts thereof of a nonionic surface active agent hereinafter to be described and (II) about 0.5 to about 10% by weight based on the weight of the oil, of a nonionic surface active agent derived from an aliphatic alcohol also to be further described.

The mixture of phosphate esters of nonionic surface active agents which is herein contemplated is a mixture of oil-soluble or oil-dispersible mono- and diphosphate esters and salts thereof. The nonionic precursors for said esters are selected from the group consisting of polyoxyalkylene ethers of alkyl phenols and aliphatic alcohols ranging from at least 8 carbon atoms to about 70 carbon atoms, derived by condensing the alcohols with an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide or mixtures thereof. Thus, said oxyalkylene groups may contain from 2 to 4 carbon atoms each. The amount of oxyalkylene groups may vary from about 10% (i.e., derived from the interaction of 1 mole alkylene oxide) up to about 47 weight percent to 75 weight percent (depending upon the oxyalkyl groups) based upon the weight of the nonionic. For example, the maximum weight percent of oxyalkylene when ethylene oxide is utilized is about 47 weight percent, while it is about 60 weight percent for propylene oxide and about 75 weight percent for butylene oxide. The ratio of monophosphate ester to diphosphate ester in the above mentioned mixture is not critical, since any mixture amounting from about 0.5% to about 10% by weight based on the weight of the oil may be used.

The nonionic surface active agent derived from an aliphatic alcohol, which is present in the water-in-oil emulsion in addition to the phosphate esters, acts as an auxiliary emulsifier. It has been surprisingly discovered that the presence of this additional surfactant contributes the

unobvious effect of making the water-in-oil emulsion very stable.

The nonionic surface active agent which is to be used in combination with the above described phosphate esters is extremely critical in obtaining a satisfactory, stable, invert emulsion. The nonionic surface active agent must be one which is dervied from an aliphatic alcohol of C_{12} to C_{24} condensed with from about 1.0 to about 3 moles of ethylene oxide, and preferably 1.5 to 2.5. Suitable alcohols include dodecyl alcohol, tridecyl alcohol, tetradecyl alcohol, pentadecyl alcohol, hexadecyl alcohol, stearyl alcohol, oleyl alcohol, primary-m-eicosyl alcohol, tricosyl alcohol, and n-tetracosyl alcohol. In addition to such alcohols, various naturally occurring mixtures which predominate in these alcohols may be used such as the mixed "coco" alcohols, tallow alcohol and the like.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nonionic oxyalkylated products which are herein contemplated as precursors for the phosphate esters are well known in the art and are derived by reacting alkyl phenols or aliphatic alcohols of at least 8 carbon atoms with alkylene oxide as, for example, disclosed in U.S. Pats. 2,213,477 and 1,970,578. The preferred alkyl phenols are those having an alkyl or a plurality of alkyl substituents having a total of at least 8 carbon atoms in the alkyl chain or chains. The preferred aliphatic alcohols are those having above about 12 carbon atoms in the molecule. The following illustrate some typical suitable phenols and alcohols which may be used to form the corresponding nonionic surface active agents which are precursors for the instantly contemplated phosphate esters:

octyl phenol (diisobutylene)
nonyl phenol (nonyl derived from propylene trimer)
dodecyl phenol (derived from propylene tetramer)
dibutyl phenol
diamyl phenol
hexadecyl phenol
octadecyl phenol, and the like

phenols containing a plurality of different alkyl groups, for example:

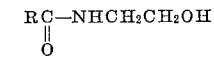
butyl amyl phenol
butyl hexyl phenol
amyl hexyl phenol
amyl heptyl phenol
ethyl heptyl phenol

as well as phenols containing a plurality of similar alkyls such as, in addition to those above:

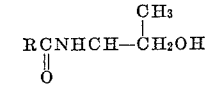
di-n-hexyl phenol
diisohexyl phenol
di-n-heptyl phenol
di-n-octyl phenol
diiso-octyl phenol
dinonyl phenol
didodecyl phenol
ditetradecyl phenol
diocta decyl phenol
tri-n-octyl phenol
trioctadecyl phenol
tri-n-butyl phenol, and the like, as well as
n-octyl alcohol
iso-octyl alcohol
n-nonyl alcohol
n-decyl alcohol
undecyl alcohol
lauryl alcohol
tridecyl (oxo) alcohol
tetradecyl alcohol
pentadecyl alcohol
hexadecyl alcohol
stearyl alcohol
oleyl alcohol

mixed "coco" alcohols
hydrogenated tallow alcohol

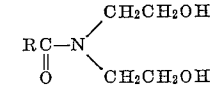
R—OH alcohols prepared from olefins of C_{12} to C_{50} by the "oxo" process, i.e., addition of $H_2C{=}O$ and hydrogenation to the alcohol: benzyl alcohol, substituted benzyl alcohols,



where R is C_5 to C_{50}



where R is C_4 to C_{50}



where R is C_3 to C_{50} and the like.

The above compounds may be easily reacted with the alkylene oxide as described above to yield the nonionic surface active agents which are then used to prepare phosphate esters employed in the compositions of the present invention.

In addition to the oxyalkylated derivatives of the aforementioned compounds, other oxyalkylated derivatives that may be employed, if desired, are the oxyalkylated derivatives of thio-alcohols, amides, sulfonamides and the like which have a reactive hydrogen atom capable of reacting with an alkylene oxide to yield an hydroxy compound which, like the compounds listed above, can also be phosphated.

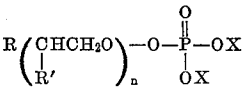
One of the methods for preparing suitable phosphate esters employed in the instant invention, involves the reaction of 1 mole of P_2O_5 with 2 to 4.5 moles of the nonionic surfactant as described and claimed in U.S. Pat. 3,004,056 by Nunn and Hesse and U.S. Pat. 3,004,057 by Nunn. As described in said Nunn and Hesse patent, the reaction between the P_2O_5 and the nonionic polyoxyalkylene ether is conducted under substantially anhydrous conditions and at a temperature below about 110° C. In its preferred form, the reaction is carried out by adding the P_2O_5 gradually, with vigorous agitation to the nonionic surface active agent in liquid form. The reaction is exothermic and cooling is in some cases necessary to keep the temperature below 110° C., since discolored and darkened products tend to be produced above this temperature. The reaction proceeds continuously during the addition of the P_2O_5 and is preferably followed by maintenance of the reaction mixture at ambient temperatures up to 110° C. for an additional period of time after completion of such addition to allow for complete solution of the P_2O_5 and reaction with the nonionic surface active agent.

By carrying out the above reaction in the presence of a small amount of a phosphorous-containing compound, selected from the group consisting of hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid, and salts and esters of phosphorous acid, preferably sodium hypophosphite or hypophosphorous acid, as described in said Nunn '057 patent, lighter colored or substantially colorless reaction products are obtained.

Monoesters and diesters can also be prepared from the corresponding triesters by reacting the triester with phosphoric acid. By varying the ratio of nonionic to acid, one can prepare either mono- or diester to the substantial exclusion of the other. A high ratio of triester to acid (2:1) produces diester, whereas a low ratio (0.5:1) produces monoester. It is also obvious that the mixture of phosphate esters may be readily prepared by merely combining one or more monophosphate esters with one or more diphosphate esters.

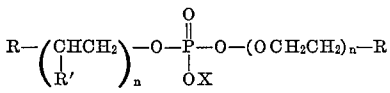
Thus, the mono- and di-phosphated products may be represented by the following formulas:

(I)



and

(II)



wherein R' represents H, or methyl; X may be hydrogen, alkali metal, alkaline earth metal, e.g., calcium, magnesium, barium, etc., ammonium or substituted ammonium, and *n* equals the number of moles of alkylene oxide necessary to yield a final product containing up to 75% by weight of the said alkylene oxide as discussed above; R is the alcohol or phenol hydrophobe nucleus.

The following examples are illustrative of the present invention and are not to be regarded as limitative. It is to be understood that all parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

Example I

A mixture of mono- and di-phosphate esters are prepared by reacting 2.7 moles of a nonionic surface active compound derived from dinonyl phenol condensed with 7 moles of ethylene oxide with 1 mole of P_2O_5 in the manner described in the examples of U.S. Pat. 3,004,056.

In general, procedures for preparing the subject emulsions involve dissolving the selected phosphate ester and the nonionic surface active agent in the selected oil and thereafter adding water slowly with sufficient stirring, whereby a water-in-oil emulsion is formed.

Example II

(A) Preparation of phosphate ester barium salt: 50 g. of the phosphate ester of Example I above are dissolved in 50 g. of Esso Base F Oil which is a non-solvent refined neutral oil with a KB value=19.1. 17.0 g. of barium hydroxide·H_2O are then added and the mixture is stirred until uniform. The resulting product is an opaque viscous liquid, the pH of a 1% solution of which in distilled water is 9.3.

(B) Preparation of water-in-oil emulsion: To 53.1 g. of Esso Base Oil F there are added 5.9 g. of the liquid prepared in Part A above and 1 g. of the nonionic surfacant derived from the condensation of oleyl alcohol with 3 moles of ethylene oxide. The mixture is stirred until a uniform product is obtained. 40 g. of water are then slowly added with high speed propeller stirring. An especially smooth, stable, non-flammable, white water-in-oil emulsion is formed.

After standing 14 days at 90° C., two thirds of the emulsion separated into a clear oil phase on top with one third of the emulsion remaining intact. However, on shaking, the water-in-oil emulsion was easily re-formed. No water separation was ever noted. This demonstrates that under the constant agitation of a pump, the water-in-oil emulsion, when in actual use, will remain very stable and completely intact.

Example III

Example II is repeated except that the nonionic surfactant employed in Part B is a condensation product of tallow alcohol plus 2 moles of ethylene oxide which yields like results.

Example IV

(A) The procedure of Example I is repeated using dodecyl phenol which has been condensed with 7 moles of ethylene oxide.

(B) To 51 parts of Solvent-Refined Midcontinent Oil (150 SUS, neutral) there are added 1.5 parts of the phosphate ester of Part A above and 4.0 parts of the nonionic surfactant described in Example III.

(C) To 43 parts of water there are added 0.5 part of barium hydroxide .8 H_2O.

(D) The aqueous solution of Part C is then slowly added to the oil prepared in Part A with stirring. An outstanding stable, non-flammable, water-in-oil emulsion is produced.

Example V

(A) Example I is again repeated except that the nonionic employed is derived from nonyl phenol condensed with 1.8 moles of ethylene oxide.

(B) To 54 parts of the oil described in Example IVB there are added 2 parts of the phosphate ester of Part A above and 1 part of the nonionic also described in Example IVB.

(C) To 43 parts of water there are added .24 part of calcium hydroxide.

(D) Parts B and C are mixed as in Example IV to produce an excellent stable, non-flammable, water-in-oil emulsion.

Example VI

Example V is repeated except that 53 parts of oil are used in Part B and 2 parts of the nonionic are employed instead of 1 part which yields like results.

Like results may also be obtained by replacing the above employed phosphate esters with mixtures of mono and di-phosphate esters derived from the following polyoxyalkylene compounds:

dinonyl phenol+4 moles ethylene oxide
dodecyl phenol+2 moles ethylene oxide
dinonyl phenol+5 moles ethylene oxide
dinonyl phenol+1.5 moles ethylene oxide
dodecyl phenol+1.8 moles ethylene oxide
octadecanol+2 moles ethylene oxide
hexadecanol+4 moles ethylene oxide
1-eicosanol+6 moles ethylene oxide
1-dotriacontanol+7 moles ethylene oxide
dodecyl phenol+5 moles ethylene oxide
hexadecyl phenol+3 moles ethylene oxide
tri-n-octyl phenol+4 moles ethylene oxide
tri-n-octyl phenol+5 moles propylene oxide
dodecyl phenol+3 moles propylene oxide
dinonyl phenol+1.5 moles propylene oxide
diisohexyl phenol+2 moles propylene oxide
tri-n-butyl phenol+2 moles propylene oxide
tri-n-butyl phenol+3 moles propylene oxide
tri-n-butyl phenol+2 moles ethylene oxide+2 moles propylene oxide
tri-n-butyl phenol+3 moles ethylene oxide
hexadecanol+3 moles propylene oxide
octadecanol+4 moles propylene oxide
butyl hexyl phenol+4 moles ethylene oxide
ethyl heptyl phenol+5 moles ethylene oxide
ethyl heptyl phenol+3 moles propylene oxide
ceryl alcohol+2 moles ethylene oxide
1-ocracosanol+4 moles ethylene oxide
1-nonacosanol+7 moles ethylene oxide
1-triacontanol+6 moles ethylene oxide
1-tetratriacontanol+5 moles ethylene oxide
1-tetratriacontanol+2 moles propylene oxide

and the like. Moreover, similar results may also be obtained by replacing the above employed nonionic surfactants with other aliphatic surfactants, such as,

dodecyl alcohol+2 moles ethylene oxide
tetradecyl alcohol+3 moles ethylene oxide
hexadecyl alcohol+1.5 moles ethylene oxide
stearyl alcohol+1.5 moles ethylene oxide
primary-m-eicosyl alcohol+1 mole ethylene oxide
n-tetracosyl alcohol+2.5 moles ethylene oxide

and the like.

Example VII

In order to demonstrate the wear and corrosion resistant properties of the instant water-in-oil emulsions, the following comparative test was carried out:

The amount of wear in a Vickers Vane type pump (Model V-104C, 8 gallons/minute delivery) was determined utilizing the water-in-oil emulsion product of Example II as compared to the amount of wear utilizing a commercially available product, Iris 902 (Shell Oil Co.). The following data illustrates the wear properties of each fluid:

Water-in-oil emulsion of Example II:
- Duration—267 hours
- Temperature—60–65° C.
- Pressure—450–500 p.s.i.
- Rate of cam ring wear—2.61 mg./hr.
- Rate of vane wear—0.303 mg./hr.

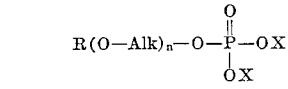
Iris 902:
- Duration—100 hours
- Temperature—45–50° C.
- Pressure—450–500 p.s.i.
- Rate of cam ring wear—5.11 mg./hr.
- Rate of vane wear—0.415 mg./hr.

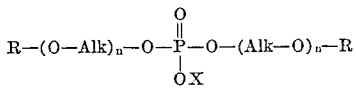
After the above test, the cam ring and vane of the experimental run utilizing the water-in-oil emulsion of Example II was found, upon visual inspection, to be clean and free from corrosion, pitting, etc.

Various modifications and variations of this invention will be obvious to a worker skilled in the art and it is understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the appended claims.

We claim:

1. A water-in-oil emulsion hydraulic fluid consisting essentially of from about a 20% to about a 60% water phase and from about a 40% to about an 80% oil phase and to which has been added (I) from about 0.5% to about 10% by weight based on the weight of the oil, of a mixture of mono- and diphosphate esters and salts thereof of the formulae





wherein Alk represents an alkylene group selected from the group consisting of ethylene, propylene, and butylene,

R represents the residue of an alkyl phenol or aliphatic alcohol from 8 to about 70 carbon atoms, X is selected from hydrogen, alkali metals, alkaline earth metals, ammonium or substituted ammonium, and *n* equals the number of moles of alkylene oxide such that the nonionic precursor of said mixture of mono- and diphosphate esters and salts thereof contains a maximum of about 47 weight percent of ethylene oxide, a maximum of about 60 weight percent of propylene oxide and a maximum of about 75 weight percent of butylene oxide depending upon the alkylene oxide used, and (II) from about 0.5% to about 10% by weight based on the weight of the oil of a nonionic surface active agent derived from the condensation of an aliphatic alcohol of from 12 to 24 carbon atoms with from about 1.5 to about 3.0 moles of ethylene oxide per mole of alcohol.

2. A water-in-oil emulsion hydraulic fluid as defined in claim **1**, wherein ingredient (II), the nonionic surface active agent, derived from an aliphatic alcohol and ethylene oxide, is the condensation product of oleyl alcohol and 3 moles of ethylene oxide.

3. A water-in-oil emulsion hydraulic fluid as defined in claim **1**, wherein ingredient (II), the nonionic surface active agent, derived from an aliphatic alcohol and ethylene oxide is the condensation product of tallow alcohol and 2 moles of ethylene oxide.

4. The water-in-oil emulsion hydraulic fluid of claim **1** wherein R is the residue of dinonyl phenol, Alk is ethylene, and X is barium.

5. The water-in-oil emulsion hydraulic fluid of claim **1** wherein R is the residue of dodecyl phenol, Alk is ethylene, and X is barium.

6. The water-in-oil emulsion hydraulic fluid of claim **1** wherein R is the residue of nonyl phenol, Alk is ethylene, and X is calcium.

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