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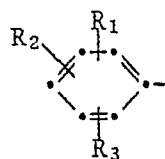
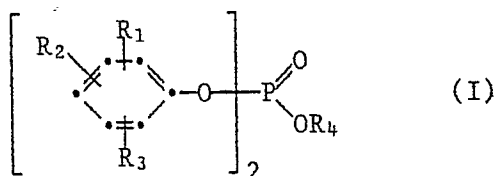
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(54) Emulsions.

(57) The invention provides an emulsion comprising
(a) a water insoluble liquid phosphate of formula I:



wherein R₁, R₂ and R₃ are as defined above,
(b) at least one emulsifying agent and (c) water.

The emulsions are useful as hydraulic fluids or metal working lubricants.

where each of R₁, R₂ and R₃ are the same or different and represent hydrogen, or an alkyl group having from 1 to 9 carbon atoms, or one or two of R₁, R₂ and R₃ are aralkyl groups having 7 to 9 carbon atoms and the other two or one are hydrogen, and R₄ represents an alkyl group having 1 to 13 carbon atoms or is a group of the formula:

Description

Emulsions

The present invention relates to stable emulsions of liquid aromatic phosphates in water, their manufacture and use as hydraulic fluids or metal working lubricants.

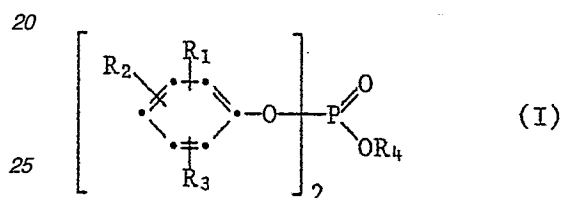
It is well known that prior art fluids such as those from petroleum oils are highly inflammable and unsuitable for use, for example as hydraulic oils in steel works where there are high fire risks.

Oil in water emulsions represent a simple solution to cheapen the higher costs of petroleum products and dramatically reduce the flammability. US 4 313 836 cites the use of a water-based hydraulic fluid and a phosphate ester but these are water soluble phosphate ester salts and require polyglycol type thickeners to provide an adequate viscosity level. Japanese patent 50/126-587 cites brominated aliphatic phosphates with water and glycols to provide stable emulsions for polyvinyl acetate and polyacrylate latexes for use in textile finishing.

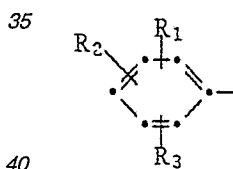
The present invention however, relates to water insoluble triaryl phosphates or alkylaryl phosphates which provide comparable viscosity ranges to those of high grade mineral oils. No thickening agents are therefore necessary, although they may be used to obtain a desired viscosity.

The present invention provides an emulsion comprising

(a) a water insoluble liquid phosphate of formula I:



where each of R_1 , R_2 and R_3 are the same or different and represent hydrogen, or an alkyl group having from 1 to 9 carbon atoms, or one or two of R_1 , R_2 and R_3 are aralkyl groups having 7 to 9 carbon atoms and the other two or one are hydrogen, and R_4 represents an alkyl group having 1 to 13 carbon atoms or is a group of the formula:



wherein R_1 , R_2 and R_3 are as defined above,
(b) at least one emulsifying agent and (c) water.

When R_1 , R_2 and R_3 are alkyl groups they may be methyl, ethyl, n-propyl, isopropyl, butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl, n-octyl or n-nonyl; they preferably have 1 to 4 carbon atoms and may be, for example methyl, ethyl, n-propyl, isopropyl, sec-butyl or t-butyl.

When R_4 is an alkyl group it may be straight or branched chain and preferably has 4 to 10 carbon atoms, most preferably 8 to 10 carbon atoms such as, for example 2-ethylhexyl or isodecyl.

Preferred phosphates are the triaryl phosphates, more preferably isopropylated phenyl phosphates or tert-butylated phenyl phosphates.

The phosphates of formula I have sufficient alkyl groups on the phenyl rings to ensure that they are liquid. Usually they comprise a mixture of different phosphates where the phenyl rings carry from 0 to 3 alkyl groups, for example those phosphates obtained by the process described in British patent specification No. 1 146 173.

Examples of water-insoluble liquid phosphates which may be used in the present invention are: tricresyl phosphate, trixylyl phosphate, tri (isopropylated-phenyl) phosphate, tri (sec-butylated phenyl) phosphate, tri (t-butylated phenyl) phosphate, tri (p-nonyl phenyl) phosphate, cresyl diphenyl phosphate, dicresyl phenyl phosphate, isodecyl diphenyl phosphate, dodecyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, phenyl dixylyl phosphate or xylyl diphenyl phosphate, and liquid mixtures of triphenyl phosphate with mono-p-benzylphenyl diphenyl phosphate or with α,α -dimethylbenzylphenyl diphenyl phosphate.

For the manufacture of the emulsion, cationic, anionic and nonionic emulsifiers are suitable, but preferably nonionic emulsifiers.

Examples of suitable cationic emulsifiers include, for instance, di-fatty acid-isopropyl-ester-dimethyl-ammoniummethyl sulphate, trimethyl-coco-ammonium chloride, trimethyl-dodecyl- or trimethyl-oleyl-ammonium

chloride and their ethoxylated derivatives, for instance, methyl-polyoxyethylene-coco-ammonium chloride with about 5 to 20 moles ethylene oxide units.

Examples of suitable anionic emulsifiers include, for instance, the mono- or di-alkyl-sulphosuccinates, such as the sodium-di-isooctyl-sulphosuccinate, the alkylbenzene-sulphonates, the mineral oil sulphonates or derivatives with ethoxylated residues of mineral acids, such as partial esters of phosphoric acid with polyoxyethylene as polyethylene glycol or the monoethers thereof, for example, the partial esters of ethoxylated lauric alcohol.

Anionic emulsifiers may be used in form of their alkali, ammonium or amine salts.

Examples of suitable nonionic emulsifiers include, for instance, the ethylene oxide adducts (EO-adducts), to straight or branched chain alkanols with at least 8 C-atoms, to fatty acids, amines, amides and alkylphenols with about 5 to about 100 EO-units, for instance, the ethoxylated lauric alcohols with about 8 EO-units, the ethoxylated palmitic acids with about 10 EO-units, the ethoxylated coco amines with about 10 EO-units, the ethoxylated tallow or oleyl amines with about 15 to 50 EO-units. The amine EO-adducts in the form of their salts may also show, dependent on the number of EO-units, more or less distinct cationic properties, too. Corresponding propylene oxide adducts or adducts from mixtures of ethylene oxide and propylene oxide may also be used.

A good guide for the selection of the proper nonionic emulsifiers is the HLB-value (Hydrophilic/Lipophilic Balance), well known to one skilled in the art. These values are known for most of the nonionic emulsifiers or they may be easily calculated.

In the case of nonionic emulsifiers, the solubility of the emulsifiers in water increases with the increase in the numbers of EO-units and hence the HLB-values. Emulsifiers with a low HLB-value, as for instance with the value 4, are soluble in oily substances and produce emulsions of the water-in-oil type. Emulsifiers with the HLB-value of about 9 and higher up to about 18 have increasing water-solubility and produce emulsions of the oil-in-water type. Preferred emulsifiers are those with an HLB-value of at least 9, and especially 10.5. The choice of the emulsifier with the correct HLB-value is also dependent on the liquid phosphate to be emulsified. There is no difficulty for the man skilled in the art to select the emulsifier with the correct HLB-value.

Mixtures of emulsifiers can be used, the average HLB-value being determined by the type of emulsion required.

It is possible to combine the nonionic emulsifier with anionic or with cationic emulsifiers.

The total amount of emulsifying agent needed to produce stable emulsions of the liquid water-insoluble phosphate are about 0.5 to 15, especially 2 to 10 % by weight related to the substance to be emulsified.

The manufacture of the emulsion is made in a way known to one skilled in the art. In principle there are two possibilities.

First: to add the oily phase to the water phase. Second: to add the water phase to the oily phase.

The latter is preferred.

According to this preferred method, a mixture of water and emulsifying agent is slowly added to the phosphate while vigorously stirring. In the initial phase the viscosity increases to a maximum, after passing through a maximum the viscosity decreases.

By using two (or more) emulsifiers with different HLB-values it is advantageous, but not necessary, to combine the emulsifier with the lower HLB-value with the liquid phosphate and to dissolve the emulsifier having the higher HLB-value in the water and then to stir the mixture of water and emulsifier into the mixture of phosphate and emulsifier.

It is also possible to operate the other way round, i.e. to stir the phosphate into the aqueous phase of water and emulsifier. In this case the formation of a maximum viscosity is not observed.

In all cases the pre-emulsion thus obtained is homogenized by means of a high pressure homogenizing device.

The ratio of phosphate to water may vary from 1:99 to 90:10, preferably from 2:98 to 80:20, and most preferably from 5:95 to 65:35.

By the use of phosphates of different viscosity and by varying the ratio of phosphate to water, emulsions can be made for a variety of uses, e.g. as hydraulic fluids or as cutting fluids in industrial applications.

The emulsions of the present invention are surprisingly more stable than the known oil-in-water emulsions.

When an oil-in-water emulsion breaks down to leave a thin oil on water film, exposure to air gives rise to a potentially explosive mixture. Serious fires and explosions have been identified from such incidents. In the case of products of the present invention the phosphate is invariably heavier than water and if the emulsion should break on standing the water layer rather than the organic layer would be in contact with air and the above situation would be avoided. In any case phosphates are safer than mineral oils used in the known emulsions because of their higher flash points and very high autoignition points.

The emulsions of the invention also have a resistance to hydrolysis which can be demonstrated by the fact that the neutralisation number changes insignificantly even after a period of 64 days at an elevated temperature of 40°C.

Low temperatures seriously affect the utility of mineral oil/water emulsions due to the freezing of the continuous phase (water) and splitting occurs. In the case of emulsions of the present invention solidification occurs at -5°C but on warming to 0°C they revert to their original mobile form. Low temperature storage problems are accordingly not as severe as with products of the prior art.

The emulsions can, of course, contain further adjuvants in addition, such as corrosion inhibitors, metal

deactivators, extreme pressure additives, viscosity index improvers, foam inhibitors and/or dispersants. Preferred foam inhibitors are silicone-based, e.g. silicones, especially in admixture with esters of higher fatty acids.

If these additional adjuvants are not soluble in water, they may be added to the non-aqueous phase prior to emulsification.

It will be understood that adjuvants which cause the emulsion to break should not be used.

The invention is illustrated by the following Examples.

Example 1:

15 parts of alkyl aryl polyglycol ether (HLB-value 17) are dissolved in 300 parts of water and this solution is added at room temperature, while vigorously stirring, to 585 parts of tri (isopropylated phenyl) phosphate (viscosity 120 mm²/sec at 25°C) containing 10 parts of glycerol trioleate and 15 parts of an organopolysiloxane as foam inhibitor.

The viscosity of the water-in-oil-emulsion first resulting during the addition of the mixture of water/emulsifier increases considerably, in the course of which a maximum is achieved after the addition of about half to two-thirds of the mixture of water/emulsifier.

In this phase the emulsion absorbs the mixture of water/emulsifier only slowly and the water-in-oil-emulsion changes into an oil-in-water-emulsion. As soon as the viscosity decreases, the mixture of water/emulsifier can be added on stirring more quickly.

Subsequently water is added with stirring to top up the volume of emulsion to 1000 parts.

This pre-emulsion is homogenized at $3 \cdot 10^7$ Pa and a temperature of about 20-30°C by a high-pressure homogenizing device.

The final "emulsion A" thus obtained is extremely stable. On standing during storage at 60°C for 28 days there is no significant physical change, and no separation occurs during centrifuging (3000 rpm (rpm = rotation per minute), 6 min).

The same procedure is repeated with liquid tri (isopropylated phenyl) phosphates having viscosities of 95, 65 and 50 mm²/s resp. The obtained emulsions are emulsion B, C and D, resp. The results of tests, conducted therewith are summarised in the following Tables 1-3.

1. Storage stability at 40°C

Table 1

Emulsion	Brookfield Viscosity (mm ² /sec) of emulsion at 23°C	Neutralisation No. (mg KOH/g) after time (days) at 40°C		Comments
Emulsion A	292	0 64	0.1 0.02	Mobile white cream
Emulsion B	282	0 64	0.24 1.03	Mobile white cream
Emulsion C	221	0 64	0.13 0.12	Mobile white cream
Emulsion D	184	0 64	0.014 0.08	Mobile white cream

Brookfield test conditions: Spindle No. 2; Stirrer speed = 5 rpm

2. Shell 4-Ball wear tests 40 kg load/1 hourTable 2

Emulsion	Additive (%)	Wear scar diameter (mm)	Comments
Emulsion A	—	0.81; 0.93	Stain
Emulsion A	0.1 % alkenyl succinic acid ester corrosion inhibitor	0.72; 0.69	No stain or rust

3. Shear Stability

6 mins. centrifuging at 3000 rpm

Table 3

Emulsion	Comments
Emulsion A	No separation
Emulsion B	No separation
Emulsion C	No separation
Emulsion D	No separation

Example 2:

A solution of 10 parts of fatty alcohol polyglycolether (HLB-value about 17) in 300 parts of water is slowly added to a mixture of 600 parts of tri (isopropylated phenyl) phosphate (viscosity 120 mm²/sec) with 40 parts of fatty alcohol polyglycolether (HLB-value 8) while vigorously stirring in the way described in Example 1.

The calculated HLB-value of both emulsifiers amounts to 9.8.

After having diluted with water to 1000 parts it is homogenized, as in Example 1.

There results an emulsion stable to storage which can easily be diluted with water to an emulsion with a content of 5 % liquid phosphate.

Example 3:

25 parts of fatty-alkyl-trimethyl-coco-ammonium chloride (HLB-value 16) are dissolved in a little amount of isopropanol and then mixed with 300 parts of water. The resulting turbid solution is added to 600 parts tri (isopropylated phenyl) phosphate (used in Example 2) in the way described in Example 1.

After having diluted with water to 1000 parts and having homogenized, a fine, stable emulsion resulted.

Example 4:

Example 3 is repeated, except that instead of the emulsifier mentioned there, 30 parts of di-fatty acid-isopropyl-ester-di-methylammonium-methylsulphate are used.

There is obtained an emulsion with properties similar to those of Example 3.

Example 5:

15 parts of the sodium salt of di-2-ethylhexyl-sulphosuccinate are dissolved in 350 parts of water. The resulting solution is added, while vigorously stirring, to 600 parts liquid tri (isopropylated phenyl) phosphate (viscosity 120 mm²/sec) in the way described in Example 1.

After having diluted with water to 1000 parts and having homogenized, a fine, stable emulsion resulted.

Example 6

330 parts of water is added, at room temperature, with vigorous stirring, to a slurry containing 585 parts trixylyl phosphate and emulsifier mixture containing 15 parts of alkyl aryl polyglycol ether (HLB-value 17) 10 parts of glycerol trioleate and 15 parts of an organopolysiloxane as foam inhibitor.

The emulsion is then diluted to 1000 parts and homogenized under pressure as per Example 1.

A stable oil-in-water emulsion is formed which has the properties listed in Table 4.

Example 7:

Example 6 is repeated except that the phosphate ester mentioned is replaced by 585 parts of isodecyl diphenyl phosphate (viscosity 12.64 mm²/sec at 40°C).

A stable oil-in-water emulsion is formed which has the properties listed in Table 4.

Example 8:

Example 6 is repeated except that the phosphate ester mentioned is replaced by 585 parts of tri(t-butylated phenyl)phosphate (viscosity 42.88 mm²/sec at 40°C).

A stable oil-in-water emulsion is formed which has the properties listed in Table 4.

Example 9:

Example 6 is repeated except that 5 parts of benzotriazole is dissolved in water phase and 0.25 parts of benzotriazole is dissolved in the phosphate ester prior to emulsification.

A stable oil-in-water emulsion is formed which has the properties listed in Table 4.

Example 10:

Example 6 is repeated except that 0.25 parts of benzotriazole and 0.25 parts half ester of propylene glycol and dodecynyl succinic acid are dissolved in the phosphate ester prior to emulsification.

The properties of the stable oil-in-water emulsion are listed in Table 4.

Example 11:

Example 6 is repeated except that 0.25 parts of a diethanolamine derivative of toluotriazole and 5 parts of triethanolamine salt of a triazine carboxylic acid are dissolved in the water phase prior to emulsification.

The properties of the stable oil-in-water emulsion are listed in Table 4.

Example 12:

A slurry containing 450 parts tri-isopropylated phenyl phosphate (viscosity 120 mm²/sec at 25°C) and 6.25 parts of a propylene oxide/ethylene oxide copolymer (HLB-value 13.5) is added at room temperature with vigorous stirring to 43.75 parts of water. During the preparation the temperature rises to 50°C.

The properties of the stable oil-in-water emulsion formed are listed in Table 4.

Example 13:

A solution of 1.75 parts polyethylene glycol (mol. wt. 4,000) in 173.25 parts water (1 % w/w solution) is added, at room temperature, with vigorous stirring to 300 parts of tri(isopropylated phenyl)phosphate (viscosity 120 mm²/sec at 25°C) which has been slurried with the 25 parts of an emulsifier mixture containing 7.8 parts of alkyl polyglycol ether (HLB-value 17), 5.0 parts of glycerol trioleate and 7.9 parts of an organopolysiloxane as foam inhibitor.

The properties of the stable oil-in-water emulsion formed are listed in Table 4.

Example 14:

Example 13 is repeated except that 1.75 parts of polyvinyl pyrrolidone (mol. wt. 10,000) replaced the polyethylene glycol. The properties of the stable oil-in-water emulsion are listed in Table 4.

Example 15:

Example 13 is repeated except that 1.75 parts of polyvinyl alcohol (75 % hydrolysed mol. wt. 2000) replaces the polyethylene glycol. The properties of the stable oil-in-water emulsion are listed in Table 4.

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Example 16:

Example 13 is repeated except that 1.75 parts of polyacrylic acid (mol. wt. 2000) replaces the polyethylene glycol. The properties of the stable oil-in-water emulsion are listed in Table 4.

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Example 17:

Example 13 is repeated except that 1.75 parts of polyacrylamide (mol. wt. 5-6 million) replaces the polyethylene glycol. The properties of the stable oil-in-water emulsion are listed in Table 4.

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Example 18:

75 parts of water are added, at room temperature, with vigorous stirring to 400 parts tri(isopropylated phenyl)phosphate (viscosity 120 mm²/sec at 25°C) containing 25 parts of propylene/ethylene oxide copolymer (HLB-value 6.4).

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A stable water-in-oil emulsion is produced having the properties listed in Table 4.

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Table 4

Example No.	pH at 23°C	Brookfield viscosity at 23°C (mm ² /sec)	Turbidity of emulsion emulsion diluted to 0.16 % phosphate content (NTU units)
6	7.5	1000	356
7	7.3	2800	326
8	7.5	1300	392
9	7.9	400	391
10	7.5	200	392
11	7.9	200	414
12	6.0	32000	143
13	6.4	1000	181
14	5.7	1200	169
15	6.1	200	174
16	3.8	200	153
17	7.0	5100	340
18	6.4	400	330*

1) NTU = nephelometric turbidity units

2) Brookfield test conditions: Spindle = No. 4

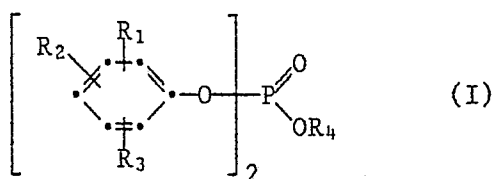
Speed = 5 rpm

* Brookfield viscosity determined using Spindle 5 at 5 rpm

** turbidity determined on 2 % soln. (based on phosphate)

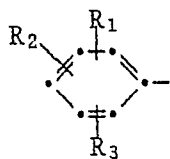
Claims

1. An emulsion comprising
(a) a water insoluble liquid phosphate of formula I:



where each of R₁, R₂ and R₃ are the same or different and represent hydrogen, or an alkyl group having

from 1 to 9 carbon atoms, or one or two of R_1 , R_2 and R_3 are aralkyl groups having 7 to 9 carbon atoms and the other two or one are hydrogen, and R_4 represents an alkyl group having 1 to 13 carbon atoms or is a group of the formula:



wherein R_1 , R_2 and R_3 are as defined above,

(b) at least one emulsifying agent and (c) water.

2. An emulsion as claimed in claim 1 in which the ratio of phosphate to water is from 2:98 to 80:20.
3. An emulsion as claimed in claim 1 in which the ratio of phosphate to water is from 5:95 to 65:35.
4. An emulsion as claimed in claim 1 in which the emulsion is of the oil-in-water type.
5. An emulsion as claimed in claim 1 in which the emulsifying agent has an HLB-value of at least 9.
6. An emulsion as claimed in claim 5 in which the emulsifying agent is a mixture of at least two emulsifiers.
7. An emulsion as claimed in claim 1 in which the emulsifying agent is nonionic.
8. An emulsion as claimed in claim 1 in which the amount of emulsifying agent is from 2 to 10 % by weight related to the substance to be emulsified.
9. An emulsion as claimed in claim 1 in which the phosphate is a triaryl phosphate.
10. An emulsion as claimed in claim 9 in which the triaryl phosphate is a tri (isopropylated phenyl) phosphate or a tri (t-butylated phenyl) phosphate.
11. An emulsion as claimed in claim 1 which contains as adjuvants a corrosion inhibitor, metal deactivator, extreme pressure additive, viscosity index improver, foam inhibitor and/or dispersant.
12. An emulsion as claimed in claim 1 in which the foam inhibitor is silicone-based.
13. An emulsion as claimed in claim 12 in which the foam inhibitor is a mixture of an ester of fatty acids and a silicone.
14. The use of an emulsion as claimed in claim 1 as a hydraulic fluid or metal working lubricant.
15. A process for preparing an emulsion as claimed in claim 1 which comprises mixing the liquid phosphate with emulsifying agent, water and possibly other adjuvants in any order and then homogenising.