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(54) **Fire resistant fluids.**

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(56) References cited:
FR-A-1 461 361
US-A-3 723 315
US-A-3 783 132
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Fire resistant fluids

This invention relates to fire resistant (difficultly inflammable) fluids based on esters of phosphoric acid. More particularly, the invention relates to a fire resistant fluid based on a phosphoric acid ester or a mixture of phosphoric acid esters and containing a corrosion and hydrolysis inhibitor.

Hydraulic fluids based on phosphoric acid esters have been used for some time. They have characteristics suitable therefor; particularly, they are not easily inflammable, so that they are used above all in systems comprising closed hydraulic circuits such as hydraulic systems of turbines and of pressure casting, continuous casting and press plants. The use of such fluids is described for example in U.S. Patent 3 468 802 and U.S. Patent 3 723 315.

Although such fluids are not easily inflammable and of relatively high thermal stability, they may, in certain applications, possess insufficient resistance to oxidation and/or hydrolysis or they may be highly corrosive to certain metals. To remedy such defects of the known fluids certain inhibitors may be added thereto. For example, certain aminopyridines may be added as antioxidants (U.S. Patent 3 783 132). Also, oxazolines and imidazolines may be added as rust inhibitors (British Patent 1 317 636). Finally, it is known to use certain amino compounds as corrosion inhibitors (U.S. Patent 3 468 802). However, many of the proposed rust inhibitors show undesirable side effects which impair the applicability of the hydraulic fluid.

In accordance with the invention there is provided a fire resistant fluid comprising a phosphate ester and a corrosion or hydrolysis inhibiting amount of piperazine or a substituted piperazine.

The fluid of the invention may be useful as a lubricant, a hydraulic fluid, a transformer oil or for a variety of other purposes wherein a fire resistant fluid is required.

The problem underlying this invention is to develop a fire resistant fluid having improved characteristics compared to those of known fluids used in hydraulic systems, especially with regard to corrosion inhibition and/or hydrolytic stability.

This is achieved by a fire resistant fluid based on a phosphoric acid ester or a mixture of phosphoric aced esters and containing piperazine and/or at least one piperazine derivative as corrosion and/or hydrolysis inhibitor.

The use of such additives in phosphate esters confers not only improved hydrolytic stability but also better corrosion inhibiting properties; particularly, the rust-preventing properties are improved.

The proportion of piperazine or piperazine derivative in fluids according to the invention is in the range of 0.005 to 5% by weight and is preferably in the range of 0.01 to 0.5% by weight.

The phosphate esters used as the base for fire resistant fluids are mainly aryl esters of phosphoric acid. The triaryl esters are particularly preferred because they are clearly superior in regard to fire resistance but diaryl alkyl phosphate esters may also be employed. The preferred triaryl phosphate esters include, inter alia, tricresyl phosphate ester, trixylyl phosphate ester, phenyl dicresyl phosphate ester, cresyl diphenyl phosphate ester and tri(isopropylphenyl) phosphate ester, di(isopropylphenyl) phenyl phosphate ester and isopropylphenyl diphenyl phosphate ester. Diphenyl-2-ethylhexyl phosphate ester is an example of the diarylalkyl phosphate ester which may be used, although with a clear loss of fire resistance in the fluid. If greater fire resistance is required halogenated phosphate esters may be used, in particular chlorinated aryl esters which, however, have considerable other disadvantages (such as corrosion).

The corrosion and hydrolysis inhibitor may be piperazine itself or a substituted piperazine. Thus, alkyl, aryl, alkaryl and aralkyl substituted piperazines may be used, and the substituent groups may themselves be substituted, for example, by halogene, hydroxy, alkoxy, amino, alkylamino or dialkylamino groups. Other substituent groups on the piperazine ring may be hydroxy, hydroxyalkyl, alkoxy, alkoxyalkyl, alkoxyaryl, amino, aminoalkyl, alkylamino, dialkylamino, alkylaminoalkyl and dialkylamino alkyl. The substitution may be made on the carbon or nitrogen atoms of the piperazine ring. Preferred types of substituted piperazine are:

Alkyl-, Dialkyl-, Trialkyl- or Tetraalkyl-piperazine,
N-alkyl-piperazine,
N,N'-Dialkyl-piperazine,
N-Aryl-piperazine,
N,N'-Diaryl-piperazine,
N-Alkylaryl-piperazine,
N,N-Di(Alkylaryl)-piperazine,
N-Hydroxyalkyl-piperazine,
N,N'-Di(hydroxyalkyl)-piperazine,
N-Aminoalkyl-piperazine, and
N,N'-Di(aminoalkyl)-piperazine.

In addition to piperazine and derivatives thereof the fluid according to the invention may also include other additives when this is desirable for particular applications. These other additives may be, for

example, metal deactivators, antioxidants and antifoaming agents.

Examples of antioxidants are:

Alkyl and non-alkylated aromatic amine:

Dioctyl-diphenylamine;
tertiary octylphenyl-α-naphthylamine;
ditertiary octylphenothiazine;
phenyl-α-naphthylamine;
N,N'-di(sec butyl)-p-phenylenediamine.

Sterically hindered phenols:

2,6-ditertiarybutyl-p-cresol;
2,6-ditertiarybutylphenol;
2,4,6-triisopropylphenol;
2,2'-thio-bis-(4-methyl-6-tert butylphenol).

Esters of thiodipropionic acid:

Dilaurylthiodipropionate ester.

Complex organic chelates:

Copper-bis(trifluoracetyl acetonate),
copper phthalocyanine, tributyl ester of EDTA.

Examples of antifoaming agents are silicones.

Example 1

The effect of the piperazine or piperazine derivatives was tested with regard to rust-preventing properties in accordance with ASTM D-665, Procedure A. The following results were obtained:

Table 1

Formulation	Test duration hours	Assessment
Phosphate ester A	24	fail, slight corrosion
Phosphate ester A	48	fail, moderate corrosion
Phosphate ester A + 0.10% Piperazine	48	pass
Phosphate ester A + 0.05% Piperazine	48	pass
Phosphate ester A + 0.03% Piperazine	48	pass
Phosphate ester A + 0.10% N,N-Dimethylpiperazine	48	pass
Phosphate ester A + 0.05% N,N-Dimethylpiperazine	48	pass
Phosphate ester A + 0.10% N-(2-Aminoethyl)-piperazine	24	pass
Phosphate ester A + 0.05% 1-(2-Hydroxyethyl)-piperazine	48	pass
Phosphate ester A + 0.03% 1-(2-Hydroxyethyl)-piperazine	48	pass
Phosphate ester A + 0.10% N-Phenyl-piperazine	24	pass
Phosphate ester A + 0.10% N-Benzyl-piperazine	48	pass
Phosphate ester B	24	fail, heavy corrosion
Phosphate ester B + 0.10% 2-Methyl-piperazine	24	pass
Phosphate ester B + 0.10% N-Methyl-piperazine	24	pass
Phosphate ester B + 0.10% N,N-Dimethyl-piperazine	24	pass
Phosphate ester B + 0.10% 1-(2-Hydroxyethyl)-piperazine	24	pass
Phosphate ester B + 0.10% Piperazine	24	pass
Phosphate ester C	48	fail, moderate corrosion
Phosphate ester C + 0.03% Piperazine	48	pass

Phosphate ester A: Triaryl phosphate ester (inhibited), 38 cSt/40°C

Phosphate ester B: Triaryl phosphate ester (uninhibited), 22 cSt/40°C

Phosphate ester C: Triaryl phosphate ester (uninhibited), 43 cSt/40°C

Example 2

The effect of the piperazine derivatives was tested with regard to hydrolytic stability in accordance with the BBC Hydrolytic Stability Test (BBC ZLC 2-5-40, 100° C, 96 hours (no clay treatment). The results of the tests are as follows:

Table 2

Formulation	Neutralization Number Increase mg KOH/g
Phosphate ester A	5.1
Phosphate ester A + 0.20% N-(2-Aminoethyl)-piperazine	1.96
Phosphate ester A + 0.20% N,N'-Dimethyl-piperazine	1.42
Phosphate ester A + 0.20% N-Methyl-piperazine	1.65
Phosphate ester A + 0.20% 2.5-Dimethyl-piperazine	1.29
Phosphate ester A + 0.20% 2-Methyl-piperazine	1.13
Phosphate ester A + 0.20% 1-(2-Hydroxyethyl)-piperazine	1.09
Phosphate ester A + 0.20% Piperazine	1.77
Phosphate ester D	0.99
Phosphate ester D + 0.05% 1-(2-Hydroxyethyl)-piperazine	0.69
Phosphate ester E + 0.05% Piperazine	0.45
Phosphate ester E + 0.05% 1-(2-Hydroxyethyl)-piperazine	0.30

Phosphate ester D: Triaryl phosphate ester (inhibited), 43 cSt/40°C

Phosphate ester E: Triaryl phosphate ester (inhibited), 43 cSt/40°C

In Tables 1 and 2, Esters A-E are mixtures of the following:

Tri(isopropylphenyl) phosphate, di(isopropylphenyl) phenyl phosphate, isopropylphenyl diphenyl phosphate and triphenyl phosphate.

Claims

1. A fire resistant fluid comprising a phosphate ester and a corrosion or hydrolysis inhibiting amount of piperazine or a substituted piperazine.

2. The fluid of Claim 1 wherein said phosphate ester is an aryl ester of phosphoric acid.

3. The fluid of Claim 2 wherein the aryl ester is a diaryl ester.

4. The fluid of Claim 3 wherein the diaryl ester is diphenyl-2-ethylhexyl phosphate.

5. The fluid of Claim 2 wehrein the aryl ester is a triaryl ester.

6. The fluid of Claim 5 wherein the triaryl ester is selected from the group consisting of tricresyl phosphate, trixylyl phosphate, phenyl dicresyl phosphate, cresyl diphenyl phosphate, and tri(isopropylphenyl) phosphate.

7. The fluid of Claim 1 wherein the corrosion or hydrolysis inhibitor is piperazine.

8. The fluid of Claim 1 wherein the corrosion inhibitor is a substituted piperazine.

9. The fluid of Claim 8 wherein the substituent is selected from the group consisting of alkyl, aryl, alkaryl, hydroxy, hydroxyalkyl, alkoxy, alkoxyalkyl, alkoxyaryl, amino, aminoalkyl, alkylamino, dialkylamino, alkylaminoalkyl and dialkylaminoalkyl.

10. The fluid of Claim 9 wherein said substituent is itself substituted with a member selected from the group consisting of halogen, hydroxy, alkoxyl, amino, alkylamino and dialkylamine.

11. The fluid of Claim 1 wherein the inhibitor is N,N'-dimethyl piperazine.

12. The fluid of Claim 1 wherein the inhibitor is 2-methyl piperazine.

13. The fluid of Claim 1 wherein the inhibitor is N-methyl piperazine.

14. The fluid of Claim 1 wherein the inhibitor is 1-(2-hydroxy) piperazine.

15. The fluid of Claim 1 wherein the inhibitor is N-(2-aminoethyl) piperazine.

16. The fluid of Claim 1 wherein the inhibitor is N-phenyl piperazine.

17. The fluid of Claim 1 wherein the inhibitor is N-benzyl piperazine.

18. The fluid of Claim 1 wherein the inhibitor is 2,5-dimethyl piperazine.

Patentansprüche

1. Feuerresistentes Fluid, gekennzeichnet durch einen Phosphatester und einen die Korrosion oder Hydrolyse inhibierenden Anteil von Piperazin oder einen substituierten Piperazin.

2. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Phosphatester ein Arylester von Phosphorsäure ist.

3. Fluid nach Anspruch 2, dadurch gekennzeichnet, daß der Arylester ein Diarylester ist.

4. Fluid nach Anspruch 3, dadurch gekennzeichnet, daß der Diarylester Diphenyl-2-äthylhexylphosphat ist.

5. Fluid nach Anspruch 2, dadurch gekennzeichnet, daß der Arylester ein Triarylester ist.

6. Fluid nach Anspruch 5, dadurch gekennzeichnet, daß der Triarylester aus der Reihe von Tricresylphosphat, Trixylylphosphat, Phenyldicresylphosphat, Cresyldiphenylphosphat und Tri(isopropylphenyl)phosphat ausgewählt ist.

7. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Korrosions- oder Hydrolyseinhibitor Piperazin ist.

8. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Korrosionsinhibitor ein substituiertes Piperazin ist.

9. Fluid nach Anspruch 8, dadurch gekennzeichnet, daß der Substituent aus der Reihe von Alkyl, Aryl, Alkaryl, Hydroxy, Hydroxyalkyl, Alkoxy, Alkoxyalkyl, Alkoxyaryl, Amino, Aminoalkyl, Alkylamino, Dialkylamino, Alkylaminoalkyl und Dialkylaminoalkyl ausgewählt ist.

10. Fluid nach Anspruch 9, dadurch gekennzeichnet, daß der Substituent selbst mit einer Gruppe aus der Reihe Halogen, Hydroxy, Alkoxyl, Amino, Alkylamino und Dialkylamino substituiert ist.

11. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor N,N'-Dimethylpiperazin ist.

12. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor 2-Methylpiperazin ist.

13. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor N-Methylpiperazin ist.

14. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor 1-(2-Hydroxy)piperazin ist.

15. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor N-(2-Aminoäthyl)piperazin ist.

16. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor N-Phenylpiperazin ist.

17. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor N-Benzylpiperazin ist.

18. Fluid nach Anspruch 1, dadurch gekennzeichnet, daß der Inhibitor 2,5-Dimethylpiperazin ist.

Revendications

1. Fluide résistant au feu comprenant un ester phosphorique et une quantité inhibant la corrosion ou l'hydrolyse de pipérazine ou d'une pipérazine substituée.

2. Fluide selon la revendication 1, dans lequel ledit ester phosphorique est un ester arylique d'acide phosphorique.

3. Fluide selon la revendication 2, dans lequel l'ester arylique est un ester diarylique.

4. Fluide selon la revendication 3, dans lequel l'ester diarylique est le phosphate de diphényle et d'éthyl-2 hexyle.

5. Fluide selon la revendication 2, dans lequel l'ester arylique est un ester triarylique.

6. Fluide selon la revendication 5, dans lequel l'ester triarylique est choisi parmi le phosphate de tricrésyle, le phosphate de trixylyle, le phosphate de phényle et le dicrésyle, le phosphate de crésyle et de diphényle et le phosphate de tri(isopropylphényle).

7. Fluide selon la revendication 1, dans lequel l'inhibiteur de corrosion ou d'hydrolyse est la pipérazine.

8. Fluide selon la revendication 1, dans lequel l'inhibiteur de corrosion est une pipérazine substituée.

9. Fluide selon la revendication 8, dans lequel le substituant est choisi parmi les groupes alkyle, aryle,

alkaryle, hydroxy, hydroxyalkyle, alcoxy, alcoxyalkyle, alcoxyaryle, amino, aminoalkyle, alkylamino, dialkylamino, alkylaminoalkyle et dialkylaminoalkyle.

10. Fluide selon la revendication 9, dans lequel ledit substituant est lui-même substitué par un groupe halogéno, hydroxy, alcoxy, amino, alkylamino ou dialkylamino.

11. Fluide selon la revendication 1, dans lequel l'inhibiteur est la N,N'-diméthylpipérazine.

12. Fluide selon la revendication 1, dans lequel l'inhibiteur est la méthyl-2 pipérazine.

13. Fluide selon la revendication 1, dans lequel l'inhibiteur est la N-méthylpipérazine.

14. Fluide selon la revendication 1, dans lequel l'inhibiteur est la (hydroxy-2)-1 pipérazine.

15. Fluide selon la revendication 1, dans lequel l'inhibiteur est la N-(amino-2 éthyl)pipérazine.

16. Fluide selon la revendication 1, dans lequel l'inhibiteur est la N-phénylpipérazine.

17. Fluide selon la revendication 1, dnas lequel l'inhibiteur est la N-benzylpipérazine.

18. Fluide selon la revendication 1, dans lequel l'inhibiteur est la diméthyl-2,5 pipérazine.