

12 **EUROPEAN PATENT APPLICATION**

21 Application number: **89116232.3**

22 Date of filing: **02.09.89**

51 Int. Cl.⁵: **C10M 169/04 , //(C10M169/04,
105:38,107:34,129:10,129:38,
129:76,133:12,137:10),
C10N30:00,C10N40:08**

30 Priority: **13.09.88 IT 2190888**

43 Date of publication of application:
21.03.90 Bulletin 90/12

84 Designated Contracting States:
AT BE CH DE ES FR GB LI LU NL SE

71 Applicant: **BP Chemicals Limited**
Belgrave House 76 Buckingham Palace Road
London, SW1W 0SU(GB)

72 Inventor: **Levrero, Lorenzo**
Corso Europa 1731-3
I-Genova(IT)
Inventor: **Granata, Francesco**
via Marco Basile 26 Palagiano
I-Taranto(IT)
Inventor: **Latorrata Rocco**
viale Stazione 62 Palagiano
I-Taranto(IT)

74 Representative: **Klausner, Erich et al**
c/o Ufficio Internazionale Brevetti Ing. C.
Gregorj S.p.A. Via Dogana 1
I-20123 Milano(IT)

54 **Fire-resistant hydraulic fluid and process of manufacture.**

57 A fire-resistant hydraulic fluid is disclosed which has an improved response to heat and flame under controlled conditions and a high degree of flame propagation resistance. The safety hydraulic fluids of the instant invention are made of at least a polyalkylene glycol, an ester and an antioxidant. Depending on the specific use, the inventive hydraulic fluid may further contain other additives such as e.g. anti-rust agents, anti-wear agents and viscosity index improvers.

A process for making the novel safety hydraulic fluid is also disclosed.

EP 0 359 071 A1

FIRE-RESISTANT HYDRAULIC FLUID AND PROCESS OF MANUFACTURE

The instant invention concerns a fire-resistant hydraulic fluid.

More particularly, the present invention concerns a hydraulic fluid having an improved response to heat and flame under controlled conditions, i.e. having a useful degree of fire resistance in industrial applications, as well as a process for making said hydraulic fluid.

5 The field of use of fire-resistant hydraulic fluids is e.g. in the hydraulic systems of the continuous casting plants for making steel billets, in the opening or closing systems of furnaces, in the loading devices of coke furnaces or lime furnaces, etc. Generally speaking, fire-resistant hydraulic fluids are employed in all the drive and power hydraulic transmission systems operating at pressures up to 700 bar in the vicinity of or under the danger of open flames or of incandescent bodies, and ambient temperatures ranging from
10 -15°C to $+150^{\circ}\text{C}$.

The present safety hydraulic fluids suitable for elevated circuit temperatures are based either on phosphoric esters (such as e.g. tricresylphosphate or trixylenylphosphate) or on organic esters, or on 9:1 mixtures of organic esters with phosphoric esters.

As it is known to those skilled in the art, fire-resistant hydraulic fluids must meet at least the following
15 three fundamental requisites, i.e. they must have:

- (i) a high degree of flame propagation resistance;
- (ii) a lubricity adequate to the operating conditions existing in the hydraulic system;
- (iii) a high operational stability.

As to the first requisite, it is known that the hydraulic fluids on the basis of phosphoric esters are the
20 most reliable, whereas those on the basis of organic esters are the least reliable. The second and third requisites are satisfied to a substantially equal degree by good quality phosphoric esters and organic esters treated with suitable additives.

The use of phosphoric esters for making fire-resistant hydraulic fluids is being phased out because of their toxicity, replacing them in most cases with organic esters.

25 On the other hand it is generally admitted that the greatest drawback of organic esters is their insufficient capability to limit flame propagation, when they catch fire. It is also known that the prior art hydraulic fluids, due to their chemical nature, are subject to decomposing during operation, thus negatively affecting their response to heat and flame, with consequent greater fire hazard.

30 Moreover, the prior art hydraulic fluids all tend - to a greater or lesser degree - to form, during operation, insoluble sludge, varnish and other deposits that clog the filters and oxidize the seat of the needle valves which are thus subject to corrosion and imperfect sealing.

In the light of the above referred drawbacks of the prior art materials it is generally recognized that a need existed for less hazardous and more stable hydraulic fluids.

35 It is therefore the main object of the present invention to provide a hydraulic safety fluid having an improved flame propagation resistance and a higher autoignition temperature than the prior art fluids.

Another object of this invention is that of providing a hydraulic safety fluid which does not decompose or which decomposes far less than prior art fluids, during operation.

40 The test method for rating the flammability of fire-resistant hydraulic fluids, in Europe, is that provided by the Sixth Luxembourg Report of the Commission of European Communities Parts III 3.1 to 3.2.2.7 inclusive entitled "Tests for Resistance to Flame". Another test method has been developed by the Factory Mutual Research Corporation: ASTM-Committee D-2 Technical Division N-Hydraulic Fluids, Section VI on Fire Resistivity. According to this method, the fluid to be tested is heated in a steel cylinder pressurized and discharged through a nozzle. The flame from a propane-air torch is introduced at points 152 mm (6 in.) and 457 mm (18 in.) from the nozzle. When the torch flame is removed from spray pattern, the duration of the
45 burning in the spray pattern is recorded. A duration of 10 seconds or more is a failure. The most critical parameter of this test method is the bulk temperature of the fluid being tested. The above referred specifications provide a temperature of 60°C .

Now, it is known that the presently employed safety hydraulic fluids based on organic esters fail the test at temperatures between 65°C and 80°C .

50 Since the high-pressure hydraulic circuits of the continuous casting plants for making steel billets are provided with heat-exchange systems which, under improper working conditions, do not allow thermostating the hydraulic fluid within a suitable temperature range above or below the pre-set temperature of 50°C , thus a hydraulic fluid should at least pass a test temperature of 75°C rather than of 60°C (which is the standard test temperature) in order to be considered sufficiently safe. This is particularly true when it comes to using such liquids in the hydraulic systems of coke furnaces since their hydraulic system is not provided

with heat exchangers.

In the light of the above outlined situation it is apparent that a need existed for an improved fire-resistant hydraulic fluid.

It is therefore the main object of the present invention to provide a less fire hazardous and less degradable hydraulic fluid. More specifically, the main object of the present invention is that of providing a hydraulic fluid with a better response to heat and flame under controlled conditions, said fluid being characterized by its capability of passing the above referred F.M. test method for spray flammability of hydraulic fluids at a test temperature higher than 60 °C, preferably at a test temperature higher than 75 °C.

According to the instant invention this object is achieved by providing a hydraulic fluid as defined in the claims.

According to the instant invention, a typical hydraulic fluid is made of at least a polyalkylene glycol (PAG), a no-phosphorus organic ester and an antioxidant.

Within the context of this invention, the expression "no-phosphorus organic ester" refers to organic esters which do not contain phosphorus in their molecule.

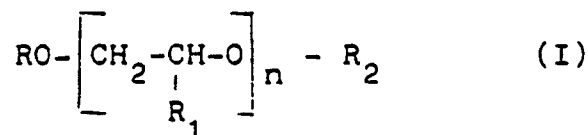
Depending on the specific use, said hydraulic fluid may further contain other additives such as e.g. anti-rust agents, anti-wear agents and viscosity index improvers.

All the above referred compounds are *per se* known in the art.

As it is known to the skilled artisan, PAGs are made by polymerizing or copolymerizing ethylene oxide, propylene oxide or/and isobutylene oxide. The copolymers can be random or block copolymers.

It is further known in the art that ethylene oxide (EO) polymers are water soluble, whereas propylene oxide (PO) polymers are not water soluble. Copolymers on the other hand will be more or less water soluble according to the amount of EO present in the copolymer molecule, whereas the oil solubility of the copolymer increases as the amount of PO increases.

The above referred EO and PO polymers and copolymers can be defined by the following formula:



where R is usually H, alkyl or aryl group

R₁ is usually H, -CH₃ or -C₂H₅

R₂ is usually H, so that :

- when R, R₁ and R₂ = H, the compound defined by the formula is polyethylene glycol (PEG); whereas
- when R = H and R₁ = -CH₃, the compound defined by the formula is a polypropylene glycol (PPG); and
- when R₁ = H or -CH₃ and R = R₂ = H, the compound defined by the formula is a copolymer.

The fire-resistant hydraulic fluid of the instant invention is preferably made using mixtures of PEGs and PPGs having a degree of polymerization of from 4 to 24.

According to the instant invention, PG polymers and/or mixtures thereof, wherein n, in the above referred formula (I) is ≥ 10, in which the ester component is soluble (with or without additives), are preferably used. It is preferred that the ester component yields perfectly homogeneous solutions at any ratio.

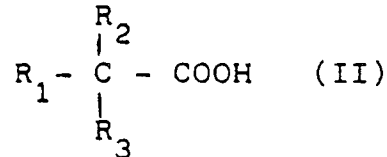
Suitable PAGs are e.g. Breox B-65-X as well as lower and higher homologues thereof. As it is known to those skilled in the art, the brand name Breox designates polyalkylene glycol fluids and lubricants manufactured by BP Chemicals, a branch of the British Petroleum Company Limited. Breox fluids and lubricants are designated by a three-part alpha-numeric symbol identifying the polymer type, viscosity and additive type. In particular the B-series are water insoluble lubricants for metal-to-metal lubrication. The number following the polymer designation represents the viscosity of the product in cS at 40 °C. The letter following the viscosity designation shows the presence of an additive which can be a special antioxidant, a rust inhibitor, an E.P. agent, or some other special purpose additive. (*)

(*) In particular the letter "X" denotes the presence of an antioxidant.

Examples of suitable monocarboxylic non-hindered fatty acids for preparing the ester component of the fire-resistant hydraulic fluids of this invention are represented by any natural or synthetic saturated or unsaturated fatty acid or mixtures thereof having from 10 to 24 carbon atoms, inclusive, such as e.g. capric acid, lauric acid, Δ⁹,10-dodecenoic acid, myristic acid, Δ⁹,10-tetradecenoic acid, pentadecanoic acid, palmitic acid, Δ⁹,10-hexadecenoic acid, margaric acid, stearic acid, oleic acid, linoleic acid, and mixtures thereof. It is to be understood that also dicarboxylic fatty acids can usefully be employed. Examples of such acids are represented e.g. by the following acids : succinic, adipic, sebacic, azelaic acid or mixtures thereof,

as well as phthalic, isophthalic acid, malic acid, fumaric acid and tetrahydrophthalic acid or mixtures thereof. According to the present invention it is also possible to use so-called hindered fatty acids. Hindered acids, also called neo-acids, are those acids having no hydrogen atoms bonded to the carbon atoms at the beta-position. Useful neo-alkyl acids have from 7 to 9 carbon atoms, such as e.g. 3,3-dimethylpentanoic acid, 3,3,6-trimethylpentanoic acid, 4,4-dimethylhexanoic acid, 4,4,5-trimethylhexanoic acid, and 5,5-dimethylhexanoic acid.

Also neo-acids and neo-alkanoic acids having from 5 to 20 carbon atoms, preferably those having from 5 to 10 carbon atoms, can be used, corresponding to the following formula



wherein

R_1 , R_2 and R_3 can be the same or different, each representing a (C_1 - C_6)-alkyl group, and R_2 , R_3 are preferably (C_1 - C_4)-alkyl groups, more preferably a methyl group.

Examples of preferred neo-alkyl acids are: 2,2-dimethyl propanoic, 2,2-dimethyl-butanoic, 2,2-dimethyl pentanoic, 2,2-dimethylhexanoic, and 2,2-dimethyl octanoic acid.

According to the instant invention, the esters suitable for admixing with the above defined PAGs may be made by reacting the carboxylic moiety of any of the above referred carboxylic acids or mixtures thereof with at least 2-3 or preferably all the hydroxyl groups of a hindered or non-hindered diol or mixtures thereof.

Concerning the carboxylic moiety, a neo-alkanoic structure is preferred.

According to the instant invention, the polyols suitable for preparing the ester component of the fire-resistant hydraulic fluid are hindered polyols having from 2 to 12 hydroxyl groups in their molecule. Preferred examples are represented e.g. by the following polyols: pentaerythritol, tetramethylol methane and/or polymers thereof (such as e.g. dipentaerythritol), trimethylolpropane, triethylolpropane, tributylolpropane. Also hindered diols such as e.g. neo-pentylglycol can be advantageously used.

Among the non-hindered diols which can be suitably used for making the inventive fire-resistant hydraulic fluids, those having from 2 to 40 carbon atoms are preferred.

As said above, the inventive fire-resistant hydraulic fluids consist of at least 3 components, viz. a PAG (as hereinabove defined) an ester (also as defined above) and an anti-oxidant.

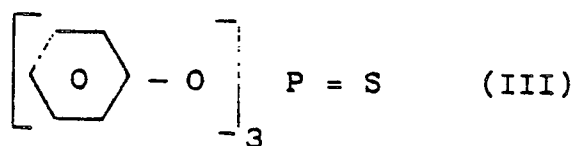
Useful anti-oxidants for making the inventive fluids are selected among the phenol derivatives, the aromatic amines as well as combinations of the two.

It is also important that products are chosen which do not darken severely. Suitable examples are represented e.g. by bisphenol-A, alpha-naphthylamine, diphenyl-alpha-naphthylamine and/or p,p'-di-ocetylphenylamine. Known anti-oxidants of this class are marketed under the trademark PARABAR. Preferably, p-cresol-di-tertiary butylates and/or hydroxytoluene butylates are used.

In order to prevent corrosion of the heat exchangers, which are made of copper and/or brass, an additive such as the one marketed under the trademark COBRATEC can be used but any other so-called metal deactivator can be added provided its solubility in the inventive fluid, within the required temperature range, is good.

Anti-wear agent compounds which do not contain active phosphorus are much preferred. Thus additives on the basis of zinc di-alkyl dithiophosphate (ZDDP) are excluded.

The product known as TPPT having the formula



contains only inactive phosphorus and can, therefore, be used, preferably in combination with the additive IRGALUBE 349 (IRGALUBE is a trademark owned by Ciba-Geigy, Switzerland).

The presence of an anti-rust agent may be required or useful. Compounds like e.g. glycol monooleate, sobitan, monooleate, dimers or trimers of oleic acid can be used. The above referred

IRGALUBE 349 besides inactivating the phosphorus contained in TPPT acts as anti-rust agent.

Another anti-rust agent which can be usefully employed is sold under the trademark LUBRIZOL 859.

Besides the above referred parameter relating to the spray flammability, there are other physico-chemical parameters which characterize a hydraulic fluid and which are useful information for the end-user.

5 The viscosity is obviously chosen to meet the machinery requirement. Preferred viscosity ranges of the inventive fire-resistant hydraulic fluid are typically from 10 to 1000 cS, more preferably of from 10 to 150 cSt.

10 In some cases the addition of viscosity index improving agents may be useful. As it is known in the art, these agents belong to either one of the following classes: 1) polymers on the basis of isobutylene and 2) acrylic copolymers. The polymers of the first class are relatively more oxidizable but have a higher shear resistance, whereas the agents of the second class are relatively less oxidizable but have a lower shear resistance.

According to the instant invention the polymers on the basis of isobutylene are preferred.

15 As referred above, hydraulic fluids must be stable under operating conditions. The performance may be assessed by the method indicated in parenthesis :

- a) Hydrolytic stability (ASTM D 2619)
- b) Air-separation capacity (ASTM D 892 or CEE LUX 5 Part III, 3-6)
- c) Water separation (ASTM D 1401)
- d) Foaming characteristics of lubricating oils (ASTM D 892)
- 20 e) Volume change of elastomeric materials in hydraulic fluids under static conditions (ASTM D 3604)
- f) Compatibility with varnishes (end-user agreed method)
- g) Corrosion resistance (CETOP/RP 48H CEE LUX 5 Part III, 3-8)
- h) Oxidability test (ASTM D 3893)

25 The lubricity of the inventive fire-resistant hydraulic fluids is rated by assessing the following parameters:

- i) Vickers test (DIN E 51389)
- ii) 4-ball wear (DIN 51350 or ASTM D 2266)
- iii) 4-ball EP (ASTM D 2783)
- iv) 4-ball wear (six hours)
- 30 v) FZG (DIN 51354)

35 It should be noted that the inventive fire-resistant hydraulic fluids, while being safer than the prior art fluids, in fact they all pass the spray flammability test at a temperature of from 75° to 85° C, they are also superior with respect to the above listed parameters. For instance, the lubricity test of the inventive fluids gives outstanding results. In fact, whereas in continuous casting steel plants a good fire resistant hydraulic fluid, i.e. one capable of meeting end-user requirements, should pass Stage 9 in DIN 51354, the inventive hydraulic fluids are capable of passing at least Stage 10.

40 Moreover, whereas the end-user specifications provide for a maximum weight loss of 60 mg on the ring and a maximum weight loss of 20 mg on the vanes (DIN E 51389 Vickers test), with the inventive hydraulic fluids the weight losses are significantly lower, viz. of from 12 to 9 mg on the ring and of from 8 to 6 mg on the vanes; typically weight losses of 9.5 mg and 6.4 mg, respectively, are obtained.

According to the instant invention, the organic ester is an ester mixture obtained by esterifying neopolyol mixtures (of the type described hereinabove) with fatty acids and neoacids (of the type described hereinabove).

45 More particularly, the esters suitable for making the inventive fire-resistant hydraulic fluid are prepared by the esterification of a neo-alkyl polyol having from 10 to 12 carbon atoms and from 2 to 6 hydroxyl groups and, preferably, not more than 7 carbon atoms and from 2 to 4 hydroxyl groups, such as, e.g. pentaerythrol, dipentaerythrol or 1,1,1-trimethylolalkanes from 5 to 7 carbon atoms, with straight chain carboxylic acids having from 4 to 12 carbon atoms or branched chain carboxylic acids having from 4 to 10 carbon atoms and a hindered neoalkaneic acid having from 5 to 20 carbon atoms, preferably from 5 to 10 carbon atoms.

50 The esterification of the neo-alkylpolyol with the straight or branched chain neo-alkyl acid is carried out using a mole ratio of the neo-alkyl polyol over the straight or branched acid and the neo-alkyl acid of 1 : (1.5 to 2) : (3 to 8) and it is allowed to proceed at 80 + 90% depending upon the quantity of water formed during the reaction.

55 At this point the unreacted acids are distilled off, preferably at low pressure.

After the removal of the unreacted acids, in order to complete the reaction there is added a sufficient quantity of straight chain carboxylic acids having from 4 to 12 carbon atoms. The esterification is preferably carried out in the presence of an inert gas, such as nitrogen, at a temperature of from 150° to 220° C and

in the presence of a solvent to facilitate the mixing in the first esterification step and to facilitate the removal of the water by azeotrope formation.

Xylene is employed as the solvent; also other aliphatic solvents of equal distillation properties may be used.

5 If the final product is to be purified, it is subjected to distillation at reduced pressure by removing the excess acidity. Subsequently, it is neutralized by means of an aqueous Na_2CO_3 solution and wash water.

The solution is then dried at reduced pressure and filtered to yield a clear product.

The present invention will now be further illustrated by way of the following examples which are not to be construed in a restrictive manner, as the skilled artisan may obviously modify and adapt these examples to render them more suitable for his specific needs, without any inventive effort on his part and without
10 departing from the scope of the instant invention.

Example 1: Neoheptanoate/pentaerythritol-n-caproate.

15

In a round bottom, 4-necked 2 l glass vessel provided with mechanical stirrer, thermometer, reflux condenser (or vacuum pump connecting means) and water trap, 2 moles (272 g) of pentaerythritol are added with 4 moles (464 g) of n-caproic acid and 8 moles (1040 g) of neoheptanoic acid and 200 g xylene. Thereafter, the reaction mixture is refluxed at $160^\circ - 175^\circ \text{C}$ until 122 ml (84.6%) reaction water is collected
20 (about 43 hours). Then the reflux condenser is disconnected and the reaction vessel is connected to the vacuum pump for removing the unreacted organic acid. The reflux condenser is then reconnected. 115 g (approx. 1 mole) n-caproic acid and 100 g xylene are added. The esterification reaction is then continued by refluxing at $175^\circ - 177^\circ \text{C}$ and until the formation of reaction water has come to an end.

Subsequently, the ester mixture is distilled under reduced pressure for removing the residual acid and then washed with a 5% Na_2CO_3 aqueous solution. The ester mixture is then added with 6 g sodium borohydride (NaBH_4) and 100 ml 0.1N NaOH and stirred for 20 hours at $50^\circ - 60^\circ \text{C}$ under nitrogen
25 atmosphere.

After cooling and separation of the water layer, the latter is discarded and the ester mixture is dissolved in xylene and washed 2 times with distilled water.

30 The so purified ester solution is desiccated under reduced pressure (1 mm Hg) and the residue is treated with 50 g infusorial earth for 2 hours at $100^\circ - 110^\circ \text{C}$ and finally filtered on diatomaceous earth. 940g of the title compound in the form of a pale yellow viscous liquid is obtained.

35

Physico-chemical characteristics:	
kinematic viscosity at 210°F (98.88°C)	approx. 5 cSt
kinematic viscosity at 100°F (37.78°C)	approx. 30 cSt
pour point	-75°F (approx. -59°)
appearance, after 60 hours	clear liquid

40

Example 2: Trimethylpropane-2,2-dimethyl-hexanoate.

45

Into a 1 l 4-necked glass vessel provided with stirrer, thermometer, reflux condenser (or vacuum pump connecting means) and water trap, are poured 54 g (0.4 mole) trimethylolpropane, 180 g (1.25 moles) 2,2-dimethylhexanoic acid and 100 g xylene. The reaction mixture is then stirred and refluxed for 28 hours at $161^\circ - 168^\circ \text{C}$, whereupon 20 ml reaction water is collected. The reaction vessel is then connected to a
50 vacuum pump (1 mm Hg) in order to remove the xylene (180°C , azeotrope) and the unreacted acid.

The residue is then dissolved in hexane and washed 3 times with a 5% Na_2CO_3 aqueous solution and then once only with distilled water.

After separation of the washing water, the reaction mixture is heated to 130°C and subjected to reduced pressure (1 mm Hg) and thereafter filtered with diatomaceous earth.

55

190 g of the title compound in the form of a pale yellow viscous liquid is obtained.

Physico-chemical characteristics:	
kinematic viscosity at 210 ° F (98.88 ° C)	6.8 cSt
kinematic viscosity at 100 ° F (37.78 ° C)	65.6 cSt
pour point	- 25 ° F (approx. - 31 ° C)
saponification number (mg KOH/g) :	315
acidity number (mg KOH/g) :	0.08
corrosion index :	22.4

10

Example 3: Pentaerythritol-2,2-dimethylpentanoate.

15

Into a 1 l 4-necked glass vessel provided with stirrer, thermometer, reflux condenser (or vacuum pump connecting means) and water trap are poured 38 g (0.28 mole) pentaerythritol, 160 g (1.21 moles) dimethylpentanoic acid and 60 g xylene. The reaction mixture is then stirred and refluxed at 168 ° -210 ° C for 32 hours to collect 21 ml of reaction water. The lateral tube is disconnected from the vessel which is connected to a vacuum pump (1 mm Hg) and heated to 173 ° C. The residue is dissolved in xylene and washed two times with a 5% Na₂CO₃ solution. It is then washed two times with distilled water. The washed ester is then desiccated at 165 ° C. By applying a reduced pressure of 1 mm Hg, 144 g of a viscous ester is obtained.

20

25

Physico-chemical characteristics:	
kinematic viscosity at 210 ° F (98.88 ° C)	approx. 14 cSt
kinematic viscosity at 100 ° F (37.78 ° C)	approx. 277 cSt
pour point	- 10 ° F (appr. - 2
saponification number (mg KOH/g)	355

30

Example 4 : Trimethylol-tallowate

Into a 1 l 4-necked glass vessel provided with stirrer, thermometer, reflux condenser (or vacuum pump connecting means) and water trap are poured 100 g tallow fatty acids and 14 g (0.12 mole) trimethylolmethane and stirred. Thereafter the reaction mixture is heated under nitrogen bubbling from the bottom of the reaction vessel in order to remove, from the reaction mass, the water vapour produced by the esterification. The reaction mixture is kept under constant stirring for 8 hours at a temperature of from 250 ° to 260 ° C. The reaction is completed when the acidity number reaches a value equal or lower than 1 or after approx. 6.5g water has been collected in the water trap.

40

45

The end product is of a brownish colour, of clear appearance at ≥ 25 ° C

Physico-mechanical characteristics:	
kinematic viscosity at 104 ° F (40 ° C)	40 ÷ 45 cSt
acidity number (mg KOH/g)	1
saponification number (mg KOH/g)	≥ 180

50

55

Example 5 : Methylolmethane-trioleate

Proceeding in the same manner as described in Example 4 but using 0.35 mole oleic acid in lieu of the tallow fatty acids

The end product is of a dark straw colour, of clear appearance at $\geq 8^\circ\text{C}$.

Physico-chemical characteristics:	
kinematic viscosity at 104°F (40°C)	$30 \div 38$ cSt
acidity number (mg KOH/g)	1
saponification number (mg KOH/g)	≥ 180

Example 6 : Pentaerythritol-tetraoleate

Into a 4-necked 1 l glass vessel provided with stirrer, thermometer, reflux condenser (or vacuum pump connecting means) and water trap are poured 100 g (0.35 mole) oleic acid, 12 g (0.088 mole) pentaerythritol, 0.1 g $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ catalysts and 100 g xylene. The reaction mixture is then stirred and heated at the reflux temperature of the xylene for 8 hours so as to remove the reaction water by means of azeotrope formation. The reaction is completed when the acidity number reaches a value equal or lower than 1 or after 6.2 g water has been collected in the trap.

The end product is of a brownish colour and consists essentially of pentaerythritol-tetraoleate.

Physico-chemical characteristics:	
kinematic viscosity at 104°F (40°C)	$110 \div 150$ cSt
acidity number (mg KOH/g)	1
saponification number (mg KOH/g)	≥ 200

In the following examples the preparation of the inventive fire-resistant hydraulic fluid is illustrated. Except when expressly stated otherwise, the quantities of the reactants are indicated in parts per weight.

Example 7	
Breox B65X	88
Pentaerythritol-tetraoleate(Ex.6)	10
Hydroxytoluene butylate	0.2
Cobratec	0.04
Irgalube TPPT	1
Irgalube 349	1

The listed components are added into a reaction vessel in the above referred order and mixed thoroughly at a temperature of from 40°C to 50°C for $\frac{1}{2}$ hour.

Physico-chemical characteristics (ranges)	
specific weight at 68 ° F (20 ° C)	0.950 ÷ 0.990
kinematic viscosity at 104 ° F (40 ° C)	60 ÷ 70 cSt
acidity number (mg KOH/g)	3 ÷ 4
saponification number (mg KOH/g)	15 ÷ 20
Cleveland open cup flash point	≥ 300
Test results	
FZG test (DIN 51354)	exceeding Stage 10
Vickers test (DIN 51389) :	loss on the ring : 9.5 mg loss on the vanes: 6.4 mg

The inventive fire-resistant hydraulic fluid shows two absorption bands in the infrared, viz.
 1710 ÷ 1720 cm⁻¹ (not very pronounced peak)
 1080 ÷ 1100 cm⁻¹ (very pronounced peak)

Example 8	
Breox B65X	88
Neoheptanoate/pentaerythritol-n-caprate (Ex.1)	10
Hydroxytoluene butylate	0.2
Cobratec	0.04
Irgalube TPPT	1
Irgalube 349	1

The listed components are added into a reaction vessel in the above referred order and mixed thoroughly at a temperature of from 40 to 50 ° C for ½ hour.

Physico-chemical characteristics(ranges):	
specific weight at 68 ° F (20 ° C)	0.950 ÷ 0.990
kinematic viscosity at 104 ° F (40 ° C)	60 ÷ 70 cSt
acidity number (mg KOH/g)	3 ÷ 4
saponification number (mg KOH/g)	20 ÷ 35
Cleveland open cup flash point	≥ 300 ° C

Example 9	
Breox B-65X	59.5
Dow Pol P 1200 (propylene oxide polymer having a MW of appr.1200)	15
Dow Pol E 600 (ethylene oxide polymer having a MW of app.600)	3
Trimethylpropane-2,2-dimethylhexanoate (Ex.2)	18
Trimethylol-tallowate (Ex.4)	2
Hydroxytoluene butylate	0.2
Cobratec	0.04
Irgalube TPPT	1
Irgalube 349	1.5

The listed components are added into a reaction vessel in the above referred order and mixed thoroughly at a temperature of 50 ° to 60 ° C for ½ hour.

Physico-chemical characteristics (ranges):	
specific weight at 68 ° F (20 ° C)	0.950 ÷ 0.990
kinematic viscosity at 104 ° F (40 ° C)	60 ÷ 70 cSt
acidity number (mg KOH/g)	3 ÷ 4
saponification number (mg KOH/g)	20 ÷ 35
Cleveland open cup flash point	≥ 300 ° C

Example 10	
Dow Pol P 1200	77
Pentaerythritol-2,2-dimethylpentanoate (Ex.3)	20
Hydroxytoluene butylate	0.2
Cobratec	0.04
Irgalube TPPT	1
Lubrizol 859	2

The listed components are added in a reaction vessel in the above referred order and mixed thoroughly at a temperature from 40 ° to 50 ° C for ½ hour.

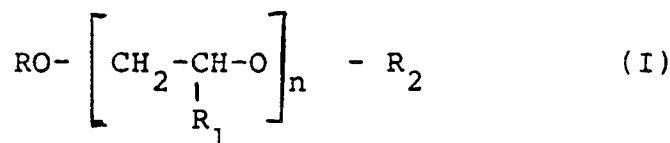
Physico-chemical characteristics (ranges):	
specific weight at 68 ° F (20 ° C)	0.950 ÷ 0.990
kinematic viscosity at 104 ° F (40 ° C)	60 ÷ 70 cSt
acidity number (mg KOH/g)	3 ÷ 4
saponification number (mg KOH/g)	30 ÷ 40
Cleveland open cup flash point	≥ 300 ° C

A homogenous mixture of a slightly strawy colour is obtained.

Claims

1. A fire-resistant hydraulic fluid having a high degree of flame propagation resistance, a lubricity adequate to the operating conditions existing in hydraulic systems, a high operational stability, and of low toxicity characterized by the fact that it contains

(i) at least a polyalkylene glycol of formula



wherein R is a hydrogen atom, an alkyl group or an aryl group,

R₁ is a hydrogen atom, -CH₃ or -C₂H₅,

R₂ is a hydrogen atom, and is an integer from 4 to 24,

(ii) a no-phosphorus organic ester, capable of yielding homogeneous solutions at any ratio, and

(iii) an antioxidant chosen among the phenyl derivatives, the aromatic amines or consisting of a mixture thereof, further characterized by the capability of passing the Factory Mutual Research Corporation Fire Resistivity Test for spray flammability at a test temperature equal to or higher than 75 ° C.

2. A fire-resistant hydraulic fluid according to claim 1, characterized in that it further contains

- (i) a corrosion inhibiting agent or a metal deactivator,
- (ii) an anti-wear agent free of active phosphorus and,
- (iii) an anti-rust agent.

3. A fire-resistant hydraulic fluid according to claim 1, characterized in that the polyalkylene glycol component is a mixture of polyethylene glycols and polypropylene glycols having a degree of polymerization of from 4 to 24.

4. A fire-resistant hydraulic fluid according to claim 1, characterized in that the polyalkylene glycol component consists of propylene and ethylene oxide polymers of formula (I), wherein n is an integer equal to or greater than 10.

5. A fire-resistant hydraulic fluid according to claim 1, characterized in that the ester component thereof is the reaction product of

(i) at least a neo-alkyl polyol having from 10 to 12 carbon atoms and from 2 to 6 hydroxy groups in its molecule, with

(ii) at least a straight chain carboxylic acid having from 4 to 12 carbon atoms in its molecule, or a branched chain carboxylic acid having from 4 to 10 carbon atoms in its molecule and a hindered neo-alkaneic acid having from 5 to 20 carbon atoms in its molecule.

6. A fire-resistant hydraulic fluid according to claim 4, characterized in that for making the ester component a 1,1,1-trimethylol-alkane having from 5 to 7 carbon atoms in its molecule is used.

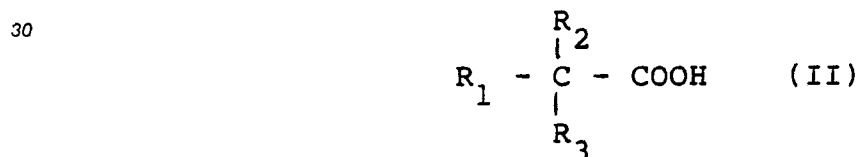
7. A fire-resistant hydraulic fluid according to claim 1, characterized in that the ester component is the reaction product of

(i) at least 1 carboxylic non-hindered saturated or unsaturated fatty acid having from 10 to 24 carbon atoms in its molecule, with

(ii) at least 2-3, or preferably all the hydroxyl groups of an hindered or a non-hindered diol or mixtures thereof.

8. A fire-resistant hydraulic fluid according to claim 1, characterized in that the ester component thereof consists of the reaction product of

(i) at least 1 neo-acid or neo-alkanoic acid having from 5 to 20 carbon atoms in its molecule, corresponding to the formula



wherein R_1 , R_2 and R_3 , which can be the same or different, each representing a (C_1-C_6) -alkyl group, and with

(ii) at least a neo-alkyl polyol having from 10 to 12 carbon atoms and from 2 to 6 hydroxyl groups in its molecule.

9. A fire-resistant hydraulic fluid according to claim 8, characterized in that the substituents R_2 and R_3 in the formula (II) acid each represents a methyl group.

10. A fire-resistant hydraulic fluid according to any one of claims 7 to 9, characterized in that for making the ester component at least a polyol is used which has from 2 to 12 hydroxyl groups in its molecule.

11. A fire-resistant hydraulic fluid according to any one of claims 7 to 9, characterized in that for making the ester component at least a non-hindered diol is used which has from 2 to 40 carbon atoms in its molecule.

12. A process for making a fire-resistant hydraulic fluid according to any of claims 1 or 2, characterized in that the components thereof are thoroughly mixed at a temperature of from 40° to 50° C.

13. A process for making the no-phosphorus organic component for making a fire-resistant hydraulic fluid according to any of claims 1 or 2, characterized by the fact that a neo-alkyl polyol is reacted, in the presence of a chemically inert gas, at a temperature of from 150° to 220° C, and in the presence of a solvent, with a straight or branched chain neoalkyl acid, using a mole ratio of the neo-alkyl polyol over the straight or branched chain acid, and the neo-alkyl acid of from 1 : (1.5 to 2) : (3 to 8), and the reaction is allowed to proceed up to an 80-90% reaction rate, depending upon the quantity of water formed during said reaction, and the unreacted acids are distilled off, whereupon said reaction is completed by adding a sufficient amount of straight chain carboxylic acids having from 4 to 12 carbon atoms in their molecule.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 017 072 (THE DOW CHEMICAL CO.) * Page 2, line 19 - page 6, line 9; page 6, example 1 *	1,3,4,7 ,10,12	C 10 M 169/04 // (C 10 M 169/04 C 10 M 105:38 C 10 M 107:34 C 10 M 129:10 C 10 M 129:38 C 10 M 129:76 C 10 M 133:12 C 10 M 137:10) C 10 N 30:00 C 10 N 40:08
A	GB-A-1 025 294 (ESSO RESEARCH & ENGINEERING CO.) * Claims 1,5,6-8 *	1,5-10	
A	US-A-4 234 497 (M.L. HONIG) * Column 2, line 28 - column 3, line 18 *	1,5-10	
A	GB-A-2 063 909 (MOBIL OIL CORP.) * Page 1, lines 3-28; page 1, lines 57,58 *	1,2,7, 10	
A	US-A-4 645 615 (H.N. DRAKE) * Column 1, lines 4-6; column 2, lines 34-46; column 3, lines 29-34 *	1,2,7, 10	
A	EP-A-0 011 730 (BASF AG) * Page 2, line 23 - page 3, line 35; page 5, lines 1-10 *	1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 263 159 (G. BERENS) * Column 3, line 60 - column 4, line 10; column 5, line 59 - column 6, line 15; column 7, lines 14-67 *	1,2,7, 11	C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-11-1989	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			