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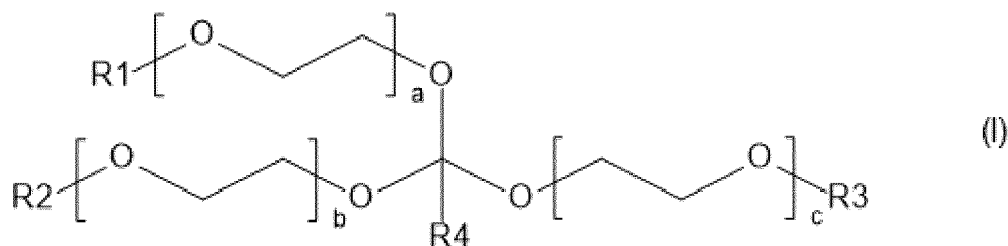
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(54) **LOW VISCOSITY FUNCTIONAL FLUID COMPOSITION**

(57) This invention relates to a functional fluid, comprising

(A) from 8 to 80% by weight, based on the total composition, of one or more ortho-ester according to formula (I)



wherein

R1, R2, R3

are independently selected from H or C₁ to C₈ alkyl groups, preferably methyl or butyl,

R4

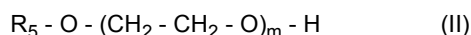
means H or C₁ to C₈ alkyl, preferably H or methyl,

a, b, c

are independently numbers from 0 to 6, preferably 3 or 4,

with the proviso that a+b+c is at least 1,

(B) from 10 to 87% by weight, based on the total composition, of one or more alkoxy glycol according to formula (II)



wherein

R₅

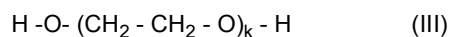
is a C₁ to C₈ alkyl residue,

m

is a number from 2 to 6,

EP 4 056 669 A1

(C) from 0 to 20 wt.-% of at least one compound according to formula (III)



wherein k is a number of 2 or higher, with the proviso that in at least 80 wt.-% of all compounds according to formula (III) k is 2 or 3,

(D) at least one additive, selected from the group consisting of corrosion inhibitor, alkalinity agents, aging protection agents, defoamers and lubricants,

the fluid comprising at most 3 wt.-% of an ester between boric acid and a glycol or polyglycol compound, and with the proviso that the combined amount of component (A) and component (B) adds up to at least 70 % of the total fluid weight.

(52) Cooperative Patent Classification (CPC): (Cont.)

C-Sets

C10M 2209/1045, C10M 2209/1085

Description

[0001] The present invention relates to a low viscosity functional fluid composition comprising a mixture of alkyl polyglycols, polyglycols and additives, the fluid being virtually free of boric acid esters of glycols or alkyl polyglycols. The fluid exhibits a low temperature kinematic viscosity of less than 900 centistokes, determined at -40°C, exhibits an equilibrium reflux boiling point (ERBP) of at least 250°C and a wet equilibrium reflux boiling point (WERBP) of at least 165°C, according to the methods described in the Federal Motor Vehicle Safety Standards (FMVSS) No 116.

[0002] The low viscosity functional fluid composition according to the present invention is useful in a variety of applications and in particular as a brake fluid, especially for new electronic or automated anti-lock brake systems which require lower viscosity fluids for satisfactory operation at low temperatures.

[0003] Functional fluid compositions based on borate esters are well known in the art. To be useful for example as DOT 4 or DOT 5.1 brake fluids, these borate ester based compositions must meet stringent physical properties and performance requirements particularly with respect to minimum dry equilibrium reflux boiling point ("ERBP"), minimum wet equilibrium reflux boiling point ("WERBP") and maximum low temperature kinematic viscosity (e.g. determined at -40°C) while maintaining adequate resistance to corrosion, stability and meeting other physical property requirements such as pH, reserve alkalinity, corrosion protection and rubber swelling.

[0004] While borate esters are advantageous to meet the DOT 4 and DOT 5.1 criteria according to Federal Motor Vehicle Safety Standards (FMVSS) No 116, especially a very high wet boiling point (wERBP), borate containing brake fluids are associated with problems. Federal Motor Vehicle Safety Standards (FMVSS) No 116 refers to 49 CFR § 571.116 in the 10-1-2016 edition and will be referred to as FMVSS in this specification.

1. Boric acid is known to be a CMR-compound (repro tox category 1). Therefore, also its esters are suspect to similar health threat (currently classified as repro tox category 2) and, therefore of potential danger during handling/filling of the brake fluid.

2. Borate-esters of alkyl glycols are more hygroscopic compared to the sole alkyl glycols, resulting in an elevated water uptake from moisture of borate-containing brake fluids, which is undesired during storage and use.

3. The content of boron in the brake fluids is associated with a certain risk of gel formation or precipitation due to salt formation of the inorganic character of boron salts, especially upon ageing of the brake fluids. As a result, particles may occur in the brake fluid and limit its performance in critical situations.

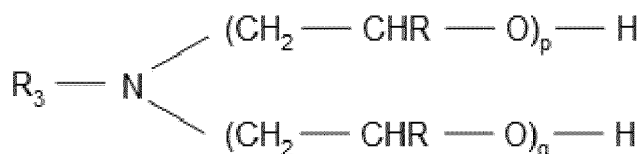
[0005] WO-00/65001 describes hydraulic fluids comprising alkoxy glycol borate esters, alkoxy glycols and corrosion inhibitors, additionally containing cyclic carboxylic acid derivatives.

[0006] WO-02/38711 describes low viscosity functional fluid compositions comprising alkoxy glycol borate esters, alkoxy glycol components and additives such as corrosion inhibitors, wherein the alkoxylation degrees of the alkoxy glycol borate esters and the alkoxy glycols are restricted to a certain narrow pattern.

[0007] US-4371448A teaches a hydraulic fluid which formally fulfils the specification DOT 5. This hydraulic fluid essentially consists of (A) about 20 to 40% by weight of at least one boric acid ester obtained from orthoboric acid, diethylene glycol and an ethylene glycol monoalkyl ether; (B) 30 to 60% by weight of at least one ethylene glycol monoalkyl ether; (C) 10 to 40% by weight of at least one bis-(ethylene glycol monoalkyl ether)-formal; (D) 0.1 to 5% by weight of at least one alkylamine; and (E) 0.05 to 5% by weight of at least one stabilizer and/or inhibitor; the percentages by weight in each case being relative to the total weight of the fluid.

[0008] EP-0750033A1 teaches a hydraulic fluid composition, especially a brake fluid composition, based on a boric ester of a glycol ether and comprising a corrosion-inhibiting system which includes: (1) at least one constituent (A) chosen from fatty amines or the salts of one or more carboxylic acids with the said amines, and (2) at least one constituent (B) chosen from the products resulting from the reaction of one or more carboxylic fatty acids with a polyoxyalkylene glycol, or from the transesterification reaction of one or more esters of carboxylic fatty acids with a polyoxyalkylene glycol.

[0009] EP-0617116A1 teaches a hydraulic fluid composition having a high boiling point, in particular a high equilibrium reflux boiling point and a low viscosity. The composition contains, as additive, at least one ether amine having a molecular weight between 120 and 300 and having the formula



in which

R_3 is linear or branched radical having at least one ether functional group and no alcohol functional group,

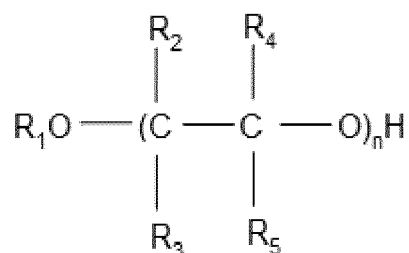
R is a methyl radical or a hydrogen atom,

p is an integer from 1 to 3 and

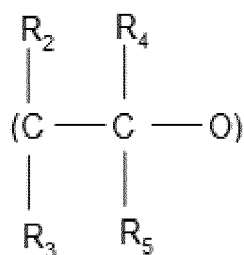
q is an integer from 0 to 2.

[0010] WO-2012/003117A1 discloses a functional fluid composition comprising

(i) an alkoxy glycol mixture in an amount of about 38% to 47% by weight of the functional fluid composition, where the alkoxy glycol mixture is comprised alkoxy glycols having the formula



with repeat unit:



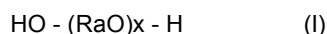
wherein

each of R_1 , R_2 , R_3 , R_4 , R_5 is either hydrogen (H) or an alkyl group containing 1 to 8 or more carbon atoms or mixtures thereof, wherein said mixture has a first alkoxy glycol component in an amount of about 36% to about 73% by weight of said mixture where $n = 3$, a second alkoxy glycol component from 17% to about 43% by weight of said mixture where $n = 4$, and a third alkoxy glycol component in an amount from about 2% to about 10% by weight of said mixture where n is greater than or equal to 5 and

(ii) a glycol borate ester in an amount of about 53% to 62% by weight of the functional fluid composition.

[0011] EP-A-0129240 teaches hydraulic fluids with a boron content of from 0 to 1% by weight, and consisting essentially of

a) 2 - 40% by weight, of an alkylene glycol of general formula (I):

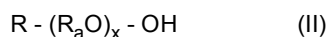


wherein

R_a is an alkylene radical having from 2 to 3 carbon atoms, and

x is an integer between 1 and 3;

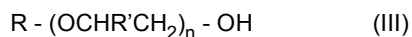
b) 15 - 65% by weight, referred to the total weight of the fluid, of an alkylene glycol mono alkylether of general formula (II);



wherein

R_a and x have the above indicated meanings, and
 R is a C_1 - C_4 alkyl;

c) 15 - 55% by weight, referred to the total weight of the fluid, of at least one poly alkylene glycol mono alkylether of general formula (III)



wherein

R is a C_1 - C_4 alkyl;
 R' is H or CH_3 and
 n is an integer whereby the molecular weight of the compound will be between 208 and 1000;

d) 0 - 54% by weight, referred to the total weight of the fluid, of the reaction product of H_3BO_3 with the alkylene glycols of formula (I), in a molar ratio of 1 : 1.5 - 3;

e) 0 - 10% by weight, referred to the total weight of the fluid, of at least one inhibitor.

[0012] DE-3627432 teaches a brake fluid based on glycols and glycol ethers, consisting essentially of

A) 30 to 80% by weight, based on the total weight of the brake fluid, of a glycol component, consisting of

a) 0 to 80% by weight diethylene glycol and / or dipropylene glycol and

b) 20 to 100% by weight of triethylene glycol, tripropylene glycol, tetraethylene glycol and / or tetrapropylene glycol, percent by weight based on the mixture of these glycols,

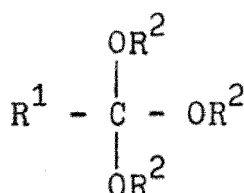
B) 20 to 70% by weight, based on the total weight of the brake fluid, of a glycol ether component, consisting of

a) 10 to 100% by weight-% of at least one glycol dialkyl ether of the following formula $R - (OAlk_1)_x - OR_1$, in which R and R_1 are an alkyl group with 1 to 4 C atoms, Alk_1 is the ethylene or a propylene group and x is an integer from 3 to 6, and

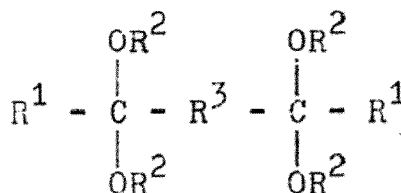
b) 0 to 90 wt.-% of at least one glycol monoalkyl ether of the following formula $R_2 - (OAlk_2)_y - OH$, in which R_2 is an alkyl group with 1 to 4 carbon atoms, Alk_2 is the ethylene or a propylene group and y is an integer from 2 to 4, percent by weight based on the mixture of these glycol ethers, and

C) 0 to 5% by weight, based on the total weight of the brake fluid, of at least one inhibitor for fluids based on glycol and glycol ethers, with the proviso that at least 14% by weight in the brake fluid of the glycol component b) are contained, weight percent based on the total weight of the brake fluid.

[0013] GB-1330468 describes brake fluid compositions containing orthoesters of the formulae A and B in combination with polyoxyalkyleneglycol esters of dicarboxylic acids and/or alkyl esters of glycols or polyglycols



A



B

[0014] Such compounds were applied in 10 wt.-% in base fluid, consisting of mainly conventional esters, such as propionates and nylonates and minor amounts of alkyl glycols. The addition of 10% of various ortho esters resulted in a less pronounced reduction of boiling point in the presence of 1 wt.-% water (minus 69°C and less, compared to -100°C reduction in the absence of ortho esters). Yet, the impact on water uptake and in the standardized WERBP test according to FMVSS no. 116 was not known. In addition, the viscosity of the functional fluids according to Castrol GB-1330468 was rather high with around 1700 cSt at -40°C.

[0015] There is a strong demand for improved high performance hydraulic fluid compositions and brake fluids having low temperature viscosity at -40°C while meeting or exceeding at the same time the minimum ERBP and especially the WERBP temperature requirements, as fulfilled by the hydraulic fluid compositions and brake fluids commonly used.

[0016] Examples of borate-free brake fluids are described in the literature

1.) DOT3/class 3 fluids, which are in general of a lower ERBP, lower WERBP and higher viscosity at -40°C), according to FMVSS.

2.) GB-1330468 (Castrol) discloses borate-free brake fluids, containing ortho esters in combinations with poly oxy-alkylene glycol ether-ester of dicarboxylic acids and/or alkyl ester of glycols or polyglycols and minor amounts of alkylglycols. Such combinations suffer from elevated viscosity at -40°C and the WERBP was not investigated.

3.) DE-3627432C2 (Hoechst) and US-2006/0264337 (BASF) disclose diethylene/triethylene glycol and dipropylene glycol based brake fluids, fulfilling just the minimum requirement of DOT 4 and ISO 4925 class 4 norm.

4.) WO-2007/005593A2 (DOW) describes compositions of brake fluids containing 0-10 wt.-% of borate ester and the use of larger quantities of butoxy-glycols, mainly butoxy-triglycol.

5.) EP-0129240A1 (Montedison S.p.A.) discloses borate-free brake fluid formulations consisting of min. 30 wt.-% diethylene glycol or higher glycols but suffering from elevated viscosity at -40°C.

[0017] These developments allow for high ERBP but suffer from a still too high viscosity at -40°C and from a low WERBP. The problem to be solved by the instant invention is to provide a hydraulic fluid having the properties mentioned below and being essentially or entirely borate free.

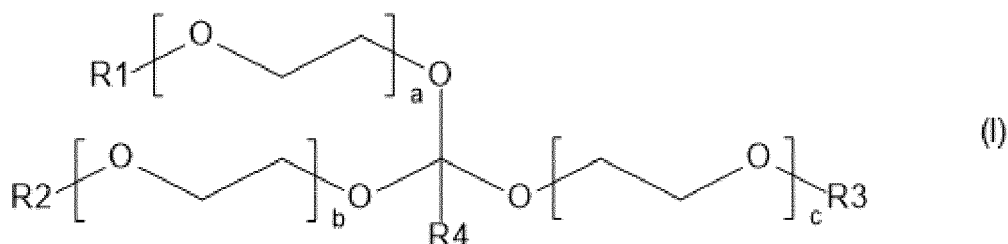
	GB-1330468 (Castrol) mixture 1	WO- 2007/005593 (DOW)	US- 2006/0264337 (BASF) "BF1"	DE- 3627432 (Examples)	EP- 0129240 Example 1	Target of the present invention
ERBP [°C]	310	270	251	237-277	250	min. 250
WERBP [°C]	Not studied	145	159	144-158	161	min. 165
Viscosity at -40°C [cSt]	1694	859	1393	1000-1450	1276	max. 900

[0018] Yet, a borate-free composition, fulfilling these criteria is not known.

[0019] According to the present invention, a functional fluid composition being essentially free from borates has been found which exhibits superior values of ERBP and of WERBP and for low temperature kinematic viscosity, while maintaining excellent resistance to corrosion, high stability and meeting other physical property requirements such as pH, reserve alkalinity and rubber swell. Especially very high WERBP values are achieved by using ortho esters as a replacement for borate esters.

[0020] In a first aspect, this invention relates to a functional fluid, comprising

(A) from 8 to 80% by weight, based on the total composition, of one or more ortho-ester according to formula (I)



wherein

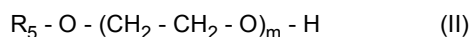
$\text{R}_1, \text{R}_2, \text{R}_3$ are independently selected from H or C_1 to C_8 alkyl groups, preferably methyl or butyl,

R_4 means H or C_1 to C_8 alkyl, preferably H or methyl,

a, b, c are independently numbers from 0 to 6, preferably 3 or 4,

with the proviso that $a+b+c$ is at least 1,

(B) from 10 to 87% by weight, based on the total composition, of one or more alkoxy glycol according to formula (II)

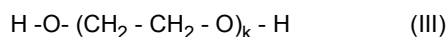


wherein

R_5 is a C_1 to C_8 alkyl residue, preferably methyl or butyl,

m is a number from 2 to 6, preferably 3 or 4,

(C) from 0 to 20, preferably 8 - 18 wt.-% of at least one compound according to formula (III)



wherein k is a number of 2 or higher, with the proviso that in at least 80 wt.-% of all compounds according to formula (III) k is 2 or 3,

(D) at least one additive, selected from the group consisting of corrosion inhibitor, alkalinity agents, aging protection agents, defoamers and lubricants,

the fluid comprising at most 3 wt.-% of an ester between boric acid and a glycol or polyglycol compound, and with the proviso that the combined amount of component (A) and component (B) adds up to at least 70 % of the total fluid weight.

[0021] In a second aspect, this invention provides the use of the functional fluid of the first aspect as a brake fluid for vehicular brakes.

[0022] In a third aspect, this invention provides for a method of operating a vehicular brake that transmits braking force through a hydraulic system, the method comprising filling the hydraulic system with a functional fluid according to the first aspect.

[0023] The functional fluid will be referred to as fluid in the following.

Component (A) - Orthoester

[0024] The orthoester used as component (A) corresponds to one or more components according to formula (I).

[0025] In formula (I), $\text{R}_1, \text{R}_2, \text{R}_3$ are independently selected from H or C_1 to C_8 alkyl groups preferably from H or C_1 to C_4 alkyl groups. In a preferred embodiment, $\text{R}_1, \text{R}_2, \text{R}_3$ are independently selected from methyl or butyl. In a more preferred embodiment, $\text{R}_1, \text{R}_2, \text{R}_3$ mean methyl. In a preferred embodiment, only one out of $\text{R}_1, \text{R}_2, \text{R}_3$ takes the meaning of H. In another preferred embodiment, the amount of orthoester according to formula (I) wherein at least one of $\text{R}_1, \text{R}_2, \text{R}_3$ takes the meaning H is less than 30 wt.-%, more preferably less than 15 wt.-%, particularly less than 10 wt.-%, on a basis of 100 wt.-% being the total amount of all orthoester according to formula (I). In a preferred embodiment, the orthoester used as component (A) corresponds to two or more components according to formula (I).

[0026] It is preferred, that the two or more orthoesters of formula (I) differ in one out of $\text{R}_1, \text{R}_2, \text{R}_3$. This may mean e.g. that one out of $\text{R}_1, \text{R}_2, \text{R}_3$ is methyl in one of the orthoesters, and one out of $\text{R}_1, \text{R}_2, \text{R}_3$ is butyl in the other of the

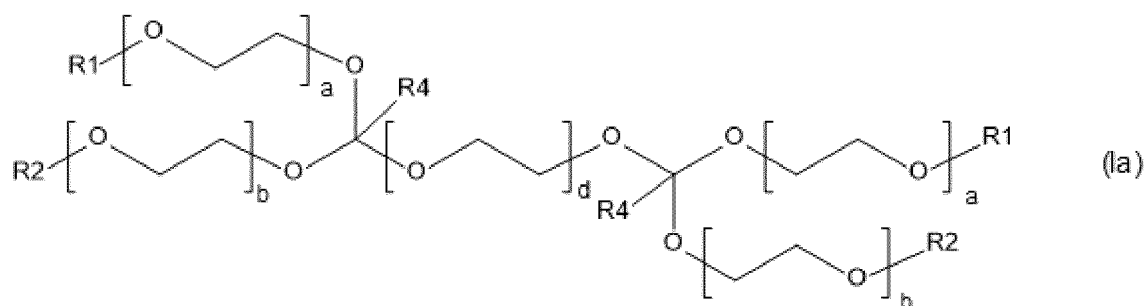
orthoesters.

[0027] In formula (I), R4 means H or C₁ to C₈ alkyl. In a preferred embodiment, R4 means H or methyl.

[0028] In formula (I), a, b, c are independently numbers from 0 to 6, with the proviso that a+b+c is at least 1, i.e. not all of a, b, c may equal zero. In a preferred embodiment, a, b, c are independently 3 or 4. In another preferred embodiment, a+b+c is at least 3, more preferably at least 6. In a preferred embodiment, the orthoester used as component (A) corresponds to two or more components according to formula (I). It is preferred, that the two or more orthoesters of formula (I) differ in one out of a, b, c., meaning that a, b, c are not all the same in the two or more orthoesters. For example, one out of a, b, c may be 3 in one of the orthoesters, and one out of a, b, c may be 4 in the other of the orthoesters.

[0029] The orthoester should be clear, homogeneous, and substantially free of salt or suspended components, e.g. such as residues of insoluble catalysts, to render a clear, homogenous functional fluid.

[0030] In a further preferred embodiment, the orthoester used as component (A) is not a single compound, but a mixture of at least two orthoesters according to formula (I) and (Ia). This means that in one embodiment, the fluid according to the first aspect not only comprises an orthoester according to formula (I), but in addition a bridged orthoester according to formula (Ia)



wherein R1, R2, R4, a and b have the same meaning as provided for formula (I), and d is a number from 0 to 6, preferably 2 or 3.

[0031] In formula (Ia), R1, R2 are independently selected from H or C₁ to C₈ alkyl groups preferably from H or C₁ to C₄ alkyl groups. In a preferred embodiment, R1, R2 are independently selected from methyl or butyl. In a more preferred embodiment, R1, R2 mean methyl. In a preferred embodiment, only one out of R1, R2 takes the meaning of H. In another preferred embodiment, the amount of orthoester according to formula (Ia) wherein at least one of R1, R2 takes the meaning H is less than 30 wt.-%, more preferably less than 15 wt.-%, particularly less than 10 wt.-%, on a basis of 100 wt.-% being the total amount of all orthoester according to formula (Ia). In a preferred embodiment, the orthoester used as component (A) corresponds to two or more components according to formula (Ia).

[0032] It is preferred, that the two or more orthoesters of formula (Ia) differ in one out of R1, R2. This may mean e.g. that one out of R1, R2 is methyl in one of the orthoesters, and one out of R1, R2 is butyl in the other of the orthoesters.

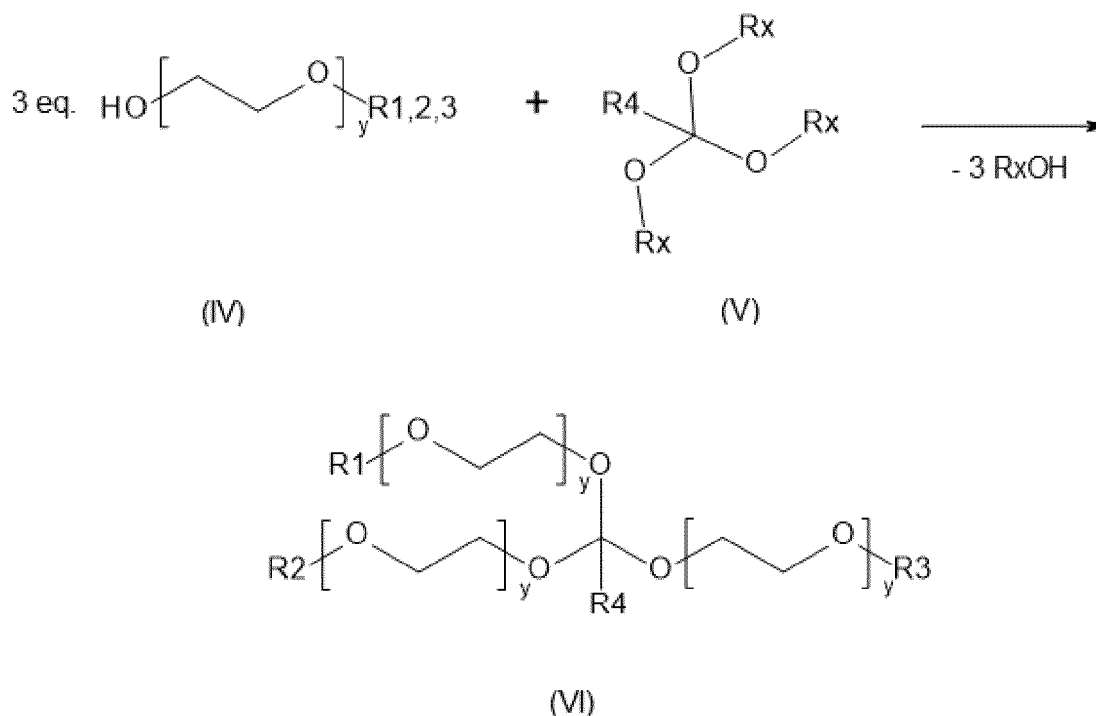
[0033] In formula (Ia), R4 means H or C₁ to C₈ alkyl. In a preferred embodiment, R4 means H or methyl.

[0034] In formula (Ia), a, b are independently numbers from 0 to 6, with the proviso that a+b is at least 1, i.e. not all of a, b, c may equal zero. In a preferred embodiment, a, b are independently 3 or 4. In another preferred embodiment, a+b is at least 3, more preferably at least 6. In a preferred embodiment, the orthoester used as component (A) corresponds to two or more components according to formula (Ia). It is preferred, that the two or more orthoesters of formula (Ia) differ in one out of a, b, meaning that a, b are not all the same in the two or more orthoesters according to formula (Ia). For example, one out of a, b may be 3 in one of the orthoesters, and one out of a, b may be 4 in the other of the orthoesters.

[0035] If a bridged orthoester according to formula (Ia) is present, its amount is preferably at most 30 wt.-%, more preferably less than 15 wt.-%, particularly less than 10 wt.-%, on a basis of 100 wt.-% being the total amount of all orthoester according to formula (I). For the purposes of this invention, the bridged orthoester according to formula (Ia) is to be regarded as part of component A). The amount of orthoester according to formula (Ia) is to be counted within the amount of component (A).

[0036] The bridging of orthoester by polyalkylene glycols has the technical effect of increasing the viscosity of the orthoester component, and therefore increasing the viscosity of the fluid of the first aspect. A larger proportion of bridged orthoesters of the formula (Ia) provides a higher viscosity of the fluid.

[0037] Orthoesters according to formula (I) and (Ia) can be synthesized according to procedures known in the art from alkyl glycols and commercially available alkyl ortho esters, according to



[0038] Useful alkyl ortho esters are selected from R₄ being a H or C₁- to C₈-alkyl residues and R_x being C₁- bis C₆-alkyl residues.

[0039] The alkyl glycol reactant of formula (IV) comprises species of ethoxylation degree of from y = 1 to y = 6, preferably of from y = 2 to y = 4, more preferably of y = 3 to y = 4. It is to be understood that the alkyl glycol reactant may be a single species, or a mixture of different species with regards to their ethoxylation degree y and/or to radicals R₁, R₂ and R₃.

[0040] Radicals R₁, R₂ and R₃ are preferably C₁- to C₄-alkyl groups and may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, preferably n-butyl or methyl.

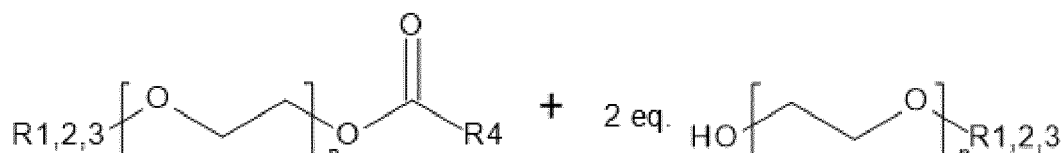
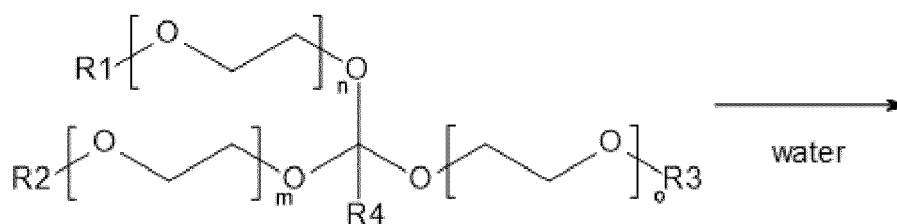
[0041] Examples of useful alkoxy glycols as starting material for component (A) of the present invention wherein R₁, R₂ or R₃ is not H include methyldiglycol, methyltriglycol, methyltetraglycol, methylpentaglycol, methylhexaglycol, ethyldiglycol, ethyltriglycol, ethyltetraglycol, ethylpentaglycol, ethylhexaglycol, n-propyl-diglycol, n-propyltriglycol, n-propyltetraglycol, n-propylpentaglycol, n-propylhexaglycol, n-butyl-diglycol, n-butyltriglycol, n-butyltetraglycol, n-butylpentaglycol, n-butylhexaglycol, n-pentyl-diglycol, n-pentyltriglycol, n-pentyltetraglycol, n-pentylpentaglycol, n-pentylhexaglycol, n-hexyldiglycol, n-hexyltriglycol, n-hexyltetraglycol, n-hexylpentaglycol, n-hexylhexaglycol, 2-ethylhexyldiglycol, 2-ethylhexyltriglycol, 2-ethylhexyltetraglycol, 2-ethylhexylpentaglycol, 2-ethylhexylhexaglycol and mixtures thereof. For the avoidance of doubt, "glycol" herein always means "ethylene glycol".

[0042] Example for useful glycols as starting material for component (A) of the present invention wherein R₁, R₂ or R₃ is H include preferably diethyleneglycol, triethyleneglycol and tetraethylene glycol and mixtures thereof.

[0043] In general, hydraulic fluids require the presence of agents providing reserve alkalinity. Such agents are e.g. amines. The required amount of the amine component is dependent on the required reserve alkalinity and the required pH value of the final functional fluids. Both reserve alkalinity and pH contribute to corrosion inhibition.

[0044] Borate-ester containing brake fluids require higher amounts of amine, usually above 1 wt.-%, in order to maintain a pH value in the range of 7.0 to 11.5, even upon hydrolysis of borate esters into the triprotic boric acid and the corresponding glycols.

[0045] In contrast, ortho-ester based brake fluids require reduced amounts of amine. Hydrolysis of ortho esters results in the formation of two equivalents of the corresponding alcohols, and one equivalent of the corresponding ester. As an example, the hydrolysis of an orthoacetate to the corresponding alcohol, and the acetic acid ester, follows this reaction path:



[0046] In a subsequent hydrolysis step, the ester (e.g. acetic acid ester) may be cleaved into the corresponding alcohol and one equivalent of the mono protic acid, e.g. acetic acid. The requirement of orthoester based fluids for reserve alkalinity is therefore reduced when compared to borate based fluids.

Component (B) - Alkylglycol ether

[0047] Component (B) of the functional fluid composition according to general formula (II) comprises species of ethoxylation degree of from $m = 2$ to $m = 6$, preferably of from $m = 2$ to $m = 4$, more preferably of $m = 3$ to $m = 4$. Component (B) may be a single species or a mixture of different species with regards to the ethoxylation degree, and/or to R5. R5 is a C_1 - to C_8 -alkyl group and may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl and 2-ethylhexyl, ethyl. More preferably, R5 is ethyl, n-butyl or methyl, most preferably n-butyl or methyl.

[0048] Examples of useful alkoxy glycols for component (B) of the present invention include methyldiglycol, methyltriglycol, methyltetraglycol, methylpentaglycol, methylhexaglycol, ethyldiglycol, ethyltriglycol, ethyltetraglycol, ethylpentaglycol, ethylhexaglycol, n-propyl-diglycol, n-propyltriglycol, n-propyltetraglycol, n-propylpentaglycol, n-propylhexaglycol, n-butyldiglycol, n-butyltriglycol, n-butyltetraglycol, n-butylpentaglycol, n-butylhexaglycol, n-pentyldiglycol, n-pentyltriglycol, n-pentyltetraglycol, n-pentylpentaglycol, n-pentyl-hexaglycol, n-hexyldiglycol, n-hexyltriglycol, n-hexyltetraglycol, n-hexylpentaglycol, n-hexylhexaglycol, 2-ethylhexyldiglycol, 2-ethylhexyltriglycol, 2-ethylhexyltetraglycol, 2-ethylhexylpentaglycol, 2-ethylhexylhexaglycol and mixtures thereof. For the avoidance of doubt, "glycol" always means "ethylene glycol". From the list above, methyltriglycol, methyltetraglycol, methylpentaglycol, ethyldiglycol, ethyltriglycol, ethyltetraglycol, n-butyldiglycol, n-butyltriglycol, n-butyltetraglycol, n-butylpentaglycol, are preferred for component (B).

[0049] In a preferred embodiment, component (B) comprises a mixture of alkoxy glycols of general formula (II) comprising solely or predominantly species with $m = 3$ and/or 4. Predominantly shall mean that at least 60% by weight, more preferably at least 75% by weight, most preferably at least 90% by weight, of component (B) comprises species with $m = 3$ and/or 4. In the last case, alkoxy glycol species with m being lower than 3, e.g. with $m = 2$, and/or with m being higher than 4, e.g. with $m = 5$ and/or $m = 6$, may be present in minor amounts, preferably less than 10% by weight, more preferably less than 8% by weight and even more preferably less than 5% by weight. Percentages of species of component (B) are given in wt.-% with the total amount of component (B) being 100 wt.-%.

[0050] In a preferred embodiment, the proportion of component (B) is 40 - 80 wt.-% of the total fluid weight.

Component (C) - Ethylene glycol oligomer

[0051] Component (C) is a polyethylene glycol according to formula (III). In formula (III), k is a number of 2, or higher. It is preferred, that k is a number from 2 - 4. More preferably, k is 2 or 3. In one preferred embodiment, component (C) is a mixture of compounds according to formula (III) wherein k is 2 or 3.

[0052] If component (C) is present, it is required that in at least 80 wt.-% of all compounds according to formula (III) k is 2 or 3, the wt.-% being relative to the total weight of all compounds according to formula (III). This means that compounds according to formula (III) wherein k is 2 or 3 make up to 18 wt.-%, preferably 3 to 15 wt.-% of the fluid, the total fluid weight being 100 wt.-%.

[0053] The total amount of component (C) in the fluid is from 0 to 20 wt.-%, preferably 4 - 18 wt.-% of the weight of

the fluid, i.e. the total weight of the fluid being 100 wt.-%. In one other preferred embodiment, component (C) is absent, i.e. the amount is 0%. In one other preferred embodiment, the amount of species of formula (III) wherein $k = 2$ is 2 - 10wt.-%. In one other preferred embodiment, the amount of species of formula (III) wherein $k = 3$ is 2 - 10 wt.-%. In one other preferred embodiment, the total amount of species according to formula (III) wherein k is 4 or higher than 4 is at most 10 wt.-%, more preferably at most 6 wt.-%. Said weight percentages provided for species according to formula (III) are provided as weight percentages of the fluid, i.e. the total weight of the fluid is 100 wt.-%. They are not provided as weight percentages of the total weight of component (C).

Component (D) - Additives

[0054] Component (D) is an additive that is required to impart particular properties to the functional fluid for performing on specifications to be fulfilled for brake fluids according to the current norms and standards FMVSS, SAE J 1703 and ISO 4925. The total amount of all components (D) in the fluid is from 0.2 to 6 wt.-%, preferably from 0.5 to 5 wt.-%.

[0055] Component (D) comprises one or more additives selected from the group consisting of corrosion inhibitors, amines as reserve alkalinity agents, stabilizing antioxidants, defoamers, lubricants and dyes.

[0056] Component (D) may comprise an amine. Amines are preferably alkyl or cycloalkyl amines, alkanol amines, alkyl amine ethoxylates and their mixtures. Preferred alkyl amines are mono- and di-(C₄- to C₂₀-alkyl)amines. Examples of suitable alkyl or cycloalkyl amines are n-butylamine, n-hexylamine, n-octylamine, 2-ethylhexylamine, isononylamine, n-decylamine, n-dodecylamine, oleylamine, d-n-propylamine, di-isopropylamine, di-n-butylamine, tri-n-butylamine, di-n-amylamine, cyclohexylamine, and salts of such amines. Examples of suitable alkanolamines are mono-, di- and trimethanolamine, mono-, di- and triethanolamine, mono-, di- and tri-n-propanolamine and mono-, di- and tri-isopropanolamine. Examples of suitable alkyl amine ethoxylates are such linear, cyclic or branched alkylamine ethoxylates carrying 1.5 to 5 EO moieties and an alkyl chain having 4 to 18 carbon atoms.

[0057] Component (D) of the present functional fluid composition may comprise, besides the Amine, at least one additive with corrosion inhibition action, although the alkylamine ethoxylates exhibit corrosion inhibition properties themselves. Suitable customary additives with corrosion inhibition properties include fatty acids such as lauric, palmitic, stearic or oleic acid; esters of phosphorus or phosphoric acid with aliphatic alcohols or aliphatic alcohol ethoxylates; such as ethyl phosphate, dimethyl phosphate, isopropyl phosphate, n-butyl phosphate, 2-ethylhexyl phosphate, triphenyl phosphite and diisopropyl phosphite; heterocyclic nitrogen containing organic compounds such as benzotriazole, tolyltriazole, 1,2,4-triazole, benzimidazole, purine, adenine and derivatives of such heterocyclic organic compounds. Of course, mixtures of the above additives with corrosion inhibition action can be used.

[0058] Defoamers may be selected from groups of oil based defoamers, such as natural oils, glycerides, waxes, powdered silica, alkoxylates such as EO/PO block copolymers, silicone based defoamers, preferably modified polyether or silicone derivatives and mixtures thereof.

[0059] The fluid may include from 0 to 5% by weight, based on the total weight of the fluid, of a lubricant. Suitable lubricants are for example, propylene oxide containing alkylene oxide polymers that are optionally substituted with a C₁ to C₄ alkyl group, triglycerides, castor oil, ricinoleic acid, and ethoxylates of castor oil or ricinoleic acid and mixtures thereof. In a preferred embodiment, the lubricants are homopolymers of propylene oxide, copolymers of propylene oxide with ethylene oxide and/or butylene oxide, mono C₁ to C₄ alkyl substituted homopolymers of propylene oxide, mono C₁ to C₄ alkyl substituted copolymers of propylene oxide with ethylene oxide and/or butylene oxide, triglycerides, castor oil, ricinoleic acid, and ethoxylates of castor oil or ricinoleic acid and mixtures thereof. In case of such ethoxylates, 1 to 50 ethoxy units are preferred. In another preferred embodiment, the propylene oxide containing alkylene oxide polymers that are optionally substituted with a C₁ to C₄ alkyl group have a number average molecular weight in the range of 150 to 3000 g/mol.

[0060] Suitable stabilizers or antioxidants are phenolic stabilizers like Bisphenols (e.g. Bisphenol A or Bisphenol M), butyl hydroxytoluene, methoxy phenols, butylated hydroxy anisole, hydroquinone derivatives; sterically hindered amines such as benzylated, alkylated or styrenated diphenylamine, styrenated phenylamine, substituted piperidine derivatives, phenothiazine derivatives or quinoline derivatives and mixtures thereof. In general, any literature known glycol stabilizing agents could be used herein.

[0061] In one preferred embodiment, the % values (A) - (D) add up to 100% by weight.

[0062] The total content of the fluid in boric acid esters is at most 3 wt.-%, preferably less than 0.3 wt.-%. Most preferably, the fluid is free of boric acid esters.

[0063] In a preferred embodiment, the combined amount of components (A) and (B) adds up to at least 70% of the fluid weight.

[0064] The functional fluid composition of the present invention exhibits superior behavior in ERBP and WERBP temperature and simultaneously in low temperature viscosity performance. It exhibits an ERBP of at least 250°C, more preferably of at least 260°C and a WERBP of at least 165°C, more preferably at least 170°C. The functional fluid composition of the present invention exhibits a low temperature kinematic viscosity of less than 900 centistokes ("cSt")

(= mm²/s), more preferably of less than 750 cSt, each determined at a temperature of -40°C. All analytical methods are described in FMVSS to which reference is made. For the purpose of this specification, ERBP and WERBP are to be determined according to FMVSS no 116.

[0065] The low viscosity functional fluid composition of the present invention is especially useful as a brake fluid, for example for vehicles such as passenger cars and trucks, especially for new electronic or automated anti-lock brake systems which require lower viscosity fluids for satisfactory operation at low temperatures.

[0066] Besides its superior behavior in ERBP and WERBP temperature and its low temperature viscosity performance, the functional fluid composition of the present invention exhibits a good corrosion protection, a good water compatibility, a mild pH value, a good stability with regard to low and high temperatures, a good oxidation stability, a good chemical stability, a good behavior towards rubber and elastomers, a good lubrication performance and good foaming behavior.

Examples for orthoesters - Synthesis

[0067] OE-A (MTG-Ortho acetate) Trimethylorthoacetate + Methyltriglycol A mixture of 160.3 g (1.33 mol) trimethyl orthoacetate and 420 mL (2.66 mol) methyl triglycol is placed under nitrogen in a 1 liter four-necked flask equipped with a stirrer and a distillation attachment including a Vigreux column and heated to 165°C within 40 min. After the constant reaction temperature had been reached, a first portion of methanol was distilled off over the course of 60 minutes. The reaction temperature was increased to 185°C and held for a further 45 minutes, a total of about 83% (71 g, 2.22 mol) of the theoretical amount of methanol being distilled off. Thereafter, a further 211 ml (1.34 mol) of methyl triglycol were metered in at constant heating power, and after one hour the reaction temperature was increased to 225°C and held for one hour, further methanol being distilled off. A further 50 ml (0.32 mol) of methyl triglycol were then metered in at constant heating power, and 1.9 g of benzoic acid were added. After 3 hours, a further 0.9 g and finally another 0.4 g of benzoic acid were added after a further hour. Finally, the mixture was stirred at a reaction temperature of 235°C for a further 2 h. A total of 140 ml / 110.6 g of methanol (3.45 mol) were distilled off, which corresponds to a conversion of 86.3%. A similar conversion rate was observed by ¹H-NMR analysis.

OE-B (MTG/MTeG-Ortho acetate) Triethylorthoacetate + Methyltriglycol (MTG) and Methyltetraglykol (MTeG)

[0068] In analogy to the synthesis procedure of OE-A, Triethylorthoacetate (2.0 mol) was reacted with MTG (4.72 mol) and MTeG (1.61 mol), resulting in the corresponding product with 91% conversion according to ¹H-NMR.

OE-C (MTeG/MTG-Orthoformate) Trimethylorthoformiate + Methyltri- and methyltetraglykol

[0069] In analogy to the synthesis procedure of OE-A, Trimethylorthoformiate (2.5 mol) was reacted with MTG (6.04 mol) and MTeG (2.01 mol), resulting in the corresponding product with 93% conversion of the starting orthoformiate according to ¹H-NMR.

OE-D (MTG-Orthoformiate)

[0070] In analogy to the synthesis procedure of OE-A, Trimethylorthoformiate (2.0 mol) was reacted with MTG (7.0 mol), resulting in the corresponding product with 93% conversion of the starting orthoformiate according to ¹H-NMR.

OE-E (MTG/TEGBE-Ortho acetate)

[0071] In analogy to the synthesis procedure of OE-A, Trimethyl ortho acetate (1.8 mol) was reacted with a mixture of 70% triethyleneglycolmonobutylether and 30% tetraethyleneglycolmonobutylether (combined 6.3 mol), resulting in the corresponding product with 88% conversion according to NMR.

OE-F (MTG/Di-Triglycol-Ortho acetate)

[0072] In analogy to the synthesis procedure of OE-A, Trimethyl ortho acetate (1.8 mol) was reacted with a mixture of 95 wt.-% triethyleneglycolmonomethylether, 2.5 wt.-% diethyleneglycol and 2.5 wt.-% triethyleneglycol (combined 5.6 mol), using benzoic acid as a catalyst, resulting in the corresponding product with 90% conversion according to NMR.

[0073] Table with physical-chemical data (viscosity, boiling point, stability at repeated boiling, even in presence of amine).

		Conversion ¹	ERBP [°C] ²	Viscosity at -40°C [mm ² /s] ³	Δ (ERBP) [°C] ⁴
MTG-Ortho acetate	OE-A	86%	259	783	-5
MTeG/MTG-Ortho acetate	OE-B	80%	263	1292	-3
MTeG/MTG-Ortho formiate	OE-C	81%	267	1488	-1
MTG-Ortho formiate	OE-D	93%	264	588	-3
MTG/TEGBE-Ortho acetate	OE-E	84%	266	1097	-6
MTG/DiTriglycol Orthoacetate	OE-F	90%	259	1208	-6
¹ Conversion of starting ortho ester to alkyl glycol ortho ester, determined by ¹ H-NMR.					
² Equilibrium reflux boiling point of the corresponding ortho ester synthesis product according to the procedure described in FMVSS no 116					
³ Viscosity of the of the corresponding ortho ester synthesis product according to ASTM D 7042					
⁴ Thermal stability of the ortho ester, calculated as: (ERBP at the fourth time of determination of the same sample) - (initial ERBP).					

20 Examples for functional fluid formulations

25 **[0074]** Table 1 shows functional fluid compositions and their performance. Percentages are wt.-% with respect to the total fluid weight, unless otherwise noted.

Table 1

	Component	Example 1 (♦)	Example 2 (♦)	Example 3 (♦)	Example 4 (♦)	Example 5 (♦)	Example 6 (♦)	Example 7 (♦)	Example 8 (♦)	Example 9 (♦)	Comparative example 1 (■)	Comparative example 2 (■)
A	OE-B [%]	27							45		(■)	
	OE-C [%]		8.5	25							(■)	
	OE-D [%]				25						(■)	
	OE-E [%]					25					(■)	
	OE-A [%]						25			36	(■)	1 (■)
	OE-F [%]							25				
B	R5=Me, m =3 (MTG) [%]	37.5	46.8	39	40.5	39	40.5	40.5	39	16	51	50.5
	R5=Me, m =4 (MTeG) [%]	18.5	23	19	17.5	17.5	17.5	17.5	8.5	20	25	24.7
	R5=butyl, m=3 (BTG) [%]	2.45	3.15	2.45	2.45	3.5	2.45	2.45	4.55	6.3	3.5	3.5
	R5=butyl, m=4 (BTeG) [%]	1.05	1.35	1.05	1.05	1.5	1.05	1.05	1.95	2.7	1.5	1.5
C	k=2 (DEG) [%]	6.25	8.1	6.25	6.25	6.25	6.25	6.25		9	9	8.9
	k=3 (TEG) [%]	6.25	8.1	6.25	6.25	6.25	6.25	6.25		9	9	8.9
D	Additive package [%]	1	1	1	1	1	1	1	1	1	1	1
	Sum [%]	100	100	100	100	100	100	100	100	100	100	100
	viscosity (- 40°C) [mm ² /s]	770	618	781	614	738	690	800	740	880	683	654
	ERBP [°C]	257	260	251	261	259	251	255	252	254	260	260

(continued)

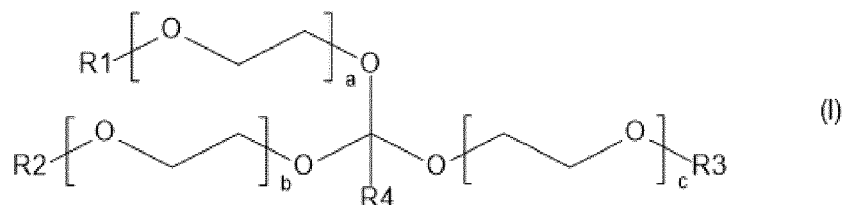
Component	Example 1 (♦)	Example 2 (♦)	Example 3 (♦)	Example 4 (♦)	Example 5 (♦)	Example 6 (♦)	Example 7 (♦)	Example 8 (♦)	Example 9 (♦)	Comparative example 1 (■)	Comparative example 2 (■)
WERBP [°C]	172	165	177	166	170	165	172	182	170	161(m)	160(■)

(♦) = according to the present invention, or according to the required specification
 (■) = not according to the invention, or not according to the required specification
 MTG = methyl triglycol, M TeG = methyl triglycol, BTG = butyl triglycol, BTeG = butyl tetraglycol, DEG = diethylene glycol,
 TEG = triethylene glycol
 The additive package added to each formulation adds up to 1 wt.-% with the following components.
 Diisopropanol amine: 0.629%, Styrenated diphenyl amine: 0.1%, Castor oil + 20 EO: 0.2%, Silicone based defoamer: 0.001%,
 Toly triazole: 0.06%, Phosphoric acid ester: 0.01%.

Claims

1. A functional fluid, comprising

(A) from 8 to 80% by weight, based on the total composition, of one or more ortho-ester according to formula (I)



wherein

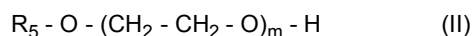
R1, R2, R3 are independently selected from H or C₁ to C₈ alkyl groups,

R4 means H or C₁ to C₈ alkyl,

a, b, c are independently numbers from 0 to 6,

with the proviso that a+b+c is at least 1,

(B) from 10 to 87% by weight, based on the total composition, of one or more alkoxy glycol according to formula (II)

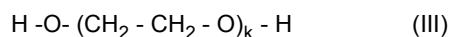


wherein

R₅ is a C₁ to C₈ alkyl residue,

m is a number from 2 to 6,

(C) from 0 to 20 wt.-% of at least one compound according to formula (III)



wherein k is a number of 2 or higher, with the proviso that in at least 80 wt.-% of all compounds according to formula (III) k is 2 or 3,

(D) at least one additive, selected from the group consisting of corrosion inhibitor, alkalinity agents, aging protection agents, defoamers and lubricants,

the fluid comprising at most 3 wt.-% of an ester between boric acid and a glycol or polyglycol compound, and with the proviso that the combined amount of component (A) and component (B) adds up to at least 70 % of the total fluid weight.

2. Fluid according to claim 1, wherein the components (A) to (D) add up to 100 wt.-%.

3. Fluid according to claim 1 or 2, wherein R1, R2, R3 are independently selected from H or C₁ to C₄ alkyl groups.

4. Fluid according to one or more of claims 1 - 3, wherein R1, R2, R3 are independently selected from methyl and butyl groups.

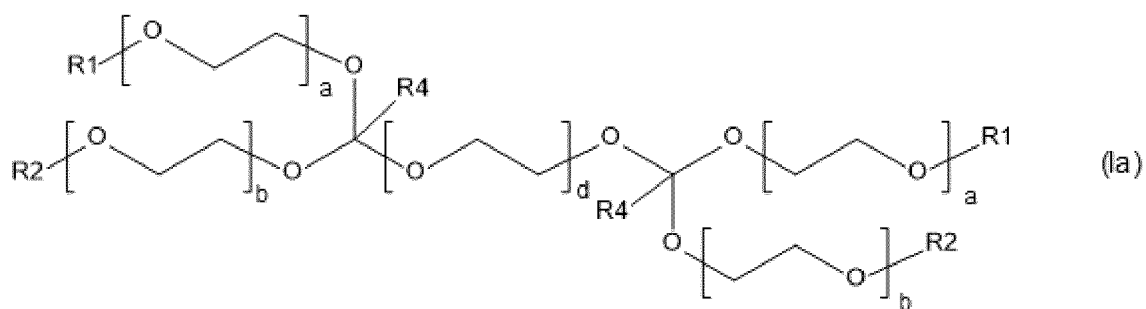
5. Fluid according to one or more of claims 1 - 4, wherein R4 is H or C₁ to C₄ alkyl.

6. Fluid according to one or more of claims 1 - 5, wherein R4 is H or methyl.

7. Fluid according to one or more of claims 1 - 6, wherein a+b+c is at least 3, more preferably at least 6.

8. Fluid according to one or more of claims 1 - 6, wherein a, b, c are independently 3 or 4.

9. Fluid according to one or more of claims 1 - 8, wherein component (A) is a mixture of at least two compounds according to formula (I) that differ in one out of R₁, R₂, R₃ or in one out of a, b, c.
- 5 10. Fluid according to one or more of claims 1 - 9, wherein in at least 60 wt.-% of all compounds according to formula (II) m is 3 or 4.
11. Fluid according to one or more of claims 1 - 9, wherein component (C) is preferably present in an amount of 4 to 18 wt.-%.
- 10 12. Fluid according to one or more of claims 1 - 11, wherein in at most 10 wt.-% of all compounds according to formula (II) m is 5 or higher.
13. Fluid according to one or more of claims 1 - 12, wherein the fluid contains at most 10 wt.-% of compounds according to formula (III) wherein k is 4 or higher, the wt.-% being relative to the total weight component C.
- 15 14. Fluid according to one or more of claims 1 - 13, wherein component (D) is present in an amount of 0.2 to 6 wt.-%, preferably 0.4 to 4.5 wt.-%.
- 20 15. Fluid according to one or more of claims 1 - 14, wherein the corrosion inhibitor is selected from the group consisting of C₈ to C₂₂ fatty acids, esters of phosphorus or phosphoric acid with C₁ to C₁₈ aliphatic alcohols, phosphites having at least one C₁ to C₁₂ hydrocarbon residue; heterocyclic organic compounds having at least one nitrogen atom as heteroatom, and mixtures thereof.
- 25 16. Fluid according to one or more of claims 1 - 15, wherein the amine is selected from the group consisting of alkyl or cycloalkyl amines, alkanol amines, alkyl amine ethoxylates and their mixtures.
17. Fluid according to one or more of claims 1 - 16, wherein the stabilizer is selected from the group consisting of substituted phenols, sterically hindered amines and mixtures thereof.
- 30 18. Fluid according to one or more of claims 1 - 17, wherein the defoamer is selected from the group consisting of glycerides, waxes, powdered silica, ethylene oxide/propylene oxide block copolymers, silicone based defoamer and mixtures thereof.
- 35 19. Fluid according to one or more of claims 1 - 18, wherein the lubricant is selected from the group consisting of homopolymers of propylene oxide, copolymers of propylene oxide with ethylene oxide and/or butylene oxide, mono C₁ to C₄ alkyl substituted homopolymers of propylene oxide, mono C₁ to C₄ alkyl substituted copolymers of propylene oxide with ethylene oxide and/or butylene oxide, triglycerides, castor oil, ricinoleic acid, and ethoxylates of castor oil or ricinoleic acid, and mixtures thereof.
- 40 20. Fluid according to one or more of claims 1 - 19, comprising 0.1 to 3 wt.-% of an amine within the component (D), weight-% being relative to the fluid weight.
- 45 21. Fluid according to one or more of claims 1 - 20, wherein the fluid's content in esters between boric acid and glycol or alkyl polyglycol compounds is less than 3 wt.-%, preferably less than 1 wt.-%, more preferably 0.1 wt.-%, the fluid being most preferably essentially free of such boric acid ester.
- 50 22. Fluid according to one or more of claims 1 - 21, the fluid having a kinematic viscosity of less than 900 centistokes, preferably less than 750 centistokes at -40°C, on an dry equilibrium reflux boiling point (ERBP) of at least 250°C and a wet equilibrium reflux boiling point (WERBP) of at least 165°C, both ERBP and WERBP to be determined according to Federal Motor Vehicle Safety Standards (FMVSS) No 116.
- 55 23. Fluid according to one or more of claims 1 - 21, wherein R₅ is a C₁- to C₄-alkyl group.
24. Fluid according to one or more of claims 1 - 23, wherein component (A) comprises a compound according to formula (Ia)



wherein d is a number from 1 to 6, in an amount of up to 30 wt.-% relative to the total weight of all compounds according to formula (I).

25. Use of a fluid according to one or more of claims 1 - 24 as brake fluid.

26. Method of operating a vehicular brake, the method comprising transmitting hydraulic pressure by a fluid according to one or more of claims 1 - 24.



EUROPEAN SEARCH REPORT

Application Number
EP 21 16 2202

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
			C10M C10N
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 28 July 2021	Examiner Pöllmann, Klaus
CATEGORY OF CITED DOCUMENTS 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		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	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 21 16 2202

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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