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(54) **DOT 4 BRAKE FLUIDS**

(76) Inventors: **Bernd Wenderoth**, Birkena (DE); **Bayram Aydin**, Ludwigshafen (DE); **Michael Roida**, Lustadt (DE); **Ralf Strauss**, Ludwigshafen (DE); **Ladislaus Meszaros**, Mutterstadt (DE); **Herbert Matzkait**, Frankenthal (DE)

Correspondence Address:
C. IRVIN MCCLELLAND
OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA, VA 22314 (US)

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(57) **ABSTRACT**

A brake fluid comprises a) from 10 to 50, preferably from 20 to 40, % by weight of diethylene glycol and/or dipropylene glycol and b) from 50 to 90, preferably from 60 to 80, % by weight of one or more monoalkyl ethers of (poly)ethylene glycol and/or (poly)propylene glycol. The novel fluids are in particular free of borate and, owing to the low hygroscopicity, are suitable for use in regions of high relative humidity.

DOT 4 BRAKE FLUIDS

[0001] The present invention relates to novel DOT 4 brake fluids, in which the addition of borates (boric acid esters) is not necessary. The brake fluids comprise

[0002] (a) from 10 to 50% by weight of diethylene glycol and/or dipropylene glycol and

[0003] (b) from 50 to 90% by weight of (poly)ethylene glycol monoalkyl ether and/or (poly)propylene glycol monoalkyl ether

and are preferably free of polyglycol dialkyl diethers.

[0004] Hydraulic fluids and in particular brake fluids for motor vehicles are subject to very high requirements with respect to their chemical and physical properties. According to the existing standards and specifications for brake fluids of the US Department of Transportation (DOT) in the Federal Motor Vehicle Safety Standard FMVSS No. 116 and the standard SAE J 1704 published by the Society of Automotive Engineers, modern brake fluids should on the one hand have a high equilibrium reflux boiling point (ERBP) and high wet ERBP, but on the other hand should also have a viscosity which changes only slightly within a wide temperature range.

[0005] Accordingly, for a DOT 4 brake fluid according to FMVSS No. 116, the specification values shown below must be complied with:

ERBP:	≧230° C.
Wet ERBP:	≧155° C.
Viscosity at −40° C.:	≦1800 mm^2/s

[0006] There are moreover more stringent requirements for sufficiently good protection of metals and nonferrous metals from corrosion by brake fluids, which can be achieved by corrosion inhibitor additives contained therein.

[0007] Commercial DOT 4 brake fluids always contain boric acid esters, for example methyltriglycol borate, which can chemically eliminate certain amounts of penetrating water from the brake fluid by hydrolysis. A disadvantage is that boric acid esters are themselves hygroscopic, with the result that such DOT 4 brake fluids, particularly in regions of high relative humidity, for example in tropical and subtropical regions, can very rapidly absorb so much moisture that, in spite of the trapping function of the boric acid esters, the operability of a brake system filled therewith can be adversely affected.

[0008] U.S. Pat. No. 3,625,899 describes DOT 4 brake fluids which contain from 54.5 to 92% of at least one boric acid ester, up to 20% of polyalkylene glycols and from 3 to 43% of polyglycol monoalkyl or dialkyl ethers, in addition to further additives.

[0009] U.S. Pat. No. 3,972,822 describes DOT 4 brake fluids which contain from 40 to 65% of polyglycol monoalkyl ethers, from 16 to 45% of polyglycols and from 10 to 19% of boric acid esters plus corrosion inhibitors.

[0010] WO 00/46325 describes DOT 4 brake fluids which contain methyltriglycol borate, glycol ethers and glycols in different amounts and an additive system.

[0011] WO 02/38711, too, discloses corresponding DOT 4 brake fluids which contain different methylpolyglycol borates, polyglycol monoalkyl ethers and corrosion inhibitors.

[0012] DE 36 27 432 C2 describes borate-free brake fluids comprising from 30 to 80% of a glycol component and up to 70% of polyglycol alkyl ether. The glycol component in turn contains from 0 to 80, preferably from 55 to 80, % by weight of diethylene glycol and/or dipropylene glycol. The polyglycol alkyl ether component contains from 0 to 90, preferably from 0 to 50, % by weight of at least one polyglycol monoalkyl ether. In selected mixing ratios, these fluids fulfill the DOT 4 specification. A disadvantage in the case of these formulations is in particular the ERBP only just above the specification limit and moreover the use of polyglycol dialkyl ethers which are more expensive to synthesize and often also lead to incompatibility reactions of rubber and sealing materials.

[0013] There is furthermore a need for low viscosity brake fluids which fulfill the DOT 4 specification.

[0014] It is an object of the present invention to provide such a brake fluid. Preferably, this brake fluid should not be very hygroscopic and should be capable of being used in regions of high relative humidity. In particular, it should be necessary to use only small amounts of boric acid esters or ideally the use of such esters should even be completely superfluous.

[0015] We have found that this object is achieved by a brake fluid comprising

[0016] a) from 10 to 50% by weight of diethylene glycol and/or dipropylene glycol and

[0017] b) from 50 to 90% by weight of one or more monoalkyl ethers of (poly)ethylene glycol or (poly)propylene glycol.

[0018] In particular, the novel fluids are free of boric acid esters.

[0019] Diethylene glycol or dipropylene glycol or a mixture of diethylene glycol and dipropylene glycol in any desired ratio may be used. Diethylene glycol is preferred.

[0020] Diethylene glycol and/or dipropylene glycol are present in the novel brake fluids in an amount of from 10 to 50, preferably from 20 to 40, % by weight.

[0021] A further component of the novel brake fluid comprises one or more monoalkyl ethers of (poly)ethylene glycols and/or (poly)propylene glycols, which are present in the novel fluids in an amount of from 50 to 90, preferably from 60 to 80, % by weight.

[0022] Examples of suitable (poly)ethylene glycols are monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol and hexaethylene glycol.

[0023] Examples of suitable (poly)propylene glycols are monopropylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, pentapropylene glycol and hexapropylene glycol.

[0024] Diethylene glycol, triethylene glycol and/or tetraethylene glycol are preferred.

[0025] The alkyl radical in the monoalkyl ethers of (poly-)ethylene glycol and (poly)propylene glycol used according to the invention is preferably a linear or branched C_1-C_6-alkyl radical. It is more preferable to use a linear or branched C_1-C_4-alkyl radical, for example methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

[0026] The alkyl radicals are in particular methyl, ethyl, isopropyl or n-butyl.

[0027] In the present invention, the use of methyldiethylene glycol, methyltriethylene glycol, methyltetraethylene glycol and/or butyltriethylene glycol is preferred.

[0028] The novel brake fluids have wet ERBPs and in particular ERBPs which are close to those which have been achieved to date with borate-free brake fluids. They are comparable with those achieved today only with borate-containing fluids. Owing to the absence of borate, however, the novel fluids are substantially less hygroscopic than borate-containing ones. This is advantageous in particular during use in tropical and subtropical regions, since, although a part of the water is bound by the addition of borate, water is also relatively rapidly absorbed. This results in each case in a deterioration in the quality of the brake fluid. In particular, this loss of quality occurs frequently in the brake system of motor vehicles but also during storage and transport of the fluids. The novel brake fluids do not have said disadvantages.

[0029] It is true that the novel brake fluids may contain different amounts of boric acid esters. However, the advantages according to the invention of low hygroscopicity are generally not achieved thereby. This is the case in particular when boric acid esters are added in the amounts customary according to the prior art.

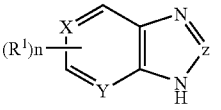
[0030] Furthermore, the novel fluids are in particular free of polyalkylene glycol dialkyl ethers. Although these too may be present in different amounts, in general the advantages of the novel brake fluids, in particular the compatibility with rubber and sealing materials, are then not achieved, this too of course being dependent on the amount of any polyalkylene glycol dialkyl ethers present.

[0031] Further polyglycols may be present as an optional component in the novel formulations. Relatively high-boiling reaction products of ethylene oxide and/or propylene oxide and/or butylene oxide with water or diol are preferably used. In particular, reaction products of mixtures of ethylene oxide and propylene oxide with water are used. The number of alkylene oxide units in said polyglycols is usually from 2 to 10, preferably 2 or 3, and in an amount of up to 5%.

[0032] The effect of these high-boiling polyglycols is that of a lubricant, which is due substantially to an improvement in the temperature-viscosity behavior. The polyglycols impart sufficient viscosity to the polyglycol monoalkyl ethers, which often have low viscosity at high temperatures, and thus ensure sufficient lubrication. Sufficient lubrication is desired since, in the components of the motor vehicle brake system, rubber or elastomers have to slide on metal with very little wear.

[0033] In a further embodiment, the novel DOT 4 brake fluids for motor vehicles furthermore contain from 0.001 to 10, preferably from 0.005 to 4, in particular from 0.005 to 1, % by weight of one or more corrosion inhibitors, for example 1H-1,2,3-benzotriazole, 1H-1,2,3-tolutriazole, hydrogenated 1H-1,2,3-tolutriazole, benzimidazole and/or derivatives thereof, alkali metal salts of phosphoric acid and phosphorous acid, fatty acids, preferably caprylic, lauric, palmitic, stearic or oleic acid, and alkali metal salts thereof, esters of phosphoric acid and of phosphorous acid, preferably ethyl phosphate, dimethyl phosphate, isopropyl phosphate, diisopropyl phosphate, butyl phosphite or dimethyl phosphite, mono- and dialkylamines which may be ethoxylated and salts thereof with mineral and fatty acids, preferably butylamine, hexylamine, octylamine, isononylamine, oleylamine, dipropylamine, diisopropylamine or dibutylamine, alkanolamines which may be ethoxylated, preferably mono-, di- or triethanolamine, N,N'-di-n-butylaminoethanol or 1,1'-iminodipropan-2-ol, cyclohexylamine, and/or nitro aromatics, preferably 3-nitrobenzaldehyde.

[0034] The novel brake fluids may also contain one or more of the heterocyclic compounds which are described in WO 01/90281 and are of the following formula



where

[0035] (i) X is N, Y is CR and Z is N or

[0036] (ii) X is N, Y is N and Z is N or CR or

[0037] (iii) X is CR, Y is N and Z is N,

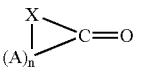
R, in each case independently of further radicals R present, being a hydrogen atom or a radical R^1,

R^1, in each case independently of further radicals R^1 present, being alkyl, aryl, aralkyl, halogen, haloalkyl, unsubstituted or alkyl-, aryl- or aralkyl-substituted amino, a heterocyclic radical, cyano, carboxyl, alkoxycarbonyl, hydroxyl or alkoxy, said organic radicals R^1 each being of 1 to 30 carbon atoms, and

n being 0, 1 or 2. Examples of preferred compounds of this type include purine, adeinine, 6-chloropurine, 2,6-dichloropurine, 6-methoxypurine, 1H-1,2,3-triazolo[4,5b]pyridine, 6-histaminopurine and 6-furfurylaminopurine.

[0038] The novel borate-free DOT 4 brake fluids may furthermore contain the formulations described in WO 02/081604 and comprising 1H-1,2,4-triazole.

[0039] The novel brake fluids may additionally contain the cyclic carboxylic acid derivatives which are mentioned in WO 00/65001 and are of the formula I



where

[0040] X is an oxygen atom or a group of the formula N—R^1,

[0041] R^1 being hydrogen or a linear or branched C_1- to C_{20}-alkyl group which additionally may be interrupted by up to 9 nonneighboring oxygen atoms and/or may carry up to 6 hydroxyl groups, or a cycloalkyl group or an unsubstituted or substituted phenyl group,

[0042] A is a group of the formula —CR^2R^3—,

[0043] R^2 and R^3 each being hydrogen or C_1- to C_8-alkyl groups which additionally may be interrupted by up to 4 nonneighboring oxygen atoms and/or may carry up to 3 hydroxyl groups, and

[0044] n is from 2 to 7.

[0045] These are suitable as components for reducing the low-temperature viscosity in the presence of water.

[0046] Further components and assistants in the novel brake fluids for motor vehicles are conventional antioxidants, e.g. phenothiazine and/or those based on phenol, and conventional antifoams and markers.

[0047] All percentages by weight stated above and below are based in each case on the total amount of the hydraulic fluid or of the brake fluid.

[0048] The novel borate-free DOT 4 brake fluids meet the requirements stated at the outset in an outstanding manner and moreover have generally good corrosion behavior compared with the prior art, i.e. very good corrosion prevention is ensured in the case of metals such as iron, steel, tin plate, cast iron (gray cast iron), lead, tin, chromium, zinc, aluminum, magnesium and alloys thereof and in the case of solder metals, for example tin solder, and in the case of nonferrous metals such as copper and alloys thereof, for example brass.

[0049] In addition to the hygroscopic properties substantially reduced owing to the freedom from borate, further advantages of the novel DOT 4 brake fluids for motor vehicles which may be singled out are their advantageous low-temperature viscosity, good water compatibility, a mild pH, good low temperature, high temperature and oxidation stability and good chemical stability, advantageous behavior toward (i.e. good compatibility with) materials such as rubbers, plastics, glue joints, fiber, elastomer and rubber seals and similar materials and good lubricating behavior.

[0050] The examples which follow illustrate the invention without restricting it.

USE EXAMPLES

[0051] The novel borate-free DOT 4 brake fluid BF1 used had the following composition:

Novel Example BF 1

[0052]

31.0%	of diethylene glycol
67.7%	of a mixture of methyldiglycol, butyldiglycol, butyltriglycol and methyltetraglycol
1.3%	of a mixture of 1,1'-iminodipropan-2-ol, bisphenol A, tolutriazole and 3-nitrobenzaldehyde

Comparative Example BF 2

[0053] (corresponds to example 5 from DE 36 27 432 C2)

39%	of diethylene glycol
26%	of triethylene glycol
24%	of triethylene glycol dimethyl ether
10%	of methyltriglycol
1%	of corrosion inhibitor (1,1'-iminodipropan-2-ol used)

[0054] Physical data:

	BF 1	BF 2 (comparison)
ERBP [° C.]:	251	234
wet ERBP [° C.]:	159 (Water absorption: 3.27%; reference RM 71 3.73%)	153 (Water absorption: 3.93%; reference RM 71 3.70%)
Viscosity −40° C.: [mm^2/s]	1393	1277

[0055] Compared with the prior art according to DE 3627432 C2, the novel borate-free DOT 4 brake fluids have in particular a substantially higher ERBP which, in the case of BF 1, easily exceeds the minimum requirement according to FMVSS No. 116 by 20° C., and a lower water absorption and, associated therewith, a higher wet ERBP.

[0056] The novel brake fluids moreover lead to very good corrosion prevention, as shown by the results below for BF 1:

[0057] Corrosion Test According to SAE J 1704, Test Duration 120 h/100° C.:

Metal	Weight change [mg/cm^2]	Appearance
Tin plate	±0.00	unchanged
Steel	+0.01	unchanged
Aluminum	±0.00	unchanged
Gray cast iron	+0.04	unchanged
Brass	−0.05	slightly tarnished
Copper	−0.05	slightly tarnished
Zinc	+0.03	tarnished

pH before/after test: 9.9/9.6

1-12. (canceled)

13. A brake fluid comprising

a) from 10 to 50% by weight of diethylene glycol and/or dipropylene glycol and

b) from 50 to 90% by weight of one or more monoalkyl ethers of (poly)ethylene glycol and/or (poly)propylene glycol.

14. The brake fluid as claimed in claim 13, which contains no boric acid esters.

15. The brake fluid as claimed in claim 13, which contains no polyalkylene glycol dialkyl ethers.

16. The brake fluid as claimed in claim 13, wherein diethylene glycol is used as component a).

17. The brake fluid as claimed in claim 13, wherein, in component b), the glycol is at least one selected from the group consisting of monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, monopropylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, pentapropylene glycol and hexapropylene glycol.

18. The brake fluid as claimed in claim 13, wherein, in component b), the alkyl radical is selected from linear and branched C_1-C_6-alkyl radicals.

19. The brake fluid as claimed in claim 13, wherein component b) is at least one selected from the group consisting of methyldiethylene glycol, methyltriethylene glycol, methyltetraethylene glycol and butyltriethylene glycol.

20. The brake fluid as claimed in claim 13, wherein reaction products of ethylene oxide and/or propylene oxide and/or butylene oxide with water or diols, are also present.

21. The brake fluid as claimed in claim 13, wherein from 0.01 to 10, % by weight of one or more corrosion inhibitors are present.

22. The brake fluid as claimed in claim 13, wherein the corrosion inhibitors are at least one selected from the group consisting of 1H-1,2,3-benzotriazole, 1H-1,2,3-tolutriazole, hydrogenated 1H-1,2,3-tolutriazole, benzimidazole and/or derivatives thereof, alkali metal salts of phosphoric acid and phosphorous acid, fatty acids, and alkali metal salts thereof, esters of phosphoric acid and of phosphorous acid, mono- and dialkylamines which may be ethoxylated and salts thereof with mineral and fatty acids, alkanolamines which may be ethoxylated, cyclohexylamine and nitro aromatics.

23. The brake fluid as claimed in claim 13, which complies with the following specification values (DOT 4):

ERBP:	≧230° C.
Wet ERBP:	≧155° C.
Viscosity at −40° C.:	≦1800 mm^2/s

24. The brake fluid as claimed in claim 13 wherein the brake fluid is utilized as a brake fluid in motor vehicles.

25. A motor vehicle brake system comprising the brake fluid as claimed in claim 13.

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