

Use of surfactants with low molecular weight for improving the filterability in hydraulic lubricants

5 **Scope of the invention**

The present invention relates to lubricating fluids having improved filterability characteristics, and to effective additives for improving the filterability characteristics of lubricating fluids such as hydraulic oils. The present invention relates more particularly to lubricating fluids and additives
10 containing an effective quantity of an agent improving filterability which contains at least one polar group and at least one lipophilic chain having 14 to 24 carbon atoms.

Technological background

15 Most lubricating oils currently in use, such as hydraulic fluids and similar fluids, contain additives which are designed to confer optimum performances as regards the prevention of wear, protection against rust, demulsibility, thermal stability, stability towards hydrolysis and oxidation stability, air release capacity, and foam prevention. Moreover, hydraulic oils
20 have to exhibit extremely good filterability properties which are measured and evaluated using a certain number of detailed filterability tests such as the AFNOR NFE 48690, 48691 and 48693, CETOP RP 124H, DENISON and PALL tests.

Unfortunately, the formulation scope required to satisfy the principal
25 performance criteria often militates against good filterability because, in general, the use of additives is harmful for filterability. For example, the use of viscosity index (VI) improvers and pour point depressors (PPD) has made it more difficult to formulate oils having a high viscosity index and/or better properties at low temperatures.

30 The filterability of hydraulic oils is currently an essential technical point because it is an important imperative for current and future formulations. Indeed, most hydraulic systems use decontamination filters. The contaminants may consist in metal particles, dust, lacquers, polymers resulting from oxidation and thermal stability factors. In fact, limiting pollution
35 by hydraulic oils has becoming a deciding factor for obtaining good performance in service, also including improved wear prevention by

reducing abrasive particles. Consequently, the trend is to reduce the porosity of the filters (in line) even further to a value of about 3 micrometres in certain cases.

Consequently, filterability tests in a dry and in a damp medium have been developed for evaluating, and offering means of improving, the filterability performance of hydraulic oils. However, in view of the very fine porosity of the filters used in these bench tests and also because of the presence of water in some of these operating procedures, the performances of hydraulic oils are sometimes lower than the acceptable criteria.

As the presence of water has an adverse effect on the filterability performance of hydraulic oils, most of the bench-scale filterability tests used at present include a period of storage of the oil artificially contaminated by water. The presence of water poses a problem because water undergoes adsorption by the calcium carbonates and calcium hydroxides forming part of the calcium salt detergents which are often present in hydraulic additives. Moreover, water interacts with the ZDDP liberating ZnO. These interactions lead to fine deposits which tend to block the filters.

Various technologies have been used in the past in an attempt to solve these problems. The most commonly used means known to date consist in using metal carboxylates in the manner described in the document GB 2 293 389, reducing the concentrations of ZDDP from about 8 mM/kg of oil to a value equal to or less than about 4 mM/kg of oil, or formulating additives with particular viscosity index improvers which are less harmful for filterability.

Summary of the invention

The inventors have discovered that it is possible to improve the filterability properties of lubricating oils by using agents improving filterability containing at least one polar group and at least one lipophilic chain having a particular length. More interestingly, if the compounds described below are used, the filterability performances are improved but this improvement obtained is not generally harmful for the principal performance criteria and may even have positive effects in certain cases.

The present invention relates in a general manner to a lubricating fluid, particularly a hydraulic oil, comprising:

1) a predominant amount of an oil having a viscosity suitable for lubrication; and

2) from 0.03% to 0.06% of an agent improving filterability, corresponding to the following formula:

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wherein Z represents a polar group containing one or more substituents chosen from:

- 10 a) phosphoric esters;
b) amides;
c) ethers;
d) amino alcohols;
e) ethoxylated amines;
15 f) mixtures thereof.

The number of said substituents forming the polar group may range from 1 to 30 but usually a number from 3 to 5 polar substituents is preferred.

As regards the lipophilic chain R forming the other portion of the agent improving filterability used in the present invention, this chain usually consists in a saturated or unsaturated hydrocarbyl chain having 14 to 24 and preferably 17 to 19 carbon atoms. The hydrocarbyl chain may be linear or branched, although linear chains are usually preferred. Although this lipophilic chain is preferably unsubstituted, it is possible to incorporate substituents or to insert heteroatoms or various groups in the chain since said insertions or substituents do not have a notable effect on the overall polarity of the molecule.

The present invention also relates to the use of agents improving filterability described in the present specification for improving the filterability of oils, particularly hydraulic oils.

The present invention also relates to a process for the production of a hydraulic fluid with improved filterability, which comprises the mixture of the following constituents:

a) a predominant amount of an oil having a viscosity suitable for lubrication; and

b) from 0.03% to 0.06% of an agent improving filterability, corresponding to the following formula:



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wherein Z represents a polar group containing one or more substituents chosen from the group comprising

- a) phosphoric esters;
- b) amides;
- 10 c) ethers;
- d) amino alcohols;
- e) ethoxylated amines;
- f) mixtures thereof,

15 and R represents a lipophilic chain having 14 to 24 carbon atoms.

Detailed description of the invention

In order to demonstrate more clearly the structural relationship
20 between the polar group and the lipophilic chain of the agents improving filterability of the present invention, examples of suitable categories of compounds are presented below.

A vast group of agents improving filterability includes those in which the polar group Z contains one or more constituents chosen from:

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- a) phosphoric esters;
- b) fatty amides;
- c) polyethers;
- d) ethoxylated amines;
- 30 e) mixtures thereof.

Each member of this group may itself form, with the appropriate hydrocarbyl chain, independent sub-groups of agents improving filterability falling within the scope of the present invention.

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A sub-group of specific phosphoric esters comprises phosphoric esters corresponding to the following formula:



wherein X represents H or R and at least one of the symbols X represents R, and R represents a saturated or unsaturated hydrocarbyl chain which may contain ether groups. The hydrocarbyl chain has 14 to 24 carbon atoms, advantageously 14 to 24 carbon atoms and preferably 17 to 19 carbon atoms. In a highly advantageous manner, R represents a group $[\text{CH}_3 - (\text{CH}_2)_{11} - \text{CH}_2 - (-\text{O} - \text{CH}_2 - \text{CH}_2 -)_3]$. An example of such phosphoric esters consists in RHODAFAC PA35 available commercially, supplied by Rhône Poulenc.

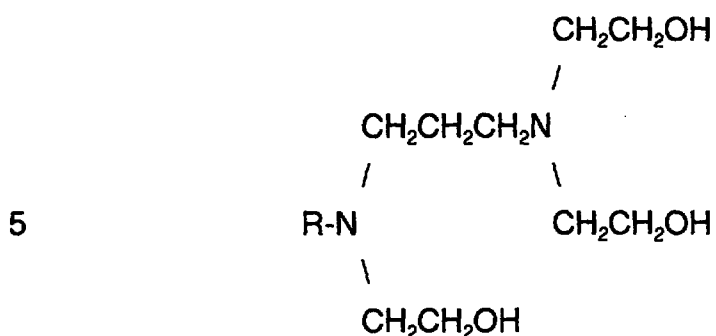
A sub-group of polyethers comprises compounds corresponding to the formula:



wherein X represents an integer from 3 to 12, preferably equal to 9, and R represents a hydrocarbyl chain having 14 to 24 carbon atoms and wherein, more advantageously, R represents a group $\text{C}_{15}\text{H}_{31}$, the polar group Z being represented by $-\text{O-(CH}_2\text{-CH}_2\text{O)}_x\text{H}$.

A suitable sub-group of ethoxylated amines comprises ethoxylated amines containing at least two ethoxy groups.

A more suitable group comprises ethoxylated amines corresponding to the following formula



wherein R represents a hydrocarbyl chain having 14 to 24 carbon atoms,
 and particularly an aliphatic chain $\text{C}_{18}\text{H}_{35}$.

A suitable sub-group of unsubstituted fatty amides comprises compounds corresponding to the following formula:



wherein R represents a hydrocarbyl chain having 14 to 24 carbon atoms and preferably 17 to 19 carbon atoms.

The concentration of the agents improving filterability described above must be adjusted such that the desired effect (improvement in the filterability characteristics of the oil) is obtained without being harmful for the other performances resulting from the action of other additives which may be present in the oil composition. More particularly, it is considered that excessive concentrations of the compounds used in the context of the present invention may have adverse effects, particularly on the oxidation stability, the thermal stability and the stability towards hydrolysis of the finished oil. For example, it has become apparent that high concentrations have adverse effects on tests such as the ASTM-D4310, ASTM-D943 and ASTM-D2619 tests.

The exact mechanism of action of the compounds used in the context of the present invention on the improvement in filterability is not fully understood. Without wishing to be bound to any particular theory, the inventors consider that there is no notable interaction in the proper sense of the word between the agents improving the filterability and the other compounds present in the lubricating oil.

However, it has become apparent that, in the competitive interactions taking place between the solid particles, polymers (VI improvers, PPD) and the water present in the oil, the polar substituents of the agents improving filterability have a preferential dispersant effect on the solid particles which makes it possible to prevent the formation of aggregates of certain dimensions and, consequently, to filter blockages. It has also become apparent that the polar substituents of the agents improving filterability of the present invention have a particular type of inhibition of the harmful effects of viscosity index improvers and pour point depressors, also due to preferential interactions with solid particles.

It has also become apparent that there is an important relationship between the polar substituents and the lipophilic chain.

It is possible to determine the choice of polar substituents and lipophilic substituents for the preparation of a particular agent improving filterability, in accordance with the present invention, by referring to the calculation of their polar/lipophilic ratio. A suitable method for calculating this ratio was described in a publication of "Atlas Chemical France" entitled "Le système HLB d'ATLAS" [the ATLAS HLB system]. In this document which is cited by way of reference in the present application, the polar/lipophilic ratio is identified by the hydrophilic/lipophilic balance (HLB).

It is possible to use a mixture of agents improving filterability, although a cumulative effect of the filterability properties is not necessarily observed. However, the inventors consider that complementary and even synergistic effects may occur if a plurality of different agents improving filterability is used in the same formulation. However, it should be borne in mind that the total concentration of the mixture of agents improving filterability should not exceed, notably, the concentrations described previously in order to avoid undesirable secondary effects which might interfere with the overall properties of the lubricating fluid formulation.

Agents improving filterability of the present invention are particularly useful for improving the filterability characteristics of lubricating oils and, preferably, hydraulic oils. They are effective independently of the presence or absence of a viscosity index improver in the oil. The improvement in filterability may be obtained for considerably different viscosity intervals. For example, in hydraulic oils and industrial oils, an improvement in filterability

may be obtained for grades ranging from ISO VG 15 to 150, preferably for grades ranging from ISO VG 32 to 68.

For example, the filterability test AFNOR NFE 48691 comprises the following steps:

- 5 - formulation of the oil
- incorporation of 0.2.% by weight of water and mixing to form an emulsion
- storage at 70°C for 72 hours, then storage at ambient temperature (24 hours)
- 10 - filtration of 300 ml of oil over a Millipore 0.8 mm filter at a pressure dependent on the rate of filtration
- measuring the time required to filter 50, 100, 200 and 300 ml of oil and calculating the corresponding IFE values.

15 In the AFNOR NFE 48691 tests, the filterability indices calculated for the test oils containing agents improving filterability have been substantially improved compared with reference formulations not containing agents improving filterability and, in fact, are close to the "ideal" filterability index which is equal to 1. Moreover, the incorporation of low concentrations of

20 agents improving filterability used in the present invention in additives does not generally prove to be harmful for other properties such as wear prevention, oxidation stability or thermal stability or the hydrolysis performances of hydraulic oils. This was measured using tests such as the

25 FZG seizing test, the Denison and Vickers Vane tests, and tests on piston pumps and the Cincinnati Milacron thermal stability tests and the ASTM D 943 and ATMD [sic] 4310 oxidation tests and the ASTM D 2619 stability towards hydrolysis test. In the manner mentioned above, it was also noted that some of the agents improving filterability may have an advantageous effect on the thermal stability and the oxidation performances.

30 The skilled person wishing to use the teachings of the present invention to prepare appropriate lubricating fluids may carry out this preparation using basic oils and additives currently available. Information concerning these other constituents is set out briefly below.

Basic lubricant

The basic lubricant may be chosen from hydraulic/transmission fluids, hydraulic brake fluids, fluids for power steering and fluids for tractors, the exact composition of which may vary slightly.

5 The lubricating oils of the present invention contain a predominant amount of an oil having a viscosity suitable for lubrication. Said oil may be any lubricating oil based on hydrocarbons, or a basic synthetic oil. It may be derived from synthetic or natural sources and it may be a paraffinic, naphthenic or asphaltic basic oil or consist in a mixture thereof.

10 In one embodiment, the oil having a viscosity suitable for lubrication is prepared from a crude mineral oil by physical separation processes such as distillation, deasphalting and dewaxing, or it may be prepared by a chemical conversion such as a catalytic or non-catalytic hydrotreatment of mineral oil fractions, or by a combination of chemical separation processes and a
15 chemical conversion; or it may consist in a basic synthetic hydrocarbon oil. Preferably, the oil having a viscosity suitable for lubrication has a kinematic viscosity from 5 to 220 cSt at 40°C.

Other additives

20 Other additives which are well known in practice may be present in the hydraulic fluid with increased filterability of the present invention. These additives may include, for example, antioxidants, viscosity index improvers, detergents, anti-rust additives, demulsifying agents, foam inhibitors, corrosion inhibitors, pour point depressors, and other anti-wear agents.

25 Examples of said additives are given below:

Antioxidants: include sterically hindered alkyl phenols such as 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol and 2,6-di-tert-butyl-4-(2-octyl-3-propanoic) phenol; N,N-di(alkylphenyl) amines; and alkylated phenylene-diamines.

30 Viscosity index improvers: include polymeric alkylmethacrylates and olefinic copolymers such as an ethylene-propylene copolymer or a styrene-butadiene copolymer.

Detergents: include calcium alkylsalicylates, calcium alkylphenates and calcium alkarylsulfonates.

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Anti-rust additives: include (short-chain) alkenylsuccinic agents [sic], partial esters thereof and nitrogen-containing derivatives thereof; and synthetic alkarylsulfonates, such as metal dinonylnaphthalene sulfonates.

Demulsifying agents: include alkoxylated phenols and phenol-
5 formaldehyde resins and synthetic alkylaryl sulfonates such as metallic dinonylnaphthalene sulfonates.

Foam inhibitors: include polymers of alkyl methacrylate and polymers of dimethylsilicone.

Corrosion inhibitors: include 2,5-dimercapto-1,3,4-thiadiazoles and
10 derivatives thereof, mercaptobenzothiazoles, alkyltriazoles and benzotriazoles.

Pour point depressors (PPD): include polymethacrylates.

Anti-wear agents: zinc alkyldithiophosphates (preferred), aryl
phosphates and phosphites, sulfur-containing esters and phosphosulfur
15 compounds, metal or ash-free dithiocarbamates.

The hydraulic fluid with increased filterability of the present invention may be produced by mixing the oil having a viscosity suitable for lubrication and the agent improving filterability together with the other additives described above which may be present in the oil having a viscosity suitable
20 for lubrication. The constituents of this mixture may interact during the mixing operation, modifying the agents improving filterability and/or the other additives.

The various preferred conditions indicated above apply both to the lubricating fluids and to the process for the production of a hydraulic fluid
25 and to the uses according to the present invention.

The present invention is illustrated in more detail by the following examples which are proposed by way of illustration of the present invention. They are not intended to limit its scope.

30 **EXAMPLES**

COMPARATIVE EXAMPLE: A formulation of basic additives containing functional quantities of zinc dithiophosphate, an ash-free dithiocarbamate, a detergent containing calcium, a phenolic antioxidant, anti-rust additives, demulsifying agents, a foam inhibitor based on a silicone polymer, were
35 mixed in such a way that the basic formulation of additives (XOIE 303J)

represents 0.80% by weight of the finished oil formulation. The finished oil formulation had a kinematic viscosity at 40°C equal to about 46 cSt.

5 COMPARATIVE EXAMPLE A: The basic formulation of additives was mixed in a refined basic oil with a solvent "A" with the addition of a PPD (of the PMA type) in a quantity of 0.2% by weight.

10 EXAMPLE 1: A quantity of 0.05% by weight of a commercial phosphoric ester "P1" (Rhodafac PA35 from Rhône Poulenc) was added to the finished oil of comparative example A.

15 EXAMPLE 2: A quantity of 0.05% by weight of a commercial phosphoric ester "P2" (CRODAFOS N3A from Croda) was added to the finished oil of comparative example A.

EXAMPLE 3: A quantity of 0.05% by weight of a commercial phosphoric ester "P3" (CRODAFOS N5A from Croda) was added to the finished oil of comparative example A.

20 EXAMPLE 4: A quantity of 0.03% by weight of a commercial fatty amide "OL" (CRODAMIDE O from Croda or Armeed O from Akzo) was added to the finished oil of comparative example A.

25 COMPARATIVE EXAMPLE B: The basic formulation of additives was mixed in a refined basic oil with a solvent "B" with the addition of a PPD (of the PMA type) in a quantity of 0.2 % by weight.

30 EXAMPLE 5: A quantity of 0.05% by weight of a commercial phosphoric ester "P1" (Rhodafac P PA35 from Rhône Poulenc) was added to the finished oil of comparative example B.

35 EXAMPLE 6: A quantity of 0.05% by weight of a commercial phosphoric ester "P2" (CRODAFOS N3A from Croda) was added to the finished oil of comparative example B.

EXAMPLE 7: A quantity of 0.05% by weight of a commercial phosphoric ester "P3" (CRODAFOS N5A from Croda) was added to the finished oil of comparative example B.

- 5 EXAMPLE 8: A quantity of 0.03% by weight of a commercial fatty amide "OL" (CRODAMIDE O from Croda or Armeed O from Akzo) was added to the finished oil of comparative example B.

- 10 COMPARATIVE EXAMPLE C: The basic formulation of additives was mixed in a refined basic oil with a solvent "C" with the addition of a PPD (of the PMA type) in a quantity of 0.2% by weight and the addition of a VI improver (of the PMA type) in a quantity of 4.65% by weight.

- 15 EXAMPLE 9: A quantity of 0.05% by weight of a commercial phosphoric ester "P1" (Rhodafac PA 35 from Rhône Poulenc) was added to the finished oil of comparative example C.

- 20 EXAMPLE 10: A quantity of 0.05% by weight of a commercial phosphoric ester P2" (CRODAFOS N3A from Croda) was added to the finished oil of comparative example C.

- 25 EXAMPLE 11: A quantity of 0.05% by weight of a commercial phosphoric ester "P3" (CRODAFOS N5A from Croda) was added to the finished oil of comparative example C.

EXAMPLE 12: A quantity of 0.03% by weight of a commercial fatty amide "OL" (CRODAMIDE O from Croda or Armeed O from Akzo) was added to the finished oil of comparative example C.

- 30 COMPARATIVE EXAMPLE D: The basic formulation of additives was mixed with a "basic formulation speciality" containing a certain quantity of a VI improver (of the PMA type).

- 35 EXAMPLE 13: A quantity of 0.05% by weight of a commercial phosphoric ester "P1" (Rhodafac PA 35 from Rhône Poulenc) was added to the finished oil of comparative example D.

EXAMPLE 14: A quantity of 0.05% by weight of a commercial phosphoric ester "P2" (CRODAFOS N3A from Croda) was added to the finished oil of comparative example D.

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EXAMPLE 15: A quantity of 0.05% by weight of a commercial phosphoric ester "P3" (CRODAFOS N5A from Croda) was added to the finished oil of comparative example D.

10 EXAMPLE 16: A quantity of 0.03% by weight of a commercial fatty amide "OL" (CRODAMIDE O from Croda or Armeed O from Akzo) was added to the finished oil of comparative example D.

15 The above-mentioned examples were evaluated in the filterability tests AFNOR NFE 48690 (A, B, C, D) and AFNOR NFE 48691 (A, B).

Table 1 below summarised the test results.

TABLE 1

Filterability tests on formulations HM and HV in oil of grade
ISO VG 46 (filterability index IF and IFE)

Filterability test	AFNOR NFE	48690	48691	48691	48690	48690	48690
Type of oil		HM	HM	HM	HM	HV	HV
Basic oils		A	B	A	B	C	D
Grade	ISO	VG46	VG46	VG46	VG46	VG46	VG46
Constituents	Amount (wt.%)						
Reference additives	XOIE 303 J	1.58	8.1	1.68	3.2	1.32	1.28
P1	0.05	1.13	1.11	1.31	1.14	1.21	1.12
P2	0.05	1.05	1.10	1.30	1.16	1.27	1.30
P3	0.05	1.10	1.11	1.16	1.11	1.23	1.26
OL	0.03	1.03	1.18	1.23	1.19	1.32	1.23

**CLAIMS**

1. A lubricating fluid comprising
- 1) a predominant amount of an oil having a viscosity suitable for
5 lubrication; and
- 2) from 0.03% to 0.06% of an agent improving filterability or a mixture thereof, corresponding to the following formula:

R-Z

wherein Z represents a polar group containing one or more substituents
10 chosen from the group consisting of

- a) phosphoric esters;
b) amides; (*mono*)
c) ethers;
d) amino alcohols;
15 e) ethoxylated amines;
f) mixtures thereof,

and R represents a lipophilic chain having 14 to 24 carbon atoms.

2. A lubricating fluid according to claim 1, wherein R contains 17 to
19 carbon atoms.
- 20 3. A lubricating fluid according to claim 1 or 2, wherein Z is chosen from the group consisting of:
- a) phosphoric esters;
b) polyethers;
c) ethoxylated amines;
25 d) mixtures thereof.

4. A lubricating fluid according to any one of claims 1 to 3, wherein the agent improving filterability is a phosphoric ester corresponding to the following formula:



wherein X represents H or R and at least one of the symbols X represents
35 R, and R represents a saturated or unsaturated hydrocarbyl chain which

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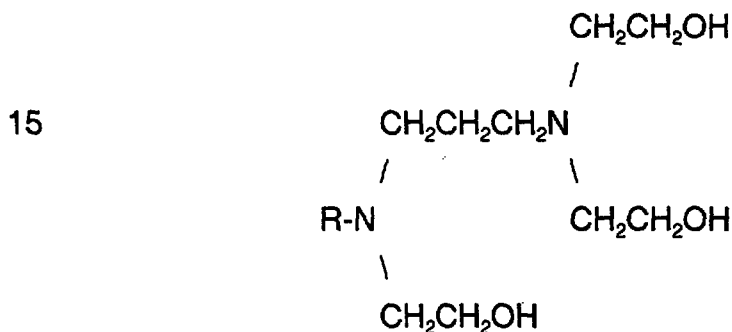


may contain ether groups, said hydrocarbyl chain having 14 to 24 carbon atoms and preferably 17 to 19 carbon atoms.

5. A lubricating fluid according to any one of claims 1 to 3, wherein the agent improving filterability is a compound corresponding to the formula
5 $R-O-(CH_2-CH_2O)_xH$ wherein X represents an integer from 3 to 12, preferably equal to 9, and R represents a hydrocarbyl chain having 14 to 24 carbon atoms, R representing preferably a $C_{11}H_{23}$ or $C_{15}H_{31}$ group.

6. A lubricating fluid according to claim 3, wherein the ethoxylated amine contains at least two ethoxy groups.

10 7. A lubricating fluid according to claim 6, wherein the agent improving filterability is a compound corresponding to the following formula:



wherein R represents a hydrocarbyl chain having 14 to 24 carbon atoms, and R represents preferably an aliphatic chain $C_{18}H_{35}$.

8. A lubricating fluid according to claim 1, wherein the agent improving filterability is an unsubstituted fatty amide corresponding to the
25 following formula:



wherein R represents a hydrocarbyl chain having 14 to 24 carbon atoms and
30 preferably 17 to 19 carbon atoms.

9. A lubricating fluid according to any one of claims 1 to 8, said lubricating fluid consisting in a hydraulic oil.

10. An additive for a lubricating fluid, comprising an effective quantity of an agent improving filterability according to any one of claims 1 to 8.

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11. The use of an effective quantity of an agent improving filterability according to any one of claims 1 to 8 as additive intended to improve the filterability of a lubricating fluid.

12. The use according to claim 11, wherein the lubricating fluid is a hydraulic oil.

13. The use according to claim 11 or 12, wherein the concentration of the agent improving filterability in the said fluid is equal to 0.03% to 0.06% by weight.

14. The use according to any one of claims 11 to 13, the said use being intended for a hydraulic system containing a piston pump having wear surfaces containing copper or a copper alloy and, optionally, a vane pump having wear surfaces containing steel.

15. A process for the production of a hydraulic fluid with improved filterability which comprises the mixture of the following constituents:

a) a predominant amount of an oil having a viscosity suitable for lubrication; and

b) from 0.03% to 0.06% of an agent improving filterability, corresponding to the following formula

R-Z

wherein Z represents a polar group containing one or more substituents chosen from the group consisting of:

a) phosphoric esters;

b) amides; (amino)

c) ethers;

d) amino alcohols;

e) ethoxylated amines;

f) mixtures thereof,

and R represents a lipophilic chain having 14 to 24 carbon atoms.

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