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(54) **ADDITIVES CONTAINING CERIUM FOR LUBRICATING COMPOSITIONS AND METHOD FOR THE PREPARATION THEREOF**

CERHALTIGE ADDITIVE FÜR SCHMIERSTOFFZUSAMMENSETZUNGEN UND
HERSTELLUNGSVERFAHREN DAFÜR

ADDITIFS CONTENANT DU CÉRIUM POUR DES COMPOSITIONS LUBRIFIANTES ET LEUR
PROCÉDÉ DE PRÉPARATION

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Description

[0001] The present invention relates to oil dispersible overbased organic salts containing Cerium and an alkaline earth metal, their synthesis method and use in lubricating oils as detergent additives, anti-friction additives, additives for extreme-pressure tribological couplings and also as additives for improving the quality of diesel engine emissions.

[0002] The use of Cerium-based compounds is well-known in the state of the art, as combustion-enhancing additives for fuels, for reducing the emissions of pollutants, such as particulate, unburned hydrocarbons, carbon monoxide and nitrogen oxides. In the USA patent 4,474,580, for example, the use of a blend of Cerium enolate and Iron enolate is described, and in the USA patent applications 2005/0160663 and 2007/015656 the use is described of compounds containing Cerium, Iron or Platinum as fuel additives.

[0003] The requirement of satisfying the increasingly severe limits relating to the emission of polluting substances in diesel engines, is leading to an increasing diffusion of the use of particulate filters or traps, often indicated with the acronym DPF (Diesel Particulate Filter). The above traps exert a physical filtering action of the exhaust gases, retaining almost all of the particles suspended in the gas. After a short period of use they become blocked by the accumulation of the particles, which causes an increase of exhaust gases counter-pressure, jeopardizing the performances of the engine. It is consequently necessary to regenerate the traps by bringing the temperature of the exhaust gases to temperature values which allow the combustion of the carbonaceous part of the particulate. This temperature can be suitably lowered with the use of additives in the fuel which exert a catalytic action. The use of fuel additives containing Cerium compounds for the catalytic regeneration of particulate filters in diesel engines, is known in the state of the art. International patent application WO 2005/012465 and the French patent FR 2873157, for example, respectively describe the use of dispersions containing Cerium oxide and solutions of Cerium nitrate as additives which are fed on the vehicle to the fuel. Patent application EP 1344812-A1, on the other hand, describes the use, as additive for diesel fuels, of overbased salts of various metals, of which preferred metals are Iron and Cerium. Some of the overbased products described in the European patent, which are dispersed in oil or solvent, are metal phenates, sulphurized metal phenates, metal salicylates, alkyl-aryl metal sulphonates and metal carboxylates, of which carboxylates are preferred. The overbased additive can be previously mixed with the fuel or mixed with the fuel on the vehicle. In that patent the synthesis of those products is not described.

[0004] There are only a few examples in the known art, however, of the use of compounds containing Cerium as additives for lubricants. It is known that some Cerium compounds give lubricating oils antiwear and antifriction properties. US patents 4,946,608 and 5,200,098, for example, describe the use of an oil dispersion of cerium fluoride as antiwear additive for lubricating oils and greases, whereas patent SU 1,721,077 describes the use of a mixture of cerium oleate with other metal-oleates as antifriction additive. Patent application JP 2004/182829 describes the use of an additive for lubricating oils containing boron and a dispersion of metal oxides, among which Cerium oxide, for improving the antifriction properties of the oil and reducing the content of toxic substances in the exhaust gases. Patent application US 2004/194454 describes a lubricating oil with antiwear properties, containing organometallic compounds of Cerium, which when fed to the fuel of a diesel engine equipped with a particulate filter (DPF), facilitates the regeneration of the filter promoting the catalytic oxidation of the particulate.

[0005] German patent DE 3926817 describes the use of lubricating oils containing cerium or cerium alloys for reducing the pollutants contained in exhaust gases.

[0006] International patent application WO 2007/022962 describes a lubricating oil containing a first combustion improver, such as for example, an alkyl benzene cerium sulphonate or a cerium phenate and a second combustion improver such as for example, an alkyl iron carboxylate or ferrocene. The two combustion improvers, dissolved or dispersed in a solvent, are effective when used in such a concentration as to introduce a quantity of about 20 ppm of Cerium and 200 ppm of Iron into the oil. The use of this oil in an internal combustion engine allows a reduction in the carbonaceous residues, an increase in the engine life, a reduction in the fuel and oil consumption and in polluting emissions.

[0007] None of the patents of the known art describes additives for lubricants based on oil dispersible compounds containing Cerium which, in addition to improving the emissions of diesel engines, also have detergent, antiwear, anti-friction properties and also an action on extreme-pressure tribological couplings.

[0008] The present invention therefore relates to oil dispersible overbased salts of organic acids containing Cerium and an alkaline earth metal, their synthesis method and use in lubricating oils as detergent additives, antiwear additives, antifriction additives, additives for extreme-pressure tribological couplings and also as additives for improving the quality of the emissions of diesel engines. In particular, the use of these additives in lubricating oils for diesel engines allows the compounds containing Cerium to be conveyed onto the particulate trap for the treatment of exhaust gases improving its efficiency. The present invention relates to overbased salts of organic acids, containing Cerium and an alkaline earth metal, dispersible in mineral oil. Here is disclosed a synthesis process of the above overbased salts, which consists in:

- i) treating Cerium compounds of organic acids with a hydroxide or oxide of an alkaline earth metal and subsequent carbonation with carbon dioxide; or

- ii) treating a mixture, consisting of Cerium compounds of organic acids and an organic acid, with a hydroxide or oxide of an alkaline earth metal and subsequent carbonation with carbon dioxide; or
 iii) treating, in a single step, an organic acid with a basic Cerium compound and with a hydroxide or oxide of an alkaline earth metal and subsequent carbonation with carbon dioxide.

[0009] The overbased salts of organic acids, containing Cerium and alkaline earth metal, object of the present invention, have a Cerium content corresponding to a ratio between the equivalents of Cerium and those of organic acid ranging from 0.1 to 1.2, preferably from 0.4 to 1 and a content of alkaline earth metal corresponding to a ratio between the equivalents of alkaline earth metal and the equivalents of organic acid ranging from 1 to 40, preferably from 5 to 30. Preferred alkaline earth metals are Magnesium and Calcium. The preferred alkaline earth metal is Calcium.

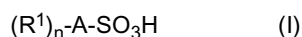
[0010] The objective of the synthesis methods is not only to prepare salts containing Cerium, but also to obtain a stable colloidal dispersion of these salts in a lubricating base. The achievement of this objective is not easy; if the synthesis is not effected with all the necessary expedients, the additive can be difficult to filter or the coagulation of the colloid may occur with the formation of gel.

[0011] The synthesis of the Cerium compounds of organic acids comprises the reaction in the presence of the following components:

- A) an organic acid or a mixture of organic acids;
- B) a basic compound of Cerium;
- C) optionally a solvent or mixture of solvents;
- D) a promoter or mixture of promoters;
- E) optionally lubricating oil.

[0012] Component A) can be:

A-1) a sulphonic acid having the formula



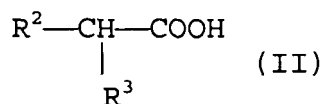
wherein R^1 is a linear or branched alkyl group containing from 6 to 40 carbon atoms or R^1 is an alkyl substituent deriving from a polymer of a C_2-C_6 olefin;

A is a C_6-C_{20} aromatic hydrocarbon, an aliphatic hydrocarbon having from 5 to 20 carbon atoms. A is preferably benzene, naphthalene, toluene, xylenes and more preferably benzene; n is zero or an integer ranging from 1 to 5, preferably 1, 2 or 3, more preferably 1 or 2.

[0013] Examples of sulphonic acids which can be used are di-alkyl benzene sulphonic acids and mono-alkyl benzene sulphonic acids. Examples of di-alkyl benzene sulphonic acids are: dinonyl benzene sulphonic acid, didecyl benzene sulphonic acid, diundecyl benzene sulphonic acid, didodecyl benzene sulphonic acid, dialkyl benzene sulphonic acids which contain alkyl substituents deriving from polypropylene, polyisobutene and poly-1-butene, or mixtures of the above acids. Examples of mono-alkyl benzene sulphonic acids which can be used are those containing alkyl substituents deriving from polypropylene, polyisobutene or mixtures of the above acids.

[0014] The preferred sulphonic acids have an acid content ranging from 60 to 99% by weight, preferably from 70 to 90% by weight and have an inorganic acidity, expressed as sulphuric acid, preferably lower than 5% by weight.

A-2) a carboxylic acid having the formula:



wherein R^2 is a linear or branched alkyl or alkenyl group, containing from 6 to 40 carbon atoms and preferably from 10 to 24;

R^3 is either hydrogen, an alkyl group containing from 1 to 4 carbon atoms, or $-CH_2COOH$.

[0015] Examples of saturated carboxylic acids having formula (II) are capric acid, lauric acid, myristic acid, stearic acid, isostearic acid, arachidic acid, behenic acid and lignoceric acid.

[0016] Examples of unsaturated carboxylic acids having formula (II) are lauroleic acid, myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, erucic acid, linoleic acid and linolenic acid. Mixtures of acids can be used, such as mixtures of synthetic and natural acids, containing both saturated and unsaturated acids.

A-3) a salicylic acid optionally substituted with linear or branched alkyl groups, in a number ranging from 1 to 3, preferably 1 to 2, containing from 6 to 40 carbon atoms.

[0017] Examples of alkyl-substituted salicylic acids are those containing alkyl substituents deriving from polypropylene, polyisobutene and poly-1-butene.

A-4) a phenol or sulphurized phenol, optionally substituted with linear or branched alkyl groups, in a number ranging from 1 to 3, preferably from 1 to 2, containing from 6 to 40 carbon atoms. Examples of phenols or alkyl-substituted sulphurized phenols are those containing alkyl substituents deriving from polypropylene, polyisobutene and poly-1-butene.

[0018] Component (A) can also be a mixture of organic acids (A-1), (A-2), (A-3) and (A-4). Component (A) is preferably a sulphonic acid.

[0019] Component (B) is a basic compound of Cerium in oxidation state (IV), such as Cerium hydroxide (IV), Cerium oxide (IV) or a mixture thereof; or a basic compound of Cerium in oxidation state (III), such as Cerium carbonate (III). The quantity of basic Cerium compound used corresponds to a ratio between the equivalents of the basic Cerium compound and the organic acid equivalents ranging from 0.2 to 2, preferably from 0.5 to 1.5.

[0020] Component (C) is a solvent or mixture of solvents selected from:

a hydrocarbon solvent which can be both aromatic and aliphatic. Examples of suitable hydrocarbon solvents include benzene; alkyl-substituted benzene, such as for example toluene, xylenes, halogen-substituted benzenes; aliphatic paraffins, such as hexane and heptane; cycloaliphatic paraffins. The preferred solvent is toluene.

[0021] The solvent, when used, is added in a quantity corresponding to a weight percentage, calculated with respect to the organic acid, ranging from 10 to 800, preferably from 50 to 400.

[0022] Component (D) is a promoter of the neutralization reaction selected from:

D-1) an alcohol containing from 1 to 20 carbon atoms, such as for example methanol or 2-ethyl hexanol.

D-2) Water, which can come from the solvent, from another promoter, it can be the reaction water, or it can be added.

D-3) a glycol, such as for example ethylene glycol or a polyalkylene glycol.

D-4) a ketone containing from 1 to 20 carbon atoms, such as cyclohexanone.

D-5) an ester of a carboxylic acid, such as ethyl acetate.

[0023] The preferred promoters are water and methanol.

[0024] The promoter is added in a quantity corresponding to a weight percentage, calculated with respect to the basic cerium compound, ranging from 5 to 800, preferably from 10 to 500.

[0025] Considering the use of the product, it is generally preferable to incorporate component (E), which is a lubricating base oil, as solvent, into the product. The lubricating base oil can be of an animal, vegetable, mineral origin, or it can be a synthetic oil. Mineral and synthetic lubricating base oils are preferred. Suitable mineral lubricating base oils are those deriving from petroleum, such as for example, naphthene-based oils, paraffin-based oils or a mixture of these. Suitable synthetic lubricating base oils are esters, such as dioctyl adipate, dioctyl sebacate, tri-decyl adipate, or polymeric hydrocarbons, such as for example, poly-alpha-olefins or liquid polyisobutenes. Particularly preferred lubricating base oils are mineral-based oils.

[0026] The lubricating base oil, when used, is added at the beginning of the reaction together with the other reagents, or during the reaction, or at the end of the reaction, in a quantity corresponding to a weight percentage, calculated with respect to the organic acid (A), ranging from 30 to 800, preferably from 50 to 300.

[0027] Other components can be optionally added to control the variation in the viscosity and improve the filterability of the product, such as for example, short-chain carboxylic acids and inorganic halides.

[0028] The synthesis of the compound of organic acids containing Cerium, can be carried out by adding components (A), (B), (D), optionally (C), and (E) to the reaction in any order. The synthesis is preferably effected by mixing all the components (A), (B), (D), optionally (C), and (E) at the beginning, or it can be carried out by initially adding component (B) to a mixture consisting of component (D) and optionally component (C) and subsequently adding component (A). In the latter case, component (E), when used, is added at the beginning together with components (D) and (C), or subsequently to component (A), or a fraction of (E) is added at the beginning together with components (D) and (C) and the remaining fraction of (E) is subsequently added to component (A).

[0029] The temperature at which the reaction is carried out ranges from 15 to 200°C, preferably from 30 to 150°C. The selection of the optimum temperature depends on the kind of solvent used.

[0030] At the end of the reaction, the product is recovered by separating, through distillation, the promoter (D), including

the reaction water, and the solvent (C), if present. If the synthesis has been effected by adding the lubricating base oil (E), the product at the end is obtained as an oil solution.

[0031] The distillation of the solvents is carried out by increasing the temperature to a maximum value of 200°C, preferably up to 160°C and maintaining the product at this temperature for the time necessary for obtaining the complete removal of the solvents. The distillation of the solvents can be effected at atmospheric pressure, or under vacuum, or partly at atmospheric pressure and partly under vacuum.

[0032] At the end the product is filtered using a filtration aid, or, alternatively, it can be centrifuged.

[0033] The synthesis method of the overbased salts of organic acids, containing Cerium and an alkaline earth metal differs depending on whether the compound to be made overbased is i) a compound of organic acids containing Cerium, or ii) a mixture of an organic compound containing Cerium with an organic acid, or iii) an organic acid.

[0034] In cases i) and ii), the synthesis method comprises the reaction between the following components:

A1) a compound of organic acids containing Cerium or a mixture of the above compound with an organic acid;

B1) a basic compound of an alkaline earth metal;

C1) a solvent or a mixture of solvents;

D1) a promoter or a mixture of promoters;

E1) optionally lubricating base oil;

F1) carbon dioxide.

[0035] The compound of organic acids containing Cerium, which is part of component (A1) is that characterized by a Cerium content corresponding to a ratio between the equivalents of Cerium and those of organic acid, from which it derives, ranging from 0.1 to 1.2, preferably from 0.4 to 1. Increasing of Cerium content lead to a more difficult formation of a stable colloidal dispersion of the overbased salt containing Cerium and an alkaline earth metal. The organic acid optionally contained in the component (A1) is equal to component (A), already described. The mixture consisting of the compound of organic acids containing Cerium and an organic acid can contain a weight percentage of the compound containing Cerium varying from 10 to 99, preferably from 40 to 90.

[0036] Component (B1) is a basic component of an alkaline earth metal, preferably a basic compound of Calcium, Magnesium, Barium, more preferably a basic compound of Calcium. The basic compound is preferably an oxide or hydroxide. Examples of bases are Calcium oxide (CaO) or Calcium hydroxide (Ca(OH)₂). Component B(1) can be completely added at the beginning of the reaction, or it can be partly added at the beginning and partly in different intermediate points of the reaction. The quantity of basic compound of alkaline earth metal used corresponds to a ratio between the equivalents of the basic compound of alkaline earth metal and those of component (A1), ranging from 1 to 40, preferably from 5 to 30.

[0037] Component (C1) is the solvent, the same as component (C), already described above. The solvent is used in a quantity corresponding to a weight percentage, calculated with respect to the component (A1), ranging from 10 to 500, preferably from 50 to 300.

[0038] Component (D1) is the promoter, the same as component (D), already described above. The promoter is added in a quantity corresponding to a weight percentage, calculated with respect to the basic compound of alkaline earth metal, ranging from 2 to 500, preferably from 5 to 300.

[0039] Component (F1) is carbon dioxide, used for carbonating the excess of component (B1) contained in the product and subsequently added to each addition of component (B1).

[0040] The carbon dioxide can be added as a gas or as a solid, preferably as a gas. The quantity of carbon dioxide used corresponds to a ratio between the equivalents of carbon dioxide and those of alkaline earth metal base, ranging from 0.6 to 1.1, preferably from 0.7 to 0.9. The carbon dioxide is preferably added in defect with respect to the base to be carbonated (oxide or hydroxide) in order to stabilize the colloidal dispersion of the product, facilitating its subsequent filtration.

[0041] Considering the use of the product, it is generally preferable to incorporate component (E1) in the product, as solvent, which is a lubricating base oil, the same as component (E), described above. The lubricating base oil, when used, is added at the beginning of the synthesis together with the other reagents, or during the synthesis, or at the end of the synthesis, in a quantity corresponding to a weight percentage, calculated with respect to component (A1) ranging from 30 to 800, preferably from 50 to 300.

[0042] Other components can be optionally added to promote the carbonation, control the variation in the viscosity and improve the filterability, such as for example short-chain carboxylic acids and inorganic halides.

[0043] The synthesis, object of the present invention, of overbased salts of organic acids, containing Cerium and an alkaline earth metal, carried out by over-basifying a compound of organic acids containing Cerium, or a mixture of said compound with an organic acid, can be effected by adding components (A1), (B1), (C1), (D1), optionally (E1) to the reaction in any order.

[0044] Component (F1) must be added subsequently to component (B1). The synthesis can be conveniently carried

out by initially adding component (B1) to a mixture consisting of component (C1) and a part of component (E1) and subsequently adding component (A1). After adding component (D1) the carbonation is carried out with carbon dioxide (component F1), after which a second part of component (E1) is added and after maturation the remaining quantity of (E1) is added. The synthesis can also be carried out by initially adding component (B1) to a mixture consisting of component (C1), component (D1) and a part of component (E1) and subsequently adding component (A1). Carbonation is then carried out with carbon dioxide (component F1), after which a second part of component (E1) is added and after maturation the remaining quantity of (E1) is added.

[0045] The temperature at which the first part of the synthesis is carried out, which consists of the neutralization and overbasifying reactions, ranges from 15°C to 200°C, preferably from 30°C to 150°C. The selection of the optimum temperature depends on the nature of the solvent used.

[0046] The carbonation reaction, on the other hand, is carried out at a temperature ranging from 10°C to 150°C, preferably from 15°C to 100°C. The addition of the carbon dioxide as gas is performed over a period of time ranging from 10 minutes to 6 hours, preferably from 1 to 4 hours. The carbonation is followed by maturation, which is carried out at a temperature ranging from 30°C to 150°C, for a time ranging from 10 minutes to 4 hours, preferably from 20 minutes to 3 hours.

[0047] At the end of the reaction, the product is recovered by separating through distillation, the promoter (D1), including the reaction water, and the solvent (C1). If the synthesis has been carried out by adding lubricating base oil (E1), the end-product is obtained as an oil-solution.

[0048] The distillation of the solvents is effected by increasing the temperature to a maximum value of 200°C, preferably up to 160°C and maintaining the product at this temperature for the time necessary for obtaining the complete removal of the solvents.

[0049] The distillation of the solvents can be effected at atmospheric pressure, or under vacuum, or partly at atmospheric pressure and partly under vacuum.

[0050] At the end, the product is filtered using a filtration coadjuvant, or, alternatively it can be centrifuged.

[0051] In case iii) in which the synthesis of the overbased salts of organic acids, containing Cerium and an alkaline earth metal is carried out in a single step using the organic acid, the synthesis method comprises reaction between the following components:

A2) An organic acid or a mixture of organic acids;

B2) A basic compound of Cerium;

C2) A basic compound of an alkaline earth metal;

D2) A solvent or mixture of solvents;

E2) A promoter or mixture of promoters;

F2) Optionally lubricating oil;

G2) Carbon dioxide.

[0052] Component (A2) is an organic acid, the same as component (A), previously described.

[0053] Component (B2) is a basic compound of Cerium the same as component (B), previously described. The quantity of basic compound of Cerium used corresponds to a ratio between the equivalents of the basic compound of Cerium and those of organic acid ranging from 0.2 to 2, preferably from 0.5 to 1.5.

[0054] Component (C2) is a basic compound of an alkaline earth metal, the same as component (B1), previously described. The quantity of basic compound of alkaline earth metal used corresponds to a ratio between the equivalents of the basic compound of alkaline earth metal and those of component (A2), ranging from 1 to 40, preferably from 5 to 30.

[0055] Component (D2) is the solvent, the same as component (C), previously described. The solvent is used in a quantity corresponding to a weight percentage, calculated with respect to component (A2), ranging from 10 to 500, preferably from 50 to 300.

[0056] Component (E2) is the promoter of the neutralization and carbonation reactions, the same as component (D), previously described. The promoter is added in a quantity corresponding to a weight percentage, calculated with respect to the sum of the basic compounds (B2) and (C2), ranging from 2 to 500, preferably from 5 to 300.

[0057] Component (G2) is carbon dioxide, which is used as component (F1), previously described. The quantity of carbon dioxide used corresponds to a ratio between the equivalents of carbon dioxide and those of the base in excess with respect to the organic acid, ranging from 0.6 to 1.1, preferably from 0.7 to 0.9. The carbon dioxide is preferably added in defect with respect to the base to be carbonated (oxide or hydroxide) in order to stabilize the colloidal dispersion of the product, facilitating its subsequent filtration.

[0058] Considering the use of the product, it is generally preferable to incorporate component (F2), which is a lubricating oil, in the product, as solvent, the same as component (E), described above. The lubricating base oil, when used, is added at the beginning of the synthesis together with the other reagents, or during the synthesis, or at the end of the synthesis, in a quantity corresponding to a weight percentage, calculated with respect to component (A2) ranging from

30 to 800, preferably from 50 to 300.

[0059] Other components can be optionally added to promote the carbonation, control the variation in the viscosity and improve the filterability, such as for example short-chain carboxylic acids and inorganic halides.

[0060] The synthesis, object of the present invention, of overbased salts of organic acids, containing Cerium and an alkaline earth metal, carried out in a single step by treating an organic acid with basic compounds of Cerium and basic compounds of alkaline earth metal, can be effected by adding components (A2), (B2), (C2), (D2), (E2), optionally (F2), to the reaction in any order.

[0061] Component (G2) must be added subsequently to components (B2) and (C2). The synthesis can be conveniently carried out, for example, by initially adding component (B2) to a mixture consisting of component (D2) and a part of component (F2) and subsequently adding component (A2). Component (C2) is then added followed by component (E2) and the carbonation is subsequently carried out with carbon dioxide (component G2), after which a second part of component (F2) is added and after maturation the remaining quantity of (F2) is added. The synthesis can also be carried out by initially adding component (B2) to a mixture consisting of component (D2), component (E2) and a part of component (F2) and subsequently adding component (A2). Component (C2) is then added and carbonation is subsequently effected with carbon dioxide (component G2), after which a second part of component (F2) is added and, after maturation, the remaining quantity of (F2) is added.

[0062] The temperature and time conditions of the various neutralization, overbasifying, carbonation and maturation phases are the same as those previously described in cases i) and ii) of the synthesis of overbased salts containing Cerium and an alkaline earth metal.

[0063] At the end of the reaction, the product is recovered by separating through distillation, the promoter (E2), including the reaction water, and the solvent (D2). If the synthesis has been carried out by adding lubricating base oil (F2), the end-product is obtained as an oil-solution.

[0064] The distillation of the solvents is effected as already described in cases i) and ii) of the synthesis of overbased salts of Cerium and alkaline earth metal. At the end, the product is filtered using a filtration aid, or, alternatively, it can be centrifuged.

[0065] The oil-dispersions of organic acids compounds containing Cerium and overbased salts of organic acids containing Cerium and alkaline earth metals, object of the present invention, can be used in lubricating compositions as additives with detergent properties, capable of limiting the formation of deposits. The overbased salts of organic acids containing Cerium and alkaline earth metals, containing a large basicity reserve, are also capable of neutralizing the acid products formed in the lubricating oil of an internal combustion engine preventing corrosion phenomena.

[0066] The compounds, object of the present invention, can also be used in lubricating compositions as additives capable of improving the antifriction and antiwear properties and as additives for extreme-pressure tribological couplings.

[0067] The above compounds can also be used in lubricating compositions for improving the quality of internal combustion engine emissions. In particular, the use of these additives in lubricating oils for diesel engines allows the compounds containing Cerium to be conveyed onto the particulate trap for the treatment of exhausted gases improving its efficacy.

[0068] A further object of the present invention therefore relates to lubricating compositions containing one or more lubricating base oils of a synthetic, mineral, vegetable or animal origin and the compounds, object of the present invention. The compounds of organic acids containing Cerium, and the overbased salts of organic acids containing Cerium and an alkaline earth metal can be used in lubricating compositions in a combination, at a concentration expressed as weight percentage with respect to the lubricating oil, ranging from 0.2 to 10, preferably from 0.5 to 7. These lubricating compositions, used for example as oils for motor vehicles, can also contain, in addition to the above additives, other detergent, antifriction, antiwear additives and supplementary additives for extreme-pressure tribological couplings, antioxidants, dispersants, additives for improving the viscosity index, additives for lowering the slip point and others.

[0069] The following examples are provided for purely illustrative and non-limiting purposes of the present invention.

Synthesis of additives containing Cerium

[0070] In examples 1-4 provided hereunder, the parameter TBN (total base number) is measured in mg KOH/g, as described in the method ASTM D2896. In these examples, the synthesis reactions of the additives containing Cerium are carried out in a Mettler RC-1 calorimeter consisting of a 5-necked jacketed glass reactor, having a volume of 2 litres, thermostat-regulated by circulation in the jacket of a fluid coming from a thermocryostat and equipped with: a mechanical blade stirrer; a Claisen condenser cooled with tap water, connected to a vacuum line and equipped with a flask for collecting the distillate; a bottom outlet with a teflon tap through which carbon dioxide is bubbled into the reaction mass; a thermocouple for measuring the temperature. The system is controlled by a computer, which allows the desired heating and cooling programs to be set. The feeding of the carbon dioxide is effected by a cylinder, positioned on a balance, which is connected to the bottom of the reactor by means of a rubber tube.

Example 1

[0071] The following reagents are added to the reactor described above: 853 g (1.333 moles) of dialkylbenzenesulphonic acid (SP1270 of Sasol Italy S.p.A.), characterized by a Molecular Weight = 480, a content of active substance (sulphonic acid content) = 75% and an inorganic acidity (H_2SO_4) = 1.8% weight; 98 g (0.471 moles) of cerium (IV) hydroxide; 80 g of methanol. The stirring is initiated and it is observed that after the addition of methanol neutralization heat develops which increases the internal temperature to about 38-40°C. The internal temperature is increased to 60°C maintaining it at this value for 2 hours. After this period, the infrared analysis of a sample taken from the reactor is effected, which reveals that the neutralization of the sulphonic acid is not complete (band at 898.5 cm^{-1}). At this point the methanol and reaction water are removed by distillation using the following heating program at atmospheric pressure:

- from 60°C to 110°C in 180 minutes
- from 110°C to 160°C in 60 minutes

[0072] When the temperature has reached 160°C, the distillation is continued, reducing the pressure to 100 mbar, for an overall time of 60 minutes, in order to remove the residual volatile substances. The quantity of distillate collected is equal to 101.7 g. At the end of the stripping, the product has a content of sediments, measured in heptane according to the method ASTM D96, equal to 1.8% by volume.

[0073] The product is treated with a quantity of filtration earth equal to 3% by weight and is filtered on a jacketed steel filter having a volume of 1 litre, with a filtering surface consisting of an 80 mesh steel net. A cake of filtering earth is prepared on the filter before the filtration. The filtration is effected at a temperature of 160°C and with a pressure of 5 atmospheres of nitrogen.

[0074] After filtration, the product has the following characteristics:

- Appearance: blackish limpid liquid
- Cerium content: 4.73% by weight
- Viscosity at 100°C: 61.56 cSt
- Sediments (method ASTM D2273): 0.1% by volume

[0075] Together with cerium (IV) sulphonate, a small quantity of Cerium (IV) sulphate, deriving from the neutralization of the sulphuric acid present as impurity in the sulphonic acid, is also formed. Assuming that the cerium (IV) sulphate remains dispersed in the product, the following parameters are calculated:

- Acid sulphonic neutralization yield = 67.3%
- Soap content = 51.9% by weight
- Cerium incorporation efficiency = 64.2%

Example 2

[0076] The following products are charged into the reactor previously described: 444 g of toluene, 177 g of methanol and 10 g of water. The stirring is initiated, 45 g of Cerium (IV) hydroxide are charged, the internal temperature is brought to 50°C and after 30 minutes 350.3 g of sulphonic acid (0.5473 moles), equal to that used in example 1, are added by means of a drop funnel. During the addition of the acid, which is effected over a period of 30 minutes, heat is developed which brings the temperature from 50 to 60°C. The same temperature is left for an hour to allow the reaction to complete (maturation) and 352 g of mineral lubricating oil SN150 of ENI/AGIP are dosed and the sediments are determined with the method ASTM D96, which prove to be 2.8% by volume. At this point the volatile substances are removed by distillation using the following heating program at atmospheric pressure:

- from 60°C to 70°C in 30 minutes
- from 70°C to 125°C in 90 minutes
- from 125°C to 160°C in 60 minutes

[0077] When the temperature has reached 160°C, the distillation is continued, reducing the pressure to 100 mbar, for an overall time of 60 minutes, in order to remove the residual volatile substances. The quantity of distillate collected is equal to 641.9 g. At the end of the stripping, the product has a content of sediments, measured in heptane according to the method ASTM D96, equal to 2% by volume.

[0078] The product is treated with a quantity of filtration earth equal to 3% by weight and is filtered on a jacketed steel filter, as described in example 1. The filtration is effected at a temperature of 160°C and with a pressure of 5 atmospheres

of nitrogen.

[0079] After filtration, the product has the following characteristics:

- Appearance: blackish limpid liquid
- Cerium content: 2.94% by weight
- Turbidity (Hach 4100 instrument): 4.43 NTU (nephelometric units)
- Viscosity at 100°C: 14.72 cSt
- Initial sediments (method ASTM D2273): 0.1% by volume

[0080] Together with cerium (IV) sulphonate, a small quantity of Cerium (IV) sulphate deriving from the neutralization of the sulphuric acid present as impurity in the sulphononic acid, is also formed. Assuming that the cerium (IV) sulphate remains dispersed in the product, the following parameters are calculated:

- Acid sulphononic neutralization yield = 87.5%
- Soap content = 34% by weight
- Cerium incorporation efficiency = 70.3%

Example 3

[0081] The following products are charged into the reactor previously described: 528.1 g of toluene, 256.53 g of lime (purity = 96%, 3.328 moles), the temperature is brought to 40°C and the mixture is stirred at this temperature for 15 minutes. 402.7 g of the compound of organic acids containing Cerium of Example 1 are subsequently added by means of a drop funnel. At the end of the addition, which is effected in about 30 minutes, 396 g of methanol and 23.3 g of water are added, maintaining the temperature at 40°C for 10 minutes. At this point the temperature is lowered to 28°C and the reactor is prepared for the carbonation phase, in which carbon dioxide is introduced into the reaction mixture, through the valve situated at the bottom of the reactor, at a flow-rate of 15 NI/hour, in order to dose 113.5 g of carbon dioxide in 165 minutes. At the end of the carbonation phase, the reaction mixture is heated from 28°C to 50°C in 30 minutes to allow the maturation of the colloidal dispersion. The temperature is maintained at 50°C for 20 minutes and 145.8 g of lubricating oil SN150 are then added. The temperature is brought from 50°C to 65°C in 40 minutes and the post-maturation sediments are determined with the method ASTM D96, proving to be 1.6% by volume. At this point the volatile substances are removed by distillation using the following heating program:

- from 65°C to 73°C in 90 minutes at atmospheric pressure
- from 73°C to 125°C in 60 minutes at atmospheric pressure, after which another fraction of SN150 oil is added, equal to 145.8 g
- from 125°C to 160°C in 60 minutes, under vacuum, at a residual pressure of 500 mbar.

[0082] When the temperature has reached 160°C, the distillation is continued, reducing the pressure to 100 mbar, for an overall time of 60 minutes, in order to remove the residual volatile substances. The quantity of distillate collected is equal to 997.3 g. At the end of the stripping, the product has a content of sediments, measured in heptane according to the method ASTM D96, equal to 1% by volume.

[0083] The product is treated with a quantity of filtration earth equal to 3% by weight and is filtered on a steel filter, as described in example 1. The filtration is effected at a temperature of 160°C and with a pressure of 5 atmospheres of nitrogen.

[0084] After filtration, the product has the following characteristics:

- Appearance: dark limpid liquid
- Calcium content: 12.71% by weight
- Cerium content: 1.71% by weight
- TBN (mg KOH/g): 351
- Initial sediments (method ASTM D2273): 0.08% by volume
- Extended sediments (method ASTM D2273): 0.08% by volume
- Turbidity (Hach 4100 instrument): 19 NTU (nephelometric units)
- Viscosity at 100°C: 58 cSt

[0085] From the analytical results, it was possible to calculate the following parameters:

- Soap content = 30.8% by weight
- CaCO_3 content = 26.02% by weight
- Ca(OH)_2 content = 3.55% by weight
- Calcium incorporation efficiency = 94.8%

Example 4

[0086] The following products are charged into the reactor previously described: 528.1 g of toluene, 38.2 g of lubricating oil SN 150, 258.3 g of lime (purity = 96%, 3.3509 moles), the temperature is brought to 40°C and the mixture is stirred at this temperature for 15 minutes. 256 g of the compound of organic acids containing Cerium of Example 1 are subsequently added by means of a drop funnel together with 109.7 g of a sulphonic acid PARABAR C9310 of INFINEUM INT Ltd, characterized by a Molecular Weight = 673, a content of active substance (content of sulphonic acid) = 83.6% by weight and having an inorganic acidity (H_2SO_4) = 0.1% by weight. At the end of the addition, which is effected in about 30 minutes, 396 g of methanol and 20.8 g of water are added, maintaining the temperature at 40°C for 10 minutes. At this point the temperature is lowered to 28°C and the reactor is prepared for the carbonation phase, in which carbon dioxide is introduced into the reaction mixture, through the valve situated at the bottom of the reactor, at a flow-rate of 15 NI/hour, in order to dose 113.5 g of carbon dioxide in 165 minutes. At the end of the carbonation phase, the reaction mixture is heated from 28°C to 50°C in 30 minutes to allow the maturation of the colloidal dispersion. The temperature is maintained at 50°C for 20 minutes and 148.6 g of lubricating oil SN150 are then added. The temperature is brought from 50°C to 65°C in 40 minutes and the post-maturation sediments are determined with the method ASTM D96, proving to be 1.6% by volume. At this point the volatile substances are removed by distillation using the procedure described in example 3. The quantity of distillate collected is equal to 996 g. At the end of the stripping, the product has a content of sediments, measured in heptane according to the method ASTM D96, equal to 1.8% by volume.

[0087] The product is treated with a quantity of filtration earth equal to 3% by weight and is filtered on a steel filter, as described in example 1. The filtration is effected at a temperature of 160°C and with a pressure of 5 atmospheres of nitrogen.

[0088] After filtration, the product has the following characteristics:

- Appearance: dark limpid liquid
- Calcium content: 13.15% by weight
- Cerium content: 1.12% by weight
- TBN (mgKOH/g): 358
- Initial sediments (method ASTM D2273): 0.1% by volume
- Turbidity (Hach 4100 instrument): 11 NTU (nephelometric units)
- Viscosity at 100°C: 102.9 cSt

[0089] From the analytical results, it was possible to calculate the following parameters:

- Soap content = 28.62 by weight
- CaCO_3 content = 25.6% by weight
- Ca(OH)_2 content = 4.4% by weight
- Calcium incorporation efficiency = 98.9%

Engine tests for the accumulation of ash on the filter

[0090] The engine test, illustrated hereunder, is suitable for evaluating the impact of the lubricant on the particulate after-treatment systems of diesel internal combustion engines. This evaluation is effected through the collection and analysis of the ash accumulated on the filter. The test is suitably accelerated with the forced increase in the oil consumption, obtained with a method described in patent US 5,913,253. This method envisages the injection of oil into the suction collector to simulate an increase in the drawing from the suction valves, from the seals on the shaft of the turbocompressor and through the ventilation circuit of the engine base. This method allows the following experimentation objectives to be reached:

- short duration of the test with respect to the normal evidence times of the phenomenon under examination;
- possibility of enhancing the phenomenon by collecting, in this case, a quantity of ash on the particulate filter (DPF) enough for the analysis;

[0091] The method selected also has the following advantages:

- it is sufficiently representative of reality as it reproduces a real phenomenon with sufficient approximation;
- the possibility of accurately dosing the quantity of oil towards the combustion chamber and totally independently of the functioning conditions of the engine.

[0092] On a plant level, the engine tests illustrated were carried out using the equipment, illustrated in the enclosed Figure, consisting of the following elements:

1. Supplementary oil tank
2. Flow-rate regulator valve
3. Oil supply pump
4. Oil heater
5. Oil injector
6. Engine suction collector
7. Engine
8. Engine discharge collector
9. Particulate filter (DPF).

[0093] The oil tank is connected to a load cell for measuring the quantity of oil consumed. The heater has the function of increasing the temperature of the oil to lower the viscosity and guarantee a sufficiently pulverized spray.

[0094] The injector is of the single-hole type normally used in Diesel engines for fuel injection.

[0095] The test bench was equipped with a continuous detection system of the quantity of oil injected. The detection of the quantity of oil consumed by the engine was obtained by weighing the oil discharged from the engine every 120 hours.

[0096] The selection of the operating conditions was aimed at reflecting effective functioning on the car when running: low, medium and high regime conditions were therefore selected, coupled with different loads in order to cover a relatively wide use of the engine.

[0097] The high load functioning period was specifically established for ensuring a sufficient regeneration of the filtering element by reaction between the oxygen present and the particulate.

[0098] The test cycle is shown in Table 1, which indicates functioning times, regime conditions, motor load and temperature of the exhaust gases (which, as can be seen, represent the main parameter capable of governing the regeneration), for a test period of 2 hours, to be suitably repeated to cover an accumulation of 120 hours, which proved optimum for the rapid screening of different oils in limited time periods

Table 1

Phase	Time	Engine charge	Engine regime	Discharge temperature
Low load accumulation	45 min	20%	3.000 rpm	300°C
regeneration	15 min	80%	4.000 rpm	550°C
Medium load accumulation	45 min	40%	2.000 rpm	350°C
regeneration	15 min	80%	4.000 rpm	550°C

Example 5

[0099] An engine test was carried out, using the apparatus described above and illustrated in the enclosed Figure and under the operating conditions indicated in Table 1, using as lubricating oil (oil 1) a semi-synthetic oil SAE 10W-40 grade, containing the additive of example 2 at a concentration equal to 0.9% by weight and the additive of example 3 at a concentration equal to 2% by weight, in addition to other additives normally used in a lubricating oil. A reference test was also effected under the same operating conditions for comparative purposes, using a second lubricating oil (oil 2), which only differs from the previous oil in the substitution of the additives containing Cerium with traditional detergents containing Calcium.

[0100] The content of the various elements present in oil 1 and in oil 2 are indicated in Table 2.

[0101] A reference gas oil was used, as fuel, for the experimentation, characterized by a very low sulphur content ($S < 10$ ppm) and without additivation.

	Oil 1	Oil 2
Phosphorous (ppm)	1070	1040
Zinc (ppm)	1180	1120
Calcium (ppm)	2560	2540
Magnesium (ppm)	270	250
Cerium (ppm)	550	0
Sulphur (ppm)	8000	8000
Sulfated ashes (wt %)	1.20	1.26

[0102] The deposit accumulated on the particulate filters was removed from the filters and subsequently characterized.

[0103] The identification of the elements and compounds present in the deposit was effected by scanning electron microscope analysis (SEM) equipped with EDX (Energy Dispersive X-Ray) module. Table 3 shows the list of elements identified and the relative percentage determined.

[0104] From Table 3, it can be deduced that, with respect to oil 1, the Cerium present in the deposit of the particulate filter represents 10% by weight of the sum of the elements P, Zn, Ca, Mg, Ce coming from the lubricant, which is the same concentration at which the Cerium is present, with respect to the same elements, in oil 1 (Table 2).

Table 3

	DPF Filter Oil 1	DPF Filter Oil 2
Phosphorous (wt %)	9.2	8.3
Zinc (wt %)	11.9	11.2
Calcium (wt %)	16.3	18.9
Magnesium (wt %)	1.6	1.6
Cerium (wt %)	4.4	0
Sulphur (wt %)	8.1	9.5

[0105] It can therefore be affirmed that the Cerium is carried by the lubricating oil onto the DPF filter, where it is available for catalyzing the combustion of the particulate, allowing the regeneration of the filter.

[0106] In these evaluations, the Sulphur has been omitted as this element is characteristic of both the lubricant and the fuel and also because it has been ascertained that most of the sulphur is not collected on the filter, but passes through it in gaseous form.

[0107] After characterizing the nature of the compounds deposited on the filter and observing both the weight of the deposits accumulated on the filter and quantity of oil consumed during the test, it was possible to quantify the compounds present, expressed in weight units of the deposit with respect to the weight unit of the oil consumed. Table 4 indicates the weight distribution of the different compounds identified.

Table 4

		Oil 1	Oil 2
CaSO ₄	g deposit/ g oil consumption	2.55E-03	2.29E-03
CaZn ₂ (PO ₄) ₂	g deposit/ g oil consumption	2.05E-03	2.03E-03
Ce	g deposit/ g oil consumption	3.25E-04	0.00E+00
Zn ₂ P ₂ O ₇	g deposit/ g oil consumption	1.03E-03	2.98E-04
Mq ₂ P ₂ O ₇	g deposit/ g oil consumption	5.47E-04	4.29E-04
Others	g deposit/ g oil consumption	0.00E+00	2.92E-04
TOTAL	g deposit/ g oil consumption	6.50E-03	5.34E-03

Evaluation of the detergent properties

[0108] The engine test described above was effected on a Volkswagen TDI engine normally used for evaluating the detergent performances of the lubricant, according to the procedure CEC L-78-T-99 which envisages running for 54 hours under prevalent high-power conditions.

[0109] The lubricant called Oil 1 was evaluated on this engine in the test described of 120 hours under mixed functioning conditions (30 hours at high power + 90 hours at intermediate power) without revealing significant engine performances variations. The oil consumption, which is considered a health index of the engine, as it tends to rise in the presence of wear or the formation of deposits which hinder the correct movement of the elastic strips, did not show any significant variations with respect to the comparative test effected on Oil 2, containing classical Calcium-based detergents, and with respect to the average consumption of the engine calculated on the values acquired during 6 different tests (Table 5)

Table 5

Oil 1	Oil 2	Average consumption of test engine
1.67 kg	1.51 kg	1.40 ± 0.25 kg

[0110] The subsequent dismantling of the engine did not show the presence of anomalies, confirming its good state of health. In conclusion, it can be affirmed that the lubricating oil called Oil 1, containing the Cerium-based additives of Example 2 and Example 3, proved to exert a correct preservation action of the good condition of the engine from problems of wear and fouling.

Example 6Evaluation of the antifriction and antiwear properties

[0111] The antifriction and antiwear properties of the overbased sulphonates containing Cerium and Calcium were evaluated according to the method DIN 51384, using the SRV test equipment. The additive tested is that of Example 3 having the following main characteristics:

- Cerium Content: 1.71% by weight
- Calcium Content: 12.71% by weight
- TBN (mg KOH/g) : 351

[0112] The behaviour with the SRV test of this additive was compared with that of a traditional overbased sulphonate containing Calcium, having the following characteristics:

- Calcium Content: 12% by weight
- TBN (mg KOH/g) : 308

[0113] The test was carried out on 5% by weight solutions of the additives in mineral lubricating oil SN 150.

[0114] The operating conditions used are the following:

- Oscillation amplitude (mm) 1
- Oscillation frequency (Hz) 50
- Load applied (N) 200
- Temperature (°C) 100
- Time (minutes) 120
- Repeatability (friction coefficient) 0.005

[0115] The results obtained are indicated in Table 6 and are expressed as:

- Friction coefficient
- Wear diameter (mm): average diameter of the wear mark on the ball
- Wear amplexness (μm): average wear degree on the disk.

[0116] From the results indicated in Table 6, it can be observed that the detergent containing Cerium and Calcium has a much better behaviour in terms of wear with respect to that containing Calcium alone. This behaviour is evident from the lower values of the diameter, but above all of the degree of wear.

Table 6

	Average friction coefficient	Wear Diameter (mm)	Wear Degree (μm)
Detergent containing Cerium/Calcium	0.098	0.418	0.54
Detergent containing Calcium	0.111	0.664	3.28

Example 7

Evaluation of the extreme pressure properties

[0117] The extreme pressure properties of the overbased sulphonates containing Cerium and Calcium were evaluated according to the method ASTM D3233 (Falex Pin & Vee Block method). The additive tested is that of Example 3, whose behaviour was compared with that of a traditional overbased sulphonate containing Calcium, whose characteristics have already been described in Example 6.

[0118] The test was carried out on solutions at 5% by weight of additives in mineral lubricating oil SN 150.

[0119] The operating conditions used are the following:

- Temperature at test start: $51.7 \pm 3^\circ\text{C}$
- Rotation rate: 290 ± 10 RPM
- Load increases: 250 lb/min

[0120] The results obtained are indicated in Table 7 and are expressed as:

- Failure load (lb)

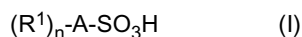
[0121] From the results indicated in the table, it can be observed that the detergent containing Cerium and Calcium has a much better behaviour with respect to that containing Calcium alone.

Table 7

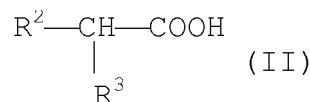
	Failure load (lb)
Detergent containing Cerium/Calcium	1750
Detergent containing Calcium	1250

Claims

1. An additive for lubricating oils comprising a metallic overbased salt of an organic acid, or a mixture of organic acids, containing Cerium and an alkaline earth metal with a Cerium content corresponding to a ratio between the equivalents of Cerium and those of organic acid ranging from 0.1 to 1.2 and a content of alkaline earth metal corresponding to a ratio between the equivalents of the alkaline earth metal and those of organic acid ranging from 1 to 40.
2. An additive for lubricating oils according to claim 1 comprising a stable, homogeneous and transparent oil-dispersion essentially consisting of:
 - i. 5-99.9% by weight of an oil; and
 - ii. 0.1-95% by weight of the metallic overbased salt.
3. An additive for lubricating oils according to claim 1 or 2, wherein the organic acid is selected from at least one of:
 - a sulphonic acid having the formula



wherein R^1 is a linear or branched alkyl group containing from 6 to 40 carbon atoms, or R^1 is an alkyl substituent deriving from a polymer of a C_2-C_6 olefin; A is a C_6-C_{20} aromatic hydrocarbon, an aliphatic hydrocarbon having from 5 to 20 carbon atoms; n is zero or an integer ranging from 1 to 5;
a carboxylic acid having the formula:



wherein R^2 is a linear or branched alkyl or alkenyl group, containing from 6 to 40 carbon atoms; R^3 is a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, or the radical $-CH_2COOH$;
a salicylic acid optionally substituted with linear or branched alkyl groups, in a number ranging from 1 to 3, containing from 6 to 40 carbon atoms;
a phenol or sulphurized phenol, optionally substituted with linear or branched alkyl groups, in a number ranging from 1 to 3, containing from 6 to 40 carbon atoms.

4. The additive for lubricating oils according to claim 1, 2 or 3, wherein the ratios between the equivalents of Cerium and those of organic acid range from 0.4 to 1 whereas the ratios between the equivalents of the alkaline earth metal and the equivalents of organic acid range from 5 to 30.
5. The additive for lubricating oils according to any of the previous claims, wherein the Cerium in the overbased salt is in oxidation state (III) or (IV).
6. The additive for lubricating oils according to any of the previous claims, wherein the alkaline earth metal is calcium, magnesium or barium.
7. The additive for lubricating oils according to any of the claims from 2 to 6, wherein the oil of component (i) is a lubricating oil selected from those of an animal, vegetable, mineral or synthetic origin.
8. A process for the synthesis of additives for lubricating oils according to any of the previous claims from 1 to 7, comprising the reaction between the following components:
 - A1. a compound of organic acids containing Cerium or a mixture of the above compound with an organic acid;
 - B1. a basic compound of an alkaline earth metal;
 - C1. a solvent or a mixture of solvents;
 - D1. a promoter or a mixture of reaction promoters;
 - E1. optionally an oil;
 - F1. carbon dioxide;

wherein the addition of components (A1), (B1), (C1), (D1), optionally (E1), is effected in any order whereas the addition of the component (F1) is effected subsequently, following component (B1).

9. The process according to claim 8, wherein the synthesis comprises:
 - initially adding component (B1) to a mixture consisting of component (C1) and a part of component (E1), subsequently adding component (A1);
 - adding component (D1);
 - carbonating the mixture obtained with component (F1);
 - adding, at the end of the carbonation, a second aliquot of component (E1); and
 - adding, after maturation, the remaining quantity of (E1).
10. The process according to claim 8, wherein the synthesis comprises:
 - initially adding component (B1) to a mixture consisting of component (C1), component (D1) and an aliquot of component (E1);

- subsequently adding component (A1);
- carbonating the mixture obtained with component (F1);
- adding a second part of component (E1);
- adding, after maturation, the remaining quantity of (E1).

11. The process according to any of the claims from 8 to 10, wherein the additive is recovered through separation, by means of distillation, of the reaction product from the reaction promoter and from the solvent and by subsequent separation, by means of filtration or centrifugation, from the insoluble by-products.

12. A process for the synthesis of additives for lubricating oils according to any of the previous claims from 1 to 7, comprising the reaction between the following components:

- A2. An organic acid or a mixture of organic acids;
- B2. A basic compound of Cerium;
- C2. A basic compound of an alkaline earth metal;
- D2. A solvent or mixture of solvents;
- E2. A promoter or a mixture of reaction promoters;
- F2. Optionally an oil;
- G2. Carbon dioxide.

wherein the addition of components (A2), (B2), (C2), (D2), (E2), optionally (F2), is effected in any order whereas the addition of the component (G2) is effected subsequently, following component (C2).

13. The process according to claim 12, wherein the synthesis comprises:

- initially adding component (B2) to a mixture consisting of component (D2) and an aliquot of component (F2), subsequently adding component (A2);
- adding component (C2) and component (E2);
- carbonating the mixture obtained with component (G2);
- adding, at the end of the carbonation, a second aliquot of component (F2); and
- adding, after maturation, the remaining quantity of (F2).

14. The process according to claim 12, wherein the synthesis comprises:

- initially adding component (B2) to a mixture consisting of component (D2), component (E2) and a part of component (F2) ;
- subsequently adding component (A2);
- add the component (C2);
- carbonating the mixture obtained with component (G2);
- adding a second part of component (F2);
- adding, after maturation, the remaining quantity of (F2).

15. The process according to any of the claims from 12 to 14, wherein the additive is recovered by separation, by means of distillation, of the reaction product from the reaction promoter and from the solvent and by subsequent separation, by means of filtration or centrifugation, from the insoluble by-products.

16. The process according to claim 8 to 11, wherein the mixture consisting of the compound of organic acids containing Cerium and an organic acid contains a weight percentage of the compound containing Cerium ranging from 10 to 99.

17. The process according to any of the claims from 8 to 16, wherein the basic compound of alkaline earth metal is selected from an oxide or hydroxide of the alkaline earth metal.

18. The process according to any of the claims from 8 to 17, wherein the solvent is used in a quantity ranging from 10 to 500% by weight, calculated with respect to component A1) or (A2), and is selected from aromatic or aliphatic hydrocarbons.

19. The process according to any of the claims from 8 to 18, wherein the reaction promoter is used in a quantity ranging from 2 to 500% by weight, calculated with respect to component B1 or the sum of components B2 and C2, and is

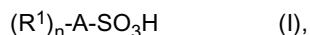
selected from an alcohol, water, a glycol, a ketone, an ester of a carboxylic acid.

20. The process according to any of the claims from 8 to 19, wherein the carbonation phase of the basic compound of the alkaline earth metal is effected with carbon dioxide in such a quantity as to have a ratio between the equivalents of carbon dioxide and those of the base of the alkaline earth metal in excess with respect to the organic acid, ranging from 0.6 to 1.1.
21. The process according to any of the claims from 8 to 20, wherein the lubricating oil, when used, is added in a quantity ranging from 30 to 800% by weight, calculated with respect to components (A1) or (A2).
22. The process according to any of the claims from 8 to 21, wherein the reaction between the components (A1)-(E1) or between the components (A2)-(F2) takes place at a temperature ranging from 15 to 200°C.
23. The process according to any of the claims from 8 to 22, wherein the carbonation phase takes place at a temperature ranging from 10 to 150°C.
24. The process according to any of the claims from 8 to 23, wherein the separation phase of the reaction product by distillation from the reaction promoter and solvent is effected by increasing the temperature at the end of the carbonation to a maximum value of 200°C.
25. Lubricating compositions comprising a base oil consisting of a lubricating oil of an animal, vegetable, mineral or synthetic origin and an additive comprising an overbased salt containing Cerium and an alkaline earth metal according to any of the previous claims from 1 to 7, used in a quantity ranging from 0.2 to 10% by weight, calculated with respect to the lubricating oil.
26. A method for reducing the emissions of polluting substances present in the exhaust gases of an internal combustion engine and/or for conveying Cerium compounds onto the particulate filter in an internal combustion engine which comprises using the lubricating composition according to claim 25.

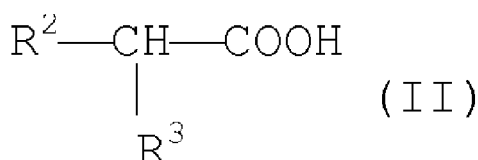
Patentansprüche

1. Additiv für Schmieröle, umfassend ein metallisches überbasisches Salz einer organischen Säure oder einer Mischung von organischen Säuren, enthaltend Cer und ein Erdalkalimetall mit einem Cer-Gehalt, entsprechend einem Verhältnis zwischen den Äquivalenten des Cers und denen der organischen Säure, in einem Bereich von 0,1 bis 1,2 und einem Gehalt an Erdalkalimetall, entsprechend einem Verhältnis zwischen den Äquivalenten des Erdalkalimetalls und denen der organischen Säure, in einem Bereich von 1 bis 40.
2. Additiv für Schmieröle gemäß Anspruch 1, umfassend eine stabile, homogene und transparente Öl-Dispersion, im Wesentlichen bestehend aus:
 - i. 5-99,9 Gew.-% eines Öls; und
 - ii. 0,1-95 Gew.-% des metallischen überbasischen Salzes.
3. Additiv für Schmieröle gemäß Anspruch 1 oder 2, worin die organische Säure ausgewählt ist aus mindestens einem aus:

einer Sulfonsäure mit der Formel



worin R¹ eine lineare oder verzweigte Alkylgruppe ist, enthaltend 6 bis 40 Kohlenstoffatome, oder R¹ ist ein Alkylsubstituent, abgeleitet von einem Polymer eines C₂-C₆-Olefins; A ist ein C₆-C₂₀-aromatischer Kohlenwasserstoff, ein aliphatischer Kohlenwasserstoff mit 5 bis 20 Kohlenstoffatomen; n ist Null oder eine Ganzzahl in einem Bereich von 1 bis 5;
einer Carbonsäure mit der Formel:



worin R² eine lineare oder verzweigte Alkyl- oder Alkenylgruppe ist, enthaltend von 6 bis 40 Kohlenstoffatome; R³ ist eine Wasserstoffatom, eine Alkylgruppe, enthaltend von 1 bis 4 Kohlenstoffatome, oder der Rest -CH₂COOH;
 einer Salizylsäure, gegebenenfalls substituiert mit linearen oder verzweigten Alkylgruppen, in einer Zahl in einem Bereich von 1 bis 3, enthaltend von 6 bis 40 Kohlenstoffatome;
 einem Phenol oder sulfuriertem Phenol, gegebenenfalls substituiert mit linearen oder verzweigten Alkylgruppen, in einer Zahl in einem Bereich von 1 bis 3, enthaltend von 6 bis 40 Kohlenstoffatomen.

4. Additiv für Schmieröle gemäß Anspruch 1, 2 oder 3, worin die Verhältnisse zwischen den Äquivalenten des Cers und denen der organischen Säure in einem Bereich von 0,4 bis 1 sind, wobei die Verhältnisse zwischen den Äquivalenten des Erdalkalimetalls und den Äquivalenten der organischen Säure in einem Bereich von 5 bis 30 liegen.
5. Additiv für Schmieröle gemäß irgendeinem der vorhergehenden Ansprüche, worin das Cer in dem überbasischen Salz im Oxidationszustand (III) oder (IV) ist.
6. Additiv für Schmieröle gemäß irgendeinem der vorhergehenden Ansprüche, worin das Erdalkalimetall Calcium, Magnesium oder Barium ist.
7. Additiv für Schmieröle gemäß irgendeinem der Ansprüche 2 bis 6, worin das Öl des Bestandteils (i) ein Schmieröl ist, ausgewählt aus denjenigen von tierischem, pflanzlichem, mineralischem oder synthetischem Ursprung.
8. Verfahren zur Synthese von Additiven für Schmieröle nach irgendeinem der vorhergehenden Ansprüche 1 bis 7, umfassend die Reaktion zwischen den folgenden Bestandteilen:

- A1. einer Verbindung einer organischen Säure, enthaltend Cer oder einer Mischung der vorgenannten Verbindungen mit einer organischen Säure;
- B1. einer basischen Verbindung eines Erdalkalimetalls;
- C1. einem Lösemittel oder einer Mischung aus Lösemitteln;
- D1. einem Promoter oder einer Mischung aus Reaktions promotern;
- E1. gegebenenfalls einem Öl;
- F1. Kohlenstoffdioxid;

worin die Zugabe der Bestandteile (A1), (B1), (C1), (D1), gegebenenfalls (E1) in einer beliebigen Reihenfolge durchgeführt wird, wobei die Zugabe des Bestandteils (F1) im Anschluss stattfindet, folgend dem Bestandteil (B1).

9. Verfahren nach Anspruch 8, worin die Synthese umfasst:

- anfängliche Zugabe von Bestandteil (B1) zu einer Mischung, bestehend aus Bestandteil (C1) und einem Teil des Bestandteils (E1), im Anschluss Zugabe von Bestandteil (A1);
- Zugabe von Bestandteil (D1);
- Karbonisierung der erhaltenen Mischung mit Bestandteil (F1);
- Zugabe, zum Ende der Karbonisierung, von einem zweiten Aliquot des Bestandteils (E1); und
- Zugabe, nach Reifung, der verbleibenden Quantität von (E1).

10. Verfahren nach Anspruch 8, worin die Synthese umfasst:

- anfängliche Zugabe von Bestandteil (B1) zu einer Mischung, bestehend aus Bestandteil (C1), Bestandteil (D1) und einem Aliquot des Bestandteils (E1);
- anschließende Zugabe von Bestandteil (A1);

- Karbonisierung der erhaltenen Mischung mit Bestandteil (F1);
- Zugabe eines zweiten Teils des Bestandteils (E1);
- Zugabe, nach Reifung, der verbleibenden Quantität von (E1).

11. Verfahren nach irgendeinem der Ansprüche 8 bis 10, worin das Additiv durch Abtrennung gewonnen wird, mittels Destillation, des Reaktionsprodukts aus dem Reaktionspromoter und aus dem Lösemittel, und durch anschließende Trennung mittels Filtration oder Zentrifugierung von den unlöslichen Nebenprodukten.

12. Verfahren zur Synthese von Additiven für Schmieröle gemäß irgendeinem der vorhergehenden Ansprüche 1 bis 7, umfassend die Reaktion zwischen den folgenden Bestandteilen:

- A2. einer organischen Säure oder einer Mischung von organischen Säuren;
- B2. einer basischen Verbindung des Cers;
- C2. einer basischen Verbindung eines Erdalkalimetalls;
- D2. einem Lösemittel oder einer Mischung von Lösemitteln;
- E2. einem Promoter oder einer Mischung von Reaktionspromotern;
- F2. gegebenenfalls einem Öl;
- G2. Kohlenstoffdioxid,

worin die Zugabe der Bestandteile (A2), (B2), (C2), (D2), (E2), gegebenenfalls (F2) in einer beliebigen Reihenfolge durchgeführt wird, wohingegen die Zugabe des Bestandteils (G2) im Anschluss stattfindet, folgend Bestandteil (C2).

13. Verfahren nach Anspruch 12, worin die Synthese umfasst:

- anfängliche Zugabe von Bestandteil (B2) zu einer Mischung, bestehend aus Bestandteil (D2) und einem Aliquot des Bestandteils (F2), anschließend Zugabe von Bestandteil (A2);
- Zugabe von Bestandteil (C2) und Bestandteil (E2);
- Karbonisierung der erhaltenen Mischung mit Bestandteil (G2);
- Zugabe, zum Ende der Karbonisierung, von einem zweiten Aliquot des Bestandteils (F2); und
- Zugabe, nach Reifung, der verbleibenden Quantität von (F2).

14. Verfahren nach Anspruch 12, worin die Synthese umfasst:

- anfängliche Zugabe von Bestandteil (B2) zu einer Mischung, bestehend aus Bestandteil (D2), Bestandteil (E2) und einem Teil von Bestandteil (F2);
- anschließende Zugabe von Bestandteil (A2);
- Zugabe von Bestandteil (C2);
- Karbonisierung der erhaltenen Mischung mit Bestandteil (G2);
- Zugabe eines zweiten Teils des Bestandteils (F2);
- Zugabe, nach Reifung, der verbleibenden Quantität von (F2).

15. Verfahren nach irgendeinem der Ansprüche 12 bis 14, worin das Additiv durch Trennung gewonnen wird, mittels Destillation des Reaktionsprodukts aus dem Reaktionspromoter und aus dem Lösemittel, und durch anschließende Abtrennung mittels Filtration oder Zentrifugierung, von den unlöslichen Nebenprodukten.

16. Verfahren nach Anspruch 8 bis 11, worin die Mischung; bestehend aus der Verbindung von organischen Säuren, enthaltend Cer, und einer organischen Säure; einen Gewichtsprozentsatz der Verbindung, enthaltend Cer, in einem Bereich von 10 bis 99 enthält.

17. Verfahren nach irgendeinem der Ansprüche 8 bis 16, worin die basische Verbindung des Erdalkalimetalls ausgewählt ist aus einem Oxid oder Hydroxid des Erdalkalimetalls.

18. Verfahren nach irgendeinem der Ansprüche 8 bis 17, worin das Lösemittel in einer Menge in einem Bereich von 10 bis 500 Gew.-%, berechnet mit Bezug auf Bestandteil (A1) oder (A2), verwendet wird, und ausgewählt ist aus aromatischen oder aliphatischen Kohlenwasserstoffen.

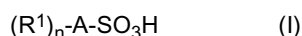
19. Verfahren nach irgendeinem der Ansprüche 8 bis 18, worin der Reaktionspromoter in einer Menge eingesetzt wird, in einem Bereich von 2 bis 500 Gew.-%, berechnet mit Bezug auf Bestandteil B1 oder der Summe der Bestandteile

B2 und C2, und ist ausgewählt aus einem Alkohol, Wasser, einem Glycol, einem Keton, einem Ester einer Carbonsäure.

20. Verfahren nach irgendeinem der Ansprüche 8 bis 19, worin die Karbonisierungsphase der basischen Verbindung des Erdalkalimetalls bewirkt wird mit Kohlenstoffdioxid in einer solchen Menge, dass ein Verhältnis zwischen den Äquivalenten des Kohlenstoffdioxids und denjenigen der Base des Erdalkalimetalls in Überschuss mit Bezug auf die organische Säure in einem Bereich von 0,6 bis 1,1 ist.
21. Verfahren nach irgendeinem der Ansprüche 8 bis 20, worin das Schmieröl bei der Verwendung in einer Menge von 30 bis 800 Gew.-%, berechnet mit Bezug auf die Bestandteile (A1) oder (A2), zugegeben wird.
22. Verfahren nach irgendeinem der Ansprüche 8 bis 21, worin die Reaktion zwischen den Bestandteilen (A1) - (E1) oder zwischen den Bestandteilen (A2) - (F2) bei einer Temperatur in einem Bereich von 15 bis 200 °C stattfindet.
23. Verfahren nach irgendeinem der Ansprüche 8 bis 22, worin die Karbonisierungsphase bei einer Temperatur in einem Bereich von 10 bis 150 °C stattfindet.
24. Verfahren nach irgendeinem der Ansprüche 8 bis 23, worin die Trennungsphase des Reaktionsprodukts durch Destillation von dem Reaktionspromoter und dem Lösemittel dadurch bewirkt wird, dass die Temperatur am Ende der Karbonisierung auf einen Maximalwert von 200 °C angehoben wird.
25. Schmierzusammensetzungen, umfassend ein Basis-Öl bestehend aus einem Schmieröl von tierischem, pflanzlichem, mineralischem oder synthetischem Ursprung und einem Additiv, umfassend ein überbasisches Salz, enthaltend Cer, und ein Erdalkalimetall gemäß irgendeinem der vorhergehenden Ansprüche 1 bis 7, verwendet in einem Bereich von 0,2 bis 10 Gew.-%, berechnet mit Bezug auf das Schmieröl.
26. Verfahren zur Reduzierung von Emissionen von verschmutzenden Substanzen, die in Abgasen einer internen Verbrennungsmaschine vorliegen und/oder zur Beförderung von Cer-Verbindungen auf den Teilchenfilter in einer internen Verbrennungsmaschine, welches die Verwendung der Schmierzusammensetzung gemäß Anspruch 25 umfasst.

Revendications

1. Adjuvant pour huiles lubrifiantes, comprenant un sel surbasique de métal d'un acide organique ou d'un mélange d'acides organiques, contenant du cérium et un métal alcalino-terreux, la teneur en cérium correspondant à un rapport entre équivalents de cérium et d'acide(s) organique(s) valant de 0,1 à 1,2, et la teneur en métal alcalino-terreux correspondant à un rapport entre équivalents de métal alcalino-terreux et d'acide(s) organique(s) valant de 1 à 40.
2. Adjuvant pour huiles lubrifiantes, conforme à la revendication 1, comprenant une dispersion huileuse stable, homogène et transparente, essentiellement constituée
 - i) de 5 à 99,9 % en poids d'une huile,
 - ii) et de 0,1 à 95 % en poids du sel surbasique de métal.
3. Adjuvant pour huiles lubrifiantes, conforme à la revendication 1 ou 2, dans lequel l'acide organique est choisi, au nombre d'au moins un, parmi
 - un acide sulfonique de formule



- dans laquelle R¹ représente un groupe alkyle linéaire ou ramifié, comportant de 6 à 40 atomes de carbone, ou R¹ représente un substituant alkyle dérivé d'un polymère d'oléfine en C₂-C₆, A représente un reste d'hydrocarbure aromatique en C₆-C₂₀ ou d'hydrocarbure aliphatique comportant de 5 à 20 atomes de carbone, et l'indice n est nul ou est un nombre entier valant de 1 à 5 ;
- un acide carboxylique de formule



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dans laquelle R² représente un groupe alkyle ou alcényle, linéaire ou ramifié, comportant de 6 à 40 atomes de carbone,

et R³ représente un atome d'hydrogène, un groupe alkyle comportant de 1 à 4 atomes de carbone, ou le groupe de formule -CH₂COOH ;

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- un acide salicylique, en option porteur de substituant(s) alkyle linéaire(s) ou ramifié(s), au nombre de 1 à 3, comportant de 6 à 40 atomes de carbone ;

- un phénol ou phénol soufré, en option porteur de substituant(s) alkyle linéaire(s) ou ramifié(s), au nombre de 1 à 3, comportant de 6 à 40 atomes de carbone.

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4. Adjuvant pour huiles lubrifiantes, conforme à la revendication 1, 2 ou 3, dans lequel le rapport entre équivalents de cérium et d'acide(s) organique(s) vaut de 0,4 à 1, et le rapport entre équivalents de métal alcalino-terreux et d'acide(s) organique(s) vaut de 5 à 30.

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5. Adjuvant pour huiles lubrifiantes, conforme à l'une des revendications précédentes, dans lequel le cérium du sel surbasique se trouve à l'état d'oxydation (III) ou (IV).

6. Adjuvant pour huiles lubrifiantes, conforme à l'une des revendications précédentes, dans lequel le métal alcalino-terreux est du calcium, du magnésium ou du baryum.

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7. Adjuvant pour huiles lubrifiantes, conforme à l'une des revendications 2 à 6, dans lequel l'huile du composant (i) est une huile lubrifiante choisie parmi celles d'origine animale, végétale, minérale ou synthétique.

8. Procédé de synthèse d'adjuvants pour huiles lubrifiantes conformes à l'une des revendications 1 à 7 précédentes, comportant le fait de faire réagir entre eux les composants suivants :

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A1) un composé d'acide(s) organique(s) contenant du cérium, ou un mélange d'un tel composé et d'un acide organique,

B1) un composé basique d'un métal alcalino-terreux,

C1) un solvant ou un mélange de solvants,

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D1) un promoteur ou un mélange de promoteurs de réaction,

E1) en option, une huile,

F1) et du dioxyde de carbone,

étant entendu que les composants (A1), (B1), (C1) et (D1) et le composant optionnel (E1) sont ajoutés dans n'importe quel ordre, mais que le composant (F1) est ajouté ultérieurement, après le composant (B1).

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9. Procédé conforme à la revendication 8, dans lequel la synthèse comporte les opérations suivantes :

- commencer par ajouter le composant (B1) à un mélange constitué du composant (C1) et d'une fraction du composant (E1), et ajouter ensuite le composant (A1) ;

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- ajouter le composant (D1) ;

- carbonater le mélange ainsi obtenu, au moyen du composant (F1) ;

- ajouter, à la fin de la carbonatation, une deuxième fraction du composant (E1) ;

- et après maturation, ajouter le reste du composant (E1).

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10. Procédé conforme à la revendication 8, dans lequel la synthèse comporte les opérations suivantes :

- commencer par ajouter le composant (B1) à un mélange constitué du composant (C1), du composant (D1) et d'une fraction du composant (E1) ;

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- ajouter ensuite le composant (A1) ;

- carbonater le mélange ainsi obtenu, au moyen du composant (F1) ;

- ajouter une deuxième fraction du composant (E1) ;

- et après maturation, ajouter le reste du composant (E1).

11. Procédé conforme à l'une des revendications 8 à 10, dans lequel on récupère l'adjuvant en séparant par distillation le produit de réaction d'avec le promoteur de réaction et le solvant, et en le séparant ensuite, par filtration ou centrifugation, d'avec les sous-produits insolubles.

12. Procédé de synthèse d'adjuvants pour huiles lubrifiantes conformes à l'une des revendications 1 à 7 précédentes, comportant le fait de faire réagir entre eux les composants suivants :

- A2) un acide organique ou un mélange d'acides organiques,
- B2) un composé basique du cérium,
- C2) un composé basique d'un métal alcalino-terreux,
- D2) un solvant ou un mélange de solvants,
- E2) un promoteur ou un mélange de promoteurs de réaction,
- F2) en option, une huile,
- G2) et du dioxyde de carbone,

étant entendu que les composants (A2), (B2), (C2), (D2) et (E2) et le composant optionnel (F2) sont ajoutés dans n'importe quel ordre, mais que le composant (G2) est ajouté ultérieurement, après le composant (C2).

13. Procédé conforme à la revendication 12, dans lequel la synthèse comporte les opérations suivantes :

- commencer par ajouter le composant (B2) à un mélange constitué du composant (D2) et d'une fraction du composant (F2), et ajouter ensuite le composant (A2) ;
- ajouter le composant (C2) et le composant (E2) ;
- carbonater le mélange ainsi obtenu, au moyen du composant (G2) ;
- ajouter, à la fin de la carbonatation, une deuxième fraction du composant (F2) ;
- et après maturation, ajouter le reste du composant (F2).

14. Procédé conforme à la revendication 12, dans lequel la synthèse comporte les opérations suivantes :

- commencer par ajouter le composant (B2) à un mélange constitué du composant (D2), du composant (E2) et d'une fraction du composant (F2) ;
- ajouter ensuite le composant (A2) ;
- ajouter le composant (C2) ;
- carbonater le mélange ainsi obtenu, au moyen du composant (G2) ;
- ajouter une deuxième fraction du composant (F2) ;
- et après maturation, ajouter le reste du composant (F2).

15. Procédé conforme à l'une des revendications 12 à 14, dans lequel on récupère l'adjuvant en séparant le produit de réaction, par distillation, du promoteur de réaction et du solvant, et en le séparant ensuite, par filtration ou centrifugation, des sous-produits insolubles.

16. Procédé conforme à l'une des revendications 8 à 11, dans lequel le mélange constitué du composé d'acide(s) organique(s) contenant du cérium et d'un acide organique contient de 10 à 99 % en poids du composé contenant du cérium.

17. Procédé conforme à l'une des revendications 8 à 16, dans lequel le composé basique de métal alcalino-terreux est choisi parmi les oxydes et hydroxydes des métaux alcalino-terreux.

18. Procédé conforme à l'une des revendications 8 à 17, dans lequel le solvant est utilisé en une proportion, calculée par rapport au composant (A1) ou (A2), de 10 à 500 % en poids, et est choisi parmi les hydrocarbures aromatiques ou aliphatiques.

19. Procédé conforme à l'une des revendications 8 à 18, dans lequel le promoteur de réaction est utilisé en une proportion, calculée par rapport au composant (B1) ou au total des composants (B2) et (C2), de 2 à 500 % en poids, et est choisi parmi un alcool, l'eau, un glycol, une cétone, et un ester d'acide carboxylique.

20. Procédé conforme à l'une des revendications 8 à 19, dans lequel la carbonatation du composé basique de métal alcalino-terreux est réalisée avec du dioxyde de carbone utilisé en une quantité telle que le rapport entre le nombre

d'équivalents de dioxyde de carbone et le nombre d'équivalents de composé basique de métal alcalino-terreux en excès par rapport à l'acide organique vaille de 0,6 à 1,1.

- 5 **21.** Procédé conforme à l'une des revendications 8 à 20, dans lequel l'huile lubrifiante, si l'on en utilise, est ajoutée en une proportion, calculée par rapport au composant (A1) ou (A2), de 30 à 800 % en poids.
- 22.** Procédé conforme à l'une des revendications 8 à 21, dans lequel la réaction entre les composants (A1) à (E1) ou entre les composants (A2) à (F2) a lieu à une température valant de 15 à 200 °C.
- 10 **23.** Procédé conforme à l'une des revendications 8 à 22, dans lequel la carbonatation a lieu à une température valant de 10 à 150 °C.
- 24.** Procédé conforme à l'une des revendications 8 à 23, dans lequel on réalise la séparation, par distillation, du produit de réaction d'avec le promoteur de réaction et le solvant en augmentant la température, à la fin de la carbonatation, 15 jusqu'à une valeur d'au plus 200 °C.
- 25.** Compositions lubrifiantes comprenant une huile de base, consistant en un huile lubrifiante d'origine animale, végétale, minérale ou synthétique, et un adjuvant comprenant un sel surbasique contenant du cérium et un métal alcalino-terreux, conforme à l'une des revendications 1 à 7 précédentes et utilisé en une proportion, calculée par rapport à 20 l'huile lubrifiante, valant de 0,2 à 10 % en poids.
- 26.** Procédé visant à réduire les émissions de polluants présents dans les gaz d'échappement d'un moteur à combustion interne et/ou à apporter des composés du cérium sur un filtre à particules d'un moteur à combustion interne, qui 25 comporte le fait d'utiliser une composition lubrifiante conforme à la revendication 25.

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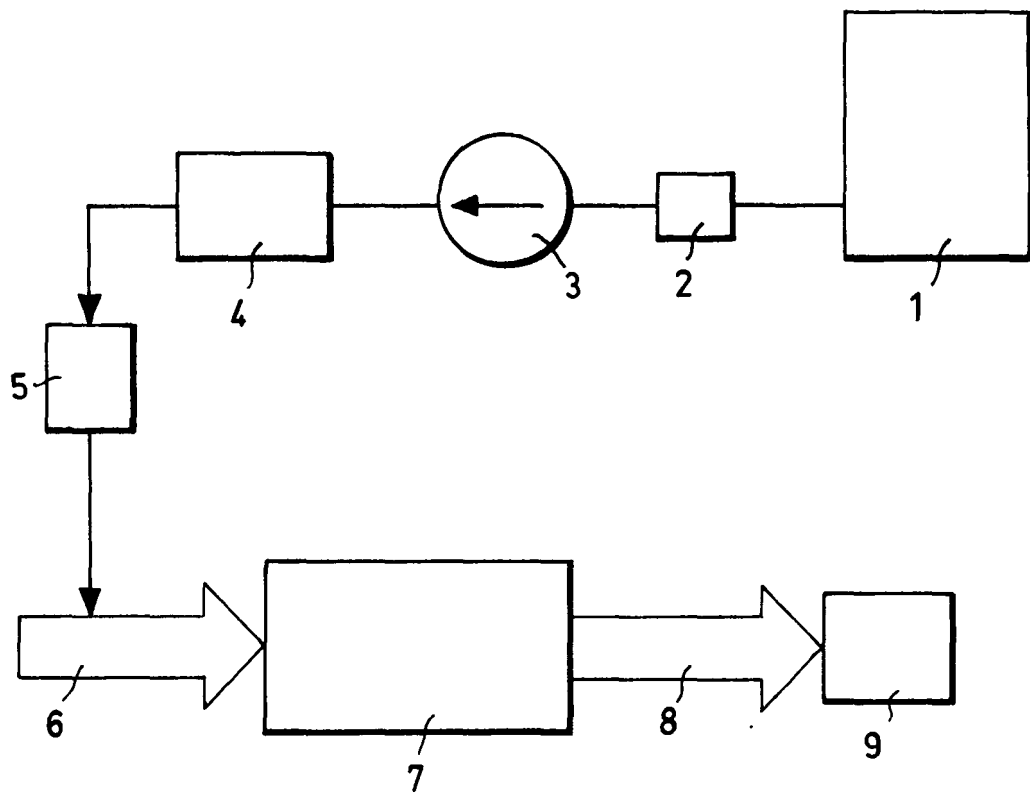
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