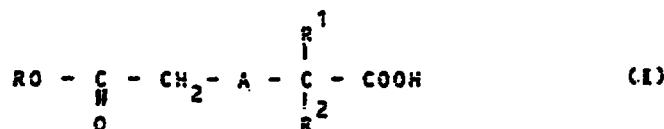


Description

The present invention relates to new compounds useful as detergent additives for lubricants, and to the lubricating compositions containing the new additives.

More particularly, a first object of the present invention is a monoester of a bicarboxy acid having the formula:



wherein R is a C1-C30 alkyl, R¹ is hydrogen or a C1-C30 alkyl, R² is a C1-C30 alkyl, and A, if present, is a C1-C30 alkylene, with the proviso that:

- a) the sum of carbon atoms contained in R, A, R¹ and R² is equal to, or greater than, 15, and
- b) when A is not present, the sum of the carbon atoms contained in R¹ and R² is smaller than 35, and their alkali metal- or alkaline earth metal salts.

The compounds having formula (I), in the form of their corresponding salts of alkali metal or of alkali-earth metal, are useful as detergent additives for lubricants.

The "detergent" lubricants are so denominated, in as much as they perform the general function of keeping engine clean.

They prevent in fact, or considerably delay, the formation of foulings and coal inside the engine, and, in particular, on the pistons and on cylinder walls thereof, and constitute hence an extremely important class of additives for lubricating oils.

Commonly used detergent additives for lubricating oils are the alkali-metal or alkali-earth-metal salts of organic acids, chemically similar to the common soaps used in the field of detergency in aqueous phase. But, as the use of these additives in lubricant bases requires them to be perfectly soluble in these bases, the selection of the organic acid to be used in the form of its metal-salt derivative is extremely important and critical.

Commonly, the alkali-metal or alkali-earth-metals salts are used of such compounds as (either vegetable or animal) natural fatty acids, higher synthetic fatty acids, sulphonic acids, phenols, sulphophenols, and so forth. As additives for lubricants, also the metal salts are known of monoesters of succinic acid substituted with hydrocarbon chains containing at least 50 carbon atoms (cfr. U.S. Pat. No. 3,632,510).

The compounds of the present invention are expediently prepared by starting from the corresponding bicarboxy-acids by esterification with an alcohol

R-OH

wherein the presence of substituents on one of the two carbon atoms in the α -position relatively to the carboxy groups allows the semiester to be selectively formed on the carboxy group, the carbon atoms in the α -position to which is not substituted.

The reaction is easily carried out by heating to above 100°C a mixture containing about equimolar amounts of the bicarboxy acid and of the alcohol, and distilling off the water which is formed during the condensation.

Operating at temperatures comprised within the range of from 150°C to 300°C in the absence of solvent is generally preferred, but it can be sometimes expedient to perform the reaction in the presence of an inert, high-boiling solvent, which may facilitate the blending. In such a case, suitable solvents can be, for example, xylene, toluene, chlorobenzene, diphenylether or mineral oils. The reaction is complete within some hours, yielding the desired semiester (I), which can be fed as such to the salification step. It may be sometimes expedient to carry out the reaction in the presence of a suitable esterification catalyst, such as, e.g., sulphuric acid, p-toluenesulphonic acid, hydrochloric acid, phosphoric acid, or other similar catalysts.

If used, such a catalyst shall be used in amounts comprised within the range of from 0.01% to 5%, or, more preferably, of from 0.1% to 2.5% by weight. When A is nothing, as an alternative to this general method for the synthesis of the semiesters, the reaction can be carried out by using, in lieu of the derivative of succinic acid, the corresponding derivative of succinic anhydride, which has an equivalent behaviour. In such a case, obviously, no water will be formed, but the reaction shall proceed in an analogous way, always

selectively leading to the semiester, wherein the esterified carboxy group is the one, the carbon atom in the α -position relatively to which is unsubstituted.

From an industrial standpoint it may be sometimes expedient to use starting products which are not individual products, but consist actually of blends of isomer or of analogous compounds, thus blends of esters of formula (I) being obtained, the chemical composition of which, and the relative proportion of the individual components of which are not easily determined. Such mixtures, which can be used as well, in the form of their corresponding metal salts, as the detergent additives, are obviously within the scope of the present invention.

The so-obtained ester-acids are then converted into their corresponding alkali-metal or alkali-earth-metal salts by being reacted with a suitable base.

The reaction is expediently carried out at a temperature comprised within the range of from room temperature to 250 °C, and, preferably, of from 80 °C to 200 °C by using an alkali-metal or alkali-earth-metal base and an inert organic diluent. Toluene, xylene, heptane, cyclohexane, mineral oils, etc., can be well used to this purpose. The base will be generally used in a stoichiometrically equivalent amount.

Alkali-metal or alkali-earth-metal bases which can be expediently used comprise the hydroxides, carbonates, bicarbonates, alkoxides and phenates of metals of the I and II Groups, and, in particular, of sodium, potassium, lithium, magnesium, calcium and barium. The procedures for salifying carboxy acids are well-known in the organic chemistry, and they therefore do not require to be described in greater detail.

The salified semiesters of formula (I), as well as their blends, can be efficaciously used as such as detergent additives for several types of lubricating compositions containing one or more lubricating oils of synthetic, mineral, vegetable or animal origin. The concentration of such additives in the lubricants is normally comprised within the range of from 0.01% to 20% by weight, and preferably of from 0.5 to 10% by weight, according to the lubricant bases used and of the required performance, although, when a particular performance, or use on particular engine types, is required, even higher amounts may be used.

A second object of the present invention are hence the lubricating compositions containing one or more lubricating oils of synthetic, mineral, vegetable or animal origin, and the alkali-metal or alkali-earth-metal salt of at least one compound of formula (I). Such lubricating compositions can obviously contain other additives, such as, e.g., antioxidants, dispersants, viscosity index improvers, fluidifiers, antiwear agents, and so on, besides other supplementary detergent additives.

Suitable bases for such lubricant compositions are, e.g., the natural oils from either vegetable or animal sources, as well as those of mineral origin, of either paraffinic or naphthenic type, but, in particular, the oils of synthetic origin commonly presently used in engine applications.

The salt derivatives of the compounds of formula (I) besides being suitable to be used as such, can be also used to the purpose of producing a further class of additives, the so-called "hyperbasic" additives. The salt derivatives of the present invention are well suitable in fact for forming a stable colloidal suspension of alkali-metal or alkali-earth-metal carbonate in oil. This gives the possibility of formulating the additive as a suspension approximately containing about 30% of alkali-metal or alkali-earth-metal carbonate, 30% of alkali-metal or alkali-earth-metal salt of one or more of the compounds of formula (I), and 40% of mineral oil. Such a formulation of the additive is stable, fluid, so to allow conveyance movements to be easily applied, as well as them to be easily formulated into the end lubricant, and is perfectly soluble in all proportions in mineral and synthetic lubricant bases.

The presence of a high amount of inorganic carbonate in the additive allows lubricants to be formulated, which contain it in concentrations of from 2% to 20%, which, besides the true detergent activity, are endowed with high neutralizing properties towards possible acidic agents they may come in contact with.

This neutralizing capability is essentially when during its use the lubricant is required to supply, besides a specific protection of mechanical components against wear, also a good protection from corrosion. This is, e.g., the case of the neutralization of sulphuric and nitric acids present in the flue gases emitted by the internal combustion engines, and of the protection from corrosive actions by water and moisture-containing corrosive agents (sea water, acidic solutions). In this field the hyperbasic derivatives are well-known of sulphonic acids and of sulphophenols, in as much as from these substrates forming stable colloidal suspensions of inorganic carbonate is possible; obtaining analogous products from organic carboxy acids is a more critical step. In this case, the structure and molecular complexity of the acid has in fact a conclusive influence on the characteristics of the additive.

Fatty acids from natural sources, e.g., are not suitable for obtaining hyperbasic derivatives; in fact, from these unstable colloidal suspensions, hence with a high trend to gelling, are obtained.

As already said, the compounds of the present invention, are, on the contrary, well fit to the formation of their corresponding hyperbasic derivatives, which yield very stable colloidal suspensions of inorganic carbonate, which are soluble in all proportions in the bases of either mineral or synthetic type, and which

give to the lubricants which contain them a performance at least equivalent, but often better than obtained with a conventional addition of commercial hyperbasic products.

The new hyperbasic derivatives of the present invention can be prepared by any of the methods known from the technical literature for the preparation of the hyperbasic sulphonates (see, e.g., U.S. Patents Nos. 2,467,176; 2,616,905; 3,057,896; 3,321,399; 3,429,811; 3,629,109; 3,671,430; 3,928,216; 4,086,170; 4,192,758; and EP-A-7257 and EP-A-7260).

A method which can be advantageously used for performing the process of rendering hyperbasic the compounds of the invention consists in forming a suspension of alkali-metal or alkali-earth-metal hydroxide in the detergent additive in the presence of alcohol and of a hydrocarbon solvent, then adding some CO₂, so to transform the oxide or hydroxide into its corresponding carbonate, removing the alcohol and the hydrocarbon solvent, while adding at the same time a certain amount of a lubricating oil which is compatible with the lubricating composition into which the additive is to be incorporated, so to directly obtain the stable colloidal suspension of the inorganic carbonate in the additive.

A third object of the present invention is hence a concentrated, stable additive, containing a high level of alkali-metals or alkali-earth-metals, consisting in a colloidal dispersion of an alkali-metal or alkali-earth-metal carbonate in mixture with the alkali-metal or alkali-earth-metal salt of at least one compound of formula (I), in oil.

According to a preferred form of practical embodiment of the invention, the alkali-metal or alkali-earth-metal carbonate is calcium carbonate, and the oil is mineral oil, due to an easier compatibility with the normal marketed lubricating oils.

On the contrary, as relates to the alkali-metal or alkali-earth-metal salt of the compound of formula (I), according to a preferred form of practical embodiment of the invention, this is selected from a group consisting of lithium, sodium, potassium, calcium, magnesium or barium salt of a compound of formula (I), wherein R is an alkyl of from 10 to 20 carbon atoms, A is nothing or an alkylene containing from 1 to 10 carbon atoms, R¹ is either hydrogen or an alkyl containing from 1 to 15 carbon atoms, and R² is an alkyl of from 1 to 15 carbon atoms.

In fact, the compounds belonging to this group, besides offering an optimum performance, as to their activity as detergents, as well as to their optimum suitability to be formulated as hyperbasic concentrates, allow also their production to start from low-cost raw materials, to be easily found on the market.

By looking more deeply into this latter aspect, the most preferred compounds of formula (I), for the time being, will be synthesized by starting from such bicarboxy acids as, e.g., 2,2,4-trimethyl-adipic acid, 2,4,4-trimethyl-adipic acid, dodecyl-succinic acid, 1,8-heptane-dicarboxy acid, 1,9-heptane-dicarboxy acid, and so forth, and alcohols R-OH of synthetic origin, wherein R contains from 12 to 20 carbon atoms, and, in particular, the C₁₂-C₁₄ or C₁₆-C₁₈ fractions, easily obtained on an industrial scale, by means of the hydroformylation (oxo-synthesis) process.

The following examples disclose in detail the preparation of some compounds of formula (I), representative of the invention, as well as of their corresponding hyperbasic derivatives, together with the characteristics of the so-obtained products.

Example 1

Semiester of trimethyladipic acid

188.2 g (1 mol) of trimethyladipic acid, consisting of the 40:60 blend of the two 2,2,4-trimethyl-:2,4,4-trimethyl-isomers is charged to a spherical reactor equipped with stirrer, thermometer, vapour condenser, together with 220 g (1 mol) of primary C₁₄-C₁₅-oxo-alcohols, consisting of a blend of derivatives having linear and branched alkyl chain.

The reaction mixture is slowly heated to 180°C and is kept at that temperature for 6 hours, with water eliminated during the reaction being condensed. The temperature is then increased up to 230°C, with a slow stream of nitrogen being fed to the reactor, to the purpose of facilitating water removal. After 2 hours at such a temperature, the release of water ends completely. The semiester derivative of trimethyladipic acid is cooled under nitrogen.

The product has a viscosity of 8.8 cSt at 100°C and of 73.2 cSt at 40°C; its neutralization number is 162 mg of KOH/g; it shows the typical I.R. absorption bands at 1,740 cm⁻¹, attributed to the ester function, and at 1,700 cm⁻¹, attributed to the carboxy function.

Example 2

Semiesters of heptadecanedicarboxy acid

328 g (1 mol) of heptadecanedicarboxy acid, consisting of the equimolar blend of the two 1,8- and 1,9-dicarboxy-isomers, is charged to a spherical reactor equipped with stirrer, thermometer, and vapour condenser, together with 210 g (1 mol) of primary C₁₂-C₁₅-oxo-alcohols, consisting of a blend of derivatives having linear and branched alkyl chain.

The reaction mixture is slowly heated to 180°C and is kept at that temperature for 6 hours, with water formed during the reaction being eliminated. The temperature is then increased up to 230°C, with a slow stream of nitrogen being fed to the reactor, to the purpose of facilitating water removal. After 2 hours at such a temperature, the release of water ends completely. The semiester derivative of heptanedicarboxy acid is cooled under a nitrogen atmosphere.

The product has the viscosity of 13.5 cSt at 100°C and of 102.3 cSt at 40°C. It shows the typical I.R. absorption bands at 1,740 cm⁻¹ and at 1,700 cm⁻¹ of the ester and carboxy groups, and its neutralization number is 120mg of KOH/g.

Example 3

Semiesters of heptadecanedicarboxy acid

The reaction is carried out as disclosed in Example 2, but with a primary C₁₄-C₁₅ oxo-alcohol constituted by only branched isomers being used.

A product with a viscosity at 100°C of 13.6 cSt, and at 40°C of 102.6 cSt, and having a neutralization number of 110 mg of KOH/g is obtained.

Example 4

Semiesters of dodecenylsuccinic acid

266 g (1 mol) of dodecenylsuccinic anhydride is reacted with 220 g (1 mol) of primary C₁₄-C₁₅-oxoalcohols, constituted by branched isomers, in a flask equipped with stirrer, thermometer, and condenser.

The reaction mixture is slowly heated to 150°C for three hours. In this case, no water is formed. After 3 hours, the reaction mass is cooled and the product is discharged. The product has a viscosity at 100°C of 10.8 cSt; a saponification number of 200 mg of KOH/g, and a neutralization number of 100 mg of KOH/g.

Example 5

Hyperbasic derivative from trimethyladipic acid (TMA) semiester

To a cylindrical reactor, provided with a jacket for temperature-control fluid circulation, equipped with stirrer, thermometer, condenser, load funnel for liquids and dipleg for gas loading, 300 g is charged of TMA semiester as prepared in Example 1, together with 470 g of toluene, 196 g of methanol, and 143 g of Ca(OH)₂ is then added over a 15-minute time, with the mixture being kept stirred. Through the gas-loading dipleg, into the mixture 57 g is delivered of carbon dioxide, with the gas flowrate being so adjusted, that it is completely absorbed. The CO₂-addition step lasts 2 hours and the temperature increases gradually up to 50°C. After the CO₂ flow is discontinued, the reaction mass is slowly heated to 65°C to the purpose of distilling off methanol.

During this distillation, through the load funnel 357 g of paraffinic mineral oil SN 150 is added. The temperature of the reaction mass is then increased to 98°C to the purpose of distilling off H₂O/toluene azeotrope, and finally to 140°C, to distill off all of toluene still present inside the reaction mixture.

The so-obtained product is treated with 40°C of a filtration coadjuvant, and is filtered over a 200-mesh wire net under a pressure of 2 abs.atm. The end product obtained has a viscosity of 33.5 cSt at 100°C, a TBN of 254 mg of KOH/g, and contains 8.9% of Ca.

The product is soluble in mineral oil in all proportions, and solutions are obtained which are perfectly clear, and free from precipitates or suspended solid matter.

Example 6

Hyperbasic derivative from heptanedicarboxy acid semiesters

250 g of heptanedicarboxy-acid semiester as prepared in Example 2 is charged to react to a reactor, provided with a jacket, equipped with stirrer, thermometer, condenser, load funnel for liquids, together with 300 g of toluene and 254 g of methanol. Within a 30-minute time, 180 g of $\text{Ca}(\text{OH})_2$ is then added.

Then, through the gas-loading dipleg, a stream is delivered of CO_2 , at such a flowrate, that it is completely absorbed. Over three hours, 80 g of CO_2 is supplied, and the temperature increases gradually up to 50° C.

After the gas flow is discontinued, the reaction mass is slowly heated to 65° C and methanol is distilled off, while through the load funnel 250 g of paraffinic mineral oil SN 150 is added. The temperature of the reactor is then increased to 98° C to the purpose of distilling off H_2O /toluene azeotrope, and finally to 140° C, to distill off all of still present toluene.

The reaction product is filtered, with the addition of a filtration coadjuvant, over a 200-mesh wire net under a pressure of 2 abs.atm.

The end product has a viscosity of 27.2 cSt at 100° C, a TBN of 315, a Ca content of 11.2%, and is perfectly soluble in all proportions in mineral and synthetic (poly-alpha-olefins, esters) lubricant bases.

Example 7

The heptanedicarboxy-acid semiester of Example 3 is treated exactly as disclosed in Example 6, to yield a hyperbasic product endowed with the following characteristics:
viscosity at 100° C: 25.1 cSt; TBN: 320; Ca: 11.5%

Example 8

Hyperbasic derivative from dodecenylsuccinic acid semiester

205 g of semiester of dodecenylsuccinic acid as prepared in Example 4 is treated inside a reactor, provided with a jacket, stirrer, thermometer, condenser, dipleg for gas loading and load funnel, with 330 g of toluene and 137 g of methanol. Within a 30-minute time, 100 g of $\text{Ca}(\text{OH})_2$ is then added.

A stream is then delivered of CO_2 , at such a flowrate, that it is completely absorbed by the reaction mixture.

Over two hours, 40 g of CO_2 is metered into the reaction mass, and the temperature increases gradually up to 50° C.

The reaction mass is heated to 65° C and methanol is distilled off, while 250 g of paraffinic mineral oil SN 150 is added. The temperature is then increased to 98° C to the purpose of distilling off H_2O /toluene azeotrope, and finally to 140° C, to distill off all the solvent.

The reaction product is filtered, with the addition of a filtration coadjuvant, over a 200-mesh wire net under a pressure of 2 abs.atm.

The product has a viscosity of 19.1 cSt at 100° C, a TBN of 246 mg of KOH/g, and a Ca content of 8.7%.

It is perfectly soluble in all proportions in mineral and synthetic (poly-alpha-olefins, esters) lubricant bases.

Evaluation of anti-rust power

The product of Example 5 was evaluated in a formulation containing 20% by weight thereof in a paraffinic mineral basis (solvent Neutral SN80), for its protective properties for iron-based materials.

The evaluation was carried out according to DIN-50017 procedure, as required for testing materials, structural components and equipment by the test methodology for saturated damp atmospheres.

By such a method, the metal specimens must be treated with the lubricant which contains the additive, and are then kept under a water-saturated atmosphere at 40° C for repeated 24-hour cycles, during which, by temperature being decreased, water is condensed on the same specimen.

The test is regarded as passed if the specimen shows rust stains, after 20 cycles, on not more than 5% of its surface.

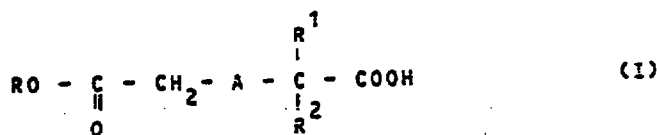
The above formulation allows a completely rust-free specimen to be obtained after 20 cycles of 24 hours.

A specimen of the same material, treated with an oil-based solution at 20% by weight of a commercial hyperbasic calcium sulphate (TBN 300 mg KOH/g; Ca = about 12%) in SN 80, after 20 24-hour cycles has more than 5% of its surface coated with rust.

Claims

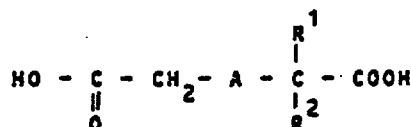
Claims for the following Contracting States : BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. Detergent additives for lubricants and lubricating compositions, selected from the compounds having the general formula:



wherein R is a C1-C30 alkyl, R¹ is hydrogen or a C1-C30 alkyl, R² is a C1-C30 alkyl, and A, if present, is a C1-C30 alkylene, with the proviso that:

- a) the sum of carbon atoms contained in R, A, R¹ and R² is equal to, or greater than, 15, and
 - b) when A is not present, the sum of the carbon atoms contained in R¹ and R² is smaller than 35, and their alkali metal- or alkaline earth metal salts.
2. A detergent additive according to Claim 1, wherein R is a C10-C20 alkyl, A, if present, is a C1-C10 alkylene, R¹ is hydrogen or a C1-C15 alkyl, and R² is a C1-C15 alkyl.
3. Process for preparing the detergent additives of formula (I) as defined in Claim 1, comprising the steps of reacting an R-OH alcohol with an equimolar amount of a bicarboxy acid:



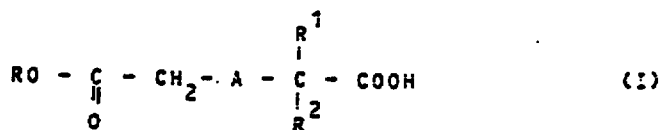
wherein R, R¹, A and R² are as defined herein, at a temperature above 100°C, and continuously removing the water as it is being formed in the reaction.

4. A lubricating composition comprising, as a detergent additive, from 0.01% to 20% by weight of an alkali metal- or alkaline earth metal salt of the compounds as defined in formula (I) of Claim 1.
5. Lubricating composition according to Claim 4, wherein the alkali metal- or alkaline earth metal salt is contained in an amount of from 0.5% to 10% by weight.
6. Lubricating composition according to Claim 4, wherein the alkali metal is selected from sodium, potassium and lithium, and the alkaline earth metal is selected from magnesium, calcium and barium.
7. A concentrated hyperbasic additive for lubricants and lubricating compositions, consisting of a colloidal dispersion, in a mineral or a synthetic oil, of an alkali metal- or alkaline earth metal carbonate, and an alkali metal- or alkaline earth metal salt of a compound as defined in formula (I) of Claim 1.
8. Concentrated hyperbasic additive according to Claim 7, wherein the alkaline earth metal carbonate is calcium carbonate.
9. Concentrated hyperbasic additive according to Claim 7, comprised of 40% of a mineral oil, 30% of calcium carbonate, and 30% of an alkali metal- or alkaline earth metal salt of a compound as defined in formula (I) of Claim 1, on a weight basis.
10. Lubricating composition containing, in one or more lubricating oil, from 2% to 20% of the concentrated hyperbasic additive as defined in Claim 7, on a weight basis.

Claims for the following Contracting States : AT, ES

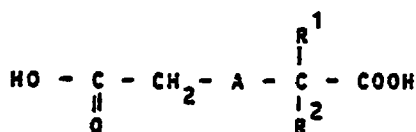


1. Process for preparing detergent additives for lubricants and lubricating compositions, selected from the compounds having the general formula:



wherein R is a C1-C30 alkyl, R¹ is hydrogen or a C1-C30 alkyl, R² is a C1-C30 alkyl, and A, if present, is a C1-C30 alkylene, with the proviso that:

- the sum of carbon atoms contained in R, A, R¹ and R² is equal to, or greater than, 15, and
- when A is not present, the sum of the carbon atoms contained in R¹ and R² is smaller than 35, and their alkali metal- or alkaline earth metal salts, characterized in that it comprises the steps of reacting an R-OH alcohol with an equimolar amount of a bicarboxy acid:



wherein R, R¹, A and R² are as defined herein, at a temperature above 100°C, and continuously removing the water as it is being formed in the reaction.

2. Process according to Claim 1, characterized in that R is a C10-C20 alkyl, A, if present, is a C1-C10 alkylene, R¹ is hydrogen or a C1-C15 alkyl, and R² is a C1-C15 alkyl.

3. Process for preparing a lubricating composition, characterized in that from 0,01% to 20% by weight of an alkali metal- or alkaline earth metal salt of the compounds as defined in formula (I) of Claim 1 is combined with a lubricant, as a detergent additive.

4. Process according to Claim 3, characterized in that the alkali metal- or alkaline earth metal salt is contained in an amount of from 0,5% to 10% by weight.

5. Process according to Claim 3, characterized in that the alkali metal is selected from sodium, potassium and lithium, and the alkaline earth metal is selected from magnesium, calcium and barium.

6. Process for preparing a concentrated hyperbasic additive for lubricants, characterized in that an alkali metal- or alkaline earth metal carbonate, and an alkali metal- or alkaline earth metal salt of a compound as defined in formula (I) of Claim 1, are colloidally dispersed in a mineral or a synthetic oil.

7. Process according to Claim 6, characterized in that the alkaline earth metal carbonate is calcium carbonate.

8. Process according to Claim 6, characterized in that 40% of a mineral oil, 30% of calcium carbonate, and 30% of an alkali metal- or alkaline earth metal salt of a compound as defined in formula (I) of Claim 1, on a weight basis, are combined to produce a lubricating composition.

9. Process for preparing a lubricating composition, characterized in that one or more lubricating oils are combined with from 2% to 20% by weight of the concentrated hyperbasic additive as defined in Claim 6.

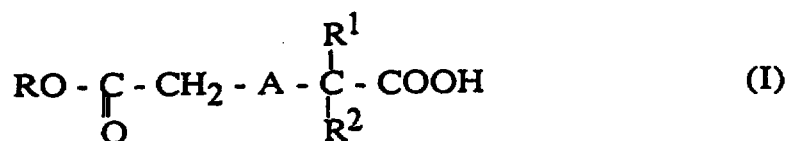
Revendications

Revendications pour les Etats contractants suivants : BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. Additifs détergents pour lubrifiants et compositions lubrifiantes, choisis parmi les composés répondant



à la formule générale :



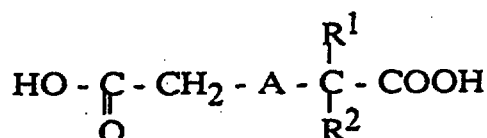
dans laquelle R représente un groupe alkyle en C₁-C₃₀, R¹ représente un atome d'hydrogène ou un groupe alkyle en C₁-C₃₀, R² représente un groupe alkyle en C₁-C₃₀ et A, s'il est présent, représente un groupe alkylène en C₁-C₃₀, étant entendu que :

- a) la somme des atomes de carbone contenus dans R, A, R¹ et R² est égale ou supérieure à 15, et
- b) lorsque A n'est pas présent, la somme des atomes de carbone contenus dans R¹ et R² est inférieure à 35,

et leurs sels de métal alcalin ou de métal alcalino-terreux.

2. Additif détergent selon la revendication 1, pour lequel R est un groupe alkyle en C₁₀-C₂₀, A, s'il est présent, est un groupe alkylène en C₁-C₁₀, R¹ est un atome d'hydrogène ou un groupe alkyle en C₁-C₁₅ et R² est un groupe alkyle en C₁-C₁₅.

3. Procédé de préparation des additifs détergents de formule (I) tels que définis dans la revendication 1, comprenant les étapes consistant à faire réagir un alcool ROH avec une quantité équimolaire d'un acide dicarboxylique de formule :



dans laquelle R, R¹, A et R² sont tels que définis ici, à une température supérieure à 100°C, et à éliminer continuellement l'eau au fur et à mesure qu'elle se forme dans la réaction.

4. Composition lubrifiante comprenant, comme additif détergent, de 0,01% à 20% en poids d'un sel de métal alcalin ou de métal alcalino-terreux des composés tels que définis par la formule (I) de la revendication 1.

5. Composition lubrifiante selon la revendication 4, dans laquelle le sel de métal alcalin ou de métal alcalino-terreux est présent en une proportion de 0,5% à 10% en poids.

6. Composition lubrifiante selon la revendication 4, pour laquelle le métal alcalin est choisi parmi le sodium, le potassium et le lithium, et le métal alcalino-terreux est choisi parmi le magnésium, le calcium et le baryum.

7. Additif hyperbasique concentré pour lubrifiants et compositions lubrifiantes, constitué d'une dispersion colloïdale, dans une huile minérale ou synthétique, d'un carbonate de métal alcalin ou de métal alcalino-terreux et d'un sel de métal alcalin ou de métal alcalino-terreux d'un composé tel que défini par la formule (I) de la revendication 1.

8. Additif hyperbasique concentré selon la revendication 7, dans lequel le carbonate de métal alcalino-terreux est le carbonate de calcium.

9. Additif hyperbasique concentré selon la revendication 7, constitué de 40% d'une huile minérale, 30% de carbonate de calcium et 30% d'un sel de métal alcalin ou de métal alcalino-terreux d'un composé tel que défini par la formule (I) de la revendication 1, les pourcentages étant exprimés en poids.

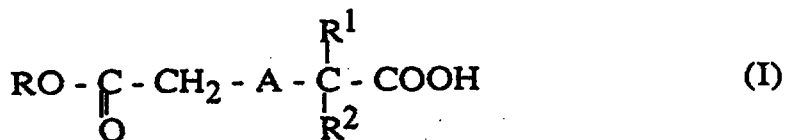
10. Composition lubrifiante contenant, dans une ou plusieurs huiles lubrifiantes, de 2% à 20% de l'additif hyperbasique concentré tel que défini dans la revendication 7, les pourcentages étant exprimés en



poids.

Revendications pour les Etats contractants suivants : AT, ES

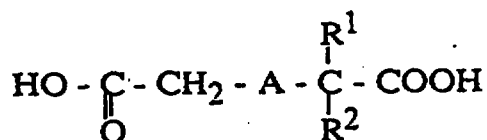
1. Procédé de préparation d'additifs détergents pour lubrifiants et compositions lubrifiantes, choisis parmi les composés répondant à la formule générale :



dans laquelle R est un groupe alkyle en C₁-C₃₀, R¹ est un atome d'hydrogène ou un groupe alkyle en C₁-C₃₀, R² est un groupe alkyle en C₁-C₃₀ et A, s'il est présent, est un groupe alkylène en C₁-C₃₀, étant entendu que :

- la somme des atomes de carbone contenus dans R, A, R¹ et R² est égale ou supérieure à 15, et
- lorsque A n'est pas présent, la somme des atomes de carbone contenus dans R¹ et R² est inférieure à 35,

et leurs sels de métal alcalin ou de métal alcalino-terreux, caractérisé en ce qu'il comprend les étapes consistant à faire réagir un alcool ROH avec une quantité équimolaire d'un acide dicarboxylique de formule :



dans laquelle R, R¹, A et R² sont tels que définis ici, à une température supérieure à 100 °C, et à éliminer continuellement l'eau au fur et à mesure qu'elle se forme dans la réaction.

- Procédé selon la revendication 1, caractérisé en ce que R est un groupe alkyle en C₁₀-C₂₀, A, s'il est présent, est un groupe alkylène en C₁-C₁₀, R¹ est un atome d'hydrogène ou un groupe alkyle en C₁-C₁₅ et R² est un groupe alkyle en C₁-C₁₅.
- Procédé de préparation d'une composition lubrifiante, caractérisé en ce qu'on combine de 0,01% à 20% en poids d'un sel de métal alcalin ou de métal alcalino-terreux des composés tels que définis par la formule (I) de la revendication 1, en tant qu'additif détergent, avec un lubrifiant.
- Procédé selon la revendication 3, caractérisé en ce que le sel de métal alcalin ou de métal alcalino-terreux est présent dans la composition en une proportion de 0,5% à 10% en poids.
- Procédé selon la revendication 3, caractérisé en ce que le métal alcalin est choisi parmi le sodium, le potassium et le lithium, et le métal alcalino-terreux est choisi parmi le magnésium, le calcium et le baryum.
- Procédé de préparation d'un additif hyperbasique concentré pour lubrifiants, caractérisé en ce qu'on forme une dispersion colloïdale, dans une huile minérale ou synthétique, d'un carbonate de métal alcalin ou de métal alcalino-terreux et d'un sel de métal alcalin ou de métal alcalino-terreux d'un composé tel que défini par la formule (I) de la revendication 1.
- Procédé selon la revendication 6, caractérisé en ce que le carbonate de métal alcalino-terreux est le carbonate de calcium.
- Procédé selon la revendication 6, caractérisé en ce que 40% d'une huile minérale, 30% de carbonate de calcium et 30% d'un sel de métal alcalin ou de métal alcalino-terreux d'un composé tel que défini par la formule (I) de la revendication 1, les pourcentages étant exprimés en poids, sont combinés pour



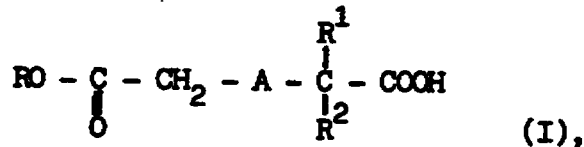
produire une composition lubrifiante.

9. Procédé de préparation d'une composition lubrifiante, caractérisé en ce qu'on combine une ou plusieurs huiles lubrifiantes avec 2% à 20% en poids de l'additif hyperbasique concentré tel que défini dans la revendication 6.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, CH, DE, FR, GB, GR, LI, LU, NL, SE

1. Detergensadditive für Schmierstoffe und Schmierstoffzusammensetzungen, ausgewählt unter Verbindungen mit der allgemeinen Formel:



20 worin

- R ein C₁-C₃₀-Alkylrest ist,
 R¹ Wasserstoff oder einen C₁-C₃₀-Alkylrest bedeutet,
 R² einen C₁-C₃₀-Alkylrest darstellt und
 A, sofern vorhanden einen C₁-C₃₀-Alkylrest bezeichnet,

25 mit der Maßgabe, daß:

- a) die Summe der R, A, R¹ und R² enthaltenen Kohlenstoffatome gleich der größer als 15 ist und
 b) wenn A nicht zugegen ist, die Summe der in R¹ und R² enthaltenen Kohlenstoffatome kleiner als 35 ist,

und ihren Alkalimetall- oder Erdalkalimetallsalzen.

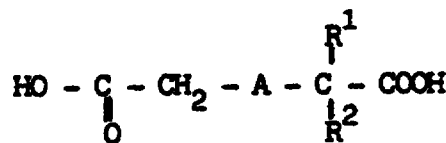
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2. Detergensadditiv nach Anspruch 1, worin

- R einen C₁₀-C₂₀-Alkylrest bedeutet,
 A, sofern zugegen, ein C₁-C₁₀-Alkylrest ist,
 R¹ Wasserstoff oder einen C₁-C₁₅-Alkylrest bedeutet und
 R² einen C₁-C₁₅-Alkylrest darstellt.

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3. Verfahren zur Herstellung der Detergensadditive der Formel (I) nach Anspruch 1, umfassend die Stufen des Umsetzens eines Alkohols R-CH mit einer äquimolaren Menge einer Dicarbonsäure:



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worin R, R¹, R² und A wie vorstehend definiert sind, bei einer Temperatur über 100°C und des kontinuierlichen Abtrenners des Wassers im Zuge seiner Bildung in der Umsetzung.

4. Schmierstoffzusammensetzung umfassend, als Detergensadditiv, 0,01 bis 20 Gew.-% eines Alkalimetall- oder Erdalkalimetallsalzes der Verbindungen, wie in Formel (I) in Anspruch 1 definiert.

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5. Schmierstoffzusammensetzung nach Anspruch 4, worin das Alkalimetall- oder Erdalkalimetallsalz in einer Menge von 0,5 bis 10 Gew.-% enthalten ist.

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6. Schmierstoffzusammensetzung nachh Anspruch 4, worin das Alkalimetall unter Natrium, Kalium und Lithium und das Erdalkalimetall unter Magnesium, Calcium und Barium ausgewählt ist.

7. Konzentriertes Überbasisches Additiv für Schmierstoffe und Schmierstoffzusammensetzungen, beste-

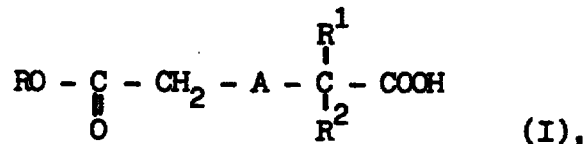


hend aus einer kolloidalen Dispersion eines Alkalimetall- oder Erdalkalimetallcarbonats und eines Alkalimetall- oder Erdalkalimetallsalzes einer Verbindung, wie in Formel (I) von Anspruch 1 definiert, in einem mineralischen oder synthetischen Öl.

8. Konzentriertes überbasisches Additiv nach Anspruch 7, worin das Erdalkalimetallcarbonat Calciumcarbonat ist.
9. Konzentriertes überbasisches Additiv nach Anspruch 7, bestehend aus 40 % eines Mineralöls, 30 % Calciumcarbonat und 30 % eines Alkalimetall- oder Erdalkalimetallsalzes einer Verbindung, wie in Formel (I) von Anspruch 1 definiert, bezogen auf Gewichtsbasis.
10. Schmierstoffzusammensetzung mit einem Gehalt an 2 bis 20% des konzentrierten überbasischen Additivs nach Anspruch 7 in einem oder in mehreren Schmierölen, bezogen auf Gewichtsbasis.

Patentansprüche für folgende Vertragsstaaten : AT, ES

1. Verfahren zur Herstellung von Detergensadditiven für Schmierstoffe und Schmierstoffzusammensetzungen, ausgewählt unter Verbindungen mit der allgemeinen Formel:



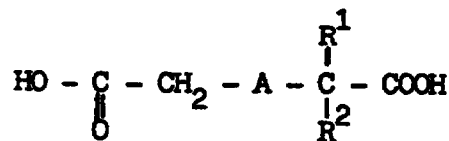
worin

- R ein C₁-C₃₀-Alkylrest ist,
 R¹ Wasserstoff oder einen C₁-C₃₀-Alkylrest bedeutet,
 R² einen C₁-C₃₀-Alkylrest darstellt und
 A, sofern vorhanden, einen C₁-C₃₀-Alkylrest bezeichnet,

mit der Maßgabe, daß:

- a) die Summe der in R, A, R¹ und R² enthaltenen Kohlenstoffatome gleich oder größer als 15 ist und
- b) wenn A nicht zugegen ist, die Summe der in R¹ und R² enthaltenen Kohlenstoffatome kleiner als 35 ist,

und ihren Alkalimetall- oder Erdalkalimetallsalzen, dadurch gekennzeichnet, daß es die Stufen des Umsetzens eines Alkohols R-OH mit einer äquimolaren Menge einer Dicarbonsäure:



worin R, R¹, R² und A wie oben definiert sind, bei einer Temperatur über 100°C und eines kontinuierlichen Abtrennens des Wassers im Zuge seiner Bildung in der Umsetzung umfaßt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß

- R ein C₁₀-C₂₀-Alkylrest ist,
 A, sofern zugegen, einen C₁-C₁₀-Alkylrest darstellt,
 R¹ für Wasserstoff oder einen C₁-C₁₅-Alkylrest steht und
 R² einen C₁-C₁₅-Alkylrest bezeichnet.

3. Verfahren zur Herstellung einer Schmierstoffzusammensetzung, dadurch gekennzeichnet, daß 0,01 bis 20 Gew.-% eines Alkalimetall- oder Erdalkalimetallsalzes der Verbindungen, wie in Formel (I) von Anspruch 1 definiert, als Detergensadditiv mit einem Schmierstoff vereinigt werden.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Alkalimetall- oder Erdalkalimetallsalz in



einer Menge von 0,5 bis 10 Gew.-% enthalten ist.

5. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß das Alkalimetall unter Natrium, Kalium und Lithium und das Erdalkalimetall unter Magnesium, Calcium und Barium ausgewählt wird.
6. Verfahren zur Herstellung eines konzentrierten überbasischen Additivs für Schmierstoffe, dadurch gekennzeichnet, daß ein Alkalimetall- oder Erdalkalimetallcarbonat und ein Alkalimetall- oder Erdalkalimetallsalz einer Verbindung, wie in Formel (I) von Anspruch 1 definiert, in einem Mineralöl oder einem synthetischen Öl kolloidal dispergiert werden.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Erdalkalimetallcarbonat Calciumcarbonat ist.
8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß 40 % eines Mineralöls, 30 % Calciumcarbonat und 30 % eines Alkalimetall- oder Erdalkalimetallsalzes einer Verbindung, wie in Formel (I) von Anspruch 1 definiert, auf Gewichtsbasis bezogen, zu einer Schmierstoffzusammensetzung vereinigt werden.
9. Verfahren zur Herstellung einer Schmierstoffzusammensetzung, dadurch gekennzeichnet, daß ein oder mehrere Schmieröle mit 2 bis 20 Gew.-% des konzentrierten überbasischen Additivs nach Anspruch 6 vereinigt werden.

