

Description

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The present invention relates to novel ammonium salts of methylphosphonic acid and to the use thereof as additives for lubricants, as well as to compositions containing the novel compounds and to a process for lubricating machine parts.

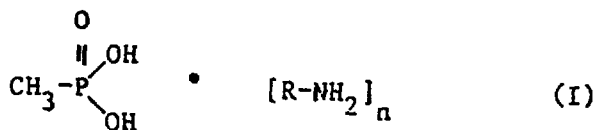
Ammonium salts of methylphosphonic acid suitable for use as anti-wear and extreme pressure additives for water-miscible hydraulic fluids are known from EP-A 12,106. The ammonium cation of these compounds contains at least one β -hydroxyethyl group, which imparts to the salts solubility in polar liquids.

α -Chloromethylphosphonic acids in combination with primary alkylamines, the alkyl moiety of which contains more than 8 carbon atoms and is preferably branched, are disclosed as extreme pressure additives in US-PS 2,858,332. Depending on the end use, the monoamino or diamino derivative is preferably used.

Furthermore, amine salts of phosphorus-containing acids of the series of phosphates, phosphonates and phosphinates have become known from FR-PS 2,132,008. The amine to be used is a phenylalkylamine and the compounds should be compatible in oil mixture particularly with elastomeric compounds.

Surprisingly, it has now been found that salts of methylphosphonic acid with primary amines, in particular salts which contain less than 2 equivalents of amine, impart unusually good extreme pressure properties to lubricants. These compounds are even superior in this respect to the very effective known thiaphosphetane derivatives.

The present invention relates to compounds of formula I



wherein n is a number from 1.0 to 2.2 and R is straight chain or branched C₈-C₃₀alkyl which may be interrupted by 1 to 5 sulfur atoms, or R is straight chain or branched C₈-C₃₀alkenyl.

R as straight chain C₈-C₃₀alkyl is n-octyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-eicosyl, n-docosyl or n-triacontyl. R as branched C₈-C₃₀alkyl may be 1,1,3,3-tetramethylbutyl, 1,1,3,3,5,5-hexamethylhexyl, 1,1,3,3,5,5,7,7-octamethyloctyl or 1,1,3,3,5,5,7,7,9,9-decamethyldecyl.

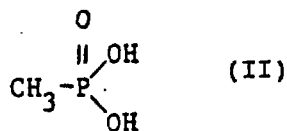
If R is C₈-C₃₀alkenyl, oleyl is particularly suitable. It is preferred to use primary amines containing a branched C₈-C₃₀alkyl radical R, in particular those containing tertiary carbon atoms and, most preferably, those containing a tertiary carbon atom in the α -position relative to the amino group. These amines can be obtained for example from branched primary alcohols which are obtained in the Oxo process in accordance with known methods. Such reactions are described by P.W. Sherwood in the Oil and Gas Journal, 1949, 71. It is preferred to use mixtures of those amines which are commercially available under the trade name of "Primenes". Thus, for example, it is possible to use the mixture "Primene[®] 81-R" (principally branched alkylamines containing 12 to 15 carbon atoms) or the mixture "Primene[®] JM-T" (principally branched primary alkylamines containing 18 to 24 carbon atoms).

A further preferred value for R is C₈-C₃₀alkyl which is interrupted by 1 to 5 sulfur atoms, in particular branched C₈-C₃₀alkyl which is interrupted by 1 to 5 sulfur atoms; particularly preferably R is -CH₂CH₂-S-alkyl (C₉-C₁₂), in particular -CH₂-CH₂-S-tert-C₁₂H₂₅ and -CH₂-CH₂-S-tert-C₉H₁₉. By tert-C₉H₁₉ and tert-C₁₂H₂₅ are meant a mixture of different isomers which are preferably characterized in that a tertiary carbon atom is in the α -position. The C₉-C₁₂alkyl radical can of course also denote a mixture of branched alkyl radicals containing a different number of carbon atoms.

Also preferred are compounds of formula I, wherein n is 1.0 to 1.5 or wherein R is C₁₀-C₃₀alkyl, in particular branched alkyl which carries a

tertiary carbon atom in the α -position relative to the amino group.

The compounds of formula I can be prepared in a manner known per se. The simplest procedure comprises reacting methylphosphonic acid of the formula II



with an amine of formula III



wherein R is as defined above. The molar ratio is in particular 1:1 to 1:2.2, preferably 1:1.5. If appropriate, a solvent or diluent is used, for example an alcohol such as methanol, which can be distilled off, for example under reduced pressure, upon completion of the reaction. The amine salt is obtained as a viscous oil.

The starting materials employed are known compounds which can be obtained in simple manner.

The compounds of formula I are employed in concentrations of 0.01 to 10% by weight, based on the total weight of the lubricant formulation. The preferred concentration range is from 0.05 to 5.0% by weight.

By virtue of their properties for effecting an enhancement of extreme pressure and anticorrosion performance, the compounds according to the invention are suitable as additives for synthetic lubricating oils or greases as well as for mineral oil-based lubricants. The compounds of the formula I can also be used in metalworking oils. Accordingly, the invention also relates to lubricants which contain compounds of formula I as well as to the use of compounds of formula I as extreme pressure and antiwear additives in lubricants. Further, the invention relates to a process for lubricating machine parts which are subject to severe shock stress, which process comprises the use of a lubricant which contains a compound of formula I.

Suitable lubricants are known to the skilled person and are described for example in "Schmiermittel-Taschenbuch", Hüthig Verlag, Heidelberg, 1974.

In addition to mineral oils, particularly suitable lubricants are for example poly- α -olefins, carboxylate-based lubricants, phosphate esters, polyalkylene glycols and mixtures of said lubricants.

The lubricant formulations can also contain other additives in order to enhance certain use properties, for example further antioxidants, metal deactivators, rust inhibitors, viscosity index improvers, pour-point depressants, dispersants/surfactants and antiwear additives.

Examples of phenolic antioxidants

1. Alkylated monophenols

2,6-di-tert-butylphenol
2-tert-butyl-4,6-dimethylphenol
2,6-di-tert-butyl-4-ethylphenol
2,6-di-tert-butyl-4-ethylphenol (sic)
2,6-di-tert-butyl-4-n-butylphenol
2,6-di-tert-butyl-4-i-butylphenol
2,6-dicyclopentyl-4-methylphenol
2-(α -methylcyclohexyl)-4,6-dimethylphenol
2,6-dioctadecyl-4-methylphenol
2,4,6-tricyclohexylphenol
2,6-di-tert-butyl-4-methoxymethylphenol

2. Alkylated hydroquinones

2,6-di-tert-butyl-4-methoxyphenol
2,5-di-tert-butylhydroquinone
2,5-di-tert-amylhydroquinone
2,6-diphenyl-4-octadecyloxyphenol

3. Hydroxylated thiodiphenyl ethers

2,2'-thio-bis(6-tert-butyl-4-methylphenol)
2,2'-thio-bis(4-octylphenol)
4,4'-thio-bis(6-tert-butyl-3-methylphenol)
4,4'-thio-bis(6-tert-butyl-2-methylphenol)

4. Alkylidene bisphenols

2,2'-methylene-bis(6-tert-butyl-4-methylphenol)
2,2'-methylene-bis(6-tert-butyl-4-ethylphenol)
2,2'-methylene-bis[4-methyl-6-(α -methylcyclohexyl)phenol]
2,2'-methylene-bis(4-methyl-6-cyclohexylphenol)
2,2'-methylene-bis(6-nonyl-4-methylphenol)
2,2'-methylene-bis(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis(6-tert-butyl-4-isobutylphenol)
2,2'-methylene-bis[6-(α -methylbenzyl)-4-nonylphenol]
2,2'-methylene-bis[6-(α , α -dimethylbenzyl)-4-nonylphenol]
4,4'-methylene-bis(6-tert-butyl-2-methylphenol)
1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane
2,6-di-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol
1,1,3-tris(5'-tert-butyl-4'-hydroxy-2'-methylphenyl)-3-n-dodecylmercapto-
butane
ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate]
di(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene
di[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methyl-
phenyl]terephthalate.

5. Benzyl compounds

1,3,5-tri(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene
di(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide
bis(3-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiolterephthalate
1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl) isocyanurate
1,3,5-tris(4'-tert-butyl-3'-hydroxy-2',6'-dimethylbenzyl) isocyanurate
dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate
calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzyl phosphonate

6. Acylaminophenols

4-hydroxylauric anilide
4-hydroxystearic anilide
2,4-bis-octylmercapto-6-(3',5'-di-tert-butyl-4'-hydroxyanilino)-s-tri-
azine
octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate

7. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

with monohydric or polyhydric alcohols, for example with methanol, octadecanol, 1,6-hexanediol, neopentylglycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-hydroxyethyl isocyanurate, dihydroxyethyloxalaldiamide.

8. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid

with monohydric or polyhydric alcohols, for example with methanol, octadecanol, 1,6-hexanediol, neopentylglycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-hydroxyethyl isocyanurate or dihydroxyethyloxalaldiamide.

9. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

for example,

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

Examples of amine antioxidants:

N,N'-diisopropyl-p-phenylenediamine

N,N'-di-sec-butyl-p-phenylenediamine

N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine

N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine

N,N'-bis(1-methylheptyl)-p-phenylenediamine

N,N'-dicyclohexyl-p-phenylenediamine

N,N'-diphenyl-p-phenylenediamine

N,N'-di(2-naphthyl)-p-phenylenediamine

N-isopropyl-N'-phenyl-p-phenylenediamine

N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine

N-cyclohexyl-N'-phenyl-p-phenylenediamine

bis-4-(p-toluenesulfonamidophenyl)amine

N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine

diphenylamine

4-isopropoxydiphenylamine

N-phenyl-1-naphthylamine
N-phenyl-2-naphthylamine
octylated diphenylamine
4-n-butylaminophenol
4-butyrylaminophenol
4-nonanoylaminophenol
4-dodecanoylaminophenol
4-octadecanoylaminophenol
bis(4-methoxyphenyl)amine
2,6-di-tert-butyl-4-dimethylaminomethylphenol
2,4'-diaminodiphenylmethane
4,4'-diaminodiphenylmethane
N,N,N'-tetramethyl-4,4'-diaminodiphenylmethane
1,2-bis(phenylamino)ethane
1,2-bis[(2-methylphenyl)amino]ethane
1,3-bis(phenylamino)propane
(o-tolyl)biguanide
bis-[4-(1',3'-dimethylbutyl)phenyl]amine

Examples of metal deactivators are:

for copper, for example: benzotriazole, tetrahydrobenzotriazole, 2-mercapto benzothiazole, 2,5-dimercaptothiadiazole, salicylidene propylene-diamine, salts of salicylaminoguanidine.

Examples of rust inhibitors are:

a) Organic acids, their esters, metal salts and anhydrides, for example: N-oleoylsarcosine, sorbitan monooleate, lead naphthenate, dodecenyl-succinic anhydride, monoalkenyl succinate, 4-nonylphenoxyacetic acid.

b) Nitrogen-containing compounds, for example:

I. Primary, secondary or tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic acids, for example oil-soluble alkylammonium carboxylates.

II. Heterocyclic compounds, for example substituted imidazolines and oxazolines.

c) Phosphorous-containing compounds, for example: amine salts of phosphoric acid partial esters.

d) Sulfur-containing compounds, for example: barium dinonylnaphthalene-sulfonates, calcium petroleum sulfonates.

Examples of viscosity index improvers are:

polymethacrylates, vinyl pyrrolidone/methacrylate copolymers, polybutene, olefin copolymers, styrene/acrylate copolymers.

Examples of pour-point depressants are:

Polymethacrylate, alkylated naphthalene derivatives

Examples of dispersants/surfactants are:

polybutenylsuccinimides, polybutenylphosphonic acid derivatives, basic magnesium, calcium and barium sulfonates and phenolates.

Examples of anti-wear additives are:

compounds which contain sulfur and/or phosphorous and/or halogen, such as sulfurised vegetable oils, zinc dialkyldithiophosphates, tritolylphosphate, chlorinated paraffins, alkyl disulfides and aryl disulfides.

Preparatory Examples 1-4:

The salts listed in the following table are obtained by reacting together appropriate molar amounts of methylphosphonic acid and primary amine.

Table

Substance No.	Formula	Properties
1	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{P} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array} \cdot [\text{iso-C}_{13}\text{H}_{27}\text{NH}_2]^{1)}$	yellow viscous liquid $n_D^{20} = 1,4612$
2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{P} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array} \cdot [\text{iso-C}_{13}\text{H}_{27}\text{NH}_2]^{1)} + 25\% \text{ Paraffin Oil}$	yellow viscous liquid
3	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{P} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array} \cdot [\text{iso-C}_{13}\text{H}_{27}\text{NH}_2]^{1)}_{1,5}$	yellow viscous liquid
4	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{P} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array} \cdot [\text{iso-C}_{20}\text{H}_{41}\text{NH}_2]^{2)}_{1,5}$	yellow viscous liquid

1) PRIMENE 81-R ®

2) PRIMENE JM-T ®

Example 5: The weld load (WL) and the wear scar diameter (WSD) are determined using the Shell four-ball machine (IP 239/73, Extreme Pressure and Wear Lubricant Test for Oils and Greases, Four-Ball Machine) as a function of the concentration of the extreme pressure additive.

WL = weld load: the load at which the 4 balls become welded together within 10 seconds

WSD = wear scar diameter: the average diameter of the scars produced on the 3 stationary balls after 10 minutes at a load of 400 N.

The test fluid employed for testing the effectiveness of the additives is a mineral oil of viscosity class ISO VG 100. The results are reported in the following table.

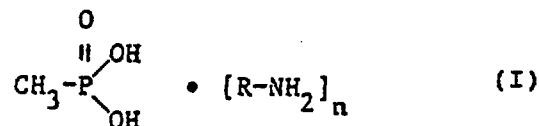
Table

Additive (Product No)	Concentration (% by weight)	W.L. (N)	WSD after 10 mins at 400 N load (mm)
-	-	1450	—
1	1.0	3750	0.50
1	2.0	6500	0.53
1	5.0	9500	—
1	10.0	9500	—



Patent claims

1. A compound of the formula I



wherein n is a number from 1.0 to 2.2 and R is straight chain or branched C₈-C₃₀alkyl which may be interrupted by one to five sulfur atoms, or wherein R is straight chain or branched C₈-C₃₀alkenyl.

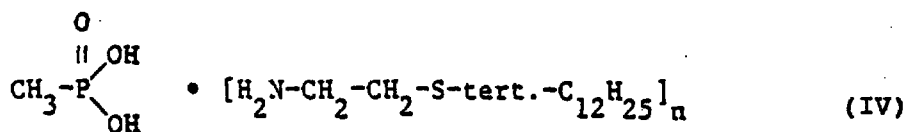
2. A compound of formula I according to claim 1, wherein n is 1.0 to 1.5.

3. A compound of formula I according to claim 1, wherein R is branched C₈-C₃₀alkyl.

4. A compound of formula I according to claim 1, wherein R is branched C₈-C₃₀alkyl which is interrupted by one to five sulfur atoms.

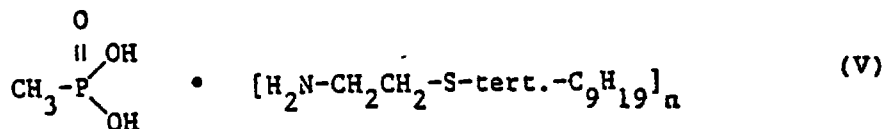
5. A compound of formula I according to claim 1, wherein R is C₁₀-C₃₀alkyl and has a tertiary carbon atom in the α-position relative to the amino group.

6. A compound of formula IV according to claim 1



wherein n is 1.

7. A compound of formula V according to claim 1



wherein n is 1.



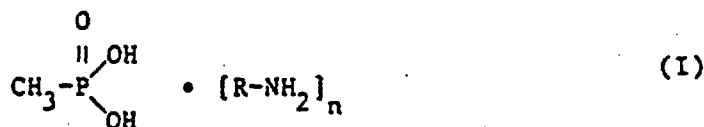
8. A compound of formula I according to claim 1, wherein the amine component used is a mixture of branched C₁₂-C₁₅alkylamines which contain a tertiary carbon atom in the α -position.
9. A compound of formula I according to claim 1, wherein the amine component used is a mixture of branched C₁₈-C₂₄alkylamines which contain a tertiary carbon atom in the α -position.
10. A lubricant containing a compound of formula I according to claim 1 as extreme pressure and antiwear additives.
11. The use of a compound of formula I according to claim 1 as extreme pressure and antiwear additives in lubricants.
12. A process for lubricating machine parts which are subject to severe shock stress, which process comprises adding a compound of formula I according to claim 1 or a mixture of such compounds to the lubricant.



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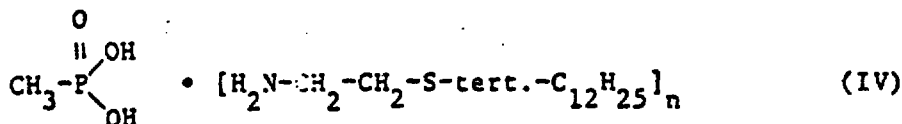
Claims

1. A compound of the formula I



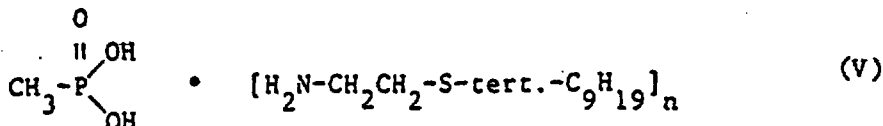
wherein n is a number from 1.0 to 2.2 and R is straight chain or branched C₈-C₃₀alkyl which may be interrupted by one to five sulfur atoms, or wherein R is straight chain or branched C₈-C₃₀alkenyl.

2. A compound of formula I according to claim 1, wherein n is 1.0 to 1.5.
 3. A compound of formula I according to claim 1, wherein R is branched C₈-C₃₀alkyl.
 4. A compound of formula I according to claim 1, wherein R is branched C₈-C₃₀alkyl which is interrupted by one to five sulfur atoms.
 5. A compound of formula I according to claim 1, wherein R is C₁₀-C₃₀alkyl and has a tertiary carbon atom in the α-position relative to the amino group.
 6. A compound of formula IV according to claim 1



wherein n is 1.

7. A compound of formula V according to claim 1



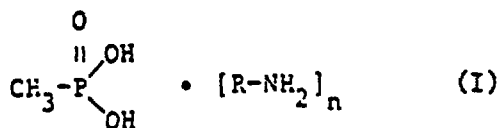
wherein n is 1.

8. A compound of formula I according to claim 1, wherein the amine component used is a mixture of branched C₁₂-C₁₅alkylamines which contain a tertiary carbon atom in the α-position.
 9. A compound of formula I according to claim 1, wherein the amine component used is a mixture of branched C₁₈-C₂₄alkylamines which contain a tertiary carbon atom in the α-position.
 10. A lubricant containing a compound of formula I according to claim 1 as extreme pressure and antiwear additives.
 11. The use of a compound of formula I according to claim 1 as extreme pressure and antiwear additives in lubricants.
 12. A process for lubricating machine parts which are subject to severe shock stress, which process comprises adding a compound of formula I according to claim 1 or a mixture of such compounds to the lubricant.

As printed:

Revendications

1. Composés répondant à la formule I:



dans laquelle n représente un nombre compris entre 1,0 et 2,2, et R représente un radical alkyle en C₈-C₃₀ linéaire ou ramifié, qui est éventuellement interrompu par un à cinq atomes de soufre ou R représente un radical alcényle en C₈-C₃₀, linéaire ou ramifié.

2. Composés de formule I selon la revendication 1 dans lesquels n désigne un nombre compris entre 1,0 et 1,5.
 3. Composés de formule I selon la revendication 1 dans lesquels R représente un radical alkyle C₈-C₃₀ ramifié.
 4. Composés de formule I selon la revendication 1 dans lesquels R représente un radical alkyle en C₈-C₃₀ ramifié et interrompu par un à cinq atomes de soufre.

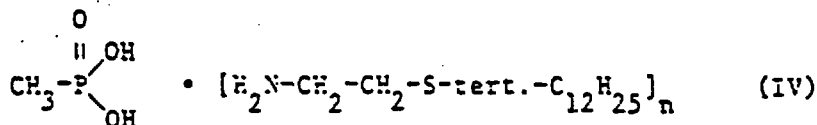


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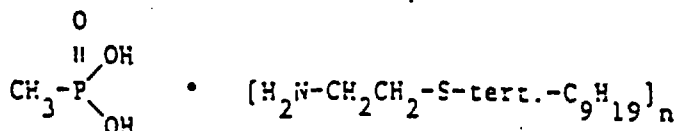
5. Composés de formule I selon la revendication 1 dans lesquels R représente un radical alkyle en C₈-C₃₀ et contient un atome de carbone tertiaire en position α par rapport au radical amino.

6. Composé selon la revendication 1, en l'espèce celui qui répond à la formule IV:



dans laquelle n désigne le nombre 1.

7. Composé selon la revendication 1, en l'espèce celui qui répond à la formule V:



dans laquelle n désigne le nombre 1.

8. Composé de formule I selon la revendication 1 dans lequel la composante amine utilisée est un mélange d'alkylamines en C₁₂-C₁₅ ramifiées qui contiennent un atome de carbone tertiaire en position α.

9. Composé de formule I selon la revendication 1 dans lequel la composante amine utilisée est un mélange d'alkylamines en C₁₈-C₂₄ ramifiées qui contiennent un atome de carbone tertiaire en position α.

10. Lubrifiants contenant des composés de formule I selon la revendication 1 comme additifs anti-usures et haute pression.

11. Application de composés de formule I selon la revendication 1 comme additifs anti-usures et haute pression dans des lubrifiants.

12. Procédé pour lubrifier des pièces de machines soumises à une forte charge par à-coups, procédé caractérisé en ce qu'on ajoute au lubrifiant un composé de formule I selon la revendication 1 ou un mélange de tels composés.

