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(54) Title: CORROSION INHIBITING COMPOSITION FOR NON-FERROUS METALS

(57) Abstract: The invention relates an additive composition for use as a metal working fluid and a process for protection of metals, particularly zinc or aluminum, against corrosion or oxidative degradation. The composition comprises an additive mixture of an alkenyl succinic half ester, a substituted imidazoline compound and amine phosphate partial ester in a functional fluid.

WO 2007/135017 A1

CORROSION INHIBITING COMPOSITION FOR NON-FERROUS METALS

The invention relates to an additive composition for use as a metal working fluid or corrosion protection oil and a process for the protection of metals, particularly zinc or aluminium alloys, against corrosion or oxidative degradation.

- 5 Additives, which have the purpose to protect metals against corrosion are commonly divided in to two classes:

Metal deactivators are used to protect yellow metals or alloys, such as copper or brass, and display their protective action in functional liquids, such as mineral oil or fuels, by deactivating the metal ions contained therein. These metal ions can have catalytic effects in undesired
10 oxidative decomposition processes of mineral oil or fuels. The protective action is explained by the formation of film-like layers on the surface of metals or by complex formation with metal ions.

Corrosion inhibitors are primary used to protect ferrous metals such as iron or steel. Analogue to metal deactivators, corrosion inhibitors, are forming also film-like layers on the surface of metals. In addition some corrosion inhibitors can prevent the corrosion, by emulsifying
15 water and minimizing therefore the direct contact of water with the metal surface.

Presently metal protection methods focus primarily on iron and copper surfaces. However, other metals, such as zinc and aluminium and their related alloys, have become very important in many technical applications. Zinc and aluminium are, for example, widely used in the
20 manufacture of automobiles. Zinc is widely used as corrosion protection coating of steels, e.g. zinc coated steel coils. Corrosion problems often occur during transport, handling and working of semi-finished metal products. Unfortunately, presently used metal deactivator compositions are less satisfactory or even unsatisfactory to protect these metal surfaces. Therefore, there is a clear need for improved metal working fluids to prevent corrosion of
25 these metals

British Patent Specification No. 795,491 discloses the preparation of alkenyl succinic half esters and their applicability as steam turbine lubricant additives.

British Patent Specification No. 1,043,488 lubricating oil compositions comprising substituted imidazoline compounds and phosphate partial esters.

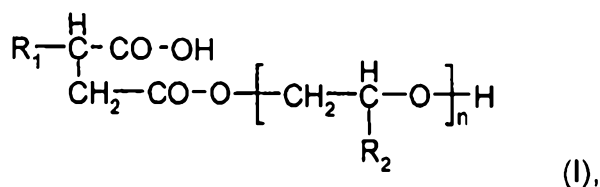
- 30 *U.S. Patent Application Publication No. 2005/0272614* discloses corrosion inhibiting compositions, wherein substituted imidazolines and neutral metal sulfonate corrosion inhibitors are present.

It has surprisingly been found that mixtures of alkenyl succinic half esters, substituted imidazoline compounds and amine phosphate partial esters in functional fluids, such as oils, prevent the corrosion of zinc, zinc coated steel and aluminum metal samples. This anticorrosive effect can be increased by the further admixture of additional anti-corrosive agents, such as substituted imidazolines and amine phosphate partial esters.

SUMMARY OF THE INVENTION

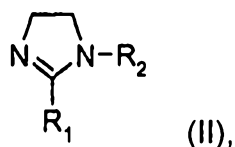
A first aspect of the invention provides a composition, which comprises

- A) An additive mixture that consists of
- a) At least one alkenyl succinic half ester of the formula



Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents hydrogen or methyl and n is a numeral from 1 to 100;

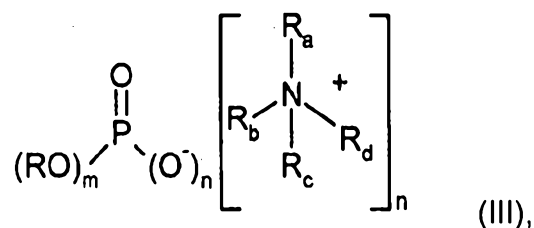
- b) At least one imidazoline compound of the formula



Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; or

Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; and

- c) At least one amine phosphate partial ester of the formula



Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxyC₂-C₁₂alkyl, amino C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

B) A functional fluid.

A second aspect of the invention provides a composition, which comprises

- a) At least one alkenyl succinic half ester (I), as defined in the first aspect,

Wherein R₁ represents C₆-C₁₈alkenyl, R₂ represents methyl and n is a numeral from 1 to 100;

- b) At least one imidazoline compound (II), as defined in the first aspect, Wherein one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; or

Wherein both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-

C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl;

c) At least one amine phosphate partial ester (III), as defined in the first aspect,

Wherein m represents 1 or 2;

n represents 2 if m represents 1; or

represents 1 if m represents 2; and

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl,

hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

d) Additional customary additives.

A third aspect of the invention provides an additive mixture that consists of

a) At least one alkenyl succinic half ester (I), as defined in the first aspect,

Wherein R₁ represents C₆-C₁₈alkenyl, R₂ represents hydrogen or methyl and n is a numeral of 0 to 100;

b) At least one imidazoline compound (II), as defined in the first aspect, Wherein one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄ alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; or

Wherein both of R₁ and R₂ represent substituents selected from the

group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; and

c) At least one amine phosphate partial ester (III), as defined in the first aspect,

Wherein m represents 1 or 2;

n represents 2 if m represents 1; or

represents 1 if m represents 2; and

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₂alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl.

A fourth aspect of the invention provides an additive mixture as defined in the third aspect, when used as a metal working fluid.

A fifth aspect of the invention provides a composition as defined in the first aspect, wherein the functional fluid B) is a non-aqueous functional liquid selected from the group consisting of: lubricants, hydraulic fluids, metal working fluids, engine coolants, transformer oils and switch gear oils.

A sixth aspect of the invention provides a process for protection against corrosion or oxidative degradation of metals, wherein the metal is exposed to a functional fluid comprising the additive mixture as defined in the third aspect.

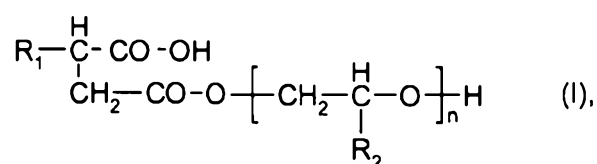
A seventh aspect of the invention provides a process for protection against corrosion or oxidative degradation of zinc, aluminium or alloys thereof, or zinc-

coated steels, wherein zinc, aluminium or alloys thereof are exposed to a functional fluid comprising the additive mixture as defined in the third aspect.

In one embodiment the present invention relates to a composition, which comprises

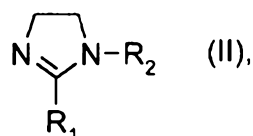
A) An additive mixture that essentially consists of

a) At least one alkenyl succinic half ester of the formula



Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents hydrogen or methyl and n is a numeral from 1 to 100;

b) At least one imidazoline compound of the formula

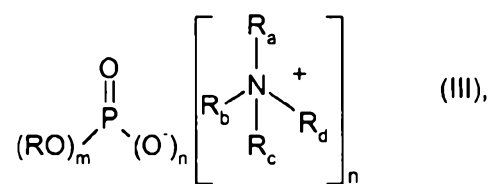


Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; or

Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; and

c) At least one amine phosphate partial ester of the formula

- 2e -



Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

- 3 -

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

B) A functional fluid.

A preferred embodiment of the invention relates to a composition, which comprises

A) An additive mixture that essentially consists of

a) At least one alkenyl succinic half ester (I), wherein

R₁ represents C₁₀-C₁₆alkenyl, R₂ represents methyl and n is a numeral from 1 to 20;

b) At least one imidazoline compound (II),

Wherein one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl; or

Wherein both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl; and

c) At least one amine phosphate partial ester (III),

Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl and amino-C₂-C₁₂alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl and hydroxy-C₂-C₁₂alkyl; and

B) A functional fluid.

A particularly preferred embodiment of the invention relates to composition, which comprises

A) An additive mixture that essentially consists of

a) At least one alkenyl succinic half ester (I), wherein

R_1 represents C_{12} - C_{16} alkenyl, R_2 represents methyl and n is a numeral from 1 to 20;

5 b) At least one imidazoline compound (II),

Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl and C_{12} - C_{18} alkenyl; or

10 Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl and C_{12} - C_{18} alkenyl; and

c) At least one amine phosphate partial ester (III),

Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

15 R represents a substituent selected from the group consisting of C_1 - C_{12} alkyl and hydroxy- C_2 - C_{12} alkyl; and

R_a , R_b , R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C_1 - C_{12} alkyl and hydroxy- C_2 - C_{12} alkyl; and

B) A functional fluid.

20 A highly preferred embodiment of the invention relates to a composition, which comprises

a) At least one alkenyl succinic half ester (I),

Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents methyl and n is a numeral from 1 to 100;

b) At least one imidazoline compound (II),

25 Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; or

30 Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl,

- 5 -

C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl;

c) At least one amine phosphate partial ester (III),

Wherein m represents 1 or 2;

5 n represents 2 if m represents 1; or

represents 1 if m represents 2; and

R represents a substituent selected from the group consisting of

C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl,

phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl,

10 C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and

C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a

substituent selected from the group consisting of C₁-C₁₂alkyl, hy-

droxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl,

15 C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cyclo-

alkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cyclo-

alkyl-C₁-C₄alkyl; and

d) Additional customary additives.

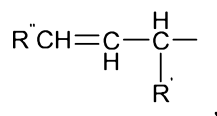
The compositions as described above are suitable as corrosion inhibitor in non-aqueous,

20 partially aqueous or aqueous functional fluids or liquids.

The expressions and terms used above and below are preferably defined as follows in the description of the present invention:

In a compound (I) R₁ defined C₆-C₁₈alkenyl is preferably straight chain or, where possible, branched radical, for example n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, or is preferably a

25 group of the partial formula



Wherein R' and R'' are independently of one another hydrogen or substantially straight chain hydrocarbyl groups, with the proviso that the total number of carbon atoms in R is within the indicated ranges. Preferably R' and R'' are C₃-C₁₅alkyl or C₃-C₁₅alkenyl groups. In a particu-

larly advantageous embodiment, R has from about 16 to about 18 C-atoms, R' is hydrogen or C₁-C₇alkyl or C₂-C₇alkenyl and R" is C₅-C₁₅alkyl or C₅-C₁₅alkenyl.

R₂ is hydrogen or preferably methyl.

In a compound (I) the index n represents a numeral from 1 to about 100. According to preferred embodiments n represents a numeral from 1 to about 20. Compounds (I) are obtainable by reacting the R-substituted succinic acid with ethylene oxide or ethylene glycol of desired chain length, if R₂ represents hydrogen, or with propylene oxide or polypropylene glycol of desired chain length, if R₂ represents methyl.

Compounds (I) are known and at least some of them are commercially available. The preparation of compounds (I) is described in *British Patent Specification No. 795,491*.

Compounds (I) are known oil soluble corrosion inhibitors, which are commercially available as solution in mineral oil, such as the product Ciba® Irgacor® L 12. Other products are Hitec® 536 commercially available from Ethyl Corp. Richmond VA, USA.

In a compound (II) one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; or

Both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl.

R₁ and R₂ defined as C₁-C₁₂alkyl is, for example, C₁-C₆alkyl, e.g. methyl, ethyl, n-propyl or isopropyl or n-butyl, sec-butyl or tert-butyl or straight-chain or branched pentyl or hexyl, and C₇-C₁₂alkyl, e.g. straight-chain or branched heptyl, octyl, isooctyl, nonyl, tert-nonyl, decyl, undecyl or dodecyl.

R₁ and R₂ defined as hydroxy-C₂-C₁₂alkyl, is e.g. 2-hydroxyethyl, dihydroxyethyl, 2- or 3-hydroxypropyl, 2-, 3-dihydroxypropyl, glyceryl or any of the above-mentioned C₄-C₁₂alkyl groups substituted by 1-3 hydroxy groups.

R₁ and R₂ defined as amino-C₂-C₁₂alkyl is e.g. 2-aminoethyl, diaminoethyl or 2- or 3-aminopropyl or any of the above-mentioned C₄-C₁₂alkyl groups substituted by 1-3 amino groups.

R₁ and R₂ defined as C₂-C₂₀alkenyl is a straight chain or, where possible, branched radical, for example vinyl, allyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl or iso-dodecenyl.

- 7 -

R₁ and R₂ defined as phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl radicals are, for example, benzyl, 1- or 2-phenethyl, 4-methyl- or 4-ethylphenyl, cumyl or 4-methylbenzyl.

According to preferred embodiments one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl; or

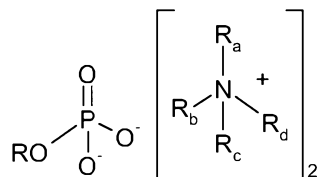
Both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl.

According to another preferred embodiment one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl and C₁₂-C₁₈alkenyl; or

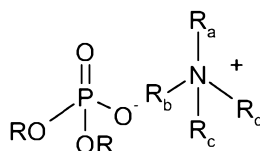
Both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl and C₁₂-C₁₈alkenyl.

Compounds (II) are known compounds and applicable oil soluble corrosion inhibitors, which are commercially available as solution in mineral oil, such as the product Ciba® Amine 0.

In a compound (III) m represents 1 or 2. In the event that m represents 1, n represents 2. Such compounds are represented by the formula



In the event that m represents 2, n represents 1. Such compounds are represented by the formula



In a compound (III) R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl.

The definitions of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl correspond to the definitions given above with regard to compounds (I) and (II).

R as well as R_a, R_b, R_c and R_d defined as C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl are, for example, cyclopentyl, cyclohexyl, cyclopentylmethyl or cyclohexylmethyl, cyclopentyl-1,1-ethyl, cyclohexyl-1,1-ethyl, cyclopentyl-1,2-ethyl, cyclohexyl-1,2-ethyl, cyclopentyl-1,2-propyl or cyclohexyl-1,2-propyl, which can be substituted on the C₄-C₈cycloalkyl groups by C₁-C₄alkyl, e.g. methyl, ethyl, n-propyl or isopropyl.

According to preferred embodiments R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl and amino-C₂-C₁₂alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl and hydroxy-C₂-C₁₂alkyl.

Amine phosphate partial ester as represented by the formula III are known compounds that can be prepared by known methods. Compounds (III) are applicable as oil soluble corrosion inhibitors and commercially available, such as the product Ciba® Irgalube® 349.

Other amine phosphate partial ester as represented by the formula III are commercially available from Rheinchemie Rheinau GmbH, Mannheim Germany, such as the products Additin® RC 3740, RC 3741 or RC 3760 (amine neutralized phosphoric acid ester of aliphatic alcohols).

The term functional liquid includes non-aqueous, partially aqueous and aqueous liquids which are in contact with metals to be protected, in particular aluminium and zinc.

Examples of non-aqueous functional liquids are fuels, e.g. hydrocarbon mixtures comprising mineral oil fractions which are liquid at room temperature and are suitable for use in internal combustion engines, e.g. internal combustion engines with external (petrol engines) or internal ignition (diesel engines), e.g. petrol having different octane contents (regular grade or premium grade petrol) or diesel fuels, and lubricants, hydraulic fluids, metal working fluids,

such as drawing oil, cutting oils, forming oils, drilling oils etc, engine coolants, transformer oils and switchgear oils.

Examples of suitable partially aqueous functional liquids are water-in-oil or oil-in-water metal working fluids, hydraulic fluids based on aqueous polyglycol/ polyglycol ether mixtures or glycol systems, and engine cooling systems based on aqueous glycol.

Examples of aqueous functional liquids are industrial cooling water, filling compositions of a water conditioning plant, steam generation systems, sea water evaporation systems, sugar evaporation systems, irrigation systems, hydrostatic boilers and heating systems or cooling systems having a closed circulation.

10 The composition according to the invention preferably comprise 0.01 to 10.0% by weight, in particular 0.02 to 3.0 % by weight, of the additive mixture, as defined above, based on the weight of the functional liquid.

Non-aqueous functional liquids are preferred, in particular base oils of lubricating viscosity, which can be used for the preparation of greases, metal working fluids, gear fluids and hydraulic fluids.

Suitable greases, metal working fluids, gear fluids and hydraulic fluids are based, for example, on mineral or synthetic oils or mixtures thereof. The lubricants are familiar to a person skilled in the art and are described in the relevant literature, such as, for example, in *Chemistry and Technology of Lubricants*; Mortier, R.M. and Orszulik, S.T. (Editors); 1992 Blackie and Son Ltd. for GB, VCH-Publishers N.Y. for U.S., ISBN 0-216-92921-0, cf. pages 208 et seq. and 269 et seq.; in *Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition* 1969, J. Wiley & Sons, New York, Vol. 13, page 533 et seq. (Hydraulic Fluids); *Performance Testing of Hydraulic Fluids*; R. Tourret and E.P. Wright, Hyden & Son Ltd. GB, on behalf of The Institute of Petroleum London, ISBN 0 85501 317 6; *Ullmann's Encyclopedia of Ind. Chem., Fifth Completely Revised Edition*, Verlag Chemie, DE-Weinheim, VCH-Publishers for U.S., Vol. A 15, page 423 et seq. (Lubricants), Vol. A 13, page 165 et seq. (Hydraulic Fluids).

The lubricants are in particular oils and greases, for example based on mineral oil, synthetic oils, or vegetable and animal oils, fats, tallow and wax or mixtures thereof. Vegetable and animal oils, fats, tallow and wax are, for example, palm kernel oil, palm oil, olive oil, colza oil, rapeseed oil, linseed oil, soy bean oil, cotton wool oil, sunflower oil, coconut oil, maize oil, castor oil, walnut oil and mixtures thereof, fish oils, and chemically modified, e.g. epoxidised or sulphoxidised or alkylated or hydrogenated, forms or forms prepared by genetic engineering, for example soy bean oil prepared by genetic engineering.

Examples of synthetic lubricants include lubricants based on aliphatic or aromatic carboxylic esters, polymeric esters, polyalkylene oxides, phosphoric acid esters, poly- α -olefins or silicones of the diester of a dibasic acid with a monohydric alcohol, e.g. dioctyl sebacate or dinonyl adipate, of a triester of trimethylolpropane with a monobasic acid or with a mixture of
5 such acids, e.g. trimethylolpropane tripelargonate, trimethylolpropane tricaprylate or mixtures thereof, of a tetra ester of pentaerythritol with a monobasic acid or with a mixture of such acids, e.g. pentaerythrityl tetracaprylate, or of a complex ester of monobasic and dibasic acids with polyhydric alcohols, e.g. a complex ester of trimethylolpropane with caprylic and sebacic acid or of a mixture thereof. Particularly suitable in addition to mineral oils are, for example,
10 poly- α -olefins, ester-based lubricants, phosphates, glycols, polyglycols and polyalkylene glycols and mixtures thereof with water.

Said lubricants or mixtures thereof can also be mixed with an organic or inorganic thickener (base fat). Metal working fluids and hydraulic fluids can be prepared on the basis of the same substances as described above for the lubricants. These are frequently also emulsions of
15 such substances in water or other liquids.

Said lubricant compositions, e.g. greases, gear fluids, metal working fluids and hydraulic fluids, may additionally contain further additives which are added in order further to improve their fundamental properties. These include: antioxidants, metal deactivators, rust inhibitors, viscosity index improvers, pour point depressants, dispersants, detergents, tackifiers,
20 thixotropic builders, dewatering agents, antifoam agents, demulsifiers, high pressure additives and antiwear additives. Such additives are added in the amounts customary in each case for the purpose, each in the range from 0.01 to 10.0% by weight. Examples of further additives follow:

1. Phenolic antioxidants

25 1.1. Alkylated monophenols: 2,6-di-tert-butyl-4-methylphenol, 2-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-iso-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, linear nonylphenols or nonylphenols which are branched in
30 the side chain, e.g. 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)-phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)-phenol and mixtures thereof

- 1.2. Alkylthiomethylphenols: 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol
- 5 1.3. Hydroquinones and alkylated hydroquinones: 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butyl-hydroquinone, 2,5-di-tert-amyl-hydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butyl-hydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenylstearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate
- 1.4. Tocopherols: α -, β -, γ - or δ -tocopherols and mixtures thereof (vitamin E)
- 10 1.5. Hydroxylated thiobiphenyl ethers: 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulphide
- 15 1.6. Alkylidene bisphenols: 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)-butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane
- 20 25 30 1.7. O-, N- and S-benzyl compounds: 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-

tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulphide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate

5 1.8. Hydroxybenzylated malonates: dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, dioctadecyl 2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecyl mercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, di-[4-(1,1,3,3-tetramethylbutyl)-phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate

1.9. Hydroxybenzyl aromatics: 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol

10 1.10. Triazine compounds: 2,4-bisooctylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 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, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate

1.11. Acylaminophenols: 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl) carbamate

20 1.12. Esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentylglycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 25 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane

1.13. Esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid (with monohydric or polyhydric alcohols), e.g. the alcohols with methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, 30 neopentylglycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)-oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane

- 1.14. Esters of beta-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with monohydric or polyhydric alcohols, e.g. the alcohols stated under 13.
- 1.15. Ester of 3,5-di-tert-butyl-4-hydroxyphenylacetic acid with monohydric or polyhydric alcohols, e.g. the alcohols stated under 13.
- 5 1.16. Amides of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g. 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
- 1.17. Ascorbic acid (vitamin C)
- 10 1.18. 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-methyl-heptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-(naphth-2-yl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulphonamido)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxy-diphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, 20 N-phenyl-2-naphthylamine, octylated diphenylamine, e.g. p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, di-(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-di-[(2-methyl-phenyl)-amino]ethane, 25 1,2-di-(phenylamino)-propane, (o-tolyl)biguanide, di-[4-(1',3'-dimethyl-butyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, mixture of mono- and dialkylated nonyldiphenylamines, mixture of mono- and dialkylated dodecyldiphenylamines, mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, mixtures 30 of mono- and dialkylated tert-butyl-diphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, mixture of mono- and dialkylated tert-butyl tert-octylphenothiazines, mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis-(2,2,6,6-tetrame-

thylpiperidin-4-yl)-hexamethylenediamine, bis-(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol

2. Further antioxidants: aliphatic or aromatic phosphites, esters of thiodipropionic acid or thiodiacetic acid or salts of dithiocarbamic or dithiophosphoric acid, 2,2,12,12-tetramethyl-5,9-dihydroxy-3,7,11-trithiatridecane and 2,2,15,15-tetramethyl-5,12-dihydroxy-3,7,10,14-tetrathiahexadecane

3. Further metal deactivators:

3.1. Benzotriazoles and derivatives thereof: 2-mercaptobenzotriazole, 2,5-dimercaptobenzotriazole, 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof, 4,5,6,7-tetrahydrobenzotriazole, 5,5'-methylenebisbenzotriazole; Mannich bases of benzotriazole or tolutriazole, such as 1-[di(2-ethylhexylaminomethyl)]tolutriazole and 1-[di(2-ethylhexylaminomethyl)]benzotriazole; alkoxyalkylbenzotriazoles, such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)benzotriazole and 1-(1-cyclohexyloxybutyl)tolutriazole

3.2. 1,2,4-Triazoles and derivatives thereof: 3-alkyl (or aryl)-1,2,4-triazoles, Mannich bases of 1,2,4-triazoles, such as 1-[di(2-ethylhexyl)aminomethyl]-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles, such as 1-(1-butoxyethyl)-1,2,4-triazole; acylated 3-amino-1,2,4-triazoles

3.3. Imidazole derivatives: 4,4'-methylenebis(2-undecyl-5-methylimidazole), bis[(N-methyl)imidazol-2-yl]carbinol octyl ether

3.4. Sulphur-containing heterocyclic compounds: 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2,5-dimercaptobenzothiadiazole and derivatives thereof; 3,5-bis[di-(2-ethylhexyl)aminomethyl]-1,3,4-thiadiazolin-2-one

3.5. Amino compounds: salicylidenepropylenediamine, salicylamino guanidine and salts thereof

4. Corrosion inhibitors:

- 4.1. Organic acids, their esters, metal salts, amine salts and anhydrides: alkyl- and alkyenylsuccinic acids and partial esters thereof with alcohols, diols or hydroxycarboxylic acids, partial amides of alkyl- and alkenylsuccinic acids, 4-nonylphenoxyacetic acid, alkoxy- and alkoxyethoxycarboxylic acids, such as dodecyloxyacetic acid, dodecyloxy(ethoxy)acetic acid and amine salts thereof, and furthermore N-oleoylsarcosine, sorbitan monooleate, lead naphthenate, alkenylsuccinic anhydrides, e.g. dodecenylsuccinic anhydride, 2-(2-carboxyethyl)-1-dodecyl-3-methylglycerol and salts thereof, in particular sodium salts and triethanolamine salts
- 5
- 4.2. Nitrogen-containing compounds:
- 4.2.1 Tertiary aliphatic and cycloaliphatic amines and amine salts of organic and inorganic acids, e.g. oil-soluble alkylammonium carboxylates, and furthermore 1-[N,N-bis-(2-hydroxyethyl)amino]-3-(4-nonylphenoxy)propan-2-ol
- 10
- 4.2.2 Heterocyclic compounds, e.g. substituted imidazolines and oxazolines, e.g. 2-heptadecenyl-1-(2-hydroxyethyl)-imidazoline
- 15
5. Sulphur-containing compounds: barium dinonylnaphthalenesulphonates, calcium petroleum sulphonates, alkylthio-substituted aliphatic carboxylic acids, esters of aliphatic 2-sulphocarboxylic acids and salts thereof
6. Viscosity index improvers: polyacrylates, polymethacrylates, vinylpyrrolidone/methacrylate copolymers, polyvinylpyrrolidones, polybutenes, olefin copolymers, styrene/acrylate copolymers, polyethers
- 20
7. Pour point depressants: poly(meth)acrylates, ethylene-vinyl acetate copolymers, alkyl polystyrenes, fumarate copolymers, alkylated naphthalene derivatives
8. Dispersants/Surfactants: polybutenylsuccinamides or polybutenylsuccinimides, polybutenylphosphonic acid derivatives, basic magnesium, calcium and barium sulphonates and phenolates
- 25
9. High pressure and antiwear additives: sulphur- and halogen-containing compounds, e.g. chlorinated paraffins, sulphonated olefins or vegetable oils (soy bean oil, rapeseed oil), alkyl or aryl di- or trisulphides, benzotriazoles or derivatives thereof, such as

bis (2-ethylhexyl)aminomethyl tolutriazoles, dithiocarbamates, such as methylenebis-dibutyl dithiocarbamate, derivatives of 2-mercaptobenzothiazole, such as 1-[N,N-bis(2-ethylhexyl)aminomethyl]-2-mercapto-1H-1,3-benzothiazole, derivatives of 2,5-dimercapto-1,3,4-thiadiazole, such as 2,5-bis(tert.nonyldithio)-1,3,4-thiadiazole

- 5 10. Substances for reducing the coefficient of friction: lard oil, oleic acid, tallow, rapeseed oil, sulphurised fats, amines. Further examples are stated in *EP-A-0 565 487*
11. Special additives for use in water/oil metal processing and hydraulic fluids:
- 11.1 Emulsifiers: petroleum sulphonates, amines, such as polyoxyethylated fatty amines, non-ionic surface-active substances
- 10 11.2 Buffers: alkanolamines
- 11.3 Biocides: triazines, thiazolinones, trisnitromethane, morpholine, sodium pyridinethiol
- 11.4 Processing speed improvers: calcium sulphonates and barium sulphonates
- 11.5 Tackifiers: acrylamide copolymer, polyisobutene resins.
- 11.6 Thixotropic builders: microcrystalline waxes, oxidized waxes and oxidized esters
- 15 11.7 Dewatering agents: polyglycol ethers, butyldiglycols.

Said components can be mixed with the lubricants in a manner known per se. It is also possible to prepare a concentrate or a so-called additive package, which can be diluted to the concentrations of use for the corresponding lubricant according to the application purposes as intended.

- 20 The ratio of component a) to component b) to component b) present in the additive mixture A) may vary within the ranges of approximately from 10 : 10 : 80 and 80 : 10 : 10 to 10 : 80 : 10% by weight.

Although the total content of the additive mixture A) in the composition is not critical, the preferred total content of the additive mixture A) in the composition is in the range between

- 25 10.0 and 0.01, preferably 10.0 and 0.1 or 3.0 and 0.1% by weight, based on the total weight of the composition.

A further embodiment of the invention relates to an additive mixture that essentially consists of

- a) At least one alkenyl succinic half ester (I),

Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents hydrogen or methyl and n is a numeral from 0 to 100;

- b) At least one imidazoline compound (II),

Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; or

Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; and

- c) At least one amine phosphate partial ester (III),

Wherein m represents 1 or 2, n represents 2, if m represents 1; or represents 1, if m represents 2;

R represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl, C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl, C_4 - C_8 cycloalkyl, C_4 - C_8 cycloalkyl- C_1 - C_4 alkyl, C_1 - C_4 alkyl- C_4 - C_8 cycloalkyl and C_1 - C_4 alkyl- C_4 - C_8 cycloalkyl- C_1 - C_4 alkyl; and

R_a , R_b , R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl, C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl, C_4 - C_8 cycloalkyl, C_4 - C_8 cycloalkyl- C_1 - C_4 alkyl, C_1 - C_4 alkyl- C_4 - C_8 cycloalkyl and C_1 - C_4 alkyl- C_4 - C_8 cycloalkyl- C_1 - C_4 alkyl.

The definitions of components a), b) and c) present in the additive mixture corresponds to the definitions of components a), b) and c) present in the compositions as defined above.

According to a preferred embodiment, the invention relates to the additive mixture, as defined above, used as additives in a metal working fluid.

The invention also relates to the process for protection against corrosion or oxidative degradation of metals, wherein the metal is exposed to a functional fluid comprising the additive mixture as defined above.

5 According to a preferred embodiment, the invention relates to the process for protection against corrosion or oxidative degradation of zinc, aluminum or alloys thereof, wherein zinc, aluminum or alloys thereof are exposed to a functional fluid comprising the additive mixture as defined above.

10 A further embodiment of the invention relates to a process for protection against corrosion or oxidative degradation of zinc, aluminum or alloys thereof, wherein zinc, aluminum or alloys thereof are exposed to a functional fluid comprising at least one alkenyl succinic half ester of the formula I as defined above, wherein R_1 represents C_6-C_{18} alkenyl, R_2 represents hydrogen or methyl and n is a numeral from 1 to 100.

The following **Examples** illustrate the invention:

Application Examples

15 A typical test procedure to test the corrosion inhibition is the climate chamber test according to DIN EN ISO 6270-2. This test is slightly modified by using several different metal samples and more severe conditions. Each sample is treated in the following test cycle:
Exposure for 8 hours in a closed climate chamber at $50 \pm 3^\circ\text{C}$, humidity ca. 100%, followed
by 16 hours in an open climate chamber, cooling at $21 \pm 3^\circ\text{C}$ and humidity approaching am-
20 bient. The test cycles are repeated until 100% corrosion is detected visually. In the event that the test sample is not corroded, the test procedure is stopped after 24 cycles.

Corrosion Inhibitor	Test Specimen	Passed test cycles	Additive treat rate
Reference oil	Zinc	19	app. 15-20%
Mixture A	Zinc	> 24	3%
Mixture B	Zinc	> 24	5%
Mixture C	Zinc	> 24	3%
Mixture D	Zinc	20	3%
Reference oil	Aluminum	0	app. 15-20%
Mixture A	Aluminum	> 15	3%
Mixture B	Aluminum	> 15	5%
Mixture C	Aluminum	> 15	3%
Mixture D	Aluminum	> 15	3%

Reference oil: As mentioned in "VDA-Prüfblatt" from May 2003; VDA 230- 201:

Mixture A = 3% Irgacor® L12 in a paraffinic base oil

Mixture B = 5% Irgalube® 349 in a paraffinic base oil

Mixture C = 0.9% IRGACOR L12; 1.5% Amine O; 0.6% IRGALUBE 349 in an naphthenic base oil

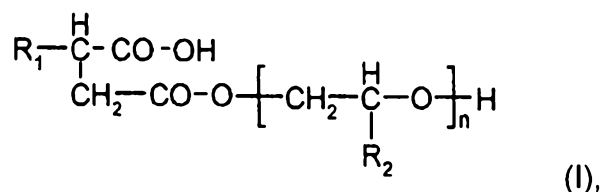
Mixture D = 0.6% IRGACOR L12; 0.9% Amine O; 1.5% IRGALUBE 349 in a paraffinic base oil.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

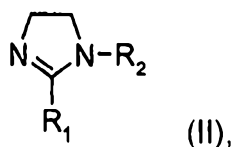
The claims defining the invention are as follows:

1. A composition, which comprises
 - A) An additive mixture that consists of
 - a) At least one alkenyl succinic half ester of the formula



Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents hydrogen or methyl and n is a numeral from 1 to 100;

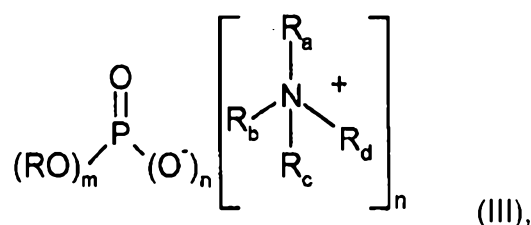
- b) At least one imidazoline compound of the formula



Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; or

Wherein both of R_1 and R_2 represent substituents selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl; and

- c) At least one amine phosphate partial ester of the formula



Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

R represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino C_2 - C_{12} alkyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl, C_1 - C_4 alkylphenyl- C_1 - C_4 alkyl, C_4 - C_8 cycloalkyl, C_4 -

C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

B) A functional fluid.

2. A composition according to claim 1, which comprises

A) An additive mixture that consists of

a) At least one alkenyl succinic half ester (I), wherein

R₁ represents C₁₀-C₁₆alkenyl, R₂ represents methyl and n is a numeral from 1 to 20;

b) At least one imidazoline compound (II),

Wherein one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl; or

Wherein both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl and C₁₂-C₁₈alkenyl; and

c) At least one amine phosphate partial ester (III),

Wherein m represents 1 or 2;

n represents 2, if m represents 1, or represents 1, if m represents 2;

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl and amino-C₂-C₁₂alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl and hydroxy-C₂-C₁₂alkyl; and

B) A functional fluid

3. A composition according to claim 1, which comprises
- A) An additive mixture that consists of
- a) At least one alkenyl succinic half ester (I) as defined in claim 1, wherein R_1 represents C_{12} - C_{16} alkenyl, R_2 represents methyl and n is a numeral from 1 to 20;
- b) At least one imidazoline compound (II) as defined in claim 1, Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl and C_{12} - C_{16} alkenyl; or
Wherein both of R_1 and R_2 represents substituents selected from the group consisting of C_1 - C_{12} alkyl and C_{12} - C_{18} alkenyl; and
- c) At least one amine phosphate partial ester (III) as defined in claim 1,
Wherein m represents 1 or 2;
 n represents 2 if m represents 1; or
represents 1 if m represents 2; and
 R represents a substituent selected from the group consisting of C_1 - C_{12} alkyl and hydroxy- C_2 - C_{12} alkyl; and
 R_a , R_b , R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C_1 - C_{12} alkyl and hydroxy- C_2 - C_{12} alkyl; and
- B) A functional fluid.
4. A composition, which comprises
- a) At least one alkenyl succinic half ester (I), as defined in claim 1,
Wherein R_1 represents C_6 - C_{18} alkenyl, R_2 represents methyl and n is a numeral from 1 to 100;
- b) At least one imidazoline compound (II), as defined in claim 1,
Wherein one of R_1 and R_2 represents hydrogen and the other one represents a substituent selected from the group consisting of C_1 - C_{12} alkyl, hydroxy- C_2 - C_{12} alkyl, amino- C_2 - C_{12} alkyl, C_2 - C_{20} alkenyl, phenyl, phenyl- C_1 - C_4 alkyl, C_1 - C_4 alkylphenyl and C_1 - C_4 alkylphenyl-

C₁-C₄alkyl; or

Wherein both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl;

c) At least one amine phosphate partial ester (III), as defined in claim 1,

Wherein m represents 1 or 2;

n represents 2 if m represents 1; or

represents 1 if m represents 2; and

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl,

hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

d) Additional customary additives.

5. An additive mixture that consists of

- a) At least one alkenyl succinic half ester (I), as defined in claim 1,
Wherein R₁ represents C₆-C₁₈alkenyl, R₂ represents hydrogen or methyl and n is a numeral of 0 to 100;
- b) At least one imidazoline compound (II), as defined in claim 1,
Wherein one of R₁ and R₂ represents hydrogen and the other one represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl,

phenyl, phenyl-C₁-C₄ alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; or

Wherein both of R₁ and R₂ represent substituents selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl and C₁-C₄alkylphenyl-C₁-C₄alkyl; and

c) At least one amine phosphate partial ester (III), as defined in claim 1,

Wherein m represents 1 or 2;

n represents 2 if m represents 1; or

represents 1 if m represents 2; and

R represents a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₂alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl; and

R_a, R_b, R_c and R_d independently of one another represent hydrogen or a substituent selected from the group consisting of C₁-C₁₂alkyl, hydroxy-C₂-C₁₂alkyl, amino-C₂-C₁₂alkyl, C₂-C₂₀alkenyl, phenyl, phenyl-C₁-C₄alkyl, C₁-C₄alkylphenyl, C₁-C₄alkylphenyl-C₁-C₄alkyl, C₄-C₈cycloalkyl, C₄-C₈cycloalkyl-C₁-C₄alkyl, C₁-C₄alkyl-C₄-C₈cycloalkyl and C₁-C₄alkyl-C₄-C₈cycloalkyl-C₁-C₄alkyl.

6. The additive mixture according to claim 5, when used as a metal working fluid.
7. A composition according to claim 1, wherein the functional fluid B) is a non-aqueous functional liquid selected from the group consisting of: lubricants, hydraulic fluids, metal working fluids, engine coolants, transformer oils and switch gear oils.
8. A process for protection against corrosion or oxidative degradation of

metals, wherein the metal is exposed to a functional fluid comprising the additive mixture according to claim 5.

9. A process for protection against corrosion of oxidative degradation of zinc, aluminium or alloys thereof, or zinc-coated steels, wherein zinc, aluminium or alloys thereof are exposed to a functional fluid comprising the additive mixture according to claim 5.
10. A composition as defined in any one of claims 1 to 4, substantially as hereinbefore described with reference to the Examples.