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New metal deactivators

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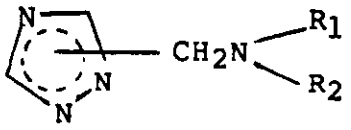
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C2C
C5F

NEW METAL DEACTIVATORS

The present invention relates to new metal deactivators, and in particular to new functional fluid compositions containing triazole derivatives as metal deactivators.

The present invention provides a composition comprising a functional fluid and, as metal deactivator, a metal deactivating proportion, preferably 0.001% to 5% by weight, on total composition, of a ring N-substituted compounds having the formula I:



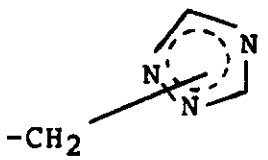
I

in which R_1 and R_2 are the same or different and each is C_1-C_{20} alkyl, C_3-C_{20} alkenyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, C_6-C_{10} aryl, or R_1 and R_2, together with the nitrogen atom to which they are each attached may form a 5-, 6- or 7-membered heterocyclic residue, or R_1 and R_2 is each a residue of formula:

$$R_3X[(\text{alkylene})O]_n(\text{alkylene})- \qquad \text{II}$$

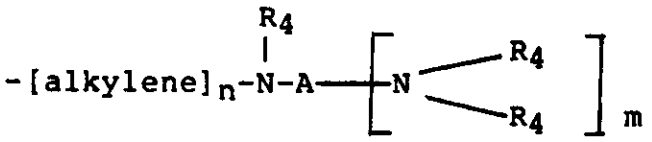
in which X is O, S or NH, R_3 is hydrogen or C_1-C_{20} alkyl, "alkylene" is a C_1-C_{12} preferably C_1-C_6 especially C_2-C_3 alkylene residue and n is O or an integer from 1 to 6, preferably O, 1, 2, 3 or 4;

or R_1 has its previous significance and R_2 is a residue of formula III:



III

or R_2 is a residue of formula III as defined above R_1 is a residue of formula IV:



IV

wherein m is 0 or 1 and, when m is 1, A is alkylene or C_6-C_{10} arylene and when m is 0, A is a residue of formula III as hereinbefore defined, and alkylene and n have their previous significance and R_4 is a residue of formula III, as hereinbefore defined.

When the group R_1 and/or R_2 and/or R_3 is a C_1-C_{20} alkyl group it may be straight- or branched chain and may be e.g. methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl or n-eicosyl.

When the group R_1 and/or R_2 is a C_3-C_{20} alkenyl group, it may be straight- or branched chain and may be e.g. prop-2-enyl, but-2-enyl, 2-methyl-prop-2-enyl, pent-2-enyl, hexa-2,4-dienyl, dec-10-enyl or eicos-2-enyl.

C_5-C_{12} cycloalkyl groups R_1 and/or R_2 may be cyclopentyl, cyclohexyl, cyclooctyl, cyclodecyl, adamantyl or cyclododecyl.

C_7-C_{13} aralkyl groups R_1 and/or R_2 are e.g. benzyl, 2-phenylethyl, benzhydryl or naphthylmethyl.

C_6-C_{10} aryl groups R_1 and/or R_2 are e.g. phenyl or naphthyl.

When R_1 and R_2 together with the nitrogen atom to which they are attached form a heterocyclic residue it may be a morpholine, pyrrolidine, piperidine or perhydroazepine residue.

C_1-C_{12} Alkylene moieties in the residue of formula (II) or IV include methylene, ethylene, 1:2- or 1:3-propylene, 1:4-butylene, 1:6-hexylene, 1:8-octylene, 1:10-decylene and 1:12-dodecylene groups.

C_6-C_{10} Arylene moieties in the residue IV include phenylene and naphthylene groups.

Specific compounds of formula I include:

1-(or 4)-(Dimethylaminomethyl) triazole

1-(or 4)-(Diethylaminomethyl) triazole

1-(or 4)-(Di-isopropylaminomethyl) triazole

1-(or 4)-(Di-n-butylaminomethyl) triazole

1-(or 4)-(Di-n-hexylaminomethyl) triazole

1-(or 4)-(Di-n-octylaminomethyl) triazole

1-(or 4)-(Di-n-decylaminomethyl) triazole

1-(or 4)-(Di-n-dodecylaminomethyl) triazole

1-(or 4)-(Di-n-octadecylaminomethyl) triazole

1-(or 4)-(Di-n-eicosylaminomethyl) triazole

1-(or 4)-[Di-(prop-2'-enyl)aminomethyl] triazole

1-(or 4)-[Di-(but-2'-enyl)aminomethyl] triazole

1-(or 4)-[Di-(eicos-2'-enyl)aminomethyl] triazole

1-(or 4)-(Di-cyclohexylaminomethyl) triazole

1-(or 4)-(Di-benzylaminomethyl) triazole

1-(or 4)-(Di-phenylaminomethyl) triazole

1-(or 4)-(4'-morpholinomethyl) triazole

1-(or 4)-(1'-pyrrolidinomethyl) triazole

1-(or 4)-(1'-piperidinomethyl) triazole

1-(or 4)-(1'-perhydroazepinomethyl) triazole

1-(or 4)-[(2',2"-dihydroxyethyl)aminomethyl] triazole

1-(or 4)-(Dibutoxypropyl-aminomethyl) triazole

1-(or 4)-(Dibutylthiopropyl-aminomethyl) triazole

1-(or 4)-(Di-butylaminopropyl-aminomethyl) triazole

N,N-Bis-(1-or 4-triazolylmethyl) laurylamine

N,N-Bis-(1-or 4-triazolylmethyl) oleylmine

N,N-Bis-(1-or 4-triazolylmethyl) ethanolamine

N,N,N',N'-Tetra(1-or 4-triazolylmethyl)ethylene diamine.

Examples of functional fluids useful as substrates for the compositions of the invention are lubricants having a mineral oil, poly-alpha olefin or synthetic carboxylic ester base; hydraulic fluids based on mineral oils, phosphate esters, aqueous polyglycol/polyglycol ether mixtures, glycol systems; oil-in-water or other water-in-oil emulsions; metal-working fluids having, as their base, mineral oil or aqueous systems; aqueous or aqueous glycol or ethylene- or propylene glycol/methanol based engine coolant compositions; and transformer and switch oils.

Examples of synthetic lubricants include lubricants based on a diester of a dibasic acid and a monohydric alcohol, for instance dioctyl sebacate or dinonyl adipate; on a triester of trimethylol propane and a monobasic acid or mixture of such acids, for instance trimethylol propane tripelargonate, trimethylol propane tricaprylate or mixtures thereof; on a tetraester of pentaerythritol and a monobasic acid or mixture of such acids, for instance pentaerythritol tetracaprylate; or on complex esters derived from monobasic acids, dibasic acids and polyhydric alcohols, for instance a complex ester derived from trimethylol propane, caprylic acid and sebacic acid; or of mixtures thereof.

Other synthetic lubricants are those known to the art-skilled and described e.g. in "Schmiermittel-Taschenbuch" (Huethig Verlag, Heidelberg 1974). Especially suitable, apart from the preferred mineral oils are e.g. phosphates, glycols, polyglcols, polyalkylene glycols and poly-alpha olefins.

Of particular interest are aqueous-based functional fluids e.g. anti-freezes, and hydraulic- and metal-working fluids. For use in this type of aqueous-based fluid, those compounds of

formula I are preferred in which R_1 and/or R_2 is a hydrophilic residue of formula II.

On the other hand, for use in oil-based functional fluids, compounds of formula I are preferred in which R_1 and/or R_2 is an oleophilic group.

In order to improve various applicational properties, the compositions of the invention may also contain other additives such as, for oil-based systems, one or more of antioxidants, other metal deactivators, rust inhibitors, viscosity-index improvers, pour-point depressants, dispersants/surfactants or anti-wear additives; and for aqueous-based systems, one or more of antioxidants, corrosion- and rust inhibitors, further metal deactivators, extreme pressure- or anti-wear additives, complexing agents, precipitation inhibitors, biocides, buffering agents and anti-foams.

For oil-based systems, examples of other additives are:

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-n-butylphenol

2,6-Di-tert.-butyl-4-i-butylphenol

2,6-Di-cyclopentyl-4-methylphenol

2-(α-Methylcyclohexyl)-4,6-dimethylphenol

2,6-Di-octadecyl-4-methylphenol

2,4,6-Tri-cyclohexylphenol

2,6-Di-tert.-butyl-4-methoxymethylphenol

2. 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

3. Hydroxylated Thiodiphenylethers

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-isobutyphenol)

2,2'-Methylene-bis-[6-(methylbenzyl)-4-nonylphenol]

2,2'Methylene-bis-[6-(-dimethylbenzyl)-4-nonylphenol]

4,4'-Methylene-bis-(6-tert.-butyl-2-methylphenol)

1,1-Bis-(5-tert.-butyl-4-hydroxy-2-methylphenol)-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-dodecyl-mercaptobutane

Ethyleneglycol-bis-[3,3-bis-(3'tert.-butyl-4'-hydroxyphenyl)-butyrate]

Di-(3-tert.-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene

Di-[3'-tert.-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert.-butyl-4-methyl-phenyl]-terephthalate

5. Benzyl Compounds

1,3,5-Tri-(3,5-di-tert.-butyl-4-hydroxybenzyl)-2,4,6-trimethyl-benzene

Di-(3,5-di-tert.-butyl-4-hydroxybenzyl)-sulfide

Bis-(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol-terephthalate

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

3,5-Di-tert.-butyl-4-hydroxybenzyl-phosphonic acid-dioctadecyl-ester

3,5-Di-tert.-butyl-4-hydroxybenzyl-phosphonic acid-monoethylester Calcium-salt

6. Acylaminophenols

4-Hydroxy-lauric acid anilide

4-Hydroxy-stearic acid anilide

2,4-Bis-octylmercapto-6-(3,5-di-tert.-butyl-4-hydroxyanilino)-s-triazine

N-(3,5-di-tert.-butyl-4-hydroxyphenyl)-carbamic acid octyl ester

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

with mono- or polyhydric alcohols e.g. with

Methanol	Diethyleneglycol
Octadecanol	Triethyleneglycol
1,6-Hexanediol	Pentaerythritol
Neopentylglycol	Tris-hydroxyethyl-isocyanurate
Thiodiethyleneglycol	Di-hydroxyethyl-oxalic acid diamide

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

with mono- or polyhydric alcohols e.g. with

Methanol	Diethyleneglycol
Octadecanol	Triethyleneglycol
1,6-Hexanediol	Pentaerythritol
Neopentylglycol	Tris-hydroxyethyl-osocyanurate
Thiodiethylenglycol	Di-hydroxyethyl-oxalic acid diamide

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

N,N'-Di-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-hexamethylene-diamine

N,N'-Di-(3,5-di-tert.-butyl-4-hydroxyphenylpropionyl)-trimethylene-diamine

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

Examples of amine antioxidants:

N,N'-Di-isopropyl-p-phenylenediamine

N,N'-Di-sec.-butyl-p-phenylenediamine

N,N'-Bis(1,4-dimethyl-pentyl)-p-phenylenediamine

N,N'-Bis(1-ethyl-3-methyl-pentyl)-p-phenylenediamine

N,N'-Bis(1-methyl-heptyl)-p-phenylenediamine

N,N'-Dicyclohexyl-p-phenylenediamine

N,N'-Diphenyl-p-phenylenediamine

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

N-Isopropyl-N'-phenyl-p-phenylenediamine

N-(1,3-dimethyl-butyl)-N'-phenyl-p-phenylenediamine

N-(1-Methyl-heptyl)-N'-phenyl-p-phenylenediamine

N-Cyclohexyl-N'-phenyl-p-phenylenediamine

4-(p-Toluol-sulfonamido)-diphenylamine

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

Diphenylamine

4-Isopropoxy-diphenylamine

N-Phenyl-1-naphthylamine

N-Phenyl-2-naphthylamine

octylated Diphenylamine

octylated N-phenyl-α(or β) naphthylamine

4-n-Butylaminophenol

4-Butyrylamino-phenol

4-Nonanoylamino-phenol

4-Dodecanoylamino-phenol

4-Octadecanoylamino-phenol

Di-(4-methoxy-phenyl)-amine

2,6-Di-tert.-butyl-4-dimethylamino-methyl-phenol

2,4'-diamino-diphenylmethane

4,4'-Diamino-diphenylmethane

N,N',N,N'-Tetramethyl-4,4'-diamino-diphenylmethane

1,2-Di-(phenylamino)-ethane

1,2-Di-[(2-methyl-phenyl)-amino]-ethane

1,3-Di-(phenylamino)-propane

(o-tolyl)-biguanide

Di-[4-(1',3'-dimethyl-butyl)-phenyl]amine

Examples of metal passivators are:

for copper e.g.

Benzotriazole, tolutriazole and derivatives thereof, Tetrahydrobenzotriazole,2-Mercaptobenzthiazole, 2,5-Dimercaptothiadiazole, Salicylidene-propylenediamine, Salts of Salicylaminoguanidine.

Examples of rust inhibitors are:

a) Organic acids, their esters, metal salts and anhydrides e.g. N-Oleoyl-sarcosine, Sorbitan-mono-oleate, lead-naphthenate, dodecenyl-succinic acid (and its partial esters and amides), 4-Nonyl-phenoxy-acetic acid.

b) nitrogen-containing compounds e.g.

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

II. Heterocyclic compounds e.g. Substituted Imidazolines and Oxazolines

c) Phosphorus-containing compounds e.g. Amine salts of phosphonic acid partial esters, Zinc dialkyldithio phosphates

d) Sulfur-containing compounds e.g. Barium-dinonylnapthalene-n-sulfonates, calcium petroleum sulfonates

Examples of viscosity-index improvers are e.g.
Polymethacrylates, Vinylpyrrolidone/Methacrylate-Copolymers, Polybutenes, Olefin-Copolymers, Styrene/Acrylate-Copolymers.

Examples of pour-point depressants are e.g.
Polymethacrylates, or alkylated Naphthalene derivatives

Examples of dispersants/surfactants are e.g.
Polybutenylsuccinic acid-amides, Polybutenylphosphonic acid derivatives, basic Magnesium-, Calcium-, and Bariumsulfonates and -phenolates.

Examples of anti-wear additives are e.g.
Sulfur- and/or Phosphorus- and/or Halogen-containing compounds e.g. sulfurised vegetable oils, zinc dialkyldithiophosphates, Tritolyl-phosphate, chlorinated Paraffins, Alkyl- and Aryldisulfides.

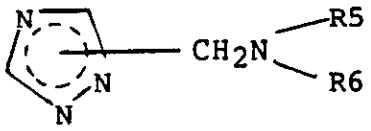
For aqueous-based systems, examples of antioxidants etc are listed hereinbefore in relation to oil-based systems and which are water-soluble.

Examples of buffering agents are borax and triethanolamine; examples of biocides are 2,4,5-trichlorophenol; and the sodium salts of 2,2'-dihydroxy-5,5'-dichlorodiphenylmethane and

orthophenylphenol, respectively; and examples of antifoams are silicones.

The compounds of formula I combine excellent metal deactivation properties with good solubility in both oil- and water-based functional fluids, respectively. Moreover, they do not form insoluble salts when used together with antiwear additives containing zinc, e.g. zinc dialkyldithiophosphates.

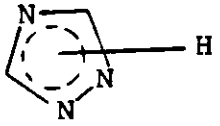
Certain ring N-substituted compounds of formula I are new, viz. those having the formula V:



V

in which R_5 and R_6 is each a residue of formula II, as hereinbefore defined.

The present invention also provides a process for producing compounds of formula V comprising reacting a compound having the formula:



VI

with formaldehyde and with an amine having the formula:

$$HNR_5R_6 \qquad \text{VII}$$

wherein R_5 and R_6 have their previous significance.

The formaldehyde reactant is conveniently used as formalin or paraformaldehyde.

The relative proportions of the reactants of formula VI and VII and of formaldehyde used will vary depending on whether the amine of formula VII is a primary or secondary amine or a di-, tri- or tetra-amine. When the amine of formula VII is a primary

amine, the molar ratios used of compound of formula VI: formaldehyde: amine VII are preferably substantially 2:2:1 or 1:1:1; when the amine VII is a secondary amine, the molar ratios used are preferably substantially 1:1:1; and when the amine VII is a diamine, the molar ratios used are preferably 4:4:1.

The process of the present invention is conveniently effected by heating all the reactants together at an elevated temperature, preferably at a temperature within the range of from 50 to 120°C, optionally in the presence of an inert solvent such as water, a C_1-C_4 alkanol, a petroleum solvent e.g. hexane, isooctane or cyclohexane or an aromatic solvent such as benzene, toluene or a xylene.

Alternatively, compound VI may be reacted first with formaldehyde to give the N-methylol compound, which can then be reacted with the amine of formula VII.

As a further alternative, the compound of formula VI may be reacted with the corresponding amine methylol compound.

The compounds of formula I have, in addition to their metal deactivation properties, valuable properties as as foam inhibitors in printing inks for use in the production of textured foamed resin materials (as described in US Patent Specification 4407882).

The following Examples 4 to 6 and 8 further illustrate the present invention. All parts and percentages given therein are by weight. The other Examples describe the production of compounds of formula I for use in compositions according to the present invention.

Example 1

3.5 parts of triazole and 12.05 parts of di-2-ethylhexylamine are mixed with 100 parts of methanol, and 4.05 parts of 36% aqueous formalin are added. The mixture is heated, under reflux, for 3 hours. The solvent is then removed under water pump vacuum. In this way, 1-di-2-ethylhexylaminomethyl triazole is obtained in 100% theory yield, having a proton NMR spectrum consistent with the given structure, a boiling point of 189°C at 0.07 m bar and the following elemental analysis:

$C_{19}H_{38}N_4$ Theory: C 70.81; H 11.80; N 17.39%

Found: C 70.83; H 11.95; N 17.73%

Example 2

7 parts of triazole, 12.9 parts of di-n-butylamine and 8.1 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 20.4 parts (97% yield) 1-N-di-n-butylaminomethyltriazole. Proton nmr spectral analysis of the product is consistent with the given structure.

Boiling point 105°/0.075 m bar

$C_{11}H_{22}N_4$ Theory: C 62.86; H 10.48; N 26.67%

Found: C 62.62; H 10.75; N 26.46%

Example 3

13.8 parts of triazole, 26.8 parts of oleylamine and 16.2 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 41.7 parts N,N-bis(1-triazolylmethyl)oleylamine, as a viscous oil.

Proton nmr spectral analysis of the product is consistent with the given structure.

$C_{24}H_{43}N_7$ Theory: C 67.13; H 10.02; N 22.84%

Found: C 67.06; H 10.25; N 22.85%

Example 4

10.5 parts of diethanolamine are added to a clear solution of 6.9 parts of triazole and 8.1 parts 36% aqueous formaldehyde in 100 parts water. The mixture is heated under reflux for 8 hours. The solvent is then removed under vacuum. In this way 1-[2,2'-dihydroxyethyl)aminomethyl] triazole is obtained in 95% yield.

Proton NMR spectral analysis is consistent with the given structure.

Boiling point 115°/0.08 m bar

$C_7H_{14}N_4O_2$ Theory: C 45.16; H 7.53; N 30.11%

Found: C 44.95; H 7.42; N 29.97%

Example 5

A 0.05% solution of the product of Example 1 is prepared in a turbine quality mineral oil containing 50 ppm of added, dissolved sulphur.

A copper strip (60 x 10 x 1 mm) is polished with 100 grade silicon carbide grit which has been picked up on cotton wool wetted with petroleum ether. The polished strip is then immediately totally immersed in the prepared solution, which is maintained at 100°C for 2 hours. After this time, the strip is removed, washed with petroleum ether, dried and its colour is compared with those of the ASTM D130 Copper Strip Corrosion Standard Chart. On this rating, 1 represents zero to slight tarnish; 2 represents moderate tarnish; 3 represents dark tarnish; and 4 represents corrosion; and the designations A, B and D indicate shadings within the numerical gradings.

The results are set out in the following Table I.

Table 1

Example	Metal Appearance/Rating	Solution Appearance
Control	Magenta - Rating 3B	colourless
5	No change - Rating 1A	colourless

Example 6

A 0.05% solution of the product of Example 4 is prepared in water containing 0.132 g/l $MgSO_4.7H_2O$ and 0.68 g/l $CaCl_2.6H_2O$ (water as used in DIN 51360 test), and the pH of the solution is adjusted to 7-8 with sodium hydroxide.

A piece of copper foil (20 x 50 x 0.1 mm) is cleaned by rubbing it with cotton wool soaked with water and powdered pumice, dried and weighed. It is then fully immersed in 50 ml. of the solution so prepared contained in a 60 ml. bottle fitted with a screw cap. The bottle is then placed for 24 hours in an oven maintained at 70°C. At the end of this time, the strip is removed, washed and dried and its colour is recorded (using the ASTM D130 colour ranking). It is then immersed for 15 seconds in 5N hydrochloric acid at 120°C, washed, dried and reweighed.

The results are summarised in Table II:

Table II

Example	Weight loss (mg)	Metal Appearance and rating	Solution Appearance
control	4.6	purple-black rating 4D	colourless
6	0.4	no change rating 1A	colourless

Example 7

6.9 Parts of triazole, 18.1 parts of dicyclohexylamine and 8.1 parts of 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 24 parts (92% yield) 1-N,N-dicyclohexylaminomethyltriazole. Proton nmr spectral analysis of the product is consistent with the given structure. Melting point 62-64°C

Example 8

A 0.05% solution of the product of Example 7 is prepared in a turbine quality mineral oil and tested as in Example 5.

The result is set out in Table III.

Table III

Example	Metal Appearance/Rating	Solution Appearance
Control	Magenta - Rating 3B	colourless
8	No change - Rating 1A	colourless

Example 9

6.9 Parts triazole, 9.7 parts diallylamine and 8.1 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted, as in Example 1, to provide 16.4 parts (89% yield) of 1-N,N-diallylaminomethyltriazole. Proton nmr spectral analysis of the product is consistent with the given structure. Boiling point 140°/0.2 m bar.

Example 10

13.8 Parts triazole, 9.3 parts aniline and 16.2 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 19.6 parts (78%) N,N-bis(triazolylmethylene)aniline as a viscous oil. Proton nmr spectral analysis of the product is consistent with the given structure.

Example 11

27.6 Parts triazole, 6 parts diaminoethane and 32.4 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 37.3 parts (97% yield) N,N,N',N'-tetra(triazolylmethylene) diaminoethane. Proton nmr spectral analysis of the product is consistent with the given structure. Melting point 127-9°C.

$C_{14}H_{20}N_{14}$ Theory: C,43.75; H,5.21; N,51.04%

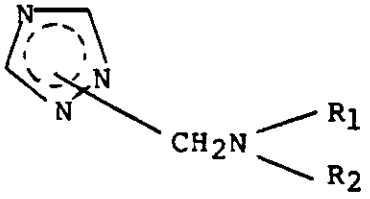
Found: C,43.22; H,5.24; N,50.74%

Example 12

34.5 Parts triazole, 10.3 parts diethylenetriamine and 40.5 parts 37% aqueous formaldehyde mixed with 100 parts of methanol are reacted as in Example 1 to provide 44.2 parts (95% yield) N,N,N',N",N"-penta(triazolylmethylene)diethylenetriamine as a viscous orange oil. Proton nmr spectral analysis is consistent with the given structure.

Claims.

1. A composition comprising a functional fluid and, as metal deactivator, a metal deactivating proportion of a ring N-substituted compound having the formula:

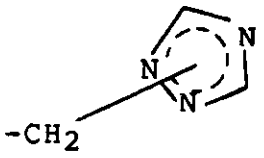


I

in which R_1 and R_2 are the same or different and each is C_1-C_{20} alkyl, C_3-C_{20} alkenyl, C_5-C_{12} cycloalkyl, C_7-C_{13} aralkyl, C_6-C_{10} aryl or R_1 and R_2, together with the nitrogen atom to which they are each attached, form a 5-, 6- or 7-membered heterocyclic residue, or R_1 and R_2 is each a residue of formula:

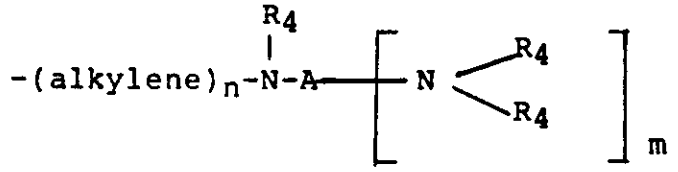
$$R_3X[(alkylene)O]_n(alkylene)- \qquad II$$

in which X is O, S or NH, R_3 is hydrogen or C_1-C_{20} alkyl, alkylene is a C_1-C_{12} alkylene residue and n is O or an integer from 1 to 6, or R_1 has its previous significance and R_2 is a residue of formula:



III

or R_2 is a residue of formula III as defined above and R_1 is residue of formula :



IV

wherein m is O or 1 and, when m is 1, A is alkylene or C_6-C_{10} arylene and when m is O, A is a residue of formula III, and alkylene and n are as defined above and R_4 is a residue of formula III as defined above.

2. Composition according to claim 1 wherein the proportion of the compound of formula I is from 0.001 to 5% by weight, based on the weight of the total composition.

3. Composition according to claim 1 or 2 wherein the functional fluid is a lubricant having a mineral oil, poly-alpha olefin or synthetic carboxylic ester base; a hydraulic fluid based on mineral oils, phosphate esters, aqueous polyglycol/polyglycol ether mixtures, glycol systems or oil-in-water or other water-in-oil emulsions; metal-working fluids having, as their base, mineral oil or aqueous systems; aqueous or aqueous glycol or ethylene- or propylene glycol/methanol based engine coolant compositions;or transformer or switch oils.

4. Composition according to claim 3 wherein the functional fluid is a lubricant based on mineral oil.

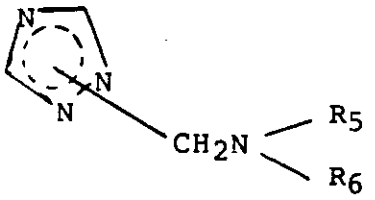
5. Composition according to claim 3 wherein the functional fluid is an aqueous-based antifreeze, -hydraulic fluid or -metal-working fluid.

6. Composition according to claim 3 wherein the functional fluid is oil-based and also contains, as further additives, one or more of antioxidants, rust inhibitors, viscosity-index improvers, pour-point depressants, dispersants/surfactants or antiwear additives.

7. Composition according to claim 3 wherein the functional fluid is aqueous-based and also contains, as further additives, one or more of antixoidants, corrosion- and rust inhibitors, further metal deactivators, extreme pressure - or antiwear additives, biocides, buffering agents and antifoams.

8. Composition according to claim 1 substantially as described with reference to Example 5, 6 or 8.

9. Ring N-substituted compounds having the formula V:

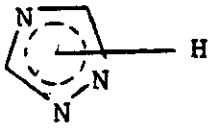


V

in which R_5 and R_6 is each a residue of formula II as defined in claim 1.

10. Compounds of formula V substantially as described with reference to Example 4.

11. Process for producing compounds of formula V comprising reacting a compound of formula:



VI

with formaldehyde and with an amine having the formula:

$$HNR_5R_6 \qquad \text{VII}$$

wherein R_5 and R_6 are as defined in claim 9.

12. Process for producing compounds of formula V substantially as described with reference to Example 4.

13. Compounds of formula V when produced by a process claimed in claim 11 or 12.

REGISTER ENTRY FOR GB2156813

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Title NEW METAL DEACTIVATORS

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RENEWAL DETAILS

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FOR THE COMPTROLLER