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(54) Title: MICROBICIDAL COMPOSITIONS

(57) Abrégé/Abstract:

There are described the use of α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol as a microbicide for the protection of industrial materials, and compositions containing this compound.



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Microbicidal Compositions

A b s t r a c t

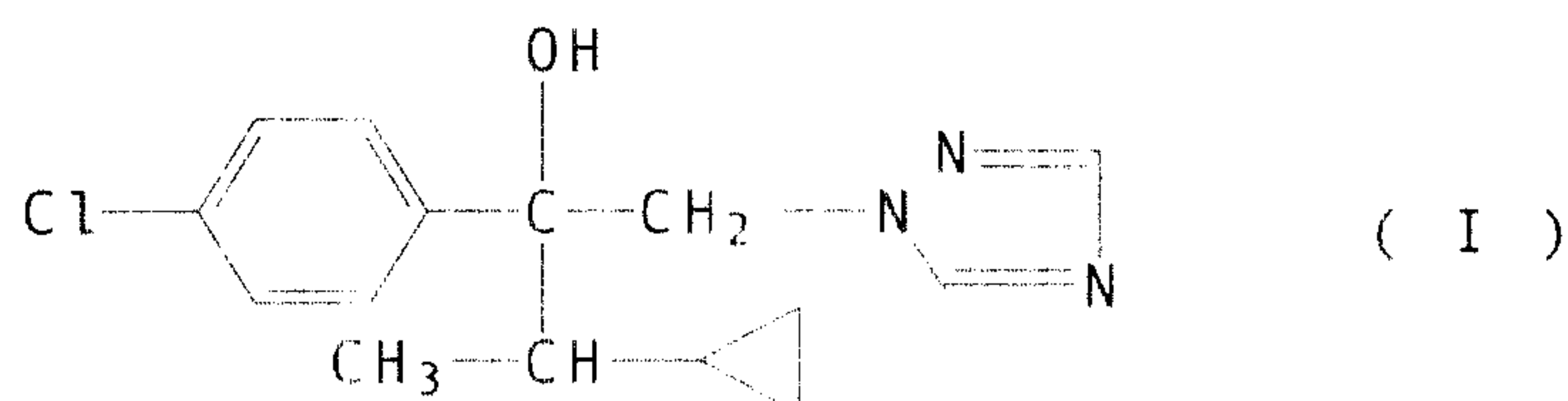
There are described the use of α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol as a microbicide for the protection of industrial materials, and compositions containing this compound.

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The invention relates to the use of the compound α -(4-chlorophenyl)- α -(1-cyclopropyl-ethyl)-1H-1,2,4-triazole-1-ethanol (cyproconazole) as a microbicide for the protection of industrial materials, and to synergistic mixtures
5 containing this compound.

It has been disclosed that the azole derivatives described in DE-OS (German Published Specification) 3,406,993 can be used for protecting plants.

In one aspect, the invention provides a microbicidal
10 composition comprising a combination of α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)

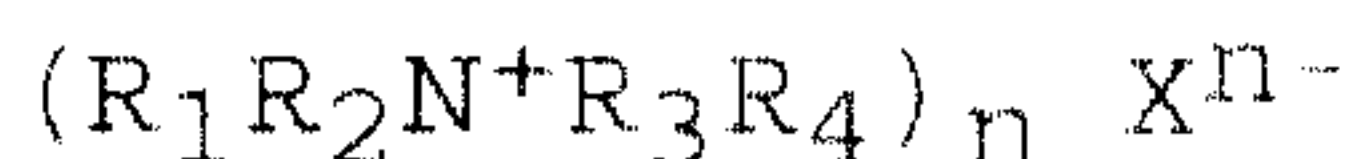


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or a metal salt thereof, or an acid addition compound thereof with at least one compound selected from the group consisting of a sulfenamide, a benzimidazole, a thiocyanate, a quaternary ammonium compound, a morpholine derivative, an
20 azole, an iodo-derivative, a phenole-derivative, a bromo-derivative, an isothiazolinone, a benzisothiazolinone, a pyridine derivative, a metal soap, a metal salt, a metal oxide, a dialkyldithiocarbamate, a nitrile-derivative, a benzthiazole, a chinoline, a boron compound, a formaldehyde
25 and a formaldehyde releasing compound, a carbamate, a nitroimine and a nitromethylene, for the protection of an industrial non-living material; with the proviso that (i) the combination does not contain 2,4,5,6-tetrachloro-isophthalonitrile and (ii) does not contain, with exception

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of benzyldimethyldodecyl-ammonium chloride and benzyldimethyltetradecyl-ammonium chloride, an ammonium salt of the general formula:



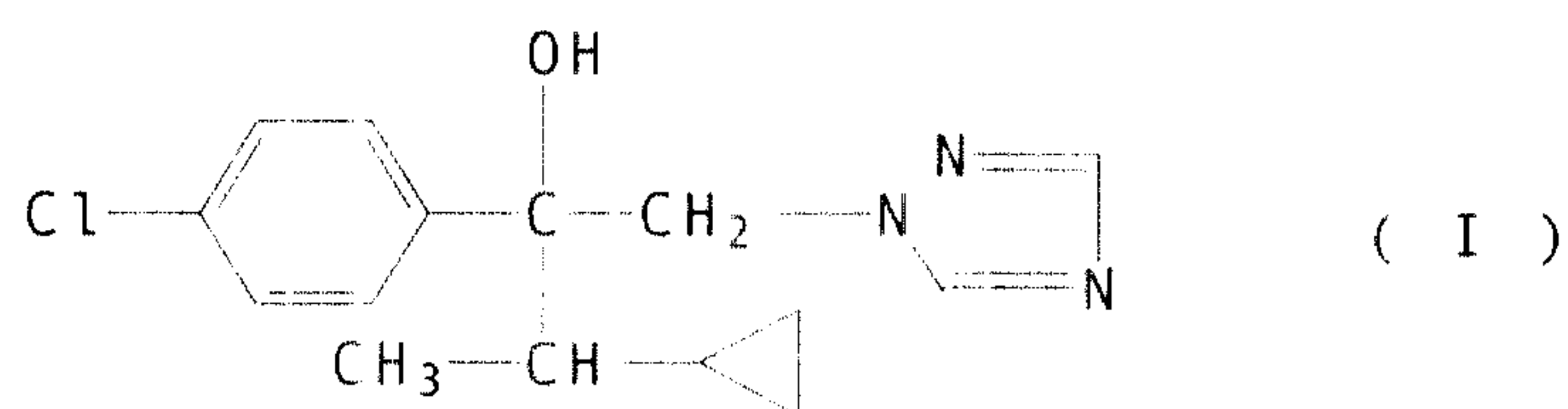
5 wherein:

R_1 to R_4 , independently, represent an organic substituent containing 1 to 18 carbon atoms, or 3 of the substituents R_1 to R_4 together with the nitrogen atom to which they are attached form a heteroaromatic system, X^{n-} represents an
10 anion of an organic or inorganic acid, and n is 1, 2 or 3.

The invention also provides for the use of the above composition for the protection of an industrial non-living material.

The invention further provides a process for the protection
15 of an industrial non-living material, comprising applying a composition as defined above to the industrial non-living material.

The invention still further provides use of a composition comprising α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-
20 1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)

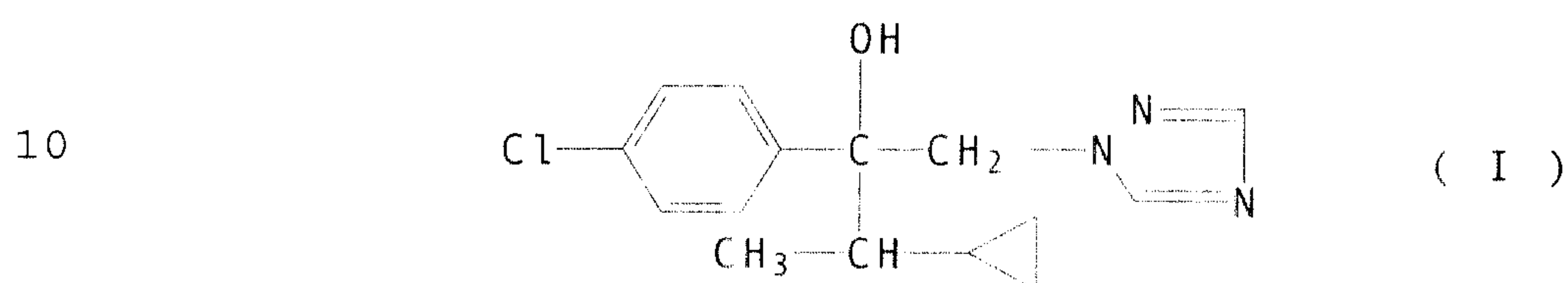


or a metal salt thereof, or an acid addition compound
25 thereof, as the only active microbicidal compound, for the protection of an industrial non-living material, excluding

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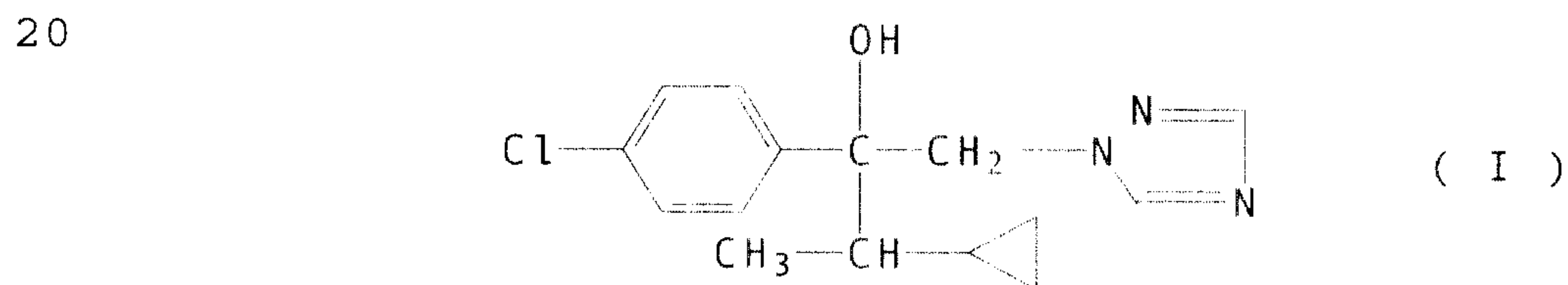
wood, brickwork and an intermediate of papermaking, in a concentration range of from 0.001 to 95 % by weight, based on the material to be protected.

The invention yet further provides a process for the protection of an industrial non-living material, comprising applying a composition comprising α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)



or a metal salt thereof, or an acid addition compound thereof, as the only active microbicidal compound, to the industrial non-living material, excluding wood, brickwork and an intermediate of papermaking, in a concentration range of from 0.001 to 95 % by weight, based on the material to be protected.

The present invention relates to the use of an azole derivative of the formula (I)



its metal salts or acid addition compounds as a microbicide for the protection of industrial materials.

The azole derivative can not only be in the form of the free base but also in the form of a metal salt complex or an acid addition salt. Suitable metal salts are preferably salts of

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metals of main groups II to IV and sub-groups I and II as well as IV to VII of the periodic table, the following being mentioned by way of example: copper, zinc, manganese, magnesium, tin, iron, calcium,

aluminium, lead, chromium, cobalt and nickel.

5 Suitable anions of the salts are those which are derived, preferably, from the following acids: hydrohalic acids such as, for example, hydrochloric acid and hydrobromic acid, furthermore phosphoric acid, nitric acid and sulphuric acid.

10 The metal salt complexes of the azole derivative can be obtained in a simple manner by customary processes, for example by dissolving the metal salt in alcohol, for example ethanol, and adding the solution to the azole fungicide. Metal salt complexes can be isolated in a known manner, for example by filtration, and, if appropriate, purified by recrystallisation.

15 The following acids are preferably suitable for preparing acid addition salts of the azole derivative: the hydrohalic acids, such as, for example, hydrochloric acid and hydrobromic acid, in particular hydrochloric acid, furthermore phosphoric acid, nitric acid, sulphuric acid, mono- and bifunctional carboxylic acids and hydroxycarboxylic acids such as, for example, acetic acid, propionic acid, 2-ethylhexanoic acid, butyric acid, mandelic acid, oxalic acid, succinic acid, 2-hydroxy-ethanedicarboxylic acid, maleic acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid, lactic acid, as well as sulphonic acids, such as, for example, 25 p-toluenesulphonic acid, p-decyl phenyl sulphonic acid, p-dodecyl phenyl sulphonic acid, 1,4-naphthalenedisulphonic acid, alkanesulphonic acids, benzoic acid and optionally substituted benzoic acids.

5 The acid addition salts of the compounds can be obtained in a simple manner by customary salt formation methods, for example by dissolving a compound in a suitable inert solvent and adding the acid, for example, hydrochloric acid, and they can be isolated in a known manner, for example by filtration, and, if appropriate, purified by washing with an inert organic solvent.

10 The compound (R*, R*)- α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol (cyproconazole) is particularly preferred.

15 Surprisingly, these compounds display a particularly powerful microbicidal, in particular fungicidal, activity against microorganisms which are relevant in the protection of materials, combined with a broad spectrum of action; they are active, above all, against moulds and wood-discolouring and wood-destroying fungi. The following groups of microorganisms may be mentioned by way of example, but without imposing any limitation:

20 A: Wood-discolouring fungi:

A1: Ascomycetes;

Ceratocystis such as Ceratocystis minor

A2: Deuteromycetes;

Aspergillus such as Aspergillus niger

25 Aureobasidium such as Aureobasidium pullulans

- 5 Dactylium such as Dactylium fusarioides
 Penicillium such as Penicillium brevicaulis or
 Penicillium variabile
 Sclerophoma such as Sclerophoma pithyophila
 Scopularia such as Scopularia phycomyces
 Trichoderma such as Trichoderma viride or
 Trichoderma lignorum
- A3: Zygomycetes:
 Mucor such as Mucor spinosus
- 10 B: Wood-destroying fungi:
- B1: Ascomycetes:
 Chaetomium such as Chaetomium globosum or
 Chaetomium alba-arenulum
 Humicola such as Humicola grisea
 15 Petriella such as Petriella setifera
 Trichurus such as Trichurus spiralis
- B2: Basidiomycetes
 Coniophora such as Coniophora puteana
 Coriolus such as Coriolus versicolor
 20 Donkioporia such as Donkioporia expansa
 Glenospora such as Glenospora graphii
 Gloeophyllum such as Gloeophyllum abietinum or
 Gloeophyllum adorum or Gl. protactum or
 Gloeophyllum sepiarium or Gl. trabeum
 25 Lentinus such as Lentinus cyathiformes or
 Lentinus edodes or Lentinus lepideus or

Lentinus grinus or L. squarrolus
Paxillus such as Paxillus panuoides
Pleurotus such as Pleurotis ostreatus
Poria such as Poria monticola or Poria placenta
or Poria vaillantii or Poria vaporaria
Serpula such as Serpula himantoides or Serpula
lacrymans
Stereum such as Stereum hirsutum
Tyromyces such as Tyromyces palustris

5

10

B3: Deuteromycetes

Alternaria such as Alternaria tenuis
Cladosporium such as Cladosporium herbarum

15

The amount of active substance employed depends on the species and the occurrence of the microorganisms, the microbial count and the medium. The optimum dosage rate for use can be determined in each case by test series. In general, however, it suffices to employ 0.001 to 20 % by weight, preferably 0.05 to 10 % by weight, of the active compound based on the material to be protected.

20

The active compound can be used as such, in the form of concentrates or generally customary formulations such as powder, granules, solutions, suspensions, emulsions or pastes.

25

The abovementioned formulations can be prepared in a manner known per se, for example by mixing the active compound with at least one solvent or diluent,

emulsifier, dispersant and/or binder or fixative, water repellent, optionally siccatives and UV stabilisers, and optionally colourants and pigments as well as other processing auxiliaries.

- 5 Suitable solvents or diluents are organochemical solvents or solvent mixtures and/or a polar organic solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture and/or water, if appropriate together with an emulsifier and/or wetting composition.
- 10 Customary water-insoluble oily or oil-type solvents of low volatility which are preferably used are the particular mineral oils/mineral-oil-containing solvent mixtures or their aromatic fractions. White spirit, petroleum or alkylbenzenes, and additionally spindle oil
- 15 and monochloronaphthalene may be mentioned as being preferred. The boiling ranges of these solvent (mixtures) of low volatility cover a range of approximately 170°C to not more than 350°C.

- 20 The above-described oily or oil-type solvents of low volatility can be replaced partially by more volatile organochemical solvents.

- To prepare a wood preservative, some of the above described solvent or solvent mixture is preferably replaced by a polar organochemical solvent or solvent mixture.
- 25 Solvents which are preferably used are those containing hydroxyl groups, ester groups, ether groups or mixtures of this functionality. Examples which may be mentioned

are esters or glycol ethers. Binders are to be understood according to the invention as being synthetic resins, binding drying oils, for example based on acrylic resins, vinyl resins, polyester resins, polyurethane resins, alkyd resins, phenol resins, hydrocarbon resins or silicone resins which can be diluted with water or are soluble, dispersible or emulsifiable in organochemical solvents. The binder used can be employed as a solution, emulsion or dispersion. Mixtures of alkyd resins and drying vegetable oil are preferably used. Alkyd resins with an oil content of between 45 and 70 % are particularly preferred.

All or some of the abovementioned binder can be replaced by a fixative (mixture) or a plasticiser (mixture). These additives are intended to prevent volatilisation of the active compound as well as crystallisation or precipitation. They preferably replace 0.01 to 30 % of the binder (based on 100 % of the binder used).

The plasticisers are from the chemical classes of the phthalic esters such as dibutyl, dioctyl or benzyl butyl phthalate, phosphoric esters such as tributyl phosphate, adipic esters such as di-(2-ethylhexyl) adipate, stearates such as butyl stearate and amyl stearate, oleates such as butyl oleate, glycerol ethers or higher-molecular-weight glycol ethers, glycerol esters as well as p-toluenesulphonic esters.

Fixatives are based, from the chemical point of view, on

polyvinyl alkyl ethers such as, for example, polyvinyl methyl ether, or ketones such as benzophenone or ethylenebenzophenone.

5 The preferred solvent or diluent is water, if appropriate in a mixture with one or more of the abovementioned solvents or diluents, emulsifiers and dispersants.

10 Industrial materials according to the invention are non-live materials which have been prepared for use in industry. For example, industrial materials which are intended to be protected by the active compound from microbial change or destruction can be glues, sizes, paper and board, textiles, leather, wood, paints and plastic articles, cooling lubricants and other materials which can be infested with, or decomposed by, micro-organisms. Parts of production plants, for example cooling-water circuits, which may be impaired by the multiplication of microorganisms may also be mentioned from amongst the materials to be protected. Preferred industrial materials beyond the scope of the invention are glues, sizes, paper and board, leather, wood, derived timber products, paints, cooling lubricants, aqueous hydraulic fluids and cooling circuits.

25 The active compound of the formula (I), or compositions or concentrates containing it, are preferably employed for protecting wood and derived timber products against microorganisms, for example against wood-destroying or wood-discolouring fungi, in particular in the protection

of tropical wood.

Wood which can be protected by the active compound of the formula (I) or by mixtures containing them is to be understood as meaning, for example, structural timber, wooden beams, railway sleepers, components of bridges, jetties, vehicles made of wood, boxes, pallets, containers, telegraph poles, wooden fences, wooden lagging, windows and doors made of wood, plywood, chipboard, joinery, or wooden products which are used, quite generally, for building houses or in building joinery.

The protection of wood is particularly effective when large-scale impregnating treatments, for example vacuum, double vacuum or pressure treatments, are used.

The active compound of the formula (I) is preferably mixed with at least one other antimicrobially active substance, fungicide and, in particular, with other active compounds, to increase the spectrum of action or to achieve particular effects such as, for example, an additional protection against insects. In many cases, this results in synergistic effect, that is to say, the activity of the mixture is greater than the activity of the individual components. Particularly preferred components for the mixtures are, for example, the following compounds:

Sulphenamides, such as dichlofluanid, tolylfluanid,

folpet and fluorfolpet;

Benzimidazoles, such as carbedazim, benomyl, fuberidazole, thiabendazole or their salts;

5 Thiocyanataes such as thiocyanatomethylthiobenzothiazole or methylene bis-thiocyanate;

Quarternary ammonium compounds such as benzyldimethyltetradecylammonium chloride, benzyldimethyldodecylammonium chloride or didecyldimethylammonium chloride;

Morpholine derivatives such as tridemorph, fenpropiomorph or falimorph;

10 Azoles such as triadimefon, triadimenol, bitertanol, tebuconazole, propioconazole, azaconazole, hexaconazole, prochloraz or bromuconazole, metconazole, penconazole, difenoconazole, fenbuconazole, opus, fensilazole.

2-(2-Chlorocyclopropyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol;

15 Iodine derivatives such as diiodomethyl-p-tolyl sulphone, 3-iodo-2-propinyl alcohol, 4-cdhlorophenyl-3-iodopropargyl formal, 3-bromo-2,3-diiido-2-propenyl ethylcarbonate, 2,3,3-triiodoallyl alcohol, 3-bromo-2,3-diiido-2-propenyl alcohol, 3-iodo-2-propinyl-n-butyl carbamate, 3-iodo-2-propinyl n-hexylcarbamate, 3-iodo-2-propinyl cyclohexylcarbamate and 3-iodo-2-propinyl phenylcarbamate; O-1-(6-Iodo-3-oxo-hex-5-myl)butylcarbamate, O-1-(6-Iodo-3-oxo-hex-5-inyl)phenylcarb-
20 amate, Nepcodide VP 305.

Phenol derivatives such as derivatives such as tribromophenol, tetrachlorophenol, 3-methyl-4-chlorophenol, dichlorophen, o-phenylphenol, m-phenylphenol, p-phenylphenol or 2-benzyl-4-chlorophenol;

5 Bromine derivatives such as 2-bromo-2-nitro-1,3-propanediol or 2-Brom-2-brommethyl-glutaridinitril;

Isothiazolinones such as N-methylisothiazolin-3-one, 5-chloro-N-methylisothiazolin-3-one, 4,5-dichloro-N-octylisothiazolin-3-one or N-octyl-isothiazolin-3-one;

Benzoisothiazolinones or 4-5-trismethylen-N-methylisothiazol-3-on;

10 Pyridines such as 1-hydroxy-2-pyridinethione (and their sodium, iron, manganese and zinc salts) or tetrachloro-4-methylsulphonylpyridine;

15 Metal soaps such as tin naphthenate, tin octoate, tin 2-ethylhexanoate, tin oleate, tin phosphate, tin benzoate, copper naphthenate, copper octoate, copper 2-ethylhexanoate, copper oleate, copper phosphate, copper benzoate, zinc naphthenate, zinc octoate, zinc 2-ethylhexanoate, zinc oleate, zinc phosphate or zinc benzoate;

Oxides such as tributyltin oxide, Cu_2O , CuO or ZnO ;

Dialkyldithiocarbamataes such as sodium and zinc salts of dialkylthiocarbamataes, tetramethylthiuram disulphide;

Nitriles such as 2,4,5,6-tetrachloroisophthalodinitrile;

Benzothiazoles such as 2-mercaptobenzothiazol;

Quinolines, such as 8-hydroxyquinoline, and their copper salts;

5 Boron compounds, such as boric acid, boric esters or borax;

10 Formaldehyde and formaldehyde-releasing compounds such as benzyl alcohol mono(poly)-hemiformal, oxazolidines, hexahydro-S-triazines, N-methylolchloroacetamide or paraformaldehyde;

Tris-N-(cyclohexyldiazeniumdioxy)-aluminium, N-(cyclohexyldiazeniumdioxy)-tributyltin or potassium salts thereof, or bis-N-(cyclohexyldiazeniumdioxy)-copper.

The following are preferably added as insecticide:

15 Phosphoric esters such as azinphos-ethyl, azinphos-methyl, 1-(4-chlorophenyl)-4-(O-ethyl,S-propyl)phosphoryloxypyrazole, chloropyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoprophos, etrimfos, fenitrothion, fenthion, heptenophos, parathion, parathion-methyl, phosalone, phoxim, 20 pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, sulfprofos, triazophos and trichlorophon;

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Carbamates such as aldicarb, bendiocarb, 2-(1-methyl-propyl)-phenyl methylcarbamate, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, cloethocarb, isoprocarb, methomyl, oxamyl, pirimicarb, promecarb, propoxur and thiodicarb;

5

Organosilicon compounds, preferably dimethyl(phenyl)-silylmethyl 3-phenoybenzyl ethers, such as dimethyl-(4-ethoxyphenyl)silylmethyl 3-phenoxybenzyl ether or (dimethylphenyl)-silyl-methyl 2-phenoxy-6-pyridylmethyl ethers such as, for example, dimethyl(9-ethoxy-phenyl)-silylmethyl 2-phenoxy-6-pyridylmethyl ether or [(phenyl)-3-(3-phenoxyphenyl)-propyl](dimethyl)-silanes, such as, for example, (4-ethoxyphenyl)-[3-(4-fluoro-3-phenoxyphenyl-propyl)]dimethyl silane.

10

Pyrethroids, such as allethrin, alphamethrin, bioresmethrin, byfenthrin, cycloprothrin, cyfluthrin, decamethrin, cyhalothrin, cypermethrin, deltamethrin, alphacyano-3-phenyl-2-methylbenzyl 2,2-dimethyl-3-(2-chloro-2-trifluoro-methylvinyl)cyclopropanecarboxylate, fenpropathrin, fenfluthrin, fenvalerate, flucythrinate, flumethrin, fluvalinate, permethrin, resmethrin and tralomethrin;

20

Nitroimines and nitromethylenes, such as 1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine (imidacloprid).

25

The mixtures, concentrates and formulations according to

the invention which have been prepared in this manner are not only active against the abovementioned fungi but also, if they contain an insecticide, against insects which destroy materials. The following insects which
 5 destroy materials may be mentioned by way of example, without imposing any limitation:

A: Dermaptera:

Sirex juvencus

Urocerus augur

10 Urocerus gigas

Urucerus gigas taignus

B: Coleoptera:

Anobium punctatum

Apate monachus

15 Bostrychus capucins

Chlorophores pilosus

Dendrobium pertinex

Dinoderus minutus

Ernobius mollis

20 Heterobostrychus brunneus

Hylotrupes bajulus

Lyctus africanus

Lyctus brunneus

Lyctus linearis

25 Lyctus planicollis

Lyctus pubescens

Minthea rugicollis

Priobium carpini

Ptilinus pecticornis

Sinoxylon spec.
 Trogoxylon aequale
 Trypto dendron spec.
 Xestobium rufovillosum
 5 Xyleborus spec.

C: Isoptera:

Coptotermes formosanus
 Cryptotermes brevis
 Heterotermes indicola
 10 Kalotermes flavicollis
 Mastotermes darwiniensis
 Reticulitermes flavipes
 Reticulitermes lucifugus
 Reticulitermes santonensis
 15 Zootermopsis nevadensis

Other active compounds which are suitable are algicides, molluscicides or active compounds against sea animals which colonise, for example, ship's bottom paints.

20 The following are particularly preferred as components in mixtures:

dichlofluanid, tolylfluanid,

benzyldimethyldodecylammonium chloride, didecyldimethyl-
ammonium chloride,

tebuconazole, propiconazole, azaconazole, hexaconazole,

3-bromo-2,3-diiodo-2-propenyl alcohol, 3-iodo-2-propinyl
n-butylcarbamate,

o-phenylphenol, m-phenylphenol, p-phenylphenol, 3-methyl-
4-chlorophenol,

5 thiocyanatomethylthiobenzothiazole,

N-methylisothiazolin-3-one, 5-chloro-N-methylisothia-
zolin-3-one, 4,5-dichloro-N-octylisothiazolin-3-one,
N-octyl-isothiazolin-3-one,

10 benzyl alcohol mono(poly)-hemiformal, N-methylolchloro-
acetamide,

phoxim,

cyfluthrin, permethrin, cypermethrin, deltamethrin,
imidacloprid.

15 The microbicidal compositions or concentrates used for
the protection of industrial materials contain the active
compound of the formula (I) in a concentration from 0.01 to
95 % by weight, in particular 0.01 to 60 % by weight, and
additionally, if appropriate, 0.001 to 95 % by weight of
one or more other suitable fungicides, insecticides or
20 other active compounds as mentioned above.

The compositions according to the invention allow in an
advantageous manner the microbicidal compositions avail-
able to date to be replaced by more effective ones. They

have good stability properties and, advantageously, a broad spectrum of action.

Example 1

Inhibition test on giant colonies of Basidiomycetes

- 5 Mycelium sections were removed from colonies of
Gloeophyllum trabeum, Coniophora puteana, Poria placenta,
Lentinus tigrinus, Coriolus versicolor and Stereum
10 sanguinolentum and incubated on an agar medium containing
malt extract peptone at 26°C. The inhibition of hyphal
growth on active-compound-containing media was compared
with the longitudinal growth on media without an addition
of active compound and rated as per cent inhibition.

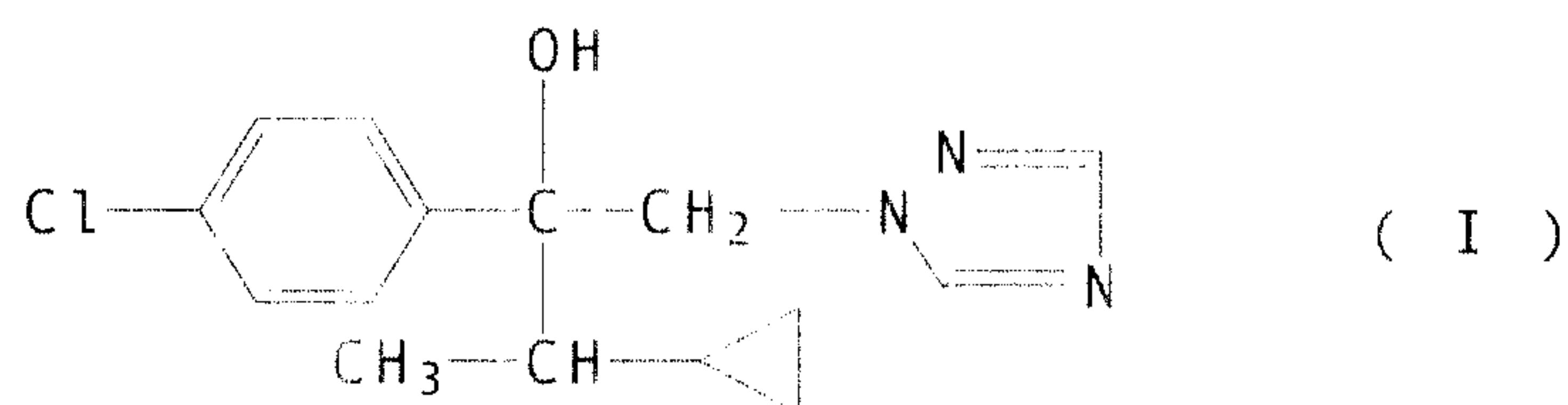
At a concentration of 10 ppm, a 100 % inhibition is obtained with the compound cyproconazole.

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CLAIMS:

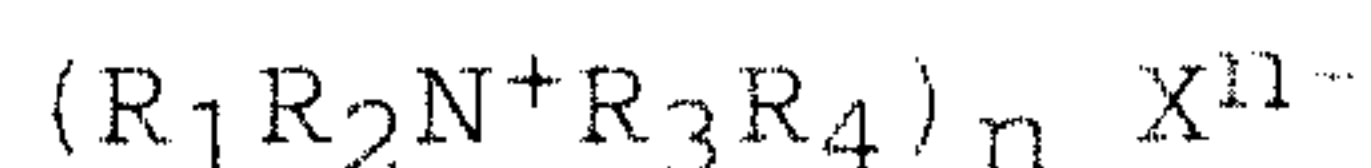
1. A microbicidal composition comprising a combination of α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)

5



or a metal salt thereof, or an acid addition compound thereof with at least one compound selected from the group consisting of a sulfenamide, a benzimidazole, a thiocyanate, a quaternary ammonium compound, a morpholine derivative, an azole, an iodo-derivative, a phenole-derivative, a bromo-derivative, an isothiazolinone, a benzisothiazolinone, a pyridine derivative, a metal soap, a metal salt, a metal oxide, a dialkyldithiocarbamate, a nitrile-derivative, a benzthiazole, a chinoline, a boron compound, a formaldehyde and a formaldehyde releasing compound, a carbamate, a nitroimine and a nitromethylene, for the protection of an industrial non-living material; with the proviso that (i) the combination does not contain 2,4,5,6-tetrachloro-isophthalonitrile and (ii) does not contain, with exception of benzyldimethyldodecyl-ammonium chloride and benzyldimethyltetradecyl-ammonium chloride, an ammonium salt of the general formula:

25



wherein:

R_1 to R_4 , independently, represent an organic substituent containing 1 to 18 carbon atoms, or 3 of the substituents R_1

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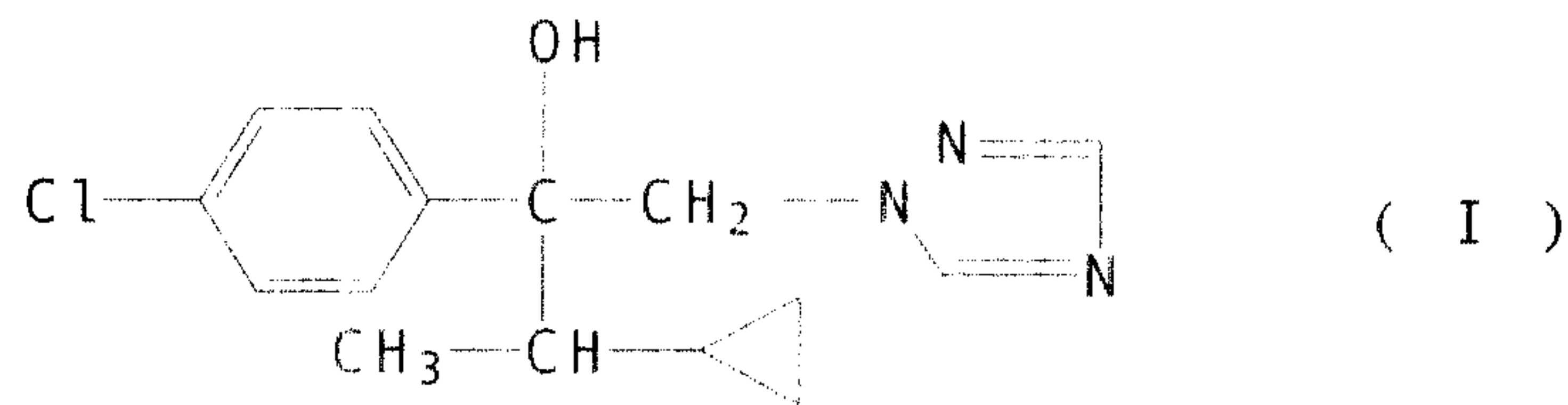
to R₄ together with the nitrogen atom to which they are attached form a heteroaromatic system,

Xⁿ⁻ represents an anion of an organic or inorganic acid, and

n is 1, 2 or 3.

- 5 2. A composition according to claim 1, comprising a combination of cyproconazole with lebuconazole.
3. A composition according to claim 1, comprising a combination of cyproconazole with propiconazole.
4. A composition according to claim 1, comprising a
10 combination of cyproconazole with a copper salt.
5. A composition according to claim 1, comprising a combination of cyproconazole with benzyl-dimethyl-tetradecyl-ammoniumchloride.
6. A composition according to claim 1, comprising a
15 combination of cyproconazole with benzyl-dimethyl-dodecyl-ammoniumchloride.
7. A composition according to any one of claims 1 to 6, comprising at least one solvent, diluent, emulsifier, dispersant binder, fixative, water repellent or a mixture
20 thereof.
8. Use of a microbicidal composition according to any one of claims 1 to 7, for the protection of an industrial non-living material.
9. Use of a composition comprising α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)
- 25

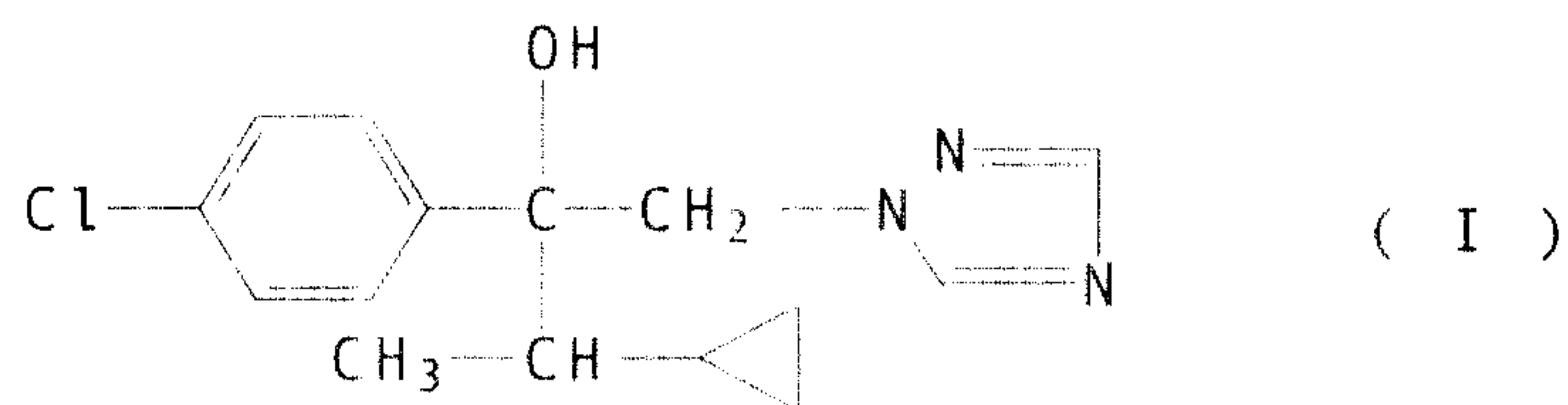
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or a metal salt thereof, or an acid addition compound thereof, as the only active microbicidal compound, for the protection of an industrial non-living material, excluding wood, brickwork and an intermediate of papermaking, in a concentration range of from 0.001 to 95 % by weight, based on the material to be protected.

10. A process for the protection of an industrial non-living material comprising applying a composition according to any one of claims 1 to 7 to the industrial non-living material.

11. A process for the protection of an industrial non-living material, comprising applying a composition comprising α -(4-chlorophenyl)- α -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol, cyproconazole, of the formula (I)



or a metal salt thereof, or an acid addition compound thereof, as the only active microbicidal compound, to the industrial non-living material, excluding wood, brickwork and an intermediate of papermaking, in a concentration range of from 0.001 to 95 % by weight, based on the material to be protected.