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(54) Title
THIOCARBAMOYL COMPOUNDS USED AS ANTIMICROBIAL AGENTS

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(71) Applicant(s)
BAYER AKTIENGESELLSCHAFT

(72) Inventor(s)
LUTZ HEUER; PETER WACHTLER; MARTIN KUGLER; HEINRICH SCHRAGE

(74) Attorney or Agent
DAVIES COLLISON CAVE , GPO Box 3876, SYDNEY NSW 2001

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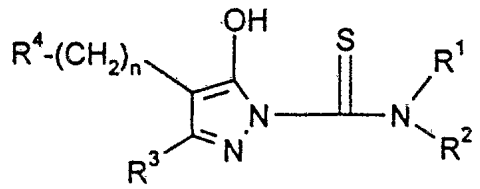
(57) Claim

1. Thiocarbamoyl compounds of the formula (I)



(I)

in which

R^1, R^2 and R^3, in each case independently of one another, represent hydrogen or methyl, and

R^4 represents cyclopentyl or cyclopentenyl,

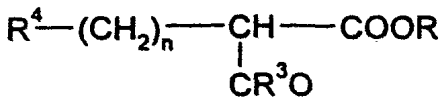
n represents the number 0 or 1,

and their metal salt complexes and acid addition products.

.../2

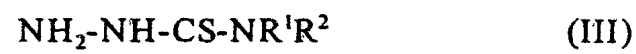
4. Method of protecting industrial materials, characterized in that compounds of the formula (I) according to Claim 1 are applied to the materials to be protected or mixed with them.

7. Process for the preparation of compounds of the formula (I), characterized in that formyl acid derivatives of the formula (II)



(II)

in which n, R^3 andR^4 have the meanings given in Claim 1 and R represents methyl, ethyl, n-, i-propyl or n-, i-, s- or t-butyl are reacted with thiosemicarbazides of the formula (III)



(III)

if desired in the presence of a diluent or solvent and/or of a base.

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(71) Anmelder (*für alle Bestimmungsstaaten ausser US*): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder (*nur für US*): HEUER, Lutz [DE/DE]; Scheiblerstrasse 83, D-47800 Krefeld (DE). WACHTLER, Peter [DE/DE]; Morgengraben 4, D-51061 Köln (DE). KUGLER, Martin [DE/DE]; Am Kloster 47, D-42799 Leichlingen (DE). SCHRAGE, Heinrich [DE/DE]; Dörperhofstrasse 31, D-47800 Krefeld (DE).

(74) Gemeinsamer Vertreter: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).

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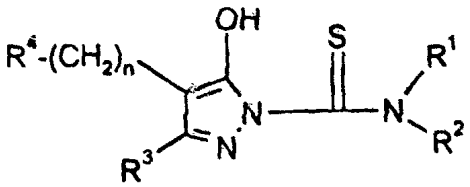
(54) Title: THIOCARBAMOYL COMPOUNDS USED AS ANTIMICROBIAL AGENTS

(54) Bezeichnung: THIOCARBAMOYLVERBINDUNGEN ALS MIKROBIZIDE

(57) Abstract

The application relates to novel thiocarbamoyl compounds of the formula (I) in which R^1, R^2, R^4 and n have the meanings given in the description.



(I)

(57) Zusammenfassung

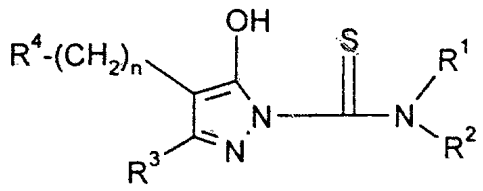
Die Anmeldung betrifft neue Thiocarbamoyl-Verbindungen der Formel (I), in denen R^1, R^2, R^3, R^4 und n die in der Beschreibung angegebene Bedeutung haben.

Thiocarbamoyl compounds as microbicides

The application relates to novel thiocarbamoyl compounds, to their preparation and to their use for protecting industrial materials.

Thiocarbamoyl compounds and their use in the protection of materials are known and are described for example in (DE 4 117 385). These compounds do however have the disadvantage that they do not in all cases have an adequate microbicidal action and, furthermore, are washed out of the materials to be protected. Consequently, long-term protection is not ensured by these known compounds.

The application therefore relates to the novel thiocarbamoyl compounds of the formula (I)



(I)

in which

R^1, R^2 and R^3, in each case independently of one another, represent hydrogen or methyl, and

R^4 represents cyclopentyl or cyclopentenyl,

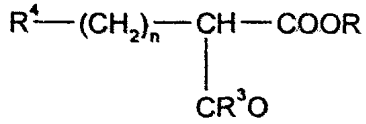
n represents the number 0 or 1,

and their metal salt complexes and acid addition products.

Particularly preferred compounds of the formula (I) are those in which R^1, R^2

and R^3 represent hydrogen and n represents the number 0 and, in particular, the compound of the formula (I) in which R^1, R^2, R^3 represent hydrogen, n represents the number 0, R^4 represents cyclopentyl.

The compounds of the formula (I) are obtained by reacting formyl acid derivatives of the formula (II)



(II)

in which n, R^3 and R^4 have the meanings given above and R represents methyl, ethyl, n-, i-propyl or n-, i-, s- or t-butyl with thiosemicarbazides of the formula (III)

$$NH_2\text{-}NH\text{-}CS\text{-}NR^1R^2 \qquad \text{(III)}$$

if desired in the presence of a diluent or solvent and/or of a base.

In this reaction, from 0.8 to 1.0 mol of thiosemicarbazide is preferably added per mole of α-formylacetic acid derivative.

Bases added are preferably sodium hydroxide, potassium hydroxide or potassium tert.-butylate, preferably in approximately equimolar amounts.

Suitable solvents or diluents are in particular alcohols such as ethanol or aromatic hydrocarbons such as toluene.

The condensation reaction is carried out within a relatively large temperature range. The thiosemicarbazone formation which takes place initially is carried out at temperatures from 20 to 110°C, preferably from 60 to 90°C. The cyclocondensation reaction which takes place after the addition of base is performed at temperatures from 20 to 100°C, preferably from 20 to 40°C.

The 1-thiocarbamoyl compounds of the formula (I) according to the invention are isolated from the reaction mixtures by known methods. The general procedure is to free the reaction mixtures from the solvent and to treat the residue with aqueous hydrochloric acid. The pyrazoles which precipitate in this procedure are separated off by filtration with suction. However, it is also possible to pour the reaction mixture directly into a large excess of dilute hydrochloric acid and to filter off the pyrazoles which are deposited as a precipitate.

The thiosemicarbazides of the formula (III) are known or are obtainable by generally known preparation methods.

The formyl acid derivatives of the formula (II) are novel and are likewise a subject of the application.

They are obtained by formylating esters of the formula (IV)

$$R^4\text{-}(CH_2)_n\text{-}CH_2\text{-}COOR \qquad (IV)$$

in which R^4, n and R have the meaning given above

with bases, for example NaH, in solvents or diluents, such as cyclohexane and DMF, for example, with amine acid esters, such as methyl or ethyl esters.

The formyl acid derivatives of the formula (II) are also obtained by hydroformylating corresponding α,β-unsaturated esters by generally known methods, as described for example in EP-417,597 or DE-2,643,205.

The active compounds of the formula (I) and the compositions according to the invention have a strong microbicidal action and can be employed in practice for combatting unwanted microorganisms. The active compounds of the formula (I) and the compositions according to the invention are suitable for protecting

industrial materials against infestation and destruction by unwanted microorganisms.

Industrial materials in the present context are non-living materials which have been prepared for use in industry. Industrial materials which are to be protected by active compounds according to the invention against microbial change or destruction can be, for example, adhesives, sizes, paper and card, textiles, leather, wood, coating compositions and articles made of plastic, cooling lubricants and other materials which may be infested or decomposed by microorganisms. In the context of the materials to be protected it is also possible to mention sections of production plants, for example cooling water circuits, which may be adversely affected by multiplication of microorganisms. In the context of the present invention, industrial materials which may be mentioned with preference are adhesives, sizes, papers and cards, leather, wood, coating compositions, cooling lubricants and heat-transfer fluids, particularly preferably coating compositions.

Microorganisms which can cause degradation of or a change in industrial materials are, for example, bacteria, fungi, yeasts, algae and slime organisms. The active compounds and compositions according to the invention preferably act against fungi, especially moulds, wood-discolouring and wood-destroying fungi (Basidiomycetes) and against slime organisms and algae.

Microorganisms of the following genera may be mentioned by way of example:
Alternaria, such as Alternaria tenuis,
Aspergillus, such as Aspergillus niger,
Chaetomium, such as Chaetomium globosum,
Coniophora, such as Coniophora puetana,
Lentinus, such as Lentinus tigrinus,
Penicillium, such as Penicillium glaucum,
Polyporus, such as Polyporus versicolor,
Aureobasidium, such as Aureobasidium pullulans,

Sclerophoma, such as Sclerophoma pityophila,
Trichoderma, such as Trichoderma viride,
Escherichia, such as Escherichia coli,
Pseudomonas, such as Pseudomonas aeruginosa,
Staphylococcus, such as Staphylococcus aureus.

Depending on their particular physical and/or chemical properties, the active compounds of the formula (I) can be converted into customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and very fine capsules in polymeric substances.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is, liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable in the main: aromatics, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, as well as water; by liquefied gaseous extenders or carriers are meant liquids which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide; as solid carriers there are suitable: for example ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly disperse silica, alumina and silicates; as solid carriers for granules there are suitable: for example crushed and fractionated

natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; as emulsifying and/or foam-forming agents there are suitable: for example non-ionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates as well as albumen hydrolysis products; as dispersing agents there are suitable: for example lignin-sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The active compounds of the formula (I) according to the invention are preferably employed for protecting coatings against infestation and destruction by unwanted microorganisms.

In the present context, a coating is to be understood as being a coat produced on a substrate by coating materials. The coating can have penetrated to a greater or lesser extent into the substrate. It may comprise one or more layers and be prepared by processes such as brushing, spraying, dipping, flow coating or the like.

The compounds of the formulae (I) are incorporated into the coating

compositions or into precursors for the preparation of the coating compositions by conventional methods, for example by mixing the active compounds with the other components.

Coating compositions according to the invention therefore contain, in addition to at least one fungicidal active compound of the formula (I), generally conventional coating components in, for example, liquid, paste-like or pulverulent form, examples being

- colorants, such as pigments or dyes, preferably pigments. Examples are titanium dioxide, zinc oxide and iron oxide.

- binders, for example oxidatively drying alkyd resins, vinyl polymers and vinyl copolymers, acrylic polymers and acrylic copolymers, polymer powders, novolaks, amino resins, polyester resins, epoxy resins, silicone resins, isocyanate resins, preferably vinyl polymers and vinyl copolymers, acrylic polymers and acrylic copolymers and other binders which can be used in water-dilutable coating materials.

In addition, the coatings contain if desired the following additives

- fillers, for example heavy spar, calcite, dolomite and talc,

- solvents, for example alcohols, ketones, esters, glycol ethers and aliphatic and aromatic hydrocarbons,

- and thickeners and thixotropic agents, dispersants and wetting agents, driers, antiskinning agents, levelling agents, antifoaming agents, corrosion inhibitors, UV absorbers, fragrances, antistatics, antifreezes.

The following coating compositions or precursors in the preparation of coating compositions may preferably be mentioned:

- Sizes and adhesives based on the known animal, vegetable or synthetic raw materials.
- Polymer dispersions, such as latex dispersions or dispersions based on other polymers.
- Starch solutions, starch dispersions or starch slurries or other products base on starch, for example printing thickeners.
- Slurries of other raw materials such as colour pigments (e.g. iron oxide pigments, carbon black pigments, titanium dioxide pigments) or slurries of fillers such as kaolin or calcium carbonate.
- Concrete additives based, for example, on molasses or ligninsulphonates.
- Bitumen emulsions.
- Precursors and intermediates of the chemical industry, for example in the production and storage of dyes.
- Inks or water colours.
- Emulsion paints for the coatings industry.
- Layers and finishes.

The effectiveness and the spectrum of action of the active compounds of the formulae (I) and/or the compositions, precursors or, quite generally, formulations which can be produced therefrom can be increased by adding, if desired, further antimicrobially active compounds, fungicides, bactericides, herbicides, insecticides or other active compounds for enlarging the spectrum of action or for obtaining particular effects such as, for example, additional protection against insects. These mixtures may possess a broader spectrum of action than the compounds according to the invention.

In this context, synergistic effects are obtained in many cases, i.e. the activity of the mixture is greater than the activity of the individual components. Examples of particularly advantageous co-components are the following compounds:

Triazoles such as:

amitrole, azocyclotin, BAS 480F, bitertanol, difenoconazole, fenbuconazole, fenchlorazole, fenethanil, fluquinconazole, flusilazole, flutriafol, imibenconazole, isozofos, myclobutanil, metconazole, epoxyconazole, paclobutrazol, penconazole, propioconazole, (±)-cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, tetraconazole, triadimefon, triadimenol, triapenthenol, triflumizole, triticonazole, uniconazole and the metal salts and acid adducts thereof.

Imidazoles such as:

imazalil, pefurazoate, prochloraz, triflumizole, 2-(1-tert-butyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol, thiazolecarboxanilides such as 2',6'-dibromo-2-methyl-4-trifluoromethoxy-4'-trifluoromethyl-1,3-thiazole-5-carboxanilide, 1-imidazolyl-1-(4'-chlorophenoxy)-3,3-dimethylbutan-2-one and the metal salts and acid adducts thereof.

Methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]3-methoxyacrylate, methyl (E)-2-[2-[6-(2-thioamidophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2-fluorophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl(E)-2-[2-[6-(2,6-difluorophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(pyrimidin-2-yloxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(5-methylpyrimidin-2-yloxy)-phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(phenyl-sulphonyloxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(4-nitrophenoxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-phenoxyphenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3,5-dimethylbenzoyl)pyrrol-1-yl]-3-methoxyacrylate, methyl (E)-2-[2-(3-methoxyphenoxy)phenyl]-3-methoxyacrylate, methyl(E)-2-[2-(2-phenylethen-1-yl)-phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3,5-dichlorophenoxy)-pyridin-3-yl]-3-methoxyacrylate, methyl (E)-2-(2-(3-(1,1,2,2-tetrafluoroethoxy)phenoxy)phenyl)-3-methoxyacrylate, methyl (E)-2-(2-[3-(alpha-hydroxybenzyl)phenoxy]phenyl)-3-methoxyacrylate, methyl (E)-2-(2-(4-phenoxypyridin-2-yloxy)phenyl)-3-methoxyacrylate, methyl (E)-2-[2-(3-n-

propyloxyphenoxy)phenyl]3-methoxyacrylate, methyl (E)-2-[2-(3-isopropyloxyphenoxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(2-fluorophenoxy)pehnoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3-ethoxyphenoxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(4-tert.-butyl-pyridin-2-yloxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(3-cyanophenoxy)phenoxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3-methylpyridin-2-yloxymethyl)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[6-(2-methylphenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(5-bromopyridin-2-yloxymethyl)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-(3-(3-iodopyridin-2-yloxy)phenoxy)phenyl]-3-methoxyacrylate, methyl(E)-2-[2-[6-(2-chloropyridin-3-yloxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate,(E),(E)methyl-2-[2-(5,6-dimethylpyrazin-2-ylmethyloximinomethyl)-phenyl]-3-methoxyacrylate, (E)methyl-2-{2-[6-(6-methylpyridin-2-yloxy)pyrimidin-4-yloxy]-phenyl}-3-methoxyacrylate, (E),(E)methyl-2-{2-(3-methoxyphenyl)methyloximinomethyl]phenyl}-3-methoxyacrylate, (E)methyl-2-{2-(6-(2-azidophenoxy)-pyrimidin-4-yloxy]phenyl}3-methoxyacrylate, (E),(E)methyl-2-{2-[6-phenylpyrimidin-4-yl)-methyloximinomethyl]phenyl}-3-methoxyacrylate, (E),(E)methyl-2-{2-[(4-chlorophenyl)-methyloximinomethyl]phenyl}-3-methoxyacrylate, (E)methyl-2-{2-[6-(2-n-propylphenoxy)-1,3,5-triazin-4-yloxy]phenyl}-3-methoxyacrylate, (E),(E)methyl-2-{2-[(3-nitrophenyl)methyloximinomethyl]phenyl}-3-methoxyacrylate;

succinate dehydrogenase inhibitors such as:

fenfuram, furcarbanil, cyclafluramid, furmecyclox, seedvax, metsulfovax, pyrocarbolid, oxycarboxin, shirlan, mebenil (mepronil), benodanil, flutolanil (Moncut); naphthalene derivatives such as terbinafine, naftifine, butenafine, 3-chloro-7-(2-aza-2,7,7-trimethyl-oct-3-en-5-ine);

sulphenamides such as dichlofluanid, tolylfluanid, folpet, fluorfolpet, captan, captofol; benzimidazoles such as carbendazim, benomyl, furathiocarb, fuberidazole, thiophonate-methyl, thiabendazole or salts thereof;

morpholine derivatives such as tridemorph, fenpropimorph, falimorph,

dimethomorph, dodemorph, aldimorph, fenpropidin and their salts with arylsulphonic acids, for example p-toluenesulphonic acid and p-dodecylphenylsulphonic acid;

dithiocarbamate, cufraneb, ferbam, mancopper, mancozeb, maneb, metam, metiram, thiram zeneb, ziram;

benzothiazoles such as 2-mercaptobenzothiazole;

benzamides such as 2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide;

boron compounds such as boric acid, boric esters, borax;

formaldehyde and formaldehyde donor compounds such as benzyl alcohol mono-(poly)-hemiformal, oxazolidines, hexa-hydro-S-triazines, N-methylolchloroacetamide, paraformaldehyde, nitropyrin, oxolinic acid, tecloftalam;

tris-N-(cyclohexyldiazeniumdioxy)-aluminium, N-(cyclohexyldiazeniumdioxy)-tributyltin and K salts, bis-N-(cyclohexyldiazeniumdioxy)-copper;

N-methylisothiazolin-3-one, 5-chloro-N-methylisothiazolin-3-one, 4,5-dichloro-N-octyl-isothiazolin-3-one, N-octyl-isothiazolin-3-one, 4,5-trimethylene-isothiazolinones, 4,5-benzisothiazolinones, N-methylolchloroacetamide;

aldehydes such as cinnamaldehyde, formaldehyde, glutaraldehyde, ß-bromocinnamaldehyde;

thiocyanates such as thiocyanatomethylthiobenzothiazole, methylenebisthiocyanate, etc.;

quaternary ammonium compounds such as benzyldimethyltetradecylammonium chloride, benzyldimethyldodecylammonium chloride, didecyldimethylammonium chloride;

iodine derivatives such as diiodomethyl p-tolyl sulphone, 3-iodo-2-propinyl alcohol, 4-chlorophenyl-3-iodopropargyl formal, 3-bromo-2,3-diiodo-2-propenyl-ethylcarbamate, 2,3,3-triiodoallyl alcohol, 3-bromo-2,3-diiodo-2-propenyl alcohol, 3-iodo-2-propinyl n-hexylcarbamate, 3-iodo-2-propinyl cyclohexylcarbamate, 3-iodo-2-propinyl phenylcarbamate;

phenol derivatives such as tribromophenol, tetrachlorophenol, 3-methyl-4-

chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophen, o-phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol and the alkali metal and alkaline earth metal salts thereof;

microbicides with an activated halogen group, such as chloroacetamide, bronopol, bronidox, tectamers such as 2-bromo-2-nitro-1,3-propanediol, 2-bromo-4'-hydroxy-acetophenone, 2,2-dibromo-3-nitrile-propionamide, 1,2-dibromo-2,4-dicyanobutane, ß-bromo-ß-nitrostyrene;

pyridines such as 1-hydroxy-2-pyridinethione (and their Na, Fe, Mn, Zn salts), tetrachloro-4-methylsulphonylpyridine, pyrimethanol, mepanipyrim, dipyrithion, 1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2(1H)-pyridine;

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

metal salts such as copper hydroxycarbonate, sodium dichromate, potassium dichromate, potassium chromate, copper sulphate, copper chloride, copper borate, zinc fluorosilicate, copper fluorosilicate;

oxides such as tributyltin oxide, Cu_2O, CuO, ZnO;

dialkyldithiocarbamates such as Na and Zn salts of dialkyldithiocarbamates, tetramethylthiuram disulphide, potassium N-methyl-dithiocarbamate;

nitriles such as 2,4,5,6-tetrachloroisophthalodinitrile, disodium cyano-dithioimidocarbamate;

quinolines such as 8-hydroxyquinoline and Cu salts thereof;

mucochloric acid, 5-hydroxy-2(5H)-furanone;

4,5-dichlorodithiazolinone, 4,5-benzodithiazolinone, 4,5-trimethylenedithiazolinone, 4,5-dichloro-(3H)-1,2-dithiol-3-one, 3,5-dimethyl-tetrahydro-1,3,5-thiadiazine-2-thione, N-(2-p-chlorobenzoylethyl)-hexaminium chloride, potassium N-hydroxymethyl-N'-methyl-dithiocarbamate, 2-oxo-2-(4-hydroxy-phenyl)acethydroximic chloride,

phenyl 2-chloro-cyano-vinyl sulphone,

phenyl 1,2-dichloro-2-cyano-vinyl sulphone;

Ag, Zn or Cu-containing zeolites alone or included in polymeric active compounds.

Very particular preference is given to mixtures with azaconazole, bromuconazole, cyproconazole, dichlobutrazol, diniconazole, hexaconazole, metaconazole, penconazole, propiconazole, tebuconazole, methyl (E)-methoximino[α-(o-tolyloxy)-o-tolyl]acetate, methyl (E)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate, methfuroxam, carboxin, fenpiclonil, 4-(2,2-difluoro-1,3-benzodioxol-4-yl)-1H-pyrrol-3-carbonitrile, butenafine, imazalil, N-methyl-isothiazolin-3-one, 5-chloro-N-methylisothiazolin-3-one, N-octylisothiazolin-3-one, benzisothiazolinones, N-(2-hydroxypropyl)-amino-methanol, benzyl alcohol (hemi)-formal, glutaraldehyde, omadine, dimethyl dicarbonate.

Furthermore, highly effective mixtures are also prepared with the following active compounds:

Fungicides:

acypetacs, 2-aminobutane, ampropylfos, anilazine, benalaxyl, bupirimate, quinomethionate, chloroneb, chlozolinate, cymoxanil, dazomet, diclomezine, dichloram, diethofencarb, dimethirimol, diocab, dithianon, dodine, drazoxolon, edifenphos, ethirimol, etridiazole, fenarimol, fenitropan, fentin acetate, fentin hydroxide, ferimzone, fluazinam, fluromide, flusulfamide, flutriafol, fosetyl, fthalide, furalaxyl, guazatine, hymexazol, iprobenfos, iprodione, isoprothiolane, metalaxyl, methasulfocarb, nitrothal-isopropyl, nuarimol, ofurace, oxadiyl, perflurazoate, pencycuron, phosdiphen, pimaricin, piperalin, procymidone, propamocarb, propineb, pyrazophos, pyrifenox, pyroquilon, quintozene, tar oils, tecnazene, thicyofen, thiophanate-methyl, tolclofos-methyl, triazoxide, trichlamide, tricyclazole, triforine, vinclozolin.

Insecticides:

Phosphoric esters such as azinphos-ethyl, azinphos-methyl, α-1(4-chlorophenyl)-4-(O-ethyl, S-propyl)phosphoryloxy-pyrazole, chlorpyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoate, ethoprophos, etrimfos, fenitrothion, fenthion, heptenophas, parathion,

parathion-methyl, phosalone, phoxim, pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, sulfprofos, triazophos and trichlorphon;

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

organosilicon compounds, preferably dimethyl(phenyl)silyl-methyl 3-phenoxybenzyl 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, silafluofen;

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

nitroimines and nitromethylenes such as 1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine (imidacloprid), N-[(6-chloro-3-pyridyl)methyl-]N^2-cyano-N^1-methylacetamide (NI-25);

abamectin, AC 303, 630, acephate, acrinathrin, alanycarb, aldoxycarb, aldrin, amitraz, azamethiphos, Bacillus thuringiensis, phosmet, phosphamidon, phosphine, prallethrin, propaphos, propetamphos, prothoate, pyraclofos, pyrethrins, pyridaben, pyridafenthion, pyriproxyfen, quinalphos, RH-7988, rotenone, sodium fluoride, sodium hexafluorosilicate, sulfotep, sulphuryl fluoride, tar oils, teflubenzuron, tefluthrin, temephos, terbufos, tetrachlorvinphos, tetramethrin, O-2-tert-butyl-pyrimidin-5-yl o-isopropyl phosphorothiate, thiocyclam, thiofanox, thiometon, tralomethrin, triflumuron, trimethacarb, vamidothion, Verticillium Lacanii, XMC, xylylcarb, benfuracarb,

bensultap, bifenthrin, bioallethrin, MERbioallethrin (S)-cyclopentenyl isomer, bromophos, bromophos-ethyl, buprofezin, cadusafos, calcium polysulphide, carbophenothion, cartap, quinomethionate, chlordane, chlorfenvinphos, chlorfluazuron, chlormephos, chloropicrin, chlorpyrifos, cyanophos, beta-cyfluthrin, alpha-cypermethrin, cyophenothrin, cyromazine, dazomet, DDT, demeton-S-methyl sulphone, diafenthiuron, dialifos, dicrotophos, diflubenzuron, dinoseb, deoxabenzofos, diaxacarb, disulfoton, DNOC, empenthrin, endosulfan, EPN, esfenvalerate, ethiofencarb, ethion, etofenprox, fenobucarb, fenoxycarb, fensulphothion, fipronil, flucycloxuron, flufenprox, flufenoxuron, fonofos, formetanate, formothion, fosmethilan, furathiocarb, heptachlor, hexaflumuron, hydramethylnon, hydrogen cyanide, hydroprene, IPSP, isazofos, isofenphos, isoprothiolane, isoxathione, iodfenphos, kadethrin, lindane, malathion, mecarbam, mephosfolan, mercurous, chloride, metam, metarthizium, anisopliae, methacrifos, methamidophos, methidathion, methiocarb, methoprene, methoxychlor, methyl isothiocyanate, metholcarb, mevinphos, monocrotophos, naled, neodiprion, sertifer NPV, nicotine, omethoate, oxydemeton-methyl, pentachlorophenol, petroleum oils, phenothrin, phenthoate, phorate;

Molluscicides:

Fentin acetate, metaldehyde, methiocarb. Niclosamide, thiodicarb, trimethacarb.

Algicides:

Copper sulphate, dichlororphen, endothal, fentin acetate, quinoclamine.

Herbicides:

acetochlor, acifluorfen, aclonifen, acrolein, alachlor, alloxydim, ametryn, amidosulfuron, amitrole, ammonium sulfamate, anilofos, asulam atrazine, aziptrotryne, benazolin, benfluralin, benfuresate, bensulfuron, bensulphide, bentazone, benzofencap, benzthiazuron, bifenox, bilanafos, borax, dichlorprop, dichlorprop-P, diclofop, diethatyl, difenoxuron, difenzoquat, diflufenican,

dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethipin, dimethylarsinic acid, dinitramine, dinoseb, dinoseb, dinoseb acetate, dinoseb, bromacil, bromobutide, bromofenoxim, bromoxynil, butachlor, butamifos, fuenachlor, butralin, butylate, carbetamide, CGA 184927, chlormethoxyfen, chloramben, chlorbromuron, chlorbutam, chlorfurenol, chloridazon, chlorimuron, chlornitrofen, chloroacetic acid, achloropicrin, chlorotoluron, chloroxuron, chlorprepham, chlorsulfuron, chlorthal, chlorthiamid, cinmethylin, cinofulsuron, clethodim, clomazone, clomeprop, clopyralid, cyanamide, cyanazine, dinoseb acetate, dinoterb, diphenamid, dipropetryn, diquat, dithiopyr, diduron, DNOC, PPX-A 788, DPX-E96361, DSMA, eglinazine, endothal, EPTC, esprocarb, ethalfluralin, ethidimuron, ethofumesate, fenoxaprop, fenoxaprop-P, fenuron, flamprop, flamprop-M, flazasulfuron, fluazifop, fluazifop-P, fluchloralin, flumeturon, fluorocgycofen, fluoronitrofen, flupropanate, flurenol, fluridone, flurochloridone, fluoroxypyr, cycloate, cycloxydim, 2,4-D, daimuron, dalapon, dazomet, 2,4-DB, desmedipham, desmetryn, dicamba, dichlorbenil, isoproturon, isouron, isoxaben, isoxapyrifop, lactofen, lenacil, linuron, LS830556, MCPA, MCPA-thioethyl, MCPB, mecoprop, mecoprop-P, mefenacet, mefluidide, metam, metamitron, metazachlor, methabenzthiazuron, methazole, methoproptryne, methyldymron, methylisothiocyanate, metobromuron, fomosafen, fosamine, furyloxyfen, glufosinate, glyphosate, haloxyfop, hexazinone, imazamethabenz, imazapyr, imazaquin, imazethapyr, ioxynil, isopropalin, propyzamide, prosulfocab, pyrazolynate, pyrazolsulfuron, pyrazoxyfen, pyributicarb, pyridate, quinclorac, quinmerac, quinocloamine, quizalofop, quizalofop-P, S-23121, sethoxydim, sifuron, simazine, simetryn, SMY 1500, sodium chlorate, sulfometuron, tar oils, TCA, metolachlor, metoxuron, metribzin, metsulfuron, molinate, monalide, monolinuron, MSMA, naproanilide, napropamide, naptalam, neburon, nicosulfuron, nipyraclofen, norflurazon, orbencarb, oaryzalin, oxadiazon, oxyfluorfen, paraquat, pebulate, pendimethalin, pentachlorophenol, pentaochlor, petroleum oils, phenmedipham, picloram, piperophos, pretilachlor, primisulfuron, prodiamine, proglinazine, propmeton, prometryn, propachlor, tebutam, tebuthiuron, terbacil, terbumeton,

terbuthylazine, terbutryn, thiazafluoron, thifensulfuron, thiobencarb, thiocarbazil, tioclorim, tralkoxydim, tri-allate, triasulfuron, tribenzuron, triclopyr, tridiphane, trietazine, trifluralin, IBI-C4874 vernolate, propanil, propaquizafop, propazine, propham.

The weight ratios of the active compounds in these active compound combinations can be varied within relatively wide ranges.

The active compound combinations preferably receive the active compound of the formula (I) to the extent of from 0.1 to 99.9%, in particular 1 to 75%, and with particular preference 5 to 50%, the remainder up to 100% being made up by one or more of the above-mentioned co-components.

The microbicidal compositions or concentrates which are used to protect the industrial materials contain the active compound or the active compound combination in a concentration of 0.01 and 95% by weight, in particular 0.1to 60% by weight.

The use concentrations of the active compounds or active compound combinations to be employed depends on the nature and occurrence of the microorganisms to be combatted and on the composition of the material to be protected. The optimum quantity for use can be determined by series of tests. In general, the application concentrations are in the range from 0.001 to 5% by weight, preferably from 0.05 to 1.0% by weight, based on the material to be protected.

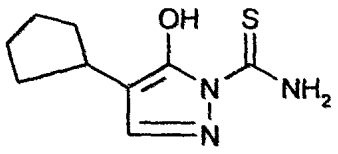
The active compounds and compositions according to the invention make it possible in an advantageous manner to replace the microbicidal compositions which have been available to date by more effective compositions. They exhibit good stability and, advantageously, have a broad spectrum of action.

The Examples which follow serve to illustrate the invention. The invention is

not limited to the Examples.

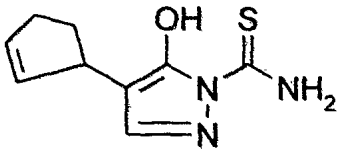
Preparation examples

Example 1



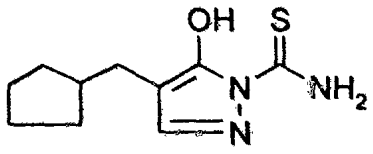
8 g of ethyl 2-formyl-2-cyclopentylacetate, prepared from the commercial 2-cyclopenteneacetic acid by esterification and formylation by known methods, were refluxed for 4 hours in 70 ml of ethanol with 3.9 g of thiosemicarbazide, 4.8 g of potassium tert.-butylate were added, and the mixture was allowed to stand for about 12 hours. Pouring onto ice/10% HCl gives 2.5℃ of the target compound of melting point m.p.: 160℃.

Example 2



Analogously to Example 1, the compound of melting point m.p. 152℃ is obtained.

Example 2



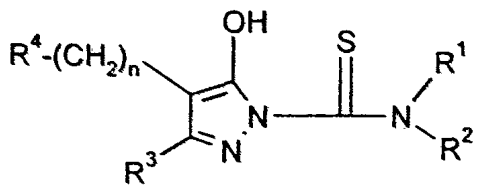
40.7 g of ethyl 3-cyclopentylpropionate are placed in 400 ml of DMF at from 0 to 5℃, and 14.4 g of sodium hydride (80% in oil) are added. After dropwise addition of 200 ml of ethyl formate, the mixture is stirred at 25℃ for 24 h. The mixture is stirred into 1.6 l of 10% HCl, extracted with 800 ml of methylene

chloride and distilled. 19.7 g (41%) are obtained of ethyl 2-formyl-3-cyclopentylpropionate of boiling point 117°C/12 mm.

9.7 g of the oil obtained were heated under reflux in 80 ml of ethanol with 4.47 g of thiosemicarbazide for 4 h, 5.5 g of potassium tert-butylate were added at 25°C, and the mixture was stirred for 24 h. The mixture was then introduced into 250 ml of 10% HCl to give, after recrystallization from ethanol, 5 g (45%) of the target compound of melting point 157°C.

Patent claims

1. Thiocarbamoyl compounds of the formula (I)



(I)

in which

R^1, R^2 and R^3, in each case independently of one another, represent hydrogen or methyl, and

R^4 represents cyclopentyl or cyclopentenyl,

n represents the number 0 or 1,

and their metal salt complexes and acid addition products.

2. Compounds of the formula (I) according to Claim 1, in which R^1, R^2 and R^3 represent hydrogen and n represents the number 0.

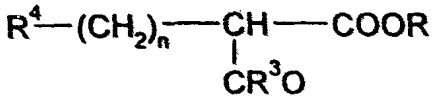
3. Compound of the formula (I) according to Claim 1, in which R^1, R^2 and R^3 represent hydrogen, n represents the number 0, R^4 represents cyclopentyl.

4. Method of protecting industrial materials, characterized in that compounds of the formula (I) according to Claim 1 are applied to the materials to be protected or mixed with them.

5. Composition for protecting industrial materials, containing at least one compound of the formula (I) according to Claim 1.

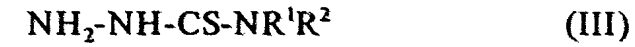
6. Use of compounds of the formula (I) according to Claim 1 for protecting materials against infestation and destruction by unwanted microorganisms.

7. Process for the preparation of compounds of the formula (I), characterized in that formyl acid derivatives of the formula (II)



(II)

in which n, R^3 andR^4 have the meanings given in Claim 1 and R represents methyl, ethyl, n-, i-propyl or n-, i-, s- or t-butyl are reacted with thiosemicarbazides of the formula (III)



(III)

if desired in the presence of a diluent or solvent and/or of a base.

DATED this 28th day of August, 1997.

BAYER AKTIENGESELLSCHAFT

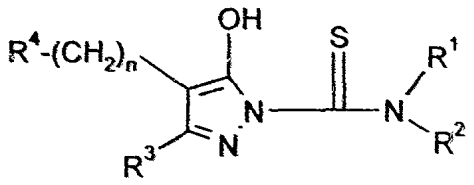
By Its Patent Attorneys

DAVIES COLLISON CAVE

Thiocarbamoyl compounds

Abstract

The application relates to novel thiocarbamoyl compounds of the formula (I)



(I)

in which

R^1, R^2, R^3, R^4 and n have the meaning given in the description.

INTERNATIONAL SEARCH REPORT

Interr ial Applicaton No
PCT/EP 94/02534

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D231/20 A01N43/56 C07C69/716 C07C69/738

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 515 934 (BAYER AG) 2 December 1992 cited in the application see page 15; claims 1,2 see page 13; example 61; table 3	1-6
X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol.104, no.13, 30 June 1982, GASTON, PA US pages 3727 - 3729 R. TAMURA ET AL. 'Palladium(0)-Catalyzed Allylic Alkylation and Amination of Allylnitroalkanes' see page 3728; Table I; Product of third item	8
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 November 1994	-6. 12. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Fink, D

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, no.21, 6 November 1974, LETCHWORTH GB pages 908 - 909 K. YAMADA ET AL. 'Total Synthesis of the Alkaloid (+/-)-Geissoschizine' see page 909; First column;Compound no. (3a)	8
X	BULLETIN DE LA SOCIETE CHIMIQUE DE FRANCE, no.10, 1969, PARIS FR pages 3694 - 3698 R. JACQUIER ET AL. 'Synthèse et équilibre céto-énolique de beta-cétoesters' see page 3698; Table VII; Second item	8
X	JOURNAL OF ORGANIC CHEMISTRY., vol.21, no.9, 16 October 1956, EASTON US pages 1022 - 1024 N.P. BUU-HOI ET AL. 'Benzocoumarins of Steroid-like Structure' see page 1023; First column; Compound no. XII	8
P,X	TETRAHEDRON LETTERS., vol.34, no.52, 24 December 1993, OXFORD GB pages 8509 - 8512 T. OHSHIMA ET AL. 'Manganese(III)-Based Oxidative Free-Radical Reaction of alpha-Allyl-beta-Keto Ester with Molecular Oxygen' see page 8510; Table; Compound no. 5b	8

INTERNATIONAL SEARCH REPORT

information on patent family members

Interr al Application No
PCT/EP 94/02534

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0515934	02-12-92	DE-A- 4117385	03-12-92
		JP-A- 5178839	20-07-93

INTERNATIONALER RECHERCHENBERICHT

Interr ales Aktenzeichen
PCT/EP 94/02534

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 6 C07D231/20 A01N43/56 C07C69/716 C07C69/738

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 6 C07D C07C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	EP,A,0 515 934 (BAYER AG) 2. Dezember 1992 in der Anmeldung erwähnt siehe Seite 15; Ansprüche 1,2 siehe Seite 13; Beispiel 61; Tabelle 3 ---	1-6
X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., Bd.104, Nr.13, 30. Juni 1982, GASTON, PA US Seiten 3727 - 3729 R. TAMURA ET AL. 'Palladium(0)-Catalyzed Allylic Alkylation and Amination of Allylnitroalkanes' siehe Seite 3728; Tabelle I; Produkt des dritten Eintrags --- -/--	8

[X] Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

[X] Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :

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"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
10. November 1994	06. 12. 94

Name und Postanschrift der Internationale Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Fink, D

Formblatt PCT/ISA/210 (Blatt 2) (Juli 1992)

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
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Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Intern ales Aktenzeichen
PCT/EP 94/02534

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