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(54) Title: ANTI-FOULING AGENT

(54) Bezeichnung: ANTIFOULING-MITTEL

(57) Abstract

The description relates to a process and agents for providing protection against fouling of objects which come into contact with sea or brackish water, containing an insecticide as the essential component.

(57) Zusammenfassung

Beschrieben wird ein Verfahren bzw. Mittel zum Schutz vor Bewuchs von Gegenständen, welche mit See- oder Brackwasser in Verbindung kommen, die als wesentliche Komponente ein Insektizid enthalten.

Anti-fouling compositions

The invention relates to a process and compositions for the protection against infestation of articles, especially ships' hulls, screens, nets, constructions, quays and signalling equipment, which come into contact with seawater or brackish water.

Infestation by species of the group Lepadomorpha (goose barnacles), such as various Lepas and Scalpellum species, or by species of the group Balanomorpha (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional resistance of ships and leads as a result, through increased energy consumption and frequent spells in dry dock, to a marked increase in the operating costs.

In addition to infestation by algae, for example Ectocarpus species and Ceramium species, particular importance attaches to infestation by sessile Entomostraca groups, which are classified under the name Cirripedia (cirriped crustaceans).

It is also known that insects can be controlled by means of active substances which act on the metamorphosis from the larval stage to the adult insect (K.H. Büchel, Pflanzenschutz und Schädlingsbekämpfung [Plant protection and pest control], Georg Thieme Verlag, Stuttgart 1977 Farm Chemicals Handbook, Meister Publ. Comp. 1993; The Agrochemical Handbook, Third Edition, Royal Society of Chemistry, Cambridge 1991).

It has now been found that the insecticides, alone or in combination with other active substances, have an outstanding anti-fouling (anti-infestation) effect.

Since conventional anti-infestation compositions have a high content of heavy metals, such as for example tin or copper, it is of advantage that by using the insecticides according to the invention it is now possible to dispense with the use of heavy metal compounds such as, for example, bis(trialkyltin) sulfides, tri-n-butyltin laurate, tri-n-butyltin chloride, copper(I) oxide, triethyltin chloride, tri-n-butyl(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulfide, antimony oxide, polymeric butyl titanate, phenyl-(bis-pyridine)-bismuth chloride, tri-n-butyltin fluoride, manganese

ethylenebisdithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, the zinc salt of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamoylzinc ethylenebisdithiocarbamate, zinc oxide, copper(I) ethylene-bis-dithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides, or substantially to reduce the concentration of these compounds.

The application therefore relates to antifouling compositions containing at least one insecticide.

Preference is given to insecticides having a development-inhibiting action which are capable of inhibiting the metamorphosis from crustacean larvae to the adult stage.

The insecticides which can be employed in accordance with the invention are generally known and can come from different structural classes.

Particularly preferred compounds in the context of the invention are benzoyl ureas such as triflumuron, chlorfluazuron, diflubenzuron, flufenoxuron, flucycloxuron, hexaflumuron, penfluron, teflubenzuron, 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-pyriyl)methyl-]N^2-cyano-N^1-methylacetamides (NI-25); 1-[4-(4-chloro-phenoxy)-3,5-dichlorophenyl]-3-(2,6-difluoro-benzoyl)-ureaandN-[[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)-phenyl]-amino]-carbonyl]-2,6-difluorobenzamide.

Preference is likewise given to development inhibitors from other structural classes, such as for example benzoic acid [2-benzoyl-1-(1,1-dimethylethyl)]-hydrazide, 2,6-dimethoxy-N-[5-]4-(pentafluoroethoxy)-phenyl[-1,3,4-thiadiazol-2-yl]-benzamide, N-cyclopropyl-1,3,5-triazine-2,4-triamine, 2-(4-phenoxyphenoxy)-ethyl ethylcarbamate, 1-(decycloxy)-4-[(6-methoxy-4-hexinyl)-oxy]benzenes, (2-propinyl)-4-methoxybenzoate, fenoxycarb, pyriproxyfen, triarathene, thiapronil, hexythiazox, clofentezine, 4-chloro-5-(6-chloro-3-pyridylmethoxy)-2-(3,4-dichlorophenyl)-pyridazin-3(2H)-ones, buprofezin, hydroprene, kinoprene, methoprene, cycloprate, gusathin, padan, paraxon, tribunil, isomers and triprene.

The active compounds mentioned here are named only by way of example; structurally related active substances having an insecticidal or development-inhibiting action are likewise suitable in principle for anti-fouling use. The following insecticides may be mentioned as preferred examples:

Phosphoric esters, such as azinphos-ethyl, azinphos-methyl, -1(4-chlorophenyl)-4-(O-ethyl, S-propyl)phosphoryloxy-pyrazol, 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, sulprofos, triazophos and trichlorphon;

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

Organosilicon compounds,preferablydimethyl(phenyl)silyl-methyl 3-phenoxybenzyl ethers, such as dimethyl-(4-ethoxyphenyl)-silylmethyl 3-phenoxybenzyl ether, or [(dimethylphenyl)silyl-methyl 2-phenoxy-6-pyridylmethyl etherssuchasfor 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, sulafluofen;

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

abamectin, AC 303, 630, acephate, acrinathrin, alanycarb, aldeoxycarb, aldrin, amitraz, azamethiphos, bacillus thuringiensis, phosmet, phosphamidon, phosphine, prallethrin, propaphos, propetamphos, prothoate, pyraclofos, pyrethrins, pyridaben, pyridafenthion, quinalphos, RH-7988, rotenone, sodium fluoride, sodium hexafluorosilicate, sulfotep, sulfuryl fluoride, tar oils, tefluthrin, temephos, terbufos, tetrachlorovinphos,

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, cadusafos, calcium polysulphide, carbophenothion, cartap, chinomethionate, chlordane, chlorfenvinphos, chlormephos, chloropicrin, chlorpyrifos, cyanophos, beta-cyfluthrin, alphacypermethrin, cyophenothrin, cyromazine, dazomet, DDT, demeton-S-methylsulphon, diafenthiuron, dialifos, DEicrotophos, dinoseb, deoxabenzofos, diaxacarb, disulfoton, DNOC, empenthrin, endosulfan, EPN, esfenvalelrate, ethiofencarb, ethion, etofenprox, fenobucarb, fensulfothion, fipronil, flufenprox, fonofos, formetanate, formoothion, fosmethilan, furathocarb, heptachlor, IPSP, isazofos, isofenphos, isoprothiolane, isoxathion, iodfenphos, Kadethrin, lindane, malthion, mecarbam, mephosfolan, mercurous, chloride, metam, Metarthizum, anisopliae, methacrifos, methamidophos, methidathion, methiocarb, methoxychlor, methyl isothiocyanate, metholcarb, mevinphos, monocrotophos, naled, Neodidprion sertifer NPV, nicotine, omethoate, oxydemeton-methyl, pentachlorophenol, petroleum oils, phenothrin, phenthoate, phorate.

Furthermore, synergistic effects are observed in the case of combinations of two or more of the insecticides mentioned. The development inhibitors according to the invention are preferably also employed in combination with algicides, herbicides, fungicides, molluscicides and/or other anti-fouling active substances, in which case synergistic effects are likewise observed.

Co-components which are employed with preference for the anti-fouling compositions according to the invention are algicides such as diuron, dichlorophen, endothal, fentin acetate, quinoclamine, molluscicides such as fentin acetate, metaldehyde, methiocarb, niclosamide, thiodicarb and trimethacarb, fungicides such as dichlofluanid, tolylfluanid, fluorfolpet, and azoles such as tebuconazole or customary anti-fouling active substances such as 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, tetrabutyldistannoxane, 2-tert-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine,4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulfide, 2,4,6-trichlorophenylmaleimide,2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine,

diodmethylparatrylsulfone, thiabendazol, tetraphenylboron pyridine salt, potassium salt, sodium salt and zinc salt of 2-pyridinethiol 1-oxide.

The anti-fouling compositions according to the invention additionally contain the customary constituents as described, for example, in Ungerer, Chem. Ind. 37 (1985), 730-732 and Williams, Antifouling Marin Coatings 1973, Park Ridge: Noyes 1973.

Customary constituents in anti-fouling coating compositions are, in particular, binders.

Examples of binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene rubbers, butadiene/acrylonitrile rubbers, butadiene/styrene/acrylonitrile rubbers, drying oils, such as linseed oil, asphalt and epoxy compounds, resin esters or modified hard resins in combination with tar or bitumen, chlorinated rubber, chlorinated polypropylene and vinyl resins.

The coating compositions also optionally contain inorganic pigments, organic pigments or dyes, which are preferably insoluble in seawater. The coating compositions may additionally contain materials such as rosin and/or rosin derivatives, in order to enable controlled release of the development inhibitors according to the invention. The coatings can additionally contain plasticizers, modifying agents which influence the rheological properties, and also other conventional constituents. The compounds according to the invention or initially mentioned combinations can also be incorporated in self-polishing anti-fouling systems.

Formulation examples, in which the active substances and/or active-substance combinations described are preferably employed, are described in DE 27 32 145 and EP 05 26 441.

Moreover, it has been found surprisingly that the mixtures of the development inhibitors according to the invention with algicides, herbicides and fungicides can also

be used as wood preservatives. These mixtures are in this case effective in particular against insects, moulds, wood-discolouring fungi and wood-destroying fungi.

The following groups of microorganisms may be mentioned by way of example, but without representing any limitation:

A: Wood-discolouring fungi:

A1: Ascomycetes
Ceratocystis such as Ceratocystis minor

A2: Deuteromycetes:
Aspergillus such as Aspergillus niger
Aureobasidium such as Aureobasidium pullulans
Dactylium such as Dactylium fusarioides
Penicillium such as Penicillium brevicaule 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 spinorus

B: Wood-destroying fungi:

B1: Ascomycetes
Chaetomium such as Chaetomium globosum or
Chaetomium alba-arenulum
Humicola such as Humicola grisea
Petriella such as Petriella setifera
Trichurus such as Trichurus spiralis

B2: Basidiomycetes:

Coniophora such as Coniophora puteana
Coriolus such as Coriolus versicolor
Donkioporia such as Donkioporia expansa
Glenospora such as glenospora graphii
Gloeophyllum such as Gloeophyllum abietinum or
Gloeophyllum adoratum or Gl. Protactum or
Gloeophyllum sepiarium or Gl. trabeum
Lentinus such as Lentinus cyathiformes or
Lentinus edodes such as Lentinus lepideus or
Lentinus grinus or L. squarrolosus
Paxillus such as Paxillus panuoides
Pleurotus such as Pleurotus 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

B3: Deuteromycetes:

Alternaria such as Alternaria tenius

Cladosporium such as Cladosporium herbarum

C. Wood-destroying insects such as

C1: Beetles

Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinus pecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthes rugicollis, Xyleborus

spec. Tryptodendron spec. Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec. Dinoderus minutus

C2: Hymenoptera

Sirex juvencus, Urocerus gigas, Urocerus gigas taignus, Urocerus augur

C3: Termites

Kalotermes flavicollis, Cryptotermers brevis, Heterotermes indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucilugus, Mastotermes darwiniensis, Zootermopsis nevadensis, Coptotermes formosanus.

These wood preservatives generally contain from 0.01 to 50 % by weight of algicides, herbicides and/or fungicides and from 0.00001 to 10 % by weight of insecticides. Furthermore, the wood preservatives generally contain more than 40 % of a mixture of solvent and/or diluent and/or organic-chemical binders or fixative, processing agent, dye, pigment, dye mixture or pigment mixture.

The mixtures contain as algicides for example:
copper sulphate, dichlororphen, endothal, fentin acetate, quinoclamine;

as herbicides for example:
acetochlor, acifluorfen, aclonifen, acrolein, alachlor, alloxydim, ametryn, amidosulfuron, amitrole, ammonium sulfamate, anilofos, asulam atrazine, aziptrotryne, benazolin, benfluralin, benfuresate, bensulfuron, bensulfide, 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, quzizalofop-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, proparil, propaquizafop, propazine, propham.

Preferred mixtures contain fungicides such as hexaconazole, tebuconazole, propiconazole, cyeproconazoleand/or 2-(1-chloro-cyclopropyl)-1-(2-chlorophenyl)-3-1H-(1,2,4-triazol-1-yl)-propan-2-ol, preferably in a weight ratio with respect to the insecticide of from 1:9 to 9:1.

Preferred additional fungicidal co-components are also:

bromuconazole, dichlobutrazol, diniconazole, penconazole, methyl (E)methoximino-[a-(o-tolyloxy)-o-tolyl)]acetate, methyl [E]-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yl-oxy]phenyl}-3-methoxyacrylate, methfuroxam, carboxin, fenpiclonil, 4(2,2-difluoro-1,3-benzodioxol-4-yl)-1H-pyrrole-3-carbonitrile, butenafine and/or 3-iodo-2-propinyl n-butylcarbamate.

In addition it is possible to employ synergistically insecticidal co-components, such as the following insecticides:

phosphoric esters such as azinphos-ethyl, azinphos-methyl, α-1(4-chlorophenyl)-4(O-ethyl, S-propyl)phosphoryloxy-pyrazol, chlorpyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoate. ethoprophos,

etrimfos, fenitrothion, fenthion, heptenophos, parathion, parathion-methl, phosalone, phoxim, pirimiphos-ethyl, pirimiphos-methyl, profenofosm prothiofos, sulfprofos, triazophos and trichlorphon;

Carbamates such as aldicarb, bendiocarb, a-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, sila fluofin

Pyrethroids such as allethrin, alphamethrin, bioresmethrin, byfenthrin, cycloprothrin, cyfluthrin, decamethrin, cyhalothrin, cypermethrin, deltramethrin, alpha-cyano-3–phenyl-2-methylbenzyl-2,2-dimethyl-3-(2-chloro-2-trifluoro-methylvinyl)cyclopropane-

carboxylate, 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^2cyano-N^1-methylacetamide (NI-25),

abamectin, AC 303, 630, acephate, acrinathrin, alanycarb, aldoxycarb, aldrin, ammoniumbifluoride, 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, sulfuryl fluoride, tar oils, teflubenzuron, tefluthrin, temephos, terbufos, tetrachlorovinphos, 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, chinomethionate, chlordane, chlorfenvinphos, chlorfluazuron, chlormephos, chloropicrin, chlorpyrifos, cyanophos, beta-cyfluthrin, alpha-cypermethrin, cyophenothrin, cyromazine, dazomet, DDT, demeton-S-methylsulphone, diafenthiuron, dialifos, dicrotophos, diflubenzuron, dinoseb, dioxabenzofos, diaxacarb, disulfoton, DNOC, empenthrin, endosulfan, EPN, esfenvalerate, ethiofencarb, ethion, etofenprox, fenobucarb, fenoxycarb, fensulfothion, fipronil, flucycloxuron, flufenprox, flufenoxuron, fonofos, formetanate, formothion, fosmethilan, furathiocarb, heptachlor, hexaflumuron, hydramethylnon, hydrogen cyanide, hydroprene, IPSP, isazofos, isofenphos, isoprothiolane, isoxathion, 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;

Particularly preferred insecticides in this context are:

chlorpyrifos, phoxim, silafluofen, cyfluthrin, cypermethrin, deltamethrin, permethrin. imidacloprid, hexaflumuron, lindane.

The synergistic effect of the mixtures is observed in mixing ratios of from 99:1 to 1:99, preferably from 3:1 to 1:3, and with very particular preference in a ratio of 1:1.

In order to obtain further increased actions against wood-destroying fungi, it is also possible to admix the following fungicides, if desired in addition to those mentioned above.

Triazoles:

amitrole, azocyclotin, BAS 480F, bitertanol, difenoconazole, fenbuconazole, fenchlorazole, fenethanil, fluquinconazole, flusilazole, flutriafol, imibenconazole, isazofos, myclobutanil, Opus, paclobutrazol,±)-cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, tetraconazole, triadimefon, triadimenol, triapenthenol, triflumizole, uniconazole;

imidazoles:

imazalil, pefurazoate, prochloraz, triflumizole,2-(1-tert.-butyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol, triazolcarboxanilides, such as 2',6'-dibromo-2methyl-4-trifluoromethoxy-4'-trifluoromethyl-1,3-triazole-5-carboxanilide.

copper salts:

copper sulfate, copper carbonate, copper chloride, copper-ammonia complexes, copper-amine complexes.

zinc salts:

zinc sulfate, zinc carbonate, zinc chloride.

mixed salts:

copper/boron mixtures, copper/chromium/boron mixtures, copper/chromium/arsenic mixtures.

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]phenoxyl]phenyl]-3-methoxyacrylate, methyl (E)-2-[3-[5-(methylpyrimidin-2-yloxy]phenoxy]phenyl]-3-methoxyacrylate,methyl(E)-2-[2-[3-(phenyl-sulfonyloxy)phenoxy]phenyl]-3-methoxyacrylate, methyl(E)-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-methoxyacrylatemethyl (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-methoxyacrylatemethyl (E)-2-[2-[3-(2-fluorophenoxy)phenoxy]phenyl]-3-methoxyacrylate,methyl (E)-2-[2-(3-ethoxyphenoxy)phenyl]-3-methoxyacrylatemethyl (E)-2-[2-(4-tert.butylpyridin-2-yloxy)phenyl]-3-methoxyacrylate, methyl (E)-2-[2-[3-(3-cyanophenoxy)phenoxy]phenyl]-3-methoxyacrylatemethyl(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-(5,6dimethylpyrazin-2-ylmethyloximinomethyl)phenyl]-3-methoxyacrylate, (E) methyl-2-{2-[6-[6-methylpyridin-2-yloxy)pyrimidin-4yloxy)-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)methyloximino methyl)phenyl}-3-methoxyacrylate, (E),(E) methyl-2-{2-[(4-cglorophenyl)-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)methyloximino methyl)phenyl}-3-methoxyacrylate.

Succinate dehydrogenase inhibitors such as:
fenfuram, furcarbanil, cyclafluramide, furmecyclox, Seedvax, metsulfovax, pyrocarbolide, 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)

sulfenamides such as dichlorofluanid, tolylfluanid, folpet, fluorfolpet; captan, captofol,

benzimidazoles, such as carbendazim, benomyl, furathiocarb, fuberidazole, thiophonat-methyl, thiabendazole or salts thereof;

thiocyanates such as thiocyanatomethylthiobenzothiazole, methylene bisthiocyanate; quaternary ammonium compounds such as benzyldimethyltetradecylammonium chloride, benzyldimethyldodecyclammonium chloride, didecyldimethylammonium chloride,

morpholine derivatives such as tridemorph, fenpropimorph, falimorph, dimethomorph, dodemorph; aldimorph, fenpropidin and arylsulfonic salts thereof, for example p-toluenesulfonic acid and p-dodecylphenyl-sulfonic acid,

iodine derivatives such as diiodomethyl p-tolyl sulfone, 3-iodo-2-propinyl alcohol, 4-chlorophenyl 3-iodopropargyl formal, 3-bromo-2,3-diiodo-2-propenyl ethylcarbamate, 2,3,3-triiodallyl alcohol,3-bromo-2,3-diiodo-2-propenyl alcohol, 6-iodo-3-oxo-hex-5-in-ol butylcarbamate, 6-iodo-3-oxo-hex-5-in-ol-phenylcarbamate,3-iod-2-propinyl-n-hexylcarbamate,3-iod-2-propinyl-cyclohexylcarbamate, 3-iodo-2-propinyl phenylcarbamate;

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

glutaraldehyde;
bromine derivatives such as 2-bromo-2-nitro-1,3-propanediol;

isothiazolinones, such as N-methylisothiazolin-3-one, 5-chloro-N-methyl-isothiazolinc-3-one, 4,5-dichloro-N-octyliso-thiazolin-3-one, N-octyl-isothiazolin-3-one;

benzisothiazolinones, 4,5-trimethylene-isothiazolinones;

pyridines or pyrimidines, such as 1-hydroxy-2-pyridinethione (and their Na, Fe, Mn, Zn salts), tetrachloro-4-methylsulfonylpyridine, pyrimethanil, mepanipyrim, dipyrithion;

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

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

dialkyldithiocarbamates, such as Na salts and Zn salts of dialkyldithiocarbamates, tetramethylthiuram disulfide;

dithiocarbamates, cufraneb, ferbam, mancopper, mancozeb, maneb, metam, metiram, thiram zineb, ziram:

nitriles such as 2,4,5,6-tetrachloroisophthalodinitrile, 2,3,5,6-tetrafluoroterephthalodinitrile;

benzthiazoles such as 2-mercaptobenzothiazole;
quinolines, such as 8-hydroxyquinoline and Cu salts thereof;

benzamides, such as 2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide (XRD-563);

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

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

tris-N-(cyclohexyldiazeniumdioxy)-aluminium,N-(cyclo-hexyldiazeniumdioxy)-tributyltin and K salts, bis-N-(cyclohexyldiazeniumdioxy)-copper.

Furthermore, highly active compounds are also produced with the following active substances:

fungicides

acypetacs, 2-aminobutane, ampropylfos, anilazine, benalaxyl, bupirimate, chinomethionate, chloroneb, chlozolinate, cymoxanil, dazomet, diclomezine, dichloram, diethofencarb, dimethirimol, dinocab, 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.

The weight ratios of the active substances in these active-substance combinations can be varied within relatively large ranges.

The active-substance combinations preferably obtain the insecticidal active substance in a proportion of from 0.1 to 99.9%, in particular from 1 to 75%, particularly preferably from 5 to 50%, the remainder to 100% being made up by one or more of the above-mentioned co-components.

The quantity of the compositions and/or concentrates employed is dependent on the nature and incidence of the insects, microorganisms, on the germ count and on the medium. The optimum quantity for use in the application can be determined in each

case by series of tests. In general, however, it is sufficient to employ from 0.001 to 20 % by weight, preferably from 0.05 to 10 % by weight, of the active-substance mixture, relative to the material to be protected.

The active-substance mixture can be used as such, in the form of concentrates or generally customary formulations, such as solutions, suspensions, emulsions or pastes.

The formulations mentioned can be prepared in a manner known per se, for example by mixing the active substances with solvents and/or diluents, emulsifier, dispersant and/or binder or fixative, water repellent, if desired siccatives and UV stabilizers, and, if desired, dyes and pigments, and also further processing auxiliaries.

The solvent and/or diluent is an organic-chemical solvent or solvent mixture and/or an oily or oil-like, relatively non-volatile organic-chemical solvent or solvent mixture and/or a polar organic-chemical solvent or solvent mixture and/or water and at least one emulsifier and/or wetting agent or consists thereof.

As organic-chemical solvents it is preferred to employ oily or oil-like solvents having an evaporation number of more than 35 and a flash point of more than 30°C, preferably more than 45°C. As such relatively non-volatile, water-insoluble, oily and oil-like solvents, use is made of appropriate mineral oils or their aromatic fractions or mineral oil-containing solvent mixtures, preferably white spirit, petroleum and/or alkylbenzene.

Those employed with advantage are mineral oils having a boiling range of from 170 to 220°C, white spirit having a boiling range of from 170 to 220°C, spindle oil having a boiling range of from 250 to 350°C, petroleum or aromatics with a boiling range from 160 to 280°C, turpentine oil and the like.

In a preferred embodiment, use is made of liquid aliphatic hydrocarbons having a boiling range of from 180 to 210°C or high-boiling mixtures of aromatic and aliphatic hydrocarbons having a boiling range of from 180 to 220°C and/or spindle oil and/or monochloronaphthalene, preferably α-monochloronaphthalene.

The organic, relatively non-volatile oily or oil-like solvents having an evaporation number of more than 35 and a flash point of above 30°C, preferably of above 45°C, can be replaced in part by readily or moderately volatile organic-chemical solvents, with the proviso that the solvent mixture likewise has an evaporation number of more than 35 and a flash point of more than 30°C, preferably more than 45°C, and that the insecticide/fungicide mixture is soluble or emulsifiable in this solvent mixture.

In accordance with a preferred embodiment, part of the organic-chemical solvent or solvent mixture is replaced or an aliphatic polar organic-chemical solvent or solvent mixture. Preferably, aliphatic organic-chemical solvents containing hydroxyl and/or ester and/or ether groups are used, such as for example glycol ethers, esters or the like.

As a solvent or diluent, water in particular is also suitable, which may be mixed with one or more of the abovementioned organic-chemical solvents or diluents, emulsifiers and dispersants.

The organic-chemical binders which are used in the context of the present invention are the synthetic resins which are known per se and which are water-dilutable and/or dispersible or emulsifiable or soluble in the organic-chemical solvents employed, and/or binding drying oils, especially binders consisting of or containing an acrylic resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation resin or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenolic resin, hydrocarbon resin, such as indene-coumarone resin, silicone resin, drying vegetable and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

The synthetic resin used as binder can be employed in the form of an emulsion, dispersion or solution. As binders it is also possible to use bitumen or bituminous substances in a proportion of up to 10 % by weight. In addition, dyes, pigments, water repellents, odour correctors and inhibitors and/or anticorrosion agents and the like which are known per se can be employed.

According to the invention, it is preferred for at least one alkyd resin or modified alkyd

resin and/or a drying vegetable oil to be contained as organic-chemical binder in the composition or in the concentrate. It is preferred according to the invention to use alkyd resins having an oil content of more than 45% by weight, preferably from 50 to 68 % by weight.

The binder mentioned can be replaced wholly or partially by a fixative (mixture) or a plasticizer (mixture). These additives are intended to prevent volatilization of the active substances and crystallization or precipitation. They preferably replace from 0.01 to 30 % of the binder (based on 100 % of the binder employed).

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

The chemical basis of fixatives, for example, is polyvinyl alkyl ethers, such as polyvinyl methyl ether, or ketones, such as benzophenone and ethylenebenzophenone, or nitrogen compounds such as alkanolamines and ammonia.

The wood which can be protected by the active-substance mixture according to the invention or by compositions containing the latter is to be understood, for example, to be: constructional timber, wooden beams, railway sleepers, bridge components, jetties, wooden vehicles, crates, pallets, containers, telephone poles, wooden panelling, wooden windows and doors, plywood, chipboard, joinery work or wooden products which are used quite generally in house building or in joinery.

Particularly effective wood protection is obtained by large-scale industrial impregnation processes, such as for example vacuum, double vacuum or pressure processes.

The microbicidal compositions or concentrates used for protecting wood and wooden materials contain the active-substance combination in a concentration of from 0.01 to

95 % by weight, in particular from 0.01 to 60 % by weight.

Preferred compositions (ready-to-use compositions) preferably contain from 0.2 to 3 % by weight, in particular from 0.5 to 2 % by weight, of a mixture of Alsystin with fungicides, herbicides and/or algicides and at least one organic-chemical solvent or solvent mixture and/or an oily or oil-like relatively non-volatile organic-chemical solvent or solvent mixture and/or a polar organic-chemical solvent or solvent mixture and/or water and emulsifier and/or wetting agent and, if desired, from 0 to 5 % by weight, preferably from 0.1 to 3 % by weight, of fixative and/or other additional agents as the residual constituent.

Particularly preferred (ready-to-use) compositions contain 2 to 30 % by weight, preferably from 5 to 22 % by weight, calculated as solids, of a synthetic-resin binder, preferably an alkyd resin and/or a drying vegetable oil, and at least one organic-chemical solvent or solvent mixture and/or an oily or oil-like relatively non-volatile organic-chemical solvent or solvent mixture and/or a polar organic-chemical solvent or solvent mixture and/or water and emulsifier and/or wetting agent and, if desired, siccatives, dyes, colour pigments, anti-settling agents and/or UV stabilizers as the residual constituent.

Concentrates for preserving wood and wooden materials preferably contain from 0.2 to 25 % by weight, preferably from 3 to 8 % by weight, of a mixture of Alsystin with fungicides, herbicides or algicides, from 5 to 40 % by weight, preferably from 10 to 30 % by weight (calculated as solids), of at least one organic-chemical binder and/or fixative or plasticizer and, in addition, an organic-chemical solvent or solvent mixture and/or an oily or oil-like relatively non-volatile organic-chemical solvent or solvent mixture and/or a polar organic-chemical solvent or solvent mixture and/or a penetration auxiliary and/or water and an emulsifier and/or wetting agent as the residual constituent.

The compositions according to the invention make it possible in an advantageous manner to replace the microbicidal compositions so far available by more effective compositions. They exhibit good stability and, advantageously, have a broad spectrum

of action.

Example 1

Instead of the direct testing of balanides, Artemia salina was used for the search for substances having a development-inhibiting effect on Crustaceae.

This saltwater crustacean is highly suitable because of its many larval stages and the already established test systems, which are recognized internationally. Because of the different sensitivities of the nauplius stages, synchronized populations were used for testing (R.B. Sleet and K. Brendel: Homogeneous populations of Artemia nauplii and their potential etc for in vitro testing in developmental toxicology, Teratogenesis, Carcinogenesis and Mtagenesis 5; 41-54 (1985)). The tests were carried out in accordance with the procedure published by Sorgeloos and co-workers (P. Sorgeloos, C.R. van der Wielen and G. Persoone: The use of Artemia nauplii for toxicity tests - a critical analysis, Ecotoxicology and Environmental Sefety 2, 249-255 (1978)).

Rating:	3 =	100 % mortality
	2 =	50 %, <100 % mortality
	1 =	20-50% mortality
	0 =	no action

Table 1 Result for some compounds according to the invention

Active substance	µg of active substance per ml of incubation medium	Rating
Alsystin	10	3
Chlorofluazuron	10	3
Methoprene	100 10	3 1-2
Hydroprene	100	3
Pyriproxylen	100 10	3 3

EXPLANATORY NOTE:

- The foregoing description is substantially as originally lodged - and is retained in this form to preserve the fullness of the initial disclosure. The restricted scope of the invention is as defined in the proposed amended claims immediately below.

- In the expression "at least one insecticide as herein defined" as employed in the proposed amended claims, the insecticide is defined as selected from the following:
  triflumuron, chlorfluazuron, diflubenzuron, flufenoxuron, flucycloxuron, hexaflumuron, penfluron, teflubenzuron, 1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine, N-[(6-chloro-3-pyriryl)methyl-]-N^2-cyano-N^1- methylacetamides (NI-25); 1-[4-(4-chloro-phenoxy)-3,5-dichlorophenyl]-3-(2,6-difluoro-benzoyl)-urea and N-[[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)-phenyl]-amino]-carbonyl]-2,6-difluorobenzamide.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for protecting articles which come into contact with seawater or brackish water characterised in that an anti-fouling composition comprising at least one insecticide as herein defined, said insecticide having a development-inhibiting action which is capable of inhibiting the metamorphosis from crustacean larvae to the adult stage
is applied to the articles, or the articles are treated with the said composition.

2. A process for protecting articles which come into contact with seawater or brackish water characterised in that an anti-fouling composition comprising at least one insecticide as herein defined, said insecticide having a development-inhibiting action which is capable of inhibiting the metamorphosis from crustacean larvae to the adult stage, and at least one algicide, herbicide, fungicide, molluscicide and/or other anti-fouling substances,
is applied to the articles, or the articles are treated with the said composition.

3. A process for protecting wood against infestation by pests characterised in that a wood treatment composition comprising at least one insecticide as herein defined, said insecticide having a development-inhibiting action which is capable of inhibiting the metamorphosis from crustacean larvae to the adult stage, and at least one algicide, herbicide or fungicide,
is applied to the wood, or the wood is treated with the said composition.

DATED this 2nd day of December, 1998.

BAYER AG

By Its Patent Attorneys

DAVIES COLLISON CAVE