

Synergistic Mixtures

The present invention relates to novel synergistically effective mixtures comprising, firstly, triadimefon and/or triadimenol and, secondly, known insecticides, to compositions based on these mixtures and to the use of these mixtures and compositions for protecting industrial materials, in particular wood and timber products, and also wood/plastic composites, against attack, damage and/or destruction by biological pests.

In principle, the person skilled in the art differentiates between structural destruction of wood by basidiomycetes and - if the wood is exposed to an environment with high humidity or soil contact - by mould fungi, and a damage of the wood by wood-destroying insects and termites and an optical impairment of the wood by wood-discolouring fungi. These destructions and impairments of the wood lead inter alia to a reduction of strength and in general to a reduced usefulness of the wood. As a consequence, wood and timber products are protected with fungicides and, if appropriate, insecticides against attack by biological pests, thus prolonging the usefulness and service life of wood and timber products.

Triazoles such as, for example, tebuconazole (cf. EP-A 254857) and cyproconazole (cf. EP-A 554833) are already known to be useful in the protection of wood against wood-destroying basidiomycetes. Their activity in the laboratory test alone is promising; however, under practical conditions, a sufficient protection of the wood is not always ensured, so that, in practical applications, these active compounds have to be combined with metals or metal salts, in particular copper salts. Thus, in practice, triazol fungicides are frequently combined with heavy metal-containing compounds, such as, for example, copper compounds, to provide, in addition to a fungicidal finish, insecticidal protection.

However, the use of heavy metal-containing compositions for the protection of wood is to be considered objectionable for ecological reasons. Accordingly, there was still a need for improved compositions for the protection of wood based on active compounds which ensure a sufficient protection of wood without the addition of heavy metals.

Triadimefon ((±)-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one) and triadimenol ((±)-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol) are known fungicides for the protection of plants against attack by fungi (cf. DE-A 2552967); however, they cannot be employed on their own in the protection of wood since the activity spectrum against the microorganisms relevant in the protection of wood has gaps (cf. EP-A 254857). An activity against insects has not been reported.

Triadimefon or triadimenol are mentioned in some literature references (for example WO 00/71314) as possible mixing partners for various active compounds for the protection of wood; however, these prior-art mixtures still require improvement in many respects and, owing to the activity gaps mentioned above, do hitherto not play any role in the protection of wood.

- 5 Accordingly, there was still a need for an improved active compound mixture based on triadimefon and/or triadimenol.

Surprisingly, it has been found that the combination of triadimefon or triadimenol, which are not effective on their own, with certain insecticides shows a synergistically enhanced activity against biological pests relevant in the protection of wood.

- 10 The present invention provides mixtures comprising synergistically effective amounts of triadimefon and/or triadimenol and at least one insecticide, preferably from the group consisting of phosphoric esters, carbamates, ureas, pyrethroides, pyrroles, phenylpyrazoles, diphenyl ethers, diacylhydrazines and nitromethylenes.

- The mixtures according to the invention show a synergistic activity against biological pests relevant in the protection of wood, i.e. the activity of the synergistic mixtures is, in an unexpected manner, higher than the sum of the activities of the active compounds in question on their own. Thus, an unforeseeable synergistic effect is present, and not just an addition of activities.

- The present invention furthermore provides the use of the synergistic mixtures according to the invention for protecting wood, timber products and wood/plastic composites against biological pests relevant in the protection of wood, in particular against wood-destroying bark beetles and termites.

- The synergistically enhanced activity has the additional advantage that, owing to the lower amount of fungicide to be used in a composition for the protection of wood according to the present invention, not only an economical advantage is obtained, but the safety risk to the environment is also reduced.

Preference is given to mixtures comprising triadimefon and/or triadimenol and at least one insecticide from the group consisting of:

- acetamiprid, allethrin, alpha-cypermethrin, beta-cyfluthrin, bifenthrin, bioallethrin, 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-pyridazinone (CAS-RN: 120955-77-3), chlorfenapyr, chlorpyrifos, clothianidin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, etofenprox, fenoxycarb, fipronil, flufenoxuron, hexaflumuron, imidacloprid, nitenpyram,

permethrin, pyriproxifen, silafluofen, tebufenozide, thiacloprid, thiamethoxam, tralomethrin, triflumuron.

Very preferred are mixtures comprising triadimefon and/or triadimenol and at least one insecticide from the group consisting of:

- 5 bifenthrin, chlorfenapyr, chlorpyrifos, clothianidin, cyfluthrin, cypermethrin, deltamethrin, etofenprox, fipronil, flufenoxuron, imidacloprid, permethrin, thiacloprid, thiamethoxam.

Especially preferred are mixtures comprising triadimefon and/or triadimenol and at least one insecticide from the group consisting of:

- 10 bifenthrin, chlorfenapyr, clothianidin, cyfluthrin, cypermethrin, deltamethrin, imidacloprid, permethrin, thiacloprid.

The weight ratios of the active compounds in the active compound mixture can be varied within a relatively wide range. Preferred are weight ratios of triadimefon and/or triadimenol to at least one of the insecticides mentioned in the range from 1000:1 to 1:1, particularly preferably from 100:1 to 2:1.

- 15 Especially preferred are active compound mixtures according to the invention comprising triadimefon and/or triadimenol and at least one of the insecticides mentioned in a weight ratio of from 50:1 to 5:1.

- 20 The synergistic mixtures according to the invention have a particularly high biocidal, in particular fungicidal and insecticidal, and also termiticidal action, combined with a broad activity spectrum against biological pests which are of relevance in the protection of materials. They are especially effective against wood-destroying basidiomycetes and insects, in particular wood-destroying beetles and termites.

The following microorganisms may be mentioned by way of example, but not by way of limitation:

- 25 *Chaetomium globosum*, *Glenospora graphii*, *Humicola gisea*, *Petriella setifera*, *Trichurus spiralis* and *Lecythophora mutabilis*, and also against *Trichoderma viride*, *Stachybotrys cartarum*, *Chephalosporium* sp. and *Acremonium* sp.

- 30 *Coniophora puteana*, *Coriolus versicolor*, *Gloeophyllum abietinum*, *Gloeophyllum trabeum*, *Lentinus tigrinus*, *Poria monticola*, *Poria placenta*, *Serpula lacrymans*, *Stereum sanguinolentum*, *Tyromyces palustris*

The following wood-destroying insects may be mentioned by way of example, but not by way of limitation:

beetles, such as, for example, *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Ahobium punctatum*, *Xestobium rufovillosum*, *Ptilinus pecticornis*, *Dendrobium pertinex*, *Ernobius mollis*, *Priobium*
 5 *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*;

hymenopterans, such as, for example, *Sirex juvencus*, *Urocera gigas*, *Urocera gigas taignus*,
Urocera augur;

10 termites, such as, for example, *Kaloterms flavicollis*, *Cryptoterms brevis*, *Heteroterms indicola*,
Reticuliterms flavipes, *Reticuliterms santonensis*, *Reticuliterms lucilugus*, *Mastoterms*
darwiniensis, *Zootermopsis nevadensis*, *Coptoterms formosanus*.

Under moist conditions, in addition to mould fungi, bacteria, such as, for example,
Caldocellulosiruptor sp., *Anaerocellum sp.*, *Clostridium* species, such as *Clostridium*
 15 *cellulovorans*, *Clostridium aldrichii*, *Cellulomonas* species, streptomycetes, *Micromonospora sp.*,
Thermomonospora sp., *Microbispora sp.* and also *Cytophaga* and *Sporocytophaga* species may
 also contribute decisively to the degradation of cellulose.

To widen the activity spectrum or to obtain particular effects, the synergistic mixtures according to
 the invention can be combined with at least one further microbically active compound. In
 20 particular, the synergistic mixture may comprise at least one further active compound from the
 group of the fungicides and antibacterially active compounds.

Preference is given in particular to mixtures with one or more of the following microbicidal
 components: dichlofluanid, tolylfluanid, carbendazim, fenpropimorph, bethoxazin, thiocyanato-
 methylthiobenzothiazol, 3-iodo-2-propynyl n-butylcarbamate, zinc pyriithione, copper pyriithione,
 25 N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine, tebuconazole, propiconazole, cyproconazole
 and copper salts.

Especially preferred are mixtures according to the invention comprising, as further component,
 dichlofluanid, tolylfluanid, bethoxazin, 3-iodo-2-propynyl butylcarbamate, zinc pyriithione or
 copper pyriithione, tebuconazole, propiconazole, cyproconazole, copper salts or a mixture of these
 30 components.

Preference is also given to mixtures with one or more of the following bactericidal components:

benzyl alcohol mono-(poly)-hemiformal, ethylene glycol hemiformal, N-(2-hydroxypropyl)amino-methanol, N-methylisothiazolin-3-one, 5-chloro-N-methylisothiazolin-3-one, 4,5-benzisothiazolinones, formaldehyde, glutardialdehyde, benzalkonium chloride, benzyldimethyltetradecylammonium chloride, benzyldimethyldodecylammonium chloride, 3-methyl-4-chlorophenol and 2-benzyl-4-chlorophenol and their alkali metal and alkaline earth metal salts, p-hydroxybenzoic esters, and also o-phenylphenol and their alkali metal and alkaline earth metal salts, bronopol, 2,2-dibromo-3-nitrilepropionamide and silver compounds.

Preference is given to active compound combinations according to the invention with the following bactericides:

benzyl alcohol mono-(poly)-hemiformal, N-methylisothiazolin-3-one, 5-chloro-N-methylisothiazolin-3-one, 4,5-benzisothiazolinones, glutardialdehyde, benzalkonium chloride, bronopol, 3-methyl-4-chlorophenol and also 2-benzyl-4-chlorophenol and the alkali metal and alkaline earth metal salts, o-phenylphenol and their alkali metal and alkaline earth metal salts, and silver compounds.

Very particular preference is given to active compound combinations with the following bactericides:

benzyl alcohol mono-(poly)-hemiformal, 4,5-benzisothiazolinone, benzalkonium chloride, bronopol, 3-methyl-4-chlorophenol and also 2-benzyl-4-chlorophenol and their sodium and potassium salts, o-phenylphenol and the sodium and potassium salts, and silver(I) compounds.

The mixtures according to the invention generally comprise 0.01 – 85 per cent by weight of triadimefon and/or triadimenol, 0.001 – 15 per cent by weight of at least one of the insecticides mentioned and, if appropriate, 0.01 – 80 per cent by weight of at least one further microbicidally active compound, in particular from the group of the active compounds mentioned above.

Preferably, the mixtures according to the invention comprise 0.1 – 40 per cent by weight of triadimefon and/or triadimenol, 0.01 – 5 per cent by weight of at least one of the insecticides mentioned and, if appropriate, 0.05 – 30 per cent by weight of at least one further microbicidally active compound, in particular from the group of the active compounds mentioned above.

The mixtures according to the invention can be prepared in a known manner, for example by grinding and/or mixing and/or granulating the active compounds in a suitable apparatus. It is also possible to dissolve, to disperse or to emulsify the active compounds individually or jointly in a suitable solvent, if appropriate with addition of further auxiliaries and additives, such as, for example, emulsifiers, and, if appropriate, to precipitate them from this solvent by adding further solvent or, if appropriate, removing the solvent to dryness by distillation.

The present invention furthermore provides the use of the active compound mixtures according to the invention for protecting industrial materials, in particular wood, timber products and wood/plastic composites, against attack, damage and/or destruction by biological pests, in particular by fungi and insects.

- 5 Depending on their particular physical and/or chemical properties, the active compounds and the active compound mixtures can be converted into the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and microencapsulations in polymeric substances.

- 10 The present invention furthermore provides microbicidal compositions comprising a synergistically effective amount of triadimefon and/or triadimenol and at least one of the insecticides mentioned and at least one diluent or solvent, if appropriate further auxiliaries and additives and also, if appropriate, at least one of the abovementioned further active compounds

- The formulations can be prepared in a known manner, for example by mixing the active compounds with extenders, i.e. liquid solvents, pressurized liquefied gases and/or solid carriers, if
15 appropriate with the use of surfactants, i.e. emulsifiers and/or dispersants and/or foam formers. If the extender used is water, it is also possible to employ, for example, organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatic compounds, such as xylene, toluene or alkylnaphthalenes, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol, and also ethers and esters thereof, ketones, such
20 as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water. Liquefied gaseous extenders or carriers are to be understood as meaning liquids which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants, such as halogenated hydrocarbons, and also butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example
25 natural ground minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and silicates. Suitable solid carriers for granules are: for example crushed and fractionated natural minerals, such as calcite, marble, pumice, sepiolite, dolomite, and also synthetic granules of inorganic and organic meals and also granules of organic material, such as sawdust, coconut shells,
30 maize cobs and tobacco stalks. Suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and also protein hydrolysates. Suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

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

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

- 10 The formulations generally comprise between 0.1 and 95 per cent by weight of active compound combination, preferably between 0.5 and 50 per cent by weight.

The microbicidal compositions or concentrates used for protecting the industrial materials comprise the active compound or the active compound combination in a concentration of from 0.005 to 95 per cent by weight, in particular from 0.1 to 50 per cent by weight.

- 15 The application concentrations of the active compounds or the active compound combinations to be used depend on the nature and the occurrence of the microorganisms to be controlled and on the composition of the material to be protected. The optimum amount to be employed can be determined by test series. In general, the application concentrations are in the range of from 0.001 to 10 per cent by weight, preferably from 0.01 to 5 per cent by weight, based on the material to be protected.

- 20 By using the active compound combinations or compositions according to the invention, it is possible to replace, in an advantageous manner, the microbicidal compositions hitherto available by more effective compositions. The compositions according to the invention have good stability and, in an advantageous manner, a broad activity spectrum.

- 25 Wood, timber products and wood/plastic composites which can be protected by the active compound mixtures according to the invention or compositions comprising them are, by way of example: construction timber, wooden beams, railway sleepers, bridge components, jetties, vehicles made of wood, boxes, palettes, containers, telephone poles, wood lagging, windows and doors made of wood, ply wood, medium density fibre board (MDF), chip board, oriented strand board (OSB), waferboard, laminated veneer lumber (LVL) or timber products which, quite generally, are used in the construction
30 of houses or building joinery, and also wood/plastic composites.

The active compounds can be applied individually or as a finished mixture, in the form of their formulations or the use forms prepared therefrom, such as ready-to-use solutions, suspensions,

pastes, soluble powders. Application is in a customary manner by treating the industrial material with the individual active compounds or the finished mixture or with a formulation or use form prepared therefrom. If the materials to be protected are wood, timber products or wood/plastic composites, the application is by customary methods, for example by spraying, painting, dipping, industrial impregnation processes, for example vacuum, double vacuum or pressure processes, and by addition to the glue or by addition via the compounder or mixer, and also via master batches.

A particularly effective protection of wood is achieved by industrial impregnation processes, for example by vacuum, double vacuum or pressure processes.

The present invention furthermore provides a method for protecting wood and timber products, where the wood or the timber product is impregnated with a synergistically effective amount of triadimefon and/or triadimenol and at least one of the insecticides mentioned and at least one diluent or solvent, if appropriate further auxiliaries and additives and also, if appropriate, at least one further active compound mentioned, by painting, spraying, vacuum, double vacuum, pressure or dipping processes. Here, the active compounds triadimefon and/or triadimenol and at least one of the insecticides mentioned can be employed either individually or as a finished mixture.

Biological Examples

The synergism was then determined using the method described by Kull et al. (F.C. Kull, P.C. Eismann, H.D. Sylvestrowicz, R.L. Mayer, Applied Microbiology 9, 538 to 541, 1961). Here, the following relationships apply:

5 $QA/Qa + QB/Qb = SI$

Qa = Concentration of substance A which corresponds to the MIC

Qb = Concentration of substance B which corresponds to the MIC

QA = Concentration of substance A in the concentration of A/B which suppresses microbial growth

10 QB = Concentration of substance B in the concentration of A/B which suppresses microbial growth

SI = Synergistic index

$SI = 1$ means additivity

$SI > 1$ means antagonism

15 $SI < 1$ means synergism

Example 1:

Various concentrations of chlorfenapyr (A), triadimefon (B) and mixtures of the two active compounds mentioned were tested against the wood-destroying basidiomycete *Gloeophyllum trabeum*. Mycel pieces were punched out of a colony of the wood-destroying organism and
20 incubated at 26°C on a nutrient agar which contained mould extract and peptone. Subsequently, the radial growth of the fungi threads with and without added active compound was compared. The stated minimum inhibitory concentration is the lowest concentration of active compound in succession at which the radial growth is suppressed completely.

Active compound	Mixing ratio	MIC [ppm]	SI
A		> 20	

A:B	1:1	10	0.5
A:B	4:6	10	0.5
A:B	3:7	10	0.5
A:B	2:8	10	0.5
B		20	

The determined index data show that the combination according to the invention of triadimefon with chlorfenapyr has, over wide ranges, a pronounced synergism.

Example 2:

- 5 Various concentrations of permethrin (A), triadimefon (B) and mixtures of the two active compounds mentioned were tested against the wood-destroying basidiomycete *Lentinus tigrinus*. Mycel pieces were punched out of a colony of the wood-destroying organism and incubated at 26°C on a nutrient agar which contained mould extract and peptone. Subsequently, the radial growth of the fungi threads with and without added active compound was compared. The stated
- 10 minimum inhibitory concentration is the lowest concentration of active compound in succession at which the radial growth is suppressed completely.

Active compound	Mixing ratio	MIC [ppm]	SI
A		>> 20	
A:B	4:6	10	0.8
A:B	3:7	6	0.51
A:B	2:8	6	0.54
A:B	1:9	6	0.57
B		10	

The determined index data show that the combination according to the invention of permethrin with triadimefon has, over wide ranges, a pronounced synergism.

Example 3:

Various concentrations of thiacloprid (A), triadimefon (B) and mixtures of the two active compounds mentioned were tested against the wood-destroying basidiomycete *Poria placenta*. Mycel pieces were punched out of a colony of the wood-destroying organism and incubated at 26°C on a nutrient agar which contained mould extract and peptone. Subsequently, the radial growth of the fungi threads with and without added active compound was compared. The stated minimum inhibitory concentration is the lowest concentration of active compound in succession at which the radial growth is suppressed completely.

Active compound	Mixing ratio	MIC [ppm]	SI
A		>> 20	
A:B	1:1	3	0.4
A:B	4:6	3	0.66
A:B	3:7	3	0.74
A:B	2:8	3	0.83
A:B	1:9	3	0.92
B		3	

The determined index data show that the combination of thiacloprid with triadimefon has, over wide ranges, a pronounced synergism.

Formulation examples:

15 **Example 1** (Technical-grade concentrate):

10% of triadimefon, 0.5% of permethrin, 24.5% of texanol, 15% of ethoxylated caster oil, 15% of sodium rhizinate/sodium dodecylbenzenesulphonate preparation, 35% of dimethyl fatty amide

Example 2 (Technical-grade concentrate):

- 5 15% of triadimefon, 0.5% of chlorfenapyr, 22.5% of Texanol, 13% of sodium rhizinate/sodium dodecylbenzene sulphonate preparation, 14% of fatty acid polyethylene glycol ether ester, 35% of dimethyl fatty amide

Example 3 (Technical-grade concentrate):

- 10 7.5% of triadimenol, 0.25% of bifenthrin, 16.25% of sodium rhizinate/sodium dodecylbenzene sulphonate preparation, 27% of ethoxylated caster oil, 49% of Texanol

Example 4 (Emulsifiable concentrate):

5.0% of triadimefon, 0.1% of thiacloprid, 2.9% of sodium rhizinate/sodium dodecylbenzene sulphonate preparation, 27% of fatty acid polyethylene glycol ether ester, 65% of Texanol

- 15 **Example 5** (Composition for impregnation):

0.3% of triadimenol, 0.01% of deltamethrin, 15% of Worléesol 31A (binder concentrate), 0.8% of Additol VXW 4940, 3.0% of ethoxylated caster oil, 3.0 % of Texanol, 77.89% of water

Example 6 (Composition for impregnation):

- 20 0.4% of triadimefon, 0.01% of cyfluthrin, 4.0% of alkyd resin, 4.0% of Dowanol DPM, 91.59% of white spirit

Example 7 (Primer):

0.2% of triadimefon, 0.2% of tebuconazole, 0.4% of tolylfluanid, 0.05% of cypermethrin, 6% of Dowanol DPM, 10% of alkyd resin, 83.2% of white spirit

Patent Claims

1. Mixtures, comprising synergistically effective amounts of triadimefon and/or triadimenol and at least one insecticidally active compound.
2. Mixtures according to Claim 1, characterized in that the insecticidally active compound is selected from the group consisting of phosphoric esters, carbamates, ureas, pyrethroids, pyrroles, phenylpyrazoles, diphenyl ethers, diacylhydrazines and nitromethylenes.
3. Mixtures according to at least one of Claims 1 and 2, characterized in that the insecticidally active compound is selected from the group consisting of: acetamiprid, allethrin, alpha-cypermethrin, beta-cyfluthrin, bifenthrin, bioallethrin, 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-pyridazinone (CAS-RN: 120955-77-3), chlorfenapyr, chlorpyrifos, clothianidin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, etofenprox, fenoxycarb, fipronil, flufenoxuron, hexaflumuron, imidacloprid, nitenpyram, permethrin, pyriproxifen, silafluofen, tebufenozide, thiacloprid, thiamethoxam, tralomethrin, triflumuron.
4. Mixtures according to at least one of Claims 1 to 3, characterized in that the insecticidally active compound is selected from the group consisting of: bifenthrin, chlorfenapyr, chlorpyrifos, clothianidin, cyfluthrin, cypermethrin, deltamethrin, etofenprox, fipronil, flufenoxuron, imidacloprid, permethrin, thiacloprid, thiamethoxam.
5. Mixtures according to at least one of Claims 1 to 4, characterized in that the weight ratio of triadimefon and/or triadimenol to insecticidally active compound is from 1000:1 to 1:1.
6. Mixtures according to at least one of Claims 1 to 5, characterized in that they comprise at least one further active compound from the group of the fungicides and antibacterially active compounds.
7. Mixtures according to at least one of Claims 1 to 6, characterized in that they comprise 0.01 – 85 per cent by weight of triadimefon and/or triadimenol, 0.001 – 15 per cent by weight of at least one insecticidally active compound and, if appropriate, 0.01 – 80 per cent by weight of at least one further microbically active compound from the group of the fungicides and antibacterially active compounds.
8. Microbicidal compositions, comprising a synergistically effective amount of triadimefon and/or triadimenol and at least one insecticidally active compound and at least one diluent or solvent, if appropriate further auxiliaries and additives and also, if appropriate, at least

one further active compound from the group of the fungicides and antibacterially active compounds.

- 5 9. Use of an active compound mixture according to at least one of Claims 1 to 7 or of a composition according to Claim 8 for protecting industrial materials, in particular wood, timber products and wood/plastic composites, against attack, damage and/or destruction by biological pests.
- 10 10. Method for protecting wood and timber products, characterized in that the wood or the timber product is impregnated with synergistically effective amounts of triadimefon and/or triadimenol and at least one insecticidally active compound and also at least one diluent or solvent, if appropriate further auxiliaries and additives, and also, if appropriate, at least one further active compound from the group of the fungicides and antibacterially active compounds, by painting, spraying, vacuum, double vacuum, pressure or dipping processes.
11. Industrial materials, comprising synergistically effective amounts of triadimefon and/or triadimenol and at least one insecticidally active compound.