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(54) **ASSOCIATIONS DE SUBSTANCES ACTIVES**
(54) **COMBINATIONS OF ACTIVE SUBSTANCES**

(57) L'invention concerne l'utilisation d'associations de substances actives comprenant des substances actives phénoliques avec des composés azoles pour la conservation de cuirs et peaux d'animaux.

(57) The present application concerns the use of active substance combinations of phenolic agents and azole compounds for use in preserving animal hides and leather.

Combinations of active compounds

Abstract

The present application relates to the use of combinations of active compounds composed of phenolic active compounds and azole compounds for the preservation of animal hides and leather.

Active compound combinations

The present application relates to the use of active compound combinations of phenolic active compounds with azole compounds for the preservation of animal hides and leather.

It is known that phenol derivatives and mixtures or formulations thereof can be used as products for the protection of materials in leather production. However, it has emerged that these compounds, used alone or in combination, do not provide sufficient protection against infections with microbes when storing hides and leather for a prolonged time.

Surprisingly, it has now been found that benzimidazoles, imidazoles, triazoles and/or morpholine derivatives in combination with phenolic compounds allow outstanding, long-term protection of the animal skins and leather during production and storage.

The invention therefore relates to the use of a combination of at least one triazole and/or at least one benzimidazole and/or at least one imidazole and/or at least one morpholine derivative with at least one phenolic compound for the protection of animal hides and leather during production and storage.

Suitable phenolic active compounds are preferably phenol derivatives, such as tribromophenol, trichlorophenol, tetrachlorophenol, nitrophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophene, o-phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol, 2,4-dichloro-3,5-dimethylphenol, 4-chlorothymol, chlorphen, triclosan, fentichlor and their ammonium, alkali metal and alkaline earth metal salts, and also their mixtures.

Suitable triazole compounds are preferably triazoles such as amitrole, azocyclotin, azaconazole, BAS 480F, bitertanol, cyproconazole, difenoconazole, fenbuconazole, fen-chlorazole, fenethanil, fluquinconazole, flusilazole, flutriafol, hexaconazole, imiben-conazole, isazofos, myclobutanil, metconazole, epoxyconazole, paclobutrazole, penconazole, propiconazole, cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cyclo-heptanol, tebuconazole, 2-(1-tert-butyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol, tetraconazole, triadimefon, triadimenol, triapenthenol, triflumizole,

triticonazole, uniconazole and their metal salts and acid adducts, and also their mixtures.

Suitable imidazoles are preferably compounds such as imazalil, pefurazoate, prochloraz, triflumizole, bifonazole, canesten, fluotimazole, miconazole, econazole, isoconazole, sulconazole and their metal salts and adducts and also their mixtures.

Suitable benzimidazoles are preferably compounds such as methyl benzimidazolyl-carbamate (MBC), benomyl, fuberidazole and thiabendazole.

Suitable morpholine derivatives are preferably compounds such as tridemorph, aldimorph, fenpropimorph, amorolfine and dodemorph.

Combinations of 3,5-dimethyl-4-chlorophenol, 2-benzyl-4-chlorophenol, p-chloro-m-cresol (CMC) and/or o-phenylphenol (OPP) as phenolic components and azoles such as tebuconazole, propiconazole, azaconazole, cyproconazole, hexaconazole, epoxyconazole and/or imazalil as further components are preferred.

Combinations of the abovementioned preferred phenols with benzimidazoles such as MBC, benomyl and/or aldimorph or tridemorph are furthermore preferred.

Combinations of CMC and/or OPP with tebuconazole and/or propiconazole are particularly preferred.

Also preferred combinations are combinations of OPP and/or CMC with MBC.

In particular, a mixture comprising CMC, OPP and tebuconazole is used.

The mixing ratios of the phenolic component to the other active compounds is generally 5 to 200, preferably 10 to 100, in particular 12 to 50, parts by weight to 1 part by weight.

The ratio of the phenolic compounds to each other can be varied within wide limits and is preferably 1:1 to 1:5 in the case of a mixture of OPP and CMC.

The abovementioned mixtures of the active compounds are generally employed in the form of formulations. The use concentration is preferably 0.1 to 1% of mixture of active compounds based on the hides or leather to be protected.

In the compositions resulting from the formulation, the mixture of active compounds preferably amounts to 10 to 50%. The compositions comprise 10 to 30% of alkali metal hydroxides and/or alkaline earth metal hydroxides, 1 to 20% of ionic and/or non-ionic emulsifiers, 5 to 30% of organic solvents such as, in particular, glycols, ketones, glycol ethers, alcohols such as ethanol, methanol, 1,2-propanediol, n-propanol or 2-propanol, and 0-0.5% of perfumes and odoriferous substances as further components. The remainder to 100% is water.

The mixtures of active compounds and the compositions which can be prepared therefrom are used according to the invention in the production of leather for protecting animal hides against infection with, and damage caused by, micro-organisms. The fact that representatives of the species Aspergillus niger, Aspergillus repens, Hormoconis resinae, Penicillium glaucum and Trichoderma viride, Penicillium species such as P. citrinum or P. glaucum, Paecilomyces variotii, Cladosporium species, and Mucor species, such as Mucor mucedo, Rhizopus species, such as Rhizopus oryzae and Rhizopus rouxii can be suppressed completely and long-term is of particular interest.

The examples which follow are intended to illustrate the invention and are not limited thereto.

Example 1

Agar plates are inoculated with conidia of the species Aspergillus niger, Aspergillus repens, Penicillium glaucum, Trichoderma viride and Hormoconis resinae. Pieces of wet chrome leather (wet blue) which have been treated with mixture I and mixture II are subsequently placed on the agar, and the samples are incubated for 28 days at 20 to 30°C and a relative atmospheric humidity of 95%.

Mixture I	Mixture II
30 parts by weight of p-chloro-m-cresol	23 parts by weight of p-chloro-m-cresol
13 parts by weight of o-phenylphenol	10 parts by weight of o-phenylphenol
	2 parts by weight of tebuconazole

In the case of the wet blues preserved with mixture I, mould had grown on the test bodies after an incubation time of only 10 days. In the case of mixture II, no infection is observed after an incubation time of 28 days.

Patent Claims

1. Use of a mixture of at least one triazole and/or at least one benzimidazole and/or at least one imidazole and/or at least one morpholine derivative with at least one phenolic compound in the production of leather for protecting animal hides and leather against microbial infection.

2. Use as claimed in Claim 1, characterized in that the microbicidal compositions are selected from amongst tribromophenol, tetrachlorophenol, nitrophenol, 3-methyl-4-chlorophenol, 3,5-dimethyl-4-chlorophenol, phenoxyethanol, dichlorophen, o-phenylphenol, m-phenylphenol, p-phenylphenol, 2-benzyl-4-chlorophenol and their alkali metal salts and alkaline earth metal salts and also their mixtures; amitrole, azocyclotin, azaconazole, BAS 480F, bitertanol, cyproconazole, difenoconazole, fenbuconazole, fenchlorazole, fenethanol, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, isazofos, myclobutanil, metconazole, epoxyconazole, paclobutrazole, penconazole, propiconazole, cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, tebuconazole, 2-(1-tert-butyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol, tetraconazole, triadimefon, triadimenol, triapenthenol, triflumizole, triticonazole, uniconazole and their metal salts and acid adducts and also their mixtures; imazalil, pefurazoate, prochloraz, triflumizole, bifonazole, canesten, fluotimazole, miconazole, econazole, isoconazole, sulconazole and their metal salts and acid adducts and also their mixtures; benomyl, fuberidazole, thiabendazole and their metal salts and acid adducts; tridemorph, aldimorph, fenpropimorph, amorolfine and dodemorph.

3. Use according to Claim 1, characterized in that combinations of 3,5-dimethyl-4-chlorophenol, 2-benzyl-4-chlorophenol, p-chloro-m-cresol (CMC) and/or o-phenylphenol (OPP) are used as phenolic components and tebuconazole, propiconazole, azaconazole, hexaconazole, epoxyconazole, imazalil, MBC, benomyl, aldimorph and/or tridemorph as further components.

4. Use according to Claim 1, characterized in that combinations of CMC and/or OPP with tebuconazole and/or propiconazole are employed.

5. Use according to Claim 1, characterized in that a mixture comprising CMC, OPP and tebuconazole is used.

6. Use according to Claim 1, characterized in that the mixing ratio of the phenolic component to the other active ingredients is generally 5 to 200 parts by weight to 1 part by weight.

7. Use according to Claim 1, characterized in that combinations of CMC and/or OPP with MBC are used.

8. Microbicidal compositions comprising a mixture according to one of Claims 1 to 7 and the components conventionally used for compositions for the protection of animal hides and leather.

9. A method of protecting animal hides and leather against microbial infection, characterized in that the hides or the leather are (is) treated with a mixture according to any of Claims 1 to 7.

10. Use of a composition according to Claims 1 to 7 for the preparation of compositions for the protection of animal hides and leather against microbial infection.