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(54) **Title:** SYNERGISTIC FUNGICIDAL AND INSECTICIDAL COMPOSITIONS COMPRISING A QUILLAY EXTRACT AND AN ACACIA NEGRA EXTRACT

(57) **Abstract:** The present invention relates to synergistic fungicidal and insecticidal mixtures, comprising at least a Quillay extract and an Acacia negra extract as defined in the description, and to compositions comprising these mixtures.

Synergistic fungicidal and insecticidal compositions comprising a Quillay extract and an Acacia negra extract

Description

The present invention relates to mixtures comprising, as active components a water-based Quillay extract and a water-based Acacia negra extract.

Quillaja saponaria, Molina, the soapbark tree, is an evergreen tree in the family Quillajaceae, native to warm temperate central Chile.

Extracts of the barksoap tree *(Quillaja saponaria* Mol.) are well-known (CAS-No. 68990-67-0) and safe cosmetic, food and pharmaceutical additives e.g. used as adjunvant in vaccine solutions. Such soapbark tree, also called China bark extract, Murillo bark extract, Panama bark extract, Quillai extract, Quillaia extract or Quillay extract, generally comprises the milled inner bark, wood, small stems, small branches and/or leaves of the soapbark tree and contains saponins, polyphenols and other ingredients.

Quillay's biocide activity has been previously described for instance in Apablaza et al (Fitopatologia 39, 2004, 144-149), where experiments are described about the control of cucurbitaceae oidium *[Erysiphe cichoracearum* DC. ex Merat and *Sphaerotheca fuliginea* (Schlecht ex Fr.) Poll] with the saponin-containing water-based Quillay extracts QL 1000 and QL 30B; said experiments provided satisfactory results in cucumber and pumpkins.

It should be noted in this respect that Quillay extract-based products (e.g. QL Agri 35, BASF SE) correspond to a 100% natural Quillay-based extract nematicide, especially indicated for the control of nematodes in vineyards and citric trees (Eur J Plant Pathol 130, 587- 596 (201 1)). It was further known that water-based Quillay extracts have antifungal activity against plant pathogenic fungal species such as *Gaeumannomyces graminis* (US 201 1/01900123 A1) and *Botrytis cinerea* (EP 2 106 698 A2).

Quillay extracts based on water extraction are commercially available e.g. under the trademark QL Agri 35 produced by Natural Response S.A., Quilpue, Chile, and marketed by Desert King Chile and BASF SE. Usually the extraction step takes place at temperatures between 5°C and 95°C, preferably at 20°C to 90°C, even more preferably aat 40°C to 90°C. It contains a minimum of 6 % of saponins, 15 % polyphenols and about 35 °Brix. One degree Brix is 1 gram of sucrose in 100 grams of solution and represents the strength of the solution as percentage by weight (% w/w) (strictly speaking, by mass). If the solution contains dissolved solids other than pure sucrose, then the °Brix is only approximate the dissolved solid content. Further suitable Quillay extracts are commercially available (trademarks QL 1000, QP 1000, QL Ultra, QL 30B and Vax Sap, produced by Natural Response S.A. Quilpue, Chile).

In the EP 1 867 230 A2, a natural product is described recording the antifungal and growth promoting effect in order to improve the productivity of plants, which comprises at least two active substances derived from a) quillay *(Quillaja saponaria),* b) quinoa *(Chenopodium quinoa),* c) tea *(Camellia spp.,* e.g. *Camellia oliefera, Camellia sinensis, Camellia chekiangoleosa, C. drupifera, C. reticulata* or *C. japonica),* and d) a saponin contained in a plant material other than (a), (b) or (c), but it does not mention any extract derived from *Acacia negra* in this composition.

Acacia negra is a fast-growing leguminous perennial tree or shrub i.a. native to South Western Australia but has been introduced nearly all over the world. Common names for it include *Acacia mearnsii, Acacia melanoxylon,* Australian Blackwood, Black Wattle, *Acacia-negra,* Australian Acacia, *Australische Akazie, Swartwattel, Uwatela, Acacia decurrens,* Acacia bark, Early black wattle, Green wattle, Sydney wattle, Wattle bark, Tan wattle, Golden teak, Brazilian teak. The tree's bark contains about 37-40% tannin compounds. The tannin compounds extracted from the bark of Acacia negra are commonly used in the production of soft leather. A range of other products, such as resins, thinners and adhesives, can also be made from bark extracts.

Various types of Acacia negra extracts are commercially available from SETA S/A, Estancia Velha - RS, 93600-000, Brazil, mainly for water and leather treatment.

It was further known that plant extracts such as the Acacia negra extract have repellant activity against exterminate termites (WO 2006/0210264).

Practical agricultural experience has shown that the repeated and exclusive application of an individual active compound in the control of harmful fungi or insects or other pests leads in many cases to a rapid selection of those fungus strains or pest isolates which have developed natural or adapted resistance against the active compound in question. Effective control of these fungi or pests with the active compound in question is then no longer possible.

To reduce the risk of the selection of resistant fungus strains or insect isolates, mixtures of different active compounds are nowadays conventionally employed for controlling harmful fungi or insects or other pests. By combining active compounds or active biological extracts having different mechanisms of action, it is possible to ensure successful control over a relatively long period of time.

It is an object of the present invention to provide, with a view to effective resistance management and effective control of phytopathogenic harmful fungi, insects or other pests, at application rates which are as low as possible, compositions which, at a reduced total amount of active compounds applied, have improved activity against the harmful fungi or pests (synergistic mixtures) and a broadened activity spectrum, in particular for certain indications.

We have accordingly found that this object is achieved by the mixtures and compositions defined herein, comprising a water-based Quillay extract and a water-based Acacia negra extract.

Thus, the present invention relates to mixtures comprising, as active components

1) a water-based Quillay extract;

and

2) a water-based Acacia negra extract

in a synergistically effective amount.

Moreover, the invention relates also to a method for controlling phytopathogenic harmful fungi, insects or other pests or for improving the health of the plants using mixtures of a Quillay extract and an Acacia negra extract and to the use of the components 1) and 2) as defined herein for preparing such mixtures, and to compositions and seed comprising these mixtures.

Moreover, we have found that simultaneous, that is joint or separate, application of a Quillay extract and an Acacia negra extract or successive application of a Quillay extract and an Acacia negra extract allows better control of harmful fungi than is possible with the individual compounds alone (synergistic mixtures). Furthermore, synergistic effects in relation with the

insecticidal and/or herbicidal action have been found with the inventive mixtures.

The terms " water-based Quillay extract" and " water-based Acacia negra extract" are to be understood that the extract of the material of the respective plant species is obtained by solid-liquid extraction wherein the liquid is water or a water-based solution comprising water-soluble solvents (such as alcohols, e.g. ethanol, propanol, butanol, benzylalcohol, cyclohexanol; glycols; DMSO; ketones, e.g. cyclohexanone; esters) and/or other auxiliaries (such as liquid carriers, solid carriers or fillers, surfactants, dispersants, emulsifiers, wetters, adjuvants, solubilizers, penetration enhancers, protective colloids, adhesion agents, thickeners, humectants, bactericides, anti-freezing agents, anti-foaming agents, tackifiers and binders).

The active component 1) of the mixture can be found on the basis of the soap bark tree *(Quillaja saponaria),* from wood, branches and the bark of the tree, which are milled. Quillaja can as well be used as an extract of flakes from branches and the bark from the soap bark tree. The extract can be based on pure water extraction or a blend of water and alcohol as a means of extraction. The extract can be used as a liquid product or it can be spray dried. The above-mentioned commercially available extracts are also suitable.

According to one embodiment, the Quillay extract contains a minimum of 2 % of saponins and 5 % polyphenols and at least 15 °Brix; more preferably a minimum of 4 % of saponins and 10 % polyphenols and at least 25 °Brix.

The active component 2) of the mixture, the Acacia negra extract is usually obtained from the bark of Acacia negra *(Acacia mearnsii)* trees. Prior to extraction, the barks of Acacia negra may be advantegously classified according to their moisture (preferably barks in good conservation conditions are used). The extraction is performed in a counter flow extraction process employing water as solvent. During this process the follwing variables are carefully controlled: time of extraction, pressure and temperature. After this stage the so-called TBC extract is obtained (tannin of low concentration), comprising approximately 12 % (w/w) total solids. Preferably, the bark of Acacia negra is pricked in a pricking type drum and the extraction of the tannin is carried out in an autoclave at about 90°C to 130°C for 1 to 10 hours. In a next stage, the TBC extract is passed through an evaporation system under vacuum where there is turned into the so-called TAC extract (tannin of high concentration) - that presents a content of total solids of approximately 50 % (w/w).

A further method for obtain the Acacia negra extract is described in Brazil Arch Biol Technol 47, 995-998 (2004).

In some embodiments of the invention, the Quillay and Acacia negra extracts are obtained by extraction from the respective plant source by employing water, alcohol or a water/alcohol solution. In some embodiments, the alcohol is ethanol or methanol.

In some embodiments, the extraction is achieved by employing a water/alcohol solution. In some embodiments, the water/alcohol solution has a watenalcohol ratio of deom 80:20 to 20:80. In further embodiments, the water/alcohol solution has a watenalcohol ratio of from 60:40 to 40:60. In further embodiments, the water/alcohol solution is 80:20 water/alcohol, 60:40 water/alcohol, 50:50 water/alcohol, 40:60 water/alcohol ratio or 20:80 water/alcohol.

The extraction time may vary without limitation from 1 to 8 hours, at or above room temperature (20°C-30°C), e.g., above 30°C, 40°C, 50°C or 60°C. In some embodiments, the extraction is carried out at a temperature between 30°C and 70°C.

In some embodiments, the extraction process comprising: treating the plant source in a

water or water/alcohol solution. Optionally, the so-extracted material may subsequently be purified by any means known in the art, including: filtration, centrifugation, re-crystallization, distillation, adsorption, chromatographic methods, fractionation, etc.

In some embodiments, the plant source is first dried and ground before being treated in the water or water/alcohol solution.

Optionally, the Quillay and/or Acacia negra extracts may be concentrated e.g. by evaporating or drying the extract-containing solution to obtain a concentrated liquid extract of the respective plant species or a dried extract of the respective plant species.

The invention also relates to a method for controlling phytopathogenic harmful fungi and/or harmful insects using mixtures of a water-based Quillay extract and a water-based Acacia negra extract and to the use of a water-based Quillay extract and a water-based Acacia negra extract for preparing such mixtures, and to compositions comprising these mixtures and seed comprising these mixtures or coated with this this mixture.

The mixtures and compositions thereof according to the invention can, in the use form as fungicides and/or insecticides, also be present together with other active substances, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers, as pre-mix or, if appropriate, not until immeadiately prior to use (tank mix).

Mixing a water-based Quillay extract and a water-based Acacia negra extract and the compositions comprising them, respectively, in the use form as fungicide with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity or in a prevention of fungicide resistance development. Furthermore, in many cases, synergistic effects are obtained.

Mixing a water-based Quillay extract and a water-based Acacia negra extract and the compositions comprising them, respectively, in the use form as insecticide with other insecticides results in many cases in an expansion of the insecticidal spectrum of activity or in a prevention of insecticide resistance development. Furthermore, in many cases, synergistic effects are obtained.

According to the present invention, it may be preferred that the mixtures comprise besides a Quillay extract and an Acacia negra extract and the compositions comprising them as component 3) a further active compound, preferably in a synergistically effective amount. Another embodiment relates to mixtures wherein the component 3) is an active compound III selected from groups A), C), D), E), F), G), I), J), K) and N):

The following list of active substances, in conjunction with which the compounds according to the invention can be used, is intended to illustrate the possible combinations but does not limit them:

A) Respiration inhibitors

- inhibitors of complex III at $Q_i$ site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate; (3S,6S,7R,8R)-3-[[(3-hydroxy-4-methoxy-2-

pyridinyl)carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1 ,5-dioxonan-7-yl 2-methylpropanoate

- other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;

C) Nucleic acid synthesis inhibitors

- phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
- others: hymexazole, octhilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;

D) Inhibitors of cell division and cytoskeleton

- tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methyl-piperidin-1 -yl)-6-(2,4,6-trifluorophenyl)-[1 ,2,4]triazolo[1 ,5-a]pyrimidine
- other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;

E) Inhibitors of amino acid and protein synthesis

- methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
- protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;

F) Signal transduction inhibitors

- MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;
- G protein inhibitors: quinoxyfen;

G) Lipid and membrane synthesis inhibitors

- Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;
- lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole;
- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyano-phenyl)-ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- compounds affecting cell membrane permeability and fatty acides: propamocarb, propamocarb-hydrochlorid
- fatty acid amide hydrolase inhibitors: 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1 -piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1 H-pyrazol-1 -yl]ethanone

I) Cell wall synthesis inhibitors

- inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defence inducers

- acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

K) Unknown mode of action

- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(1,2,3,4-tetrahydro-naphthalen-1-yl)-amide, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1,2,3,4-tetrahydro-naphthalen-1-yl-amide, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1 H-pyrazol-1-yl]ethanone, methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, A/-Methyl-2-{1-[(5-methyl-3-trifluoromethyl-1 H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-A/-[(1 R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzoimidazole,
2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;

N) Herbicides

- acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet, mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, pretilachlor, propachlor, thenylchlor;
- amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate;
- aryloxyphenoxypropionat.es: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quizalofop, quizalofop-P-tefuryl;
- Bipyridyls: diquat, paraquat;
- (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate;
- cyclohexanediones: butroxydim, clethodim, cycloxydim, profoxydim, sethoxydim, tepraloxydim, tralkoxydim;
- dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin;
- diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen;
- hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil;
- imidazolinones: imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr;
- phenoxy acetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPB, Mecoprop;
- pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate;
- pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram,

picolinafen, thiazopyr;

- sulfonyl ureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1 ,2-b]pyridazin-3-yl)sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea;
- triazines: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron, metribuzin, prometryn, simazine, terbuthylazine, terbutryn, triaziflam;
- ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, methabenzthiazuron,tebuthiuron;
- other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, ortho-sulfamuron, penoxsulam, propoxycarbazone, pyribambenz-propyl, pyribenzoxim, pyriftalid, pyriminobac-methyl, pyrimisulfan, pyrithiobac, pyroxasulfone, pyroxsulam;
- others: amicarbazone, aminotriazole, anilofos, beflubutamid, benazolin, bencarbazone,benfluresate, benzofenap, bentazone, benzobicyclon, bicyclopyrone, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthal, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoquat, *Drechslera monoceras,* endothal, ethofumesate, etobenzanid, fenoxasulfone, fentrazamide, flumiclorac-pentyl, flumioxazin, flupoxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsonic acid, naptalam, oxadiargyl, oxadiazon, oxaziclomefone, pentoxazone, pinoxaden, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, quinoclamine, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrione, tembotrione, thiencarbazone, topramezone, (3-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-phenoxy]-pyridin-2-yloxy)-acetic acid ethyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3-chloro-6-(4-chloro-phenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxy-phenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3-chloro-6-(4-chloro-3-dimethylamino-2-fluoro-phenyl)-pyridine-2-carboxylic acid methyl ester.

The compounds III, their preparation and their biological activity e.g. against harmful fungi, pests or weed is known (e.g.: http://www.alanwood.net/pesticides/); many of these substances are commercially available.:

It is preferred that the mixtures comprise as compounds III fungicidal compounds that are independently of each other selected from the groups A), C), D), E), F), G), I), J) and K), more preferably in combination with an organic acid such as citric acid, lactic acid or ascorbic acid.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group C) and particularly selected from metalaxyl, (metalaxyl-M) mefenoxam, ofurace.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group D) and particularly selected from benomyl, carbendazim,

thiophanate-methyl, ethaboxam, fluopicolide, zoxamide, metrafenone, pyriofenone.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group E) and particularly selected from cyprodinil, mepanipyrim, pyrimethanil.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group F) and particularly selected from iprodione, fludioxonil, vinclozolin, quinoxyfen.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group G) and particularly selected from dimethomorph, flumorph, iprovalicarb, benthiavalicarb, mandipropamid, propamocarb.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group I) and particularly selected from carpropamid and fenoxanil.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group J) and particularly selected from acibenzolar-S-methyl, probenazole, tiadinil, fosetyl, fosetyl-aluminium, $H_3PO_3$ and salts thereof.

Preference is also given to mixtures comprise as compound III (component 3) at least one active substance selected from group K) and particularly selected from cymoxanil, proquinazid and A/-methyl-2-{1 -[(5-methyl-3-trifluoromethyl-1 H-pyrazol-1 -yl)-acetyl]-piperidin-4-yl}-A/-[(1 R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide.

The mixtures and compositions according to the invention are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, including soil-borne fungi, which derive especially from the classes of the Plasmodiophoromycetes, Peronosporomycetes (syn. Oomycetes), Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes (syn. Fungi imperfecti). Some are systemically effective and they can be used in crop protection as foliar fungicides, fungicides for seed dressing and soil fungicides. Moreover, they are suitable for controlling harmful fungi, which inter alia occur in wood or roots of plants.

The mixtures and compositions according to the invention are particularly important in the control of a multitude of phytopathogenic fungi on various cultivated plants, such as cereals, e. g. wheat, rye, barley, triticale, oats or rice; beet, e. g. sugar beet or fodder beet; fruits, such as pomes, stone fruits or soft fruits, e. g. apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries, blackberries or gooseberries; leguminous plants, such as lentils, peas, alfalfa or soybeans; oil plants, such as rape, mustard, olives, sunflowers, coconut, cocoa beans, castor oil plants, oil palms, ground nuts or soybeans; cucurbits, such as squashes, cucumber or melons; fiber plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruits or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceous plants, such as avocados, cinnamon or camphor; energy and raw material plants, such as corn, soybean, rape, sugar cane or oil palm; corn; tobacco; nuts; coffee; tea; bananas; vines (table grapes and grape juice grape vines); hop; turf; natural rubber plants or ornamental and forestry plants, such as flowers, shrubs, broad-leaved trees or evergreens, e. g. conifers; and on the plant propagation material, such as seeds, and the crop material of these plants.

Preferably the inventive mixtures and compositions are used for controlling a multitude of

fungi on field crops, such as potatoes sugar beets, tobacco, wheat, rye, barley, oats, rice, corn, cotton, soybeans, rape, legumes, sunflowers, coffee or sugar cane; fruits; vines; ornamentals; or vegetables, such as cucumbers, tomatoes, beans or squashes.

The term "plant propagation material" is to be understood to denote all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants, including seedlings and young plants, which are to be transplanted after germination or after emergence from soil. These young plants may also be protected before transplantation by a total or partial treatment by immersion or pouring.

Preferably, treatment of plant propagation materials with the inventive combination of compound I and compounds II and compositions thereof, respectively, is used for controlling a multitude of fungi on cereals, such as wheat, rye, barley and oats; rice, corn, cotton and soybeans.

The term "cultivated plants" is to be understood as including plants which have been modified by breeding, mutagenesis or genetic engineering including but not limiting to agricultural biotech products on the market or in development (cf. http://www.bio.org/speeches/pubs/er/agri_products.asp). Genetically modified plants are plants, which genetic material has been so modified by the use of recombinant DNA techniques that under natural circumstances cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-transtional modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

The inventive mixtures and compositions are particularly suitable for controlling the following plant diseases:

*Albugo* spp. (white rust) on ornamentals, vegetables (e. g. *A. Candida)* and sunflowers (e. g. *A. tragopogonis); Altemaria* spp. (Alternaria leaf spot) on vegetables, rape *(A. brassicola* or *brassicae),* sugar beets *(A. tenuis),* fruits, rice, soybeans, potatoes (e. g. *A. solani or A. alternata*), tomatoes (e. g. *A. solani or A. altemata)* and wheat; *Aphanomyces* spp. on sugar beets and vegetables; *Ascochyta* spp. on cereals and vegetables, e. g. *A. tritici* (anthracnose) on wheat and *A. hordei* on barley; *Bipolaris* and *Drechslera* spp. (teleomorph: *Cochliobolus* spp.) on corn (e. g. *D. maydis),* cereals (e. g. *B. sorokiniana:* spot blotch), rice (e. g. *B. oryzae)* and turfs; *Blumeria* (formerly *Erysiphe) graminis* (powdery mildew) on cereals (e. g. on wheat or barley); *Botrytis cinerea* (teleomorph: *Botryotinia fuckeliana:* grey mold) on fruits and berries (e. g. strawberries), vegetables (e. g. lettuce, carrots, celery and cabbages), rape, flowers, vines, forestry plants and wheat; *Bremia lactucae* (downy mildew) on lettuce;

*Ceratocystis* (syn. *Ophiostoma)* spp. (rot or wilt) on broad-leaved trees and evergreens, e. g. *C. ulmi* (Dutch elm disease) on elms; *Cercospora* spp. (Cercospora leaf spots) on corn, rice, sugar beets (e. g. *C. beticola),* sugar cane, vegetables, coffee, soybeans (e. g. *C. sojina or C. kikuchii)* and rice; *Cladosporium* spp. on tomatoes (e. g. *C. fulvum:* leaf mold) and cereals, e. g. *C. herbarum* (black ear) on wheat; *Claviceps purpurea* (ergot) on cereals; *Cochliobolus* (anamorph: *Helminthosporium* of *Bipolaris)* spp. (leaf spots) on corn (C. *carbonum),* cereals (e. g. *C. sativus,* anamorph: *B. sorokiniana)* and rice (e. g. *C. miyabeanus,* anamorph: *H. oryzae); Colle-*

*totrichum* (teleomorph: *Glomerella)* spp. (anthracnose) on cotton (e. g. *C. gossypii),* corn (e. g. *C. graminicola),* soft fruits, potatoes (e. g. *C. coccodes:* black dot), beans (e. g. *C. lindemuthianum)* and soybeans (e. g. *C. truncatum* or *C. gloeosporioides); Corticium* spp., e. g. *C. sasakii* (sheath blight) on rice; *Corynespora cassiicola* (leaf spots) on soybeans and ornamentals; *Cycloconium* spp., e. g. *C. oleaginum* on olive trees; *Cylindrocarpon* spp. (e. g. fruit tree canker or young vine decline, teleomorph: *Nectria* or *Neonectria* spp.) on fruit trees, vines (e. g. *C. liriodendri,* teleomorph: *Neonectria linodendrr.* Black Foot Disease) and ornamentals; *Dematophora* (teleomorph: *Rosellinia)* necatrix (root and stem rot) on soybeans; *Diaporthe* spp., e. g. *D. phaseolorum* (damping off) on soybeans; *Drechslera* (syn. *Helminthosporium,* teleomorph: *Pyrenophora)* spp. on corn, cereals, such as barley (e. g. *D. teres,* net blotch) and wheat (e. g. *D. tritici-repentis:* tan spot), rice and turf; Esca (dieback, apoplexy) on vines, caused by *Formitiporia* (syn. *Phellinus) punctata, F. mediterranea, Phaeomoniella chlamydospora* (earlier *Phaeoacremonium chlamydosporum), Phaeoacremonium aleophilum* and/or *Botryosphaeria obtusa; Elsinoe* spp. on pome fruits (*E. pyri),* soft fruits (*E. veneta:* anthracnose) and vines (*E. ampelina:* anthracnose); *Entyloma oryzae* (leaf smut) on rice; *Epicoccum* spp. (black mold) on wheat; *Erysiphe* spp. (powdery mildew) on sugar beets (*E. betae),* vegetables (e. g. *E. pisi),* such as cucurbits (e. g. *E. cichoracearum),* cabbages, rape (e. g. *E. cruciferarum); Eutypa lata* (Eutypa canker or dieback, anamorph: *Cytosporina lata,* syn. *Libertella blepharis)* on fruit trees, vines and ornamental woods; *Exserohilum* (syn. *Helminthosporium)* spp. on corn (e. g. *E. turcicum);* *Fusarium* (teleomorph: *Gibberella)* spp. (wilt, root or stem rot) on various plants, such as F. *graminearum* or F. *culmorum* (root rot, scab or head blight) on cereals (e. g. wheat or barley), F. *oxysporum* on tomatoes, F. *solani* on soybeans and F. *verticillioides* on corn; *Gaeumannomyces graminis* (take-all) on cereals (e. g. wheat or barley) and corn; *Gibberella* spp. on cereals (e. g. *G. zeae)* and rice (e. g. *G. fujikuroi:* Bakanae disease); *Glomerella cingulata* on vines, pome fruits and other plants and *G. gossypii* on cotton; Grainstaining complex on rice; *Guignardia bidwellii* (black rot) on vines; *Gymnosporangium* spp. on rosaceous plants and junipers, e. g. *G. sabinae* (rust) on pears; *Helminthosporium* spp. (syn. *Drechslera,* teleomorph: *Cochliobolus)* on corn, cereals and rice; *Hemileia* spp., e. g. *H. vastatrix* (coffee leaf rust) on coffee; *Isariopsis clavispora* (syn. *Cladosporium vitis)* on vines; *Macrophomina phaseolina* (syn. *phaseoli)* (root and stem rot) on soybeans and cotton; *Microdochium* (syn. *Fusarium) nivale* (pink snow mold) on cereals (e. g. wheat or barley); *Microsphaera diffusa* (powdery mildew) on soybeans; *Monilinia* spp., e. g. *M. laxa, M. fructicola* and *M. fructigena* (bloom and twig blight, brown rot) on stone fruits and other rosaceous plants; *Mycosphaerella* spp. on cereals, bananas, soft fruits and ground nuts, such as e. g. *M. graminicola* (anamorph: *Septoria tritici,* Septoria blotch) on wheat; *Peronospora* spp. (downy mildew) on cabbage (e. g. *P. brassicae),* rape (e. g. *P. parasitica),* onions (e. g. *P. destructor),* tobacco *(P. tabacina)* and soybeans (e. g. *P. manshurica); Phakopsora pachyrhizi* and *P. meibomiae* (soybean rust) on soybeans; *Phialophora* spp. e. g. on vines (e. g. *P. tracheiphila* and *P. tetraspora)* and soybeans (e. g. *P. gregata:* stem rot); *Phoma lingam* (root and stem rot) on rape and cabbage and *P. betae* (root rot, leaf spot and damping-off) on sugar beets; *Phomopsis* spp. on sunflowers, vines (e. g. *P. viticola:* can and leaf spot) and soybeans (e. g. stem rot: *P. phaseoli,* teleomorph: *Diaporthe phaseolorum); Physoderma maydis* (brown spots) on corn; *Phytophthora* spp. (wilt, root, leaf, fruit and stem root) on various plants, such as paprika and cucurbits (e. g. *P. capsici),* soybeans (e. g. *P. megasperma,* syn. *P. sojae),* potatoes and tomatoes (e. g. *P. infestans:* late blight) and broad-

leaved trees (e. g. *P. ramorum:* sudden oak death); *Plasmodiophora brassicae* (club root) on cabbage, rape, radish and other plants; *Plasmopara* spp., e. g. *P. viticola* (grapevine downy mildew) on vines and *P. halstedii* on sunflowers; *Podosphaera* spp. (powdery mildew) on rosaceous plants, hop, pome and soft fruits, e. g. *P. leucotricha* on apples; *Polymyxa* spp., e. g. on cereals, such as barley and wheat (P. *graminis)* and sugar beets (P. *betae)* and thereby transmitted viral diseases; *Pseudocercosporella herpotrichoides* (eyespot, teleomorph: *Tapesia yallundae)* on cereals, e. g. wheat or barley; *Pseudoperonospora* (downy mildew) on various plants, e. g. P. *cubensis* on cucurbits or P. *humili* on hop; *Pseudopezicula tracheiphila* (red fire disease or , rotbrenner' , anamorph: *Phialophora)* on vines; *Puccinia* spp. (rusts) on various plants, e. g. P. *triticina* (brown or leaf rust), P. *striiformis* (stripe or yellow rust), P. *hordei* (dwarf rust), P. *graminis* (stem or black rust) or P. *recondita* (brown or leaf rust) on cereals, such as e. g. wheat, barley or rye, and asparagus (e. g. P. *asparagi); Pyrenophora* (anamorph: *Drechslera) tritici-repentis* (tan spot) on wheat or P. feres (net blotch) on barley; *Pyricularia* spp., e. g. P. *oryzae* (teleomorph: *Magnaporthe grisea,* rice blast) on rice and P. *grisea* on turf and cereals; *Pythium* spp. (damping-off) on turf, rice, corn, wheat, cotton, rape, sunflowers, soybeans, sugar beets, vegetables and various other plants (e. g. P. *ultimum* or P. *aphanidermatum); Ramularia* spp., e. g. *R. collo-cygni* (Ramularia leaf spots, Physiological leaf spots) on barley and *R. beticola* on sugar beets; *Rhizoctonia* spp. on cotton, rice, potatoes, turf, corn, rape, potatoes, sugar beets, vegetables and various other plants, e. g. *R. solani* (root and stem rot) on soybeans, *R. solani* (sheath blight) on rice or *R. cerealis* (Rhizoctonia spring blight) on wheat or barley; *Rhizopus stolonifer* (black mold, soft rot) on strawberries, carrots, cabbage, vines and tomatoes; *Rhynchosporium secalis* (scald) on barley, rye and triticale; *Sarocladium oryzae* and S. *attenuatum* (sheath rot) on rice; *Sclerotinia* spp. (stem rot or white mold) on vegetables and field crops, such as rape, sunflowers (e. g. S. *sclerotiorum)* and soybeans (e. g. S. *rolfsii* or S. *sclerotiorum); Septoria* spp. on various plants, e. g. S. *glycines* (brown spot) on soybeans, S. *tritici* (Septoria blotch) on wheat and S. (syn. *Stagonospora)* nodorum (Stagonospora blotch) on cereals; *Uncinula* (syn. *Erysiphe) necator* (powdery mildew, anamorph: *Oidium tuckeri)* on vines; *Setospaeria* spp. (leaf blight) on corn (e. g. S. *turcicum,* syn. *Helminthosporium turcicum)* and turf; *Sphacelotheca* spp. (smut) on corn, (e. g. S. *reiliana:* head smut), sorghum und sugar cane; *Sphaerotheca fuliginea* (powdery mildew) on cucurbits; *Spongospora subterranea* (powdery scab) on potatoes and thereby transmitted viral diseases; *Stagonospora* spp. on cereals, e. g. S. *nodorum* (Stagonospora blotch, teleomorph: *Leptosphaeria* [syn. *Phaeosphaeria] nodorum)* on wheat; *Synchytrium endobioticum* on potatoes (potato wart disease); *Taphrina* spp., e. g. *T. deformans* (leaf curl disease) on peaches and *T. pruni* (plum pocket) on plums; *Thielaviopsis* spp. (black root rot) on tobacco, pome fruits, vegetables, soybeans and cotton, e. g. *T. basicola* (syn. *Chalara elegans); Tilletia* spp. (common bunt or stinking smut) on cereals, such as e. g. *T. tritici* (syn. *T. caries,* wheat bunt) and *T. controversa* (dwarf bunt) on wheat; *Typhula incarnata* (grey snow mold) on barley or wheat; *Urocystis* spp., e. g. *U. occulta* (stem smut) on rye; *Uromyces* spp. (rust) on vegetables, such as beans (e. g. *U. appendiculatus,* syn. *U. phaseoli)* and sugar beets (e. g. *U. betae); Ustilago* spp. (loose smut) on cereals (e. g. *U. nuda* and *U. avaenae),* corn (e. g. *U. maydis:* corn smut) and sugar cane; *Venturia* spp. (scab) on apples (e. g. *V. inaequalis)* and pears; and *Verticillium* spp. (wilt) on various plants, such as fruits and ornamentals, vines, soft fruits, vegetables and field crops, e. g. *V. dahliae* on strawberries, rape, potatoes and tomatoes.

In particular, the mixtures and compositions of the present invention are effective against plant pathogens in speciality crops such as vine, fruits, hop, vegetables and tabacco - see the above list.

Plant propagation materials may be treated with the mixtures and compositions of the invention prophylactically either at or before planting or transplanting.

The invention also relates to agrochemical compositions comprising an auxiliary and at least a water-based Quillay extract and a water-based Acacia negra extract according to the invention.

An agrochemical composition comprises a fungicidally or insecticidally effective amount of a water-based Quillay extract and a water-based Acacia negra extract. The term "effective amount" denotes an amount of the composition or of the water-based Quillay extract and the Acacia negra extract, which is sufficient for controlling harmful fungi or harmful pests on cultivated plants or in the protection of materials and which does not result in a substantial damage to the treated plants. Such an amount can vary in a broad range and is dependent on various factors, such as the fungal or pest species to be controlled, the treated cultivated plant or material, the climatic conditions.

The mixtures comprising a water-based Quillay extract and a water-based Acacia negra extract and the compositions thereof, respectively, are also particularly suitable for controlling the following harmful insects from the order of the

lepidopterans (Lepidoptera), for example *Agrotis ypsilon, Agrotis segetum, Alabama argillacea, Anticarsia gemmatalis, Argyresthia conjugella, Autographa gamma, Bupalus piniarius, Cacoecia murinana, Capua reticulana, Cheimatobia brumata, Choristoneura fumiferana, Choristoneura occidentalis, Cirphis unipuncta, Cydia pomonella, Dendrolimus pini, Diaphania nitidalis, Diatraea grandiosella, Earias insulana, Elasmopalpus lignosellus, Eupoecilia ambiguella, Evetria bouliana, Feltia subterranea, Galleria mellonella, Grapholitha funebrana, Grapholitha molesta, Heliothis armigera, Heliothis virescens, Heliothis zea, Hellula undalis, Hibemia defoliaria, Hyphantria cunea, Hyponomeuta malinellus, Keiferia lycopersicella, Lambdina fiscellaria, Laphygma exigua, Leucoptera coffeella, Leucoptera scitella, Lithocolletis blancardella, Lobesia botrana, Loxostege sticticalis, Lymantria dispar, Lymantria monacha, Lyonetia clerkella, Malacosoma neustria, Mamestra brassicae, Orgyia pseudotsugata, Ostrinia nubilalis, Panolis flammea, Pectinophora gossypiella, Peridroma saucia, Phalera bucephala, Phthorimaea operculella, Phyllocnistis citrella, Pieris brassicae, Plathypena scabra, Plutella xylostella, Pseudoplusia includens, Rhyacionia frustrana, Scrobipalpula absoluta, Sitotroga cerealella, Sparganothis pilleriana, Spodoptera frugiperda, Spodoptera littoralis, Spodoptera litura, Thaumatopoea pityocampa, Tortrix viridana, Trichoplusia ni* and *Zeiraphera canadensis,*

beetles (Coleoptera), for example *Agrilus sinuatus, Agriotes lineatus, Agriotes obscurus, Amphimallus solstitialis, Anisandrus dispar, Anthonomus grandis, Anthonomus pomorum, Atomaria linearis, Blastophagus piniperda, Blitophaga undata, Bruchus rufimanus, Bruchus pisorum, Bruchus lentis, Byctiscus betulae, Cassida nebulosa, Cerotoma trifurcata, Ceuthorrhynchus assimilis, Ceuthorrhynchus napi, Chaetocnema tibialis, Conoderus vespertinus, Crioceris asparagi, Diabrotica longicornis, Diabrotica speciosa, Diabrotica 12-punctata, Diabrotica virgifera, Diloboderus abderus, Epilachna varivestis, Epitrix hirtipennis, Eutinobothrus brasiliensis, Hylobius abietis, Hypera brunneipennis, Hypera postica, Ips typographus, Lema bilineata, Lema melanopus, Leptinotarsa decemlineata, Limonius californicus, Lissorhoptrus oryzophilus, Mela-*

*notus communis, Meligethes aeneus, Melolontha hippocastani, Melolontha melolontha, Oulema oryzae, Ortiorrhynchus sulcatus, Oryazophagus oryzae, Otiorrhynchus ovatus, Phaedon cochleariae, Phyllotreta chrysocephala, Phyllophaga sp., Phyllophaga cuyabana, Phyllophaga triticophaga, Phyllopertha horticola, Phyllotreta nemorum, Phyllotreta striolata, Popillia japonica, Sitona lineatus* and *Sitophilus granaria,*

dipterans (Diptera), for example *Aedes aegypti, Aedes vexans, Anastrepha ludens, Anopheles maculipennis, Ceratitis capitata, Chrysomya bezziana, Chrysomya hominivorax, Chrysomya macellaria, Contarinia sorghicola, Cordylobia anthropophaga, Culex pipiens, Dacus cucurbitae, Dacus oleae, Dasineura brassicae, Fannia canicularis, Gasterophilus intestinalis, Glossina morsitans, Haematobia irritans, Haplodiplosis equestris, Hylemyia platura, Hypoderma lineata, Liriomyza sativae, Liriomyza trifolii, Lucilia caprina, Lucilia cuprina, Lucilia sericata, Lycoria pectoralis, Mayetiola destructor, Musca domestica, Muscina stabulans, Oestrus ovis, Oscinella frit, Pegomya hysocyami, Phorbia antiqua, Phorbia brassicae, Phorbia coarctata, Rhagoletis cerasi, Rhagoletis pomonella, Tabanus bovinus, Tipula oleracea* and *Tipula paludosa,*

thrips (Thysanoptera), e.g. *Frankliniella fusca, Frankliniella occidentalis, Frankliniella tritici, Scirtothrips citri, Thrips oryzae, Thrips paImi* and *Thrips tabaci,*

hymenopterans (Hymenoptera), e.g. *Acromyrmex ambuguus, Acromyrmex crassispinus, Acromyrmex heiery, Acromyrmex landolti, Acromyrmex subterraneus, Athalia rosae, Atta capiguara, Atta cephalotes, Atta laevigata, Atta robusta, Atta sexdens, Atta texana, Hoplocampa minuta, Hoplocampa testudinea, Monomorium pharaonis, Solenopsis geminata* and *Solenopsis invicta,*

heteropterans (Heteroptera), e.g. *Acrosternum hilare, Blissus leucopterus, Cyrtopeltis notatus, Dichelops furcatus, Dysdercus cingulatus, Dysdercus intermedius, Euchistos heros, Eurygaster integriceps, Euschistus impictiventris, Leptoglossus phyllopus, Lygus lineolaris, Lygus pratensis, Nezara viridula, Piesma quadrata, Piezodorus guildini, Solubea insularis* and *Thyanta perditor,*

Hemiptera and Homoptera, e.g. *Acrosternum hilare, Blissus leucopterus, Cyrtopeltis notatus, Diaphorina citri, Dysdercus cingulatus, Dysdercus intermedius, Eurygaster integriceps, Euschistus impictiventris, Leptoglossus phyllopus, Lygus lineolaris, Lygus pratensis, Nezara viridula, Piesma quadrata, Solubea insularis , Thyanta perditor, Acyrthosiphon onobrychis, Adelges laricis, Aphidula nasturtii, Aphis fabae, Aphis forbesi, Aphis pomi, Aphis gossypii, Aphis grossulariae, Aphis schneideri, Aphis spiraecola, Aphis sambuci, Acyrthosiphon pisum, Aulacorthum solani, Brachycaudus cardui, Brachycaudus helichrysi, Brachycaudus persicae, Brachycaudus prunicola, Brevicoryne brassicae, Capitophorus horni, Cerosipha gossypii, Chaetosiphon fragaefolii, Cryptomyzus ribis, Dreyfusia nordmannianae, Dreyfusia piceae, Dysaphis radicola, Dysaulacorthum pseudosolani, Dysaphis plantaginea, Dysaphis pyri, Empoasca fabae, Hyalopterus pruni, Hyperomyzus lactucae, Macrosiphum avenae, Macrosiphum euphorbiae, Macrosiphon rosae, Megoura viciae, Melanaphis pyrarius, Metopolophium dirhodum, Myzodes persicae, Myzus ascalonicus, Myzus cerasi, Myzus varians, Nasonovia ribis-nigri, Nilaparvata lugens, Pemphigus bursarius, Perkinsiella saccharicida, Phorodon humuli, Psylla mail, Psylla piri, Rhopalomyzus ascalonicus, Rhopalosiphum maidis, Rhopalosiphum padi, Rhopalosiphum insertum, Sappaphis mala, Sappaphis mail, Schizaphis graminum, Schizoneura lanuginosa, Sitobion avenae, Trialeurodes vaporariorum, Toxoptera aurantiiand, Viteus vitifolii, Cimex lectularius, Cimex hemipterus, Reduvius senilis, Triatoma spp., andArilus critatus,*

termites (Isoptera), *e.g. Calotermes flavicollis, Comitermes cumulans, Heterotermes tenuis, Leucotermes flavipes, Neocapritemes opacus, Procomitermes triacifer; Reticulitermes lucifugus, Syntermes molestus, and Termes natalensis,*

orthopterans (Orthoptera), e.g. *Acheta domestica, Blatta orientalis, Blattella germanica, Forficula auricularia, Gryllotalpa gryllotalpa, Locusta migratoria, Melanoplus bivittatus, Melanoplus femur-rubrum, Melanoplus mexicanus, Melanoplus sanguinipes, Melanoplus spretus, Nomadacris septemfasciata, Periplaneta americana, Schistocerca americana, Schistocerca peregrina, Stauronotus maroccanus* and *Tachycines asynamorus,*

Arachnoidea, such as arachnids, e.g. of the families Argasidae, Ixodidae and Sarcoptidae, such as *Amblyomma americanum, Amblyomma variegatum, Argas persicus, Boophilus annulatus, Boophilus decoloratus, Boophilus microplus, Dermacentor silvarum, Hyalomma truncatum, Ixodes ricinus, Ixodes rubicundus, Ornithodorus moubata, Otobius megnini, Dermanyssus gallinae, Psoroptes ovis, Rhipicephalus appendiculatus, Rhipicephalus evertsi, Sarcoptes scabiei,* and *Eriophyidae spp.* such as *Aculus schlechtendali, Phyllocoptrata oleivora* and *Eriophyes sheldoni; Tarsonemidae spp.* such as *Phytonemus pallidus* and *Polyphagotarsonemus latus; Tenuipalpidae spp.* such as *Brevipalpus phoenicis; Tetranychidae spp.* such as *Tetranychus cinnabarinus, Tetranychus kanzawai, Tetranychus pacificus, Tetranychus telarius* and *Tetranychus urticae, Panonychus ulmi, Panonychus citri,* and *Oligonychus pratensis.*

In particular, the inventive mixtures are suitable for combating pests of the orders Coleoptera, Lepidoptera, Thysanoptera, Homoptera, Isoptera, and Orthoptera.

They are also suitable for controlling the following plant parasitic nematodes such as *Meloidogyne, Globodera,Heterodera, Radopholus, Rotylenchulus, Pratylenchus* and other genera.

The Quillay extract and the Acacia negra extract can be converted into customary types of agrochemical compositions, e. g. solutions, emulsions, suspensions, dusts, powders, pastes, granules, pressings, capsules, and mixtures thereof. Examples for composition types are suspensions (e.g. SC, OD, FS), emulsifiable concentrates (e.g. EC), emulsions (e.g. EW, EO, ES, ME), capsules (e.g. CS, ZC), pastes, pastilles, wettable powders or dusts (e.g. WP, SP, WS, DP, DS), pressings (e.g. BR, TB, DT), granules (e.g. WG, SG, GR, FG, GG, MG), insecticidal articles (e.g. LN), as well as gel formulations for the treatment of plant propagation materials such as seeds (e.g. GF). These and further compositions types are defined in the " Catalogue of pesticide formulation types and international coding system" , Technical Monograph No. 2, 6th Ed. May 2008, CropLife International.

The compositions are prepared in a known manner, such as described by Mollet and Grubemann, Formulation technology, Wiley VCH, Weinheim, 2001 ; or Knowles, New developments in crop protection product formulation, Agrow Reports DS243, T&F Informa, London, 2005.

Suitable auxiliaries are solvents, liquid carriers, solid carriers or fillers, surfactants, dispersants, emulsifiers, wetters, adjuvants, solubilizers, penetration enhancers, protective colloids, adhesion agents, thickeners, humectants, repellents, attractants, feeding stimulants, compatibilizers, bactericides, anti-freezing agents, anti-foaming agents, colorants, tackifiers and binders.

Suitable solvents and liquid carriers are water and organic solvents, such as mineral oil fractions of medium to high boiling point, e.g. kerosene, diesel oil; oils of vegetable or animal origin; aliphatic, cyclic and aromatic hydrocarbons, e. g. toluene, paraffin, tetrahydronaphthalene, al-

kylated naphthalenes; alcohols, e.g. ethanol, propanol, butanol, benzylalcohol, cyclohexanol; glycols; DMSO; ketones, e.g. cyclohexanone; esters, e.g. lactates, carbonates, fatty acid esters, gamma-butyrolactone; fatty acids; phosphonates; amines; amides, e.g. N-methylpyrrolidone, fatty acid dimethylamides; and mixtures thereof.

Suitable solid carriers or fillers are mineral earths, e.g. silicates, silica gels, talc, kaolins, limestone, lime, chalk, clays, dolomite, diatomaceous earth, bentonite, calcium sulfate, magnesium sulfate, magnesium oxide; polysaccharides, e.g. cellulose, starch; fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas; products of vegetable origin, e.g. cereal meal, tree bark meal, wood meal, nutshell meal, and mixtures thereof.

Suitable surfactants are surface-active compounds, such as anionic, cationic, nonionic and amphoteric surfactants, block polymers, polyelectrolytes, and mixtures thereof. Such surfactants can be used as emusifier, dispersant, solubilizer, wetter, penetration enhancer, protective colloid, or adjuvant. Examples of surfactants are listed in McCutcheon's, Vol.1 : Emulsifiers & Detergents, McCutcheon's Directories, Glen Rock, USA, 2008 (International Ed. or North American Ed.).

Suitable anionic surfactants are alkali, alkaline earth or ammonium salts of sulfonates, sulfates, phosphates, carboxylates, and mixtures thereof. Examples of sulfonates are alkylarylsulfonates, diphenylsulfonates, alpha-olefin sulfonates, lignine sulfonates, sulfonates of fatty acids and oils, sulfonates of ethoxylated alkylphenols, sulfonates of alkoxylated arylphenols, sulfonates of condensed naphthalenes, sulfonates of dodecyl- and tridecylbenzenes, sulfonates of naphthalenes and alkylnaphthalenes, sulfosuccinates or sulfosuccinamates. Examples of sulfates are sulfates of fatty acids and oils, of ethoxylated alkylphenols, of alcohols, of ethoxylated alcohols, or of fatty acid esters. Examples of phosphates are phosphate esters. Examples of carboxylates are alkyl carboxylates, and carboxylated alcohol or alkylphenol ethoxylates.

Suitable nonionic surfactants are alkoxylates, N-subsituted fatty acid amides, amine oxides, esters, sugar-based surfactants, polymeric surfactants, and mixtures thereof. Examples of alkoxylates are compounds such as alcohols, alkylphenols, amines, amides, arylphenols, fatty acids or fatty acid esters which have been alkoxylated with 1 to 50 equivalents. Ethylene oxide and/or propylene oxide may be employed for the alkoxylation, preferably ethylene oxide. Examples of N-subsititued fatty acid amides are fatty acid glucamides or fatty acid alkanolamides. Examples of esters are fatty acid esters, glycerol esters or monoglycerides. Examples of sugar-based surfactants are sorbitans, ethoxylated sorbitans, sucrose and glucose esters or alkylpolyglucosides. Examples of polymeric surfactants are home- or copolymers of vinylpyrrolidone, vinylalcohols, or vinylacetate.

Suitable cationic surfactants are quaternary surfactants, for example quaternary ammonium compounds with one or two hydrophobic groups, or salts of long-chain primary amines. Suitable amphoteric surfactants are alkylbetains and imidazolines. Suitable block polymers are block polymers of the A-B or A-B-A type comprising blocks of polyethylene oxide and polypropylene oxide, or of the A-B-C type comprising alkanol, polyethylene oxide and polypropylene oxide. Suitable polyelectrolytes are polyacids or polybases. Examples of polyacids are alkali salts of polyacrylic acid or polyacid comb polymers. Examples of polybases are polyvinylamines or polyethyleneamines.

Suitable adjuvants are compounds, which have a neglectable or even no pesticidal activity themselves, and which improve the biological performance of the compound I on the target.

Examples are surfactants, mineral or vegetable oils, and other auxilaries. Further examples are listed by Knowles, Adjuvants and additives, Agrow Reports DS256, T&F Informa UK, 2006, chapter 5.

Suitable thickeners are polysaccharides (e.g. xanthan gum, carboxymethylcellulose), anorganic clays (organically modified or unmodified), polycarboxylates, and silicates.

Suitable bactericides are bronopol and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones. Suitable anti-freezing agents are ethylene glycol, propylene glycol, urea and glycerin. Suitable anti-foaming agents are silicones, long chain alcohols, and salts of fatty acids. Suitable colorants (e.g. in red, blue, or green) are pigments of low water solubility and water-soluble dyes. Examples are inorganic colorants (e.g. iron oxide, titan oxide, iron hexacyanoferrate) and organic colorants (e.g. alizarin-, azo- and phthalocyanine colorants). Suitable tackifiers or binders are polyvinylpyrrolidone, polyvinylacetates, polyvinyl alcohols, polyacrylates, biological or synthetic waxes, and cellulose ethers.

According to the invention, the solid material of the Acacia negra extract and Quillay extract are considered as active components (e.g. to be obtained after drying or evaporation of the extraction medium).

In accordance with the present invention, the (weight) ratios used herein for the Acacia negra extract and/or Quillay extract are based on the total weight of the dry content (solid material) of the respective extract(s).

The agrochemical compositions generally comprise between 0.01 and 95%, preferably between 0.1 and 90%, and in particular between 0.5 and 75%, by weight of active components.

Solutions for seed treatment (LS), suspoemulsions (SE), flowable concentrates (FS), powders for dry treatment (DS), water-dispersible powders for slurry treatment (WS), water-soluble powders (SS), emulsions (ES), emulsifiable concentrates (EC) and gels (GF) are usually employed for the purposes of treatment of plant propagation materials, particularly seeds. The compositions in question give, after two-to-tenfold dilution, active components concentrations of from 0.01 to 60% by weight, preferably from 0.1 to 40%, in the ready-to-use preparations. Application can be carried out before or during sowing. Methods for applying or treating compound I and compound II and compositions thereof, respectively, on to plant propagation material, especially seeds include dressing, coating, pelleting, dusting, soaking and in-furrow application methods of the propagation material. Preferably, compound I and compound II or the compositions thereof, respectively, are applied on to the plant propagation material by a method such that germination is not induced, e.g. by seed dressing, pelleting, coating and dusting.

When employed in plant protection, the amounts of active components applied are, depending on the kind of effect desired, from 0.001 to 10 kg per ha, preferably from 0.005 to 2 kg per ha, more preferably from 0.05 to 0.9 kg per ha, in particular from 0.1 to 0.75 kg per ha.

In treatment of plant propagation materials such as seeds, e.g. by dusting, coating or drenching seed, amounts of active components of from 0.1 to 10000 g, preferably from 1 to 2000 g, more preferably from 1 to 500 g and most preferably from 5 to 100 g, per 100 kilogram of plant propagation material (preferably seed) are generally required.

When used in the protection of materials or stored products, the amount of active components applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of

active components per cubic meter of treated material.

Various types of oils, wetters, adjuvants, fertilizer, or micronutrients, and further pesticides (e.g. herbicides, insecticides, fungicides, growth regulators, safeners) may be added to the active substances or the compositions comprising them as premix or, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention in a weight ratio of 1:100 to 100:1 , preferably 1:10 to 10:1 .

According to one embodiment, a polyether polymethylsiloxane copolymer may be added to the composition accoding to the invention, preferably in a weight ratio of 1:100 to 100:1 , more preferably in a weight ratio of 1:10 to 10:1 , in particular in a weight ratio of 1:5 to 5:1 based on the total weight of the dry content of Quillay extract and Acacia negra extract together.

According to a further embodiment, a mineral oil or a vegetable oil may be added to the composition according to the invention, preferably in a weight ratio of 1:100 to 100:1 , more preferably in a weight ratio of 1:10 to 10:1 , in particular in a weight ratio of 1:5 to 5:1 based on the total weight of the dry content of Quillay extract and Acacia negra extract together.

The user applies the composition according to the invention usually from a predosage device, a knapsack sprayer, a spray tank, a spray plane, or an irrigation system. Usually, the agrochemical composition is made up with water, buffer, and/or further auxiliaries to the desired application concentration and the ready-to-use spray liquor or the agrochemical composition according to the invention is thus obtained. Usually, 20 to 2000 liters, preferably 50 to 400 liters, of the ready-to-use spray liquor are applied per hectare of agricultural useful area.

According to one embodiment, individual components of the composition according to the invention such as parts of a kit or parts of a binary or ternary mixture may be mixed by the user himself in a spray tank and further auxiliaries may be added, if appropriate.

In the binary mixtures and compositions according to the invention the weight ratio of the component 1) and the component 2) generally depends from the properties of the active components used, usually it is in the range of from 1:100 to 100:1 , regularly in the range of from 1:50 to 50:1 , preferably in the range of from 1:20 to 20:1 , more preferably in the range of from 1:10 to 10:1 , even more preferably in the range of from 1:4 to 4:1 and in particular in the range of from 1:2 to 2:1 .

According to further embodiments of the binary mixtures and compositions, the weight ratio of the component 1) and the component 2) usually is in the range of from 100:1 to 1:1 , regularly in the range of from 50:1 to 1:1 , preferably in the range of from 20:1 to 1:1 , more preferably in the range of from 10:1 to 1:1 , even more preferably in the range of from 4:1 to 1:1 and in particular in the range of from 2:1 to 1:1 .

According to further embodiments of the binary mixtures and compositions, the weight ratio of the component 1) and the component 2) usually is in the range of from 1:1 to 1:100, regularly in the range of from 1:1 to 1:50, preferably in the range of from 1:1 to 1:20, more preferably in the range of from 1:1 to 1:10, even more preferably in the range of from 1:1 to 1:4 and in particular in the range of from 1:1 to 1:2.

In the ternary mixtures, i.e. compositions according to the invention comprising the component 1) and component 2) and a compound III (component 3), the weight ratio of component 1) and component 2) depends from the properties of the active substances used, usually it is in the range of from 1:100 to 100:1 , regularly in the range of from 1:50 to 50:1 , preferably in the range of from 1:20 to 20:1 , more preferably in the range of from 1:10 to 10:1 and in particular in the

range of from 1:4 to 4:1, and the weight ratio of component 1) and component 3) usually it is in the range of from 1:100 to 100:1 , regularly in the range of from 1:50 to 50:1 , preferably in the range of from 1:20 to 20:1 , more preferably in the range of from 1:10 to 10:1 and in particular in the range of from 1:4 to 4:1 .

Preferably, the mixtures and/or the compositions thereof according to the invention comprise 10 - 90% by weight of the component 1), and 10 - 90% by weight of the component 2), based on the total amount of the components 1) and 2) calculated as dry matter (solid material) thereof.Any further active components are, if desired, added in a ratio of from 20:1 to 1:20 to the component 1).

In the mixtures and compositions, the compound ratios are advantageously chosen so as to produce a synergistic effect.

The term "synergstic effect" is understood to refer in particular to that defined by Colby's formula (Colby, S. R., "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, pp. 20-22, 1967).

The term "synergistic effect" is also understood to refer to that defined by application of the Tammes method, (Tammes, P. M. L , "Isoboles, a graphic representation of synergism in pesticides", Netherl. J. Plant Pathol. 70, 1964).

The components can be used individually or already partially or completely mixed with one another to prepare the composition according to the invention. It is also possible for them to be packaged and used as combination such as a kit of parts.

The fungicidal and insecticidal action of the compositions according to the invention can be shown by the tests described below.

Lab trials

Components used:

TAC: Acacia negra extract 90%* (w/w) WP

QL Agri: Quillay extract 35%* (w/v) SL, BASF SE

Break Thru: Polyether polymethylsiloxane copolymer (additive)

* based on the total weight of the dry content (solid material) of respective extract

Use example 1: Control of *Trialeudores vaporarorium* adults (whitefiels) on tomato *(Lycopersicum esculentum)* leaves (San Francisco Mostazal. VI R. November 201 1, Chile)

Young tomato leaves were excised and placed with a certain number of whitefly alive petri dishes, then the initial number of whiteflies alive was counted. All treatments had similar number of adults of white flies. The experiments were performed with four replicates. The experimental design was a complete randomized block. In all treatments except the control water was used for dilution of the products. Application date was November 4, 201 1.

For application of the treatments a hand sprayer with a capacity of one liter was used. The applications were directed to each of the Petri dishes aiming to achieve a good coverage reaching a volume of water estimated to 1500 L per hectare.

The white flies adults alive were counted again 14 days after application (DAA).

To calculate the effectiveness of control, we used the Henderson & Titon formula. These percentages were converted into efficacies.

The mortality (%) was calculated based on the counted number of whiteflies alive according the Abbots formula as follows:

$$M = (1 - \alpha/\beta) \cdot 100$$

a corresponds to the number of white flies alive before appl. and

β corresponds to the number of white flies alive 14 days after treatment

The expected mortality of active component mixtures were determined using the adapted Colby's formula [R.S. Colby, " Calculating synergistic and antagonistic responses of herbicide combinations", Weeds 15, 20-22 (1967)] and compared with the observed mortalities.

| | | Number of individuals alive | | | | |
|---|---|---|---|---|---|---|
| Treatment | Dosage (mL or g / 100 L) | Before appl. | 14DAA | Efficacy (%) | Mortality (%) observed | Mortality (%) expected |
| Water control | n.a. | 10.25 | 12.75 | | -24.39 | |
| QL Agri | 150 mL | 10.75 | 3.25 | 75.70 | 69.77 | |
| QL Agri | 100 mL | 9.75 | 8.75 | 27.85 | 10.26 | |
| QL Agri | 50 mL | 10 | 11.75 | 5.54 | -17.50 | |
| TAC | 150 g | 8.75 | 4.25 | 60.95 | 51.43 | |
| TAC | 100 g | 10.5 | 11.5 | 11.95 | -9.52 | |
| TAC | 50 g | 9.75 | 11.5 | 5.18 | -17.95 | |
| Break Thru | 50 mL | 10.75 | 14 | -4.7 | -30.23 | |
| QL Agri +TAC | 150 mL + 50 g | 9.5 | 2 | 83.08 | **78.95** | **64.34** |
| QL Agri +TAC | 100 mL + 100 g | 10.5 | 2.5 | 80.86 | **76.19** | **1.71** |
| QL Agri +TAC | 50 mL + 150 g | 10.5 | 3 | 77.03 | **71.43** | **42.93** |
| QL Agri +TAC + Break Thru | 50 mL + 150 g + 50 mL | 10 | 2.25 | 81.91 | 77.50 | |

Use example 2: Control of *Panonychus ulmi* adults (mites) on apple leaves (San Francisco Mostazal. VI R. November 201 1, Chile)

Five apple leaves *(Malus domestica)* were excised from apple plants grown in glass house and placed with a certain number of whitefly alive and placed in petri dishes, then the initial number of mites alive was counted. All treatments had similar number of adults of mites. The experiments were performed with four replicates. The experimental design was a complete randomized block. In all treatments except the control water was used for dilution of the products.

For application of the treatments a hand sprayer with a capacity of one liter was used. The applications were directed to each of the Petri dishes aiming to achieve a good coverage reaching a volume of water estimated to 1500 L per hectare.

The mite adults alive were counted again 14 days after application (DAA).

Assessments of mortality were made by counting the dead insects. To calculate the effectiveness of control, we used the Henderson & Titon formula. These percentages were converted into efficacies.

| | | Number of individuals alive | | | | |
|---|---|---|---|---|---|---|
| **Treatment** | **Dosage (mL or g / 100 L)** | **Before appl.** | **14DAA** | **Efficacy (%)** | **Mortality (%) observed** | **Mortality (%) expected** |
| Water control | n.a. | 24.25 | 230.75 | | -851 .55 | |
| QL Agri | 150 mL | 24.25 | 4.5 | 98.05 | 81.44 | |
| QL Agri | 100 mL | 26.50 | 13 | 94.84 | 50.94 | |
| QL Agri | 50 mL | 25 | 58.25 | 75.51 | -133 | |
| TAC | 150 g | 32.25 | 4 | 98.70 | 87.60 | |
| TAC | 100 g | 27.5 | 8.75 | 96.66 | 68.18 | |
| TAC | 50 g | 23.75 | 59.5 | 73.67 | -150.53 | |
| Break Thru | 50 mL | 32.5 | 251 .5 | 18.67 | -673.85 | |
| QL Agri +TAC | 150 mL + 50 g | 30.5 | 2.25 | 99.22 | **92.62** | **53.51** |
| QL Agri +TAC | 100 mL+ 100 g | 31.75 | 2.25 | 99.26 | **92.91** | **84.39** |
| QL Agri +TAC | 50 mL + 150 g | 29.25 | 2 | 99.28 | **93.16** | **71.10** |
| QL Agri +TAC + Break Thru | 50 mL + 150 g + 50 mL | 31.25 | 1.5 | 99.50 | 95.20 | |

Use examples 3 and 4: Control of *Diaspidiotus pemiciosus (San Jose Scale SJS) black stage* on almond and apple shoots (Lab trial September 2012, Chile)

Excised apple and almond shoots with black cap stage of San Jose Scale insects *(Diaspidiotus pemiciosus)* were used. The experiments were performed with four replicates for almond (use example 3) and with 8 replicates for apple shoots (use example 4). Application date was August 30, 2012.

For application of the treatments a hand sprayer with a capacity of one liter was used. The applications were directed to each of the Petri dishes aiming to achieve a good coverage reaching a volume of water estimated to 2000 L per hectare. The base of the shoots was mantained in water and with wax on the top to avoid dehydratation.

The evaluation was done by counting the number of SJS total and alive, using a pin for take off the cap, 30 days after the application. Mortality was determined using Abbofs formula.

Results from Use example 3 on almond shoots:

| Treatment | Dosage (mL or g / 100 L) | Mortality (%) observed | Mortality (%) expected |
|---|---|---|---|
| Water control | n.a. | - | |
| QL Agri | 400 mL | 51.4 | |
| QL Agri | 100 mL | 14.3 | |
| QL Agri | 50 mL | -7.1 | |
| TAC | 300 g | 50 | |
| TAC | 150 g | 44.3 | |
| Mineral oil | 2000 mL | 57.1 | |
| QL Agri +TAC | 100 mL + 300 g | **64.3** | **57.1** |
| QL Agri +TAC | 50 mL + 150 g | **58.6** | **40.3** |
| QL Agri +TAC + Mineral oil | 50 g + 150 g + 2000 mL | **100** | **84.7** |

Results from Use example 4 on apple shoots:

| Treatment | Dosage (mL or g / 100 L) | Mortality (%) observed | Mortality (%) expected |
|---|---|---|---|
| Water control | n.a. | - | |
| QL Agri | 400 mL | 55.9 | |
| QL Agri | 100 mL | 29.4 | |
| QL Agri | 50 mL | 12.5 | |
| TAC | 300 g | 62.5 | |
| TAC | 150 g | 63.2 | |
| Mineral oil | 2000 mL | 55.5 | |
| QL Agri +TAC | 100 mL + 300 g | **69.1** | **73.5** |
| QL Agri +TAC | 50 mL + 150 g | **66.2** | **67.8** |
| QL Agri +TAC + Mineral oil | 50 mL + 150 g + 2000 mL | **100** | **86.3** |

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We claim:

1. A mixture comprising, as active components:

1) a water-based Quillay extract

and

2) a water-based Acacia negra extract

in a synergistically effective amount.

2. The mixture according to claim 1, wherein component 1) and component 2) are present in a total weight ratio of from 100:1 to 1:100 based on the total weight of the solid material (dry matter) of component 1) and component 2).

3. The mixture according to claim 2, wherein the total weight ratio is from 4:1 to 1:4.

4. The mixture according to claim 2, wherein the total weight ratio is from 2:1 to 1:2.

5. The mixture according to any of the claims 1 to 2, comprising
10 - 90% by weight of the component 1), and
10 - 90% by weight of the component 2), based on the total amount of the components 1) and 2) calculated as dry matter.

6. An agrochemical composition, comprising an auxiliary and a mixture as defined in any one of claims 1 to 5.

7. The composition according to claim 6, comprising
10 - 90% by weight of the component 1) based on the total weight of the dry matter (solid material) of component 1), and
10 - 90% by weight of the component 2), based on the total weight of the dry matter (solid material) of component 2).

8. The composition according to any of the claims 6 to 7, comprising as an auxiliary an organic acid, a mineral oil or a vegetable oil.

9. The composition according to any of the claim 8, wherein the auxiliary is selected from citric acid, lactic acid and ascorbic acid.

10. The composition according to any of the claims 6 to 9, further comprising as active component 3) a further active compound.

11. The composition according to claim 10, wherein the further active compound is a compound III selected from groups A), C), D), E), F), G), I), J), K) and N):

A) Respiration inhibitors

- inhibitors of complex III at Q; site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1 ,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1 ,5-dioxonan-7-yl] 2-methylpropanoate; (3S,6S,7R,8R)-3-[[(3-hydroxy-4-methoxy-2-pyridinyl)carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1 ,5-dioxonan-7-yl 2-methylpropanoate
- other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;

C) Nucleic acid synthesis inhibitors

- phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
- others: hymexazole, octhilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;

D) Inhibitors of cell division and cytoskeleton

- tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methylpiperidin-1 -yl)-6-(2,4,6-trifluorophenyl)-[1 ,2,4]triazolo[1 ,5-a]pyrimidine
- other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;

E) Inhibitors of amino acid and protein synthesis

- methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
- protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;

F) Signal transduction inhibitors

- MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;
- G protein inhibitors: quinoxyfen;

G) Lipid and membrane synthesis inhibitors

- Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;

- lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole;
- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyanophenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- compounds affecting cell membrane permeability and fatty acids: propamocarb, propamocarb-hydrochlorid
- fatty acid amide hydrolase inhibitors: 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1 H-pyrazol-1-yl]ethanone

I) Cell wall synthesis inhibitors

- inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defence inducers

- acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

K) Unknown mode of action

- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide,
N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine,
N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, 2-{1 -[2-(5-methyl-3-trifluoromethyl-pyrazole-1 -yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(1 ,2,3,4-tetrahydro-naphthalen-1-yl)-amide, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1 ,2,3,4-tetrahydro-naphthalen-1-yl-amide, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-l H-pyrazol-1-yl]ethanone, methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, A/-Methyl-2-{1-[(5-methyl-3-trifluoromethyl-1 H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-A/-[(1 R)-1 ,2,3,4-tetrahydronaphthalen-1 -yl]-4-thiazolecarboxamide, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1 H-benzoimidazole, 2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;

N) Herbicides

- acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet, mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, preti-

lachlor, propachlor, thenylchlor;

- amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate;
- aryloxyphenoxypropionates: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quizalofop, quizalofop-P-tefuryl;
- Bipyridyls: diquat, paraquat;
- (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate;
- cyclohexanediones: butroxydim, clethodim, cycloxydim, profoxydim, sethoxydim, tepraloxydim, tralkoxydim;
- dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin;
- diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen;
- hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil;
- imidazolinones: imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr;
- phenoxy acetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPB, Mecoprop;
- pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate;
- pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram, picolinafen, thiazopyr;
- sulfonyl ureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1 ,2-b]pyridazin-3-yl)sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea;
- triazines: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron, metribuzin, prometryn, simazine, terbuthylazine, terbutryn, triaziflam;
- ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, methabenzthiazuron,tebuthiuron;
- other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, ortho-sulfamuron, penoxsulam, propoxycarbazone, pyribambenz-propyl, pyribenzoxim, pyriftalid, pyriminobac-methyl, pyrimisulfan, pyrithiobac, pyroxasulfone, pyroxsulam;
- others: amicarbazone, aminotriazole, anilofos, beflubutamid, benazolin, bencarbazone,benfluresate, benzofenap, bentazone, benzobicyclon, bicyclopyrone, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthai, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoquat , *Drechslera monoceras,* endothal, ethofumesate, etobenzanid, fenoxasulfone, fentrazamide, flumiclorac-pentyl, flumioxazin, flupoxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsonic acid, naptalam, oxadiargyl, oxadiazon, oxaziclomefone,

pentoxazone, pinoxaden, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, quinoclamine, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrione, tembotrione, thiencarbazone, topramezone, (3-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-phenoxy]-pyridin-2-yloxy) -acetic acid ethyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3-chloro-6-(4-chloro-phenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxy-phenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3-chloro-6-(4-chloro-3-dimethylamino-2-fluoro-phenyl)-pyridine-2-carboxylic acid methyl ester.

12. A method for controlling harmful insects, which method comprises treating the pest, their habitat, breeding grounds, their locus or the plants to be protected against pest attack, the soil or plant propagation material, with a mixture as defined in any one of claims 1 to 5 or with a composition as defined in any of the claims 6 to 11.

13. A method for controlling phytopathogenic harmful fungi, comprising treating the fungi, their habitat or the seed, the soil or the plants to be protected against fungal attack with an effective amount of the mixture as defined in any one of claims 1 to 5 or of the composition as defined in any of the claims 6 to 11.

14. A plant propagation material, comprising the mixture as defined in any one of claims 1 to 5 or the composition as defined in any of the claims 6 to 11 in an amount of from 0.01 g to 10 kg per 100 kg of plant propagation material.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/075142

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N65/20 A01N65/34 A01P7/04 A01P3/00
ADD.

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)
A01N

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 practicable, search terms used)
EPO-Internal , BIOSIS, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | EP 1 862 072 A2 (NOR NATUR APS [DK] ) 5 December 2007 (2007-12-05) | 1-14 |
| A | US 2005/074508 Al (SAN MARTIN RICARDO [CL] ) 7 Apri l 2005 (2005-04-07) | 1 |
| A | US 5 270 083 A ( L0TZ W ROBERT [US] ) 14 December 1993 (1993-12-14) | 1 |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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"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

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 10 January 2013 | 18/01/2013 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Bertrand, Franck |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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