METHOD OF MOLLUSC CONTROL

A method of controlling mollusc damage to plants in horticulture or agriculture comprises treating the plant's propagation material with a combination of, as active ingredients, at least (a) clothianidin and prothioconazole, (b) clothianidin, fluoxastrobin and prothioconazole, (c) clothianidin, tebuconazole, triazoxide and prothioconazole, (d) imidacloprid and prothioconazole, (e) thiamethoxam, tebuconazole and fludioxonil, (f) imidacloprid and carboxin, (g) thiamethoxam, tefluthrin, azoxystrobin and tebuconazole, or (h) imidacloprid and tebuconazole.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
METHOD OF MOLLUSC CONTROL

The present invention relates to a method for improving the growing characteristics of a plant, in particular by protecting the plant propagation material of the plant against damage by molluscs, which method comprises a defined treatment of the plant propagation material; a plant propagation material so treated; and a composition for such treatment.

Molluscs are serious pests, especially of cereals, such as wheat, barley, oats and oil seed rape. The molluscs consume the seeds, seed growing points, and seedlings and thereby reduce the plant stand and yield of the crop.

Molluscs, such as slugs and snails, in horticulture and agriculture are a massively increasing problem. They can cause severe plant damage by feeding, and can also bring about undesirable soiling by slug and snail mucus and faeces. Changes in the management of crops (such as minimum tillage, direct drilling, and high organic matter build up in the soil) have led to increased population densities of slugs and snails and more severe damage on crops. The obligation to dispense with burning stubble fields - which is based on an ecological approach - and to manage the straw through other ways suggests that the existing mollusc problems, especially slug problems, are being made worse. Slugs feed vigorously above and below the surface on seeds, growing points, shoots and roots along with other organic matter they can find.

Current chemical control measures (bait pellets) often do not give adequate protection to plants, and pose an environmental hazard to mammals, and can often not be applied in a timely manner due to weather conditions and crop stand. In addition, at very early growing stages and when fields are dry, the molluscs do not come above ground which means baits are not effective, and crops are damaged.

There is, therefore, a demand for an effective management of this nuisance in horticulture and agriculture.

It has been found that treating plant propagation material before it is sown or planted with a combination of defined active ingredients provides surprisingly effective management against molluscs, and an increase in crop stand.
Accordingly, in a first aspect the present invention provides a method of controlling mollusc damage to plants in horticulture or agriculture comprises treating the plant's propagation material with a combination of, as active ingredients, at least (a) clothianidin and prothioconazole, (b) clothianidin, fluoxastrobin and prothioconazole, (c) clothianidin, tebuconazole, triazoxide and prothioconazole, (d) imidacloprid and prothioconazole, (e) thiamethoxam, tebuconazole and fludioxonil, (f) imidacloprid and carboxin, (g) thiamethoxam, tefluthrin, azoxystrobin and tebuconazole, or (h) imidacloprid and tebuconazole.

In a second aspect the present invention provides a plant propagation material treated with a combination defined in the first aspect.

In a third aspect the present invention provides a composition, preferably plant propagation material treatment composition, comprising a combination defined in the first aspect.

In an embodiment of the third aspect, a molluscidal plant propagation material, preferably molluscidal seed, treatment composition is made available.

The present invention is believed to prevent damage to the plant propagation material and organs that grow at later point in time by molluscs, and thus improve the growth characteristics of the plant through improved control of such molluscs.

Accordingly, in a further aspect the present invention provides a method of protecting plant propagation material and organs that grow at a later point in time against damage by molluscs, which method comprises treating the propagation material with a combination defined in the first aspect.

Also, the present invention provide a method of reducing the damage caused by molluscs to plant propagation material and organs that grow at a later point in time, which method comprises treating the propagation material with a combination defined in the first aspect.

The combinations of the invention are preventatively and/or curatively valuable active ingredients with a very favourable biocidal spectrum in the field of mollusc control, even at low use concentrations, and are well tolerated by warm blooded species, fish and plants. The combinations of the invention make it possible to treat seeds and other plant propagation materials with lower amounts of acutely toxic biocides than is known from the prior art.
The combinations of the invention are active against all or individual developmental stages of normally sensitive, but also resistant, molluscs, especially those mollusc stages that are foraging. Using the combination, it is possible to control, i.e., contain or destroy, mollusc damage in particular on plants, mainly on useful plants and ornamentals in agriculture, in horticulture and in forests.

The molluscicidal action of the combinations of the invention according to the invention correspond to reduction of the damage caused by molluscs to plant propagation material and organs that grow at a later point in time and may manifest (i) directly, i.e., in destruction of the molluscs, either immediately or only after some time has elapsed, or indirectly, for example in a reduced oviposition and/or hatching rate, the good action corresponding to a destruction rate (mortality) of at least 50 to 60%, or (ii) through repellancy of the molluscs, for example, by a reduction in the seed hollowing, and any signs of changes in the mollusc behaviour, such as paralysis, reduced movement, swellings or deformation, or (iii) through a combination of (i) and (ii).

The present invention, therefore, provides methods and materials for the prevention, control, and eradication, of mollusc infestation and, more particularly, mollusc-related damage to plants.

An amount of the combination that is effective to cause such prevention, control, and/or eradication will be referred to herein as an "effective amount" or a "molluscicidal-effective amount".

The combinations of the invention demonstrate synergistically enhanced action resulting in, for example, reduced damage to the plant by molluscs, lower rates of application of the individual active ingredients for such control, a longer duration of action and all together higher crop yields. The increase in advantageous properties achieved with the combinations of the invention are significantly greater than the activity to be expected by the individual components. In particular, it has now been found, surprisingly, that, for example, the activity of the treatment of the combinations of the invention on the plant propagation material, compared with the activity of the individual active ingredients, are not merely additive, as may essentially be expected, but that a synergistic effect exists. This effect can be calculated according to the Colby formula.

The term "synergistic", independently of the combination, is not, however, in any way limited in this context to the molluscicidal activity, but refers equally to other advantageous properties.
Examples of such advantageous properties that may be mentioned are: a broadening of the spectrum of pesticidal activity to other pests, for example to resistant strains; a reduction in the rate of application of the active ingredients; adequate control of the pests with the aid of the combinatons, even at a rate of application at which the individual active ingredients are totally ineffective; advantageous behaviour during formulating and/or upon application, for example upon grinding, sieving, emulsifying, dissolving or dispersing; increased storage stability; improved stability to light; more advantageous degradability; improved toxicological and/or ecotoxicological behavior; improved crop characteristics including: emergence, crop yields, more developed root system, tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, less fertilizers needed, less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, improved plant vigor, and early germination; or any other advantages familiar to a person skilled in the art.

The improvement in the growing (or growth) characteristics of a plant can manifest in a number of different ways, but ultimately it results in a better production of the plant. It can, for example, manifest in improving the yield and/or vigour of the plant or quality of the harvested product from the plant.

As used herein the phrase "improving the yield" of a plant relates to an increase in the yield of a product (e.g., as measured by plant biomass, grain or fruit yield, protein content, carbohydrate or oil content or leaf area) of the plant by a measurable amount over the yield of the same product of the plant produced under the same conditions, but without the application of the subject method. It is preferred that the yield be increased by at least about 0.5%, more preferred that the increase be at least about 1%, even more preferred is about 2%, and yet more preferred is about 4%, or more. Yield can be expressed in terms of an amount by weight or volume of a product of the plant on some basis. The basis can be expressed in terms of time, growing area, weight of plants produced, amount of a raw material used, or the like.

As used herein the phrase "improving the vigour" of a plant relates to an increase or improvement of the vigour rating, or the stand (the number of plants per unit of area), or the plant height, or the plant canopy, or the visual appearance (such as greener leaf colour), or the root rating, or emergence, or protein content, or increased tillering, or bigger leaf blade, or less dead basal leaves, or stronger tillers, or less fertilizer needed, or less seeds needed, or more productive tillers, or earlier flowering, or early grain maturity, or less plant verse
(lodging), or increased shoot growth, or earlier germination, or any combination of these factors, or any other advantages familiar to a person skilled in the art, by a measurable or noticeable amount over the same factor of the plant produced under the same conditions, but without the application of the subject method.

When it is said that a method is capable of "improving the yield and/or vigour" of a plant, the present method results in an increase in either the yield, as described above, or the vigor of the plant, as described above, or both the yield and the vigor of the plant.

The combinations of the invention can also be used to treat stored products for protection against molluscs.

In a further aspect, the present invention also provides a method of controlling mollusc damage to plants in horticulture or agriculture comprises treating the plant’s propagation material with a combination of, as active ingredients, at least three active ingredients from (I) one or more of (i) one or more of a neonicotinoid, (ii) one or more of a pyrethroid, (iii) one or more of a macrolide, (iv) one or more of flubendiamide (3-iodo-N-(2-mesyl-1,1-dimethylethyl)-N-{4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-o-tolyl]phthalamide) and a compound of formula A-1 below.

\[
\begin{align*}
\text{H}_3\text{C} & \text{O} \\
\text{Br} & \\
\text{Cl} & \\
\text{N} & \text{H} \\
\text{N} & \text{CH}_3
\end{align*}
\]

(v) one or more of a fiprole and (vi) one or more of metaldehyde, methiocarb, thiodicarb, cinnamaldehyde and 3,5-dimethoxycinnamic acid, and (II) one or more of a fungicide compound selected from, benalaxyl, benalaxyl-M, fuberidazole, thiram, fludioxonil, thiabendazole, azyxystrobin, pyraclostrobin, fluoxastrobin, bitertanol, cyproconazole, difenoconazole, diniconazole, prochloraz, fluquinconazole, flutriafol, metalaxyl, metalaxyl-M (mefenoxam), prothioconazole, tebuconazole, triadimenol, triticonazole, triazoxide, cyprodinil, carboxin and silthiofam.
In another aspect, the present invention provides a method of controlling mollusc damage to plants in horticulture or agriculture comprises treating the plant's propagation material with a combination of, as active ingredients, at least two active ingredients from (i) one or more of a neonicotinoid, (ii) one or more of a pyrethroid, (iii) one or more of a macrolide, (iv) one or more of flubendiamide (3-iodo-N-(2-methyl-1,1-dimethyllethyl)-N-{4-[1,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-o-toly]phthalamide) and a compound of formula A-1 below.

(v) one or more of a fiprole and (vi) one or more of metaldehyde, methiocarb, thiodicarb, cinnamaldehyde and 3,5-dimethoxycinnamic acid, and (ii) one or more of a fungicide compound selected from, benalaxyl, benalaxyl-M, fuberidazole, thiabendazole, azoxytrobin, pyraclostrobin, fluoxastrobin, bitertanol, cyproconazole, difenoconazole, diniconazole, prochloraz, fluquinconazole, flutriafol, metalaxyl, metalaxyl-M, prothioconazole, tebuconazole, triadimenol, triticonazole, triazole, cyprodinil, carboxin and silthiofam.

The present invention also makes available, in respect of each of the combinations defined in the two preceding paragraphs above, further methods and compositions as detailed in respect of the first aspect above.

The combinations of the invention are found to demonstrate unexpected molluscicidal action, especially against slugs. Molluscs which may be controlled by methods and compositions of the present invention are preferably molluscs comprised in the gastropod class, more preferably the subclass pulmonata, even more preferably snails and slugs, and most preferably include, for example, Ampullariidae; Arion (A. ater, A. circumscriptus, A. hortensis, A. rufus); Bradybaenidae (Bradybaena fruticum); Cepaea (C. hortensis, C. Nemoralis); ochlodina; Deroceras (D. agrestis, D. empiroricum, D. laeve, D. reticulatum); Discus (D. rotundatus); Euomphalia; Galba (G. trunculata); Helicelium (H. itala, H. obvia); Helicidae Helicogona arbustorum; Helicodiscus; Helix (H. aperta); Limax (L. cinereoniger, L. flavus, L. marginatus, L. maximus, L. tenellus); Lymnaea; Milax (M. gagates, M. marginatus, M. sowerbyi); Opeas; Pomacea (P. canaticulata); Vallonia
and Zanitoides. The combinations according to the present invention are particularly effective against Deroceras, such as Deroceras reticulatum.

In an aspect, the present invention is a method comprising

(i) treating plant propagation material with a combination as defined herein,
(ii) planting or sowing the treated plant propagation material, and
(iii) achieving control of molluscs at the site of planting or sowing.

Even distribution of the active ingredients and adherence thereof to the propagation materials is desired during propagation material treatment. Treatment could vary from a thin film (dressing) of the formulation containing the active ingredient(s) on a plant propagation material, such as a seed, where the original size and/or shape are recognizable to an intermediary state (such as a coating) and then to a thicker film (such as pelleting with many layers of different materials (such as carriers, for example, clays; different formulations, such as of other active ingredients; polymers; and colourants) where the original shape and/or size of the seed is no longer recognisable.

Accordingly, in the second aspect, the active ingredients are adhered to the propagation material, such a seed. The treated propagation material, consequently, demonstrates resistance to molluscs and pests as a result of the treatment.

The combination of the invention can be treated simultaneously, or sequentially, in any order, on to the propagation material. Similarly if there is more than one active ingredient in (I) or (II), then those active ingredients can be treated simultaneously, or sequentially, in any order, on to the propagation material.

In the instance it is applied sequentially, an active ingredient (e.g., from (I)) in the form of a suitable product, such as seed treatment formulation, could be applied to the propagation material, and then a second active ingredient (e.g., from (II)), in the form of a separate formulation, could be applied later, resulting in, for example, a layered treatment of the propagation material.

Preferably, active ingredients are applied simultaneously on to the propagation material. In such a case, the combination is mixed before treatment on to the propagation material from separate formulations (products), each containing at least one active ingredient, or is available as a single composition containing all of the active ingredients (e.g. (I) and (II)).
In the event the combination is present in a single composition (known as a pre-mix product or formulation), the composition consists essentially, preferably consists, as active ingredients, of a combination as defined herein.

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

Parts of plant and plant organs that grow at later point in time are any sections of a plant that develop from a plant propagation material, such as a seed. Parts of plant, plant organs, and plants can also benefit from the pathogenic and/or pest damage protection achieved by the application of the combination on to the plant propagation material. In an embodiment, certain parts of plant and certain plant organs that grow at later point in time can also be considered as plant propagation material, which can themselves be applied (or treated) with the combination; and consequently, the plant, further parts of the plant and further plant organs that develop from the treated parts of plant and treated plant organs can also benefit from the pathogenic and/or pest damage protection achieved by the application of the combination on to the certain parts of plant and certain plant organs.

Methods for applying or treating pesticidal active ingredients, mixtures and compositions thereof on to plant propagation material, especially seeds, are known in the art, and include dressing, coating, pelleting and soaking application methods of the propagation material. In a preferred embodiment, the combination is applied or treated on to the plant propagation material by a method such that the germination is not induced; generally seed soaking induces germination because the moisture content of the resulting seed is too high. Accordingly, examples of suitable methods for applying (or treating) a plant propagation material, such as a seed, is seed dressing, seed coating or seed pelleting and alike.

It is preferred that the plant propagation material is a seed. Although it is believed that the present method can be applied to a seed in any physiological state, it is preferred that the seed be in a sufficiently durable state that it incurs no damage during the treatment process.
-9-
Typically, the seed would be a seed that had been harvested from the field; removed from
the plant; and separated from any cob, stalk, outer husk, and surrounding pulp or other non-
seed plant material. The seed would preferably also be biologically stable to the extent that
the treatment would cause no biological damage to the seed. It is believed that the
treatment can be applied to the seed at any time between harvest of the seed and sowing of
the seed or during the sowing process (seed directed applications). The seed may also be
primed, according to techniques understood by a skilled person, either before or after the
treatment.

The seed treatment occurs to an unsown seed, and the term "unsown seed" is meant to
include seed at any period between the harvest of the seed and the sowing of the seed in the
ground for the purpose of germination and growth of the plant.

Treatment to an unsown seed is not meant to include those practices in which the active
ingredient is applied to the soil but would include any application practice that would target
the seed during the planting process.

Preferably, the treatment occurs before sowing of the seed so that the sown seed has been
pre-treated with the combination. In particular, seed coating or seed pelleting are preferred in
the treatment of the combinations according to the invention. As a result of the treatment,
the active ingredients in the combination are adhered on to the seed and therefore available
for pathogenic and/or pest control, especially molluscidal control.

The weight ratio of any two actives ingredients (e.g. (I) and (II)) and amount used on the
propagation material varies according to specific active ingredient (e.g., abamectin is
generally applied at a lower rate than thiamethoxam), type of propagation material (e.g.,
seed or tuber) and plant (for example, wheat seeds generally have less active ingredients
adhered thereto than oil seed rape seeds based on equivalent weight of seeds) and is such
that the combinations are an effective amount to provide the desired molluscidal action and
can be determined by biology trials.

The weight ratio of any combination of active ingredients is generally selected as to give the
desired, for example synergistic, action. In general, the weight ratio between any two active
ingredients is from 7:1 to 1:7, more preferably 5:1 to 1:5, especially from 2.5:1 to 1:2.5,
advantageously preferably, 1:1.5 to 1:5:1.
The application rates can, therefore, range from 6g to 250kg of a combination per 100kg of seeds. Generally, the combined application rate of a combination for cereal seeds range from 23g to 740g, preferably 50g to 600g, per 100kg of seeds; and the combined application rate of a combination for oil seed rape seeds can range from 700g to 25kg, preferably 1.5kg to 20kg, per 100kg of seeds.

Examples of application rates in cereals, such as wheat, barley, can be in the range of:
- clothianidin – 10-200, preferably 25-100, such as 45-55;
- prothioconazole – 2-40, preferably 5-10, such as 7-12;
- fluoxastrobin – 1.5-20, preferably 3-10, such as 4-6;
- tebuconazole – 0.5-12, preferably 1-6, such as 2-4;
- triazoxide – 0.5-8, preferably 1-4, such as 1.5-2.5;
- imidacloprid – 8.5-140, preferably 16-70, such as 30-50;
- thiamethoxam – 10-200, preferably 20-100, such as 30-60;
- fludixonil – 1.5-20, preferably 3-10, such as 4-6;
- carboxin – 15-280, preferably 30-140, such as 60-80;
- tefluthrin – 5-80, preferably 10-40, such as 17-25;
- azoxystrobin – 1.5-20, preferably 3-10, such as 4-6;

each in grams per 100kg of seeds.

In an embodiment of each aspect of the invention, the combination is one of (I) and two or more of (II), as active ingredients.

In an embodiment, independent of other embodiments and aspects, (i) the neonicotinoid is from one or more of acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, thiamethoxam. Preferred neonicotinoid insecticides include clothianidin, thiacloprid, imidacloprid and thiamethoxam. Particularly preferred neonicotinoid insecticides include thiamethoxam and imidacloprid.

In an embodiment, independent of other embodiments and aspects, (ii) the pyrethroid is from one or more of alpha-cypermethrin, beta-cyfluthrin, beta-cypermethrin, bifenthrin, bioallethrin, bioresmethrin, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin, cyphenothrin, deltamethrin, empenthrin, esfenvalerate, fenpropathrin, fenvalerate, flucythrinate, flumethrin, gamma-cyhalothrin, imiprothrin, lambda-cyhalothrin, methothrin, metofluthrin, permethrin, phenothrin, prallethrin, resmethrin, tau-fluvalinate, tefluthrin, tetramethrin, theta-cypermethrin, tralomeprin, transfluthrin, and zeta-cypermethrin. Preferred pyrethroid insecticides include tefluthrin, beta-
cyfluthrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, deltamethrin and lambda cyhalothrin.

In an embodiment, independent of other embodiments and aspects, (iii) the macrolide is selected from abamectin, emamectin, spinosad, doramectin, eprinomectin, ivermectin, selamectin, and substituted milbemectins, such a compound of formula

\[ R = CH_2 \text{ ca. 80\% (A4)} \]
\[ R = H \text{ ca. 20\% (A3)} \]

Preferably the macrolide is selected from emamectin, abamectin, spinosad, and a compound of formula

\[ R = CH_2 \text{ ca. 80\% (A4)} \]
\[ R = H \text{ ca. 20\% (A3)} \]

In an embodiment, independent of other embodiments and aspects, (v) is fipronil.

In an embodiment, independent of other embodiments and aspects, (vi) is metaldehyde.

In an embodiment, independent of other embodiments and aspects, the one or more of a compound (I) is selected from thiamethoxam, imidacloprid, clothianidin, tefluthrin, beta-cyfluthrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-
cypermethrin, fipronil and metaldehyde; especially selected from thiamethoxam, imidacloprid, clothianidin, fipronil and metaldehyde

Preferably the fungicide compound (II) is selected from (a) a strobilurin compound, (b) a DMI compound, (c) a benzimidazole compound, (d) a benzotriazine compound, (e) a phenylpyrrole compound, (f) an anilinopyrimidine compound, (g) a carboxamide compound, (h) a phenylamide: acylalanine, (i) a multi-site class.

In an embodiment, independent of other embodiments and aspects, (a) the strobilurin compound is from one or more of a strobilurin type: methoxyacrylate compound, strobilurin type: oxazolidinedione compound, strobilurin type: imidazolinone compound, strobilurin type: oximinoacetamide compound, strobilurin analogue: dihydrodioxazine compound, strobilurin type: oximinoacetate compound, and strobilurin type: methoxycarbarnate compound.

In an embodiment, independent of other embodiments and aspects, (a) the strobilurin compound is from one or more of fluoxastrobin, fenamidone, azoxytrobibin, picoxystrobin, pyraclostrobin, famoxadone, dimoxystrobin, metominostrobin, kresoxim-methyl, and trifloxystrobin. Advantageous strobilurin compounds are fluoxastrobin, pyraclostrobin and azoxytrobibin.

In an embodiment, independent of other embodiments and aspects, (b) the DMI compound is from one or more of a DMI: piperazine compound, DMI: triazole compound, DMI: imidazole compound, and DMI: pyrimidine compound.

The DMI: piperazine compound is triformine.

The DMI: triazole compound is selected from one or more of azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, paclobutrazol, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, and triticonazole.

The DMI: imidazole compound is selected from imazalil, oxpoconazole fumarate, pefurazoate, penconazole, prochloraz, and triflumizole.

The DMI: pyridine compound is pyrifenox.
The DMI: pyrimidine compound is fenarimol.

In an embodiment, independent of other embodiments and aspects, (b) the DMI compound
is from one or more of bitertanol, cyproconazole, difenoconazole, diniconazole,
fluquinconazole, fluatriafol, metconazole, prothioconazole, tebuconazole, triadimefon,
triamidinol, triticonazole, prochloraz and imazalil.

In an embodiment, independent of other embodiments and aspects, (c) the benzimidazole
compound is from one or more of carbendazim, furberidazole and thiabendazole;
advantageously one or more of furberidazole and thiabendazole.

In an embodiment, independent of other embodiments and aspects, (d) the benzotriazine
compound is triazoxide.

In an embodiment, independent of other embodiments and aspects, (e) the phenylpyrrole
compound is from one or more of fenpiclonil and fludioxonil.

In an embodiment, independent of other embodiments and aspects, (f) the anilinopyrimidine
compound is from one or more cyprodinil and pyrimethanil.

In an embodiment, independent of other embodiments and aspects, (g) the carboxamide
compound is from one or more of boscalid, carboxin and silthiofam; advantageously one or
more carboxin and silthiofam.

In an embodiment, independent of other embodiments and aspects, (h) the
phenylamide:acylalanine compound is one or more of benalaxyl, benalaxyl-M, metalaxyl,
metalaxyl-M; advantageously one or more of metalaxyl and metalaxyl-M.

In an embodiment, independent of other embodiments and aspects, the fungicide is selected
from a multi-site class compound such as thiram, copper hydroxide, iminoctadine and
mancozeb, especially thiram.

In an embodiment, independent of other embodiments and aspects, the one or more
fungicides (II) is selected from one or more of thiram, benalaxyl, benalaxyl-M, furberidazole,
thiabendazole, azoxystrobin, pyraclostrobin, fluoxastrobin, bitertanol, cyproconazole,
-14-
difenconazole, prochloraz, diniconazole, prothioconazole, fluquinconazole, flutriafol, metalaxyl, metalaxyl-M, prothioconazole, tebuconazole, triadimenol, triticonazole, fludioxonil, triazoxide, cyprodinil, carboxin and silthiofam; especially pyraclostrobin, fluoxastrobin, fluquinconazole, prothioconazole, tebuconazole, carboxin, fludioxonil, prochloraz, difenoconazole, mefenoxam.

Accordingly, a preferred combination according to the invention is
(A) at least three from:

(I) thiamethoxam, imidacloprid, clothianidin, tefluthrin, beta-cyfluthrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, fipronil and metaldehyde; especially selected from thiamethoxam, imidacloprid, clothianidin, fipronil and metaldehyde, and

(II) thiram, benalaxyl, benalaxyl-M, fuberdaizole, thiabendazole, azoxystrobin, pyraclostrobin, fluoxastrobin, bitertanol, cyproconazole, difenoconazole, prochloraz, diniconazole, prothioconazole, fluquinconazole, flutriafol, metalaxyl, metalaxyl-M, prothioconazole, tebuconazole, triadimenol, triticonazole, fludioxonil, triazoxide, cyprodinil, carboxin and silthiofam; especially pyraclostrobin, fluoxastrobin, fluquinconazole, prothioconazole, tebuconazole, carboxin, fludioxonil, prochloraz, difenoconazole, mefenoxam.

or

(B) at least two from

(I) thiamethoxam, imidacloprid, clothianidin, tefluthrin, beta-cyfluthrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, fipronil and metaldehyde; especially selected from thiamethoxam, imidacloprid, clothianidin, fipronil and metaldehyde, and

(II) benalaxyl, benalaxyl-M, fuberdaizole, thiabendazole, azoxystrobin, pyraclostrobin, fluoxastrobin, bitertanol, cyproconazole, difenoconazole, prochloraz, diniconazole, prothioconazole, fluquinconazole, flutriafol, metalaxyl, metalaxyl-M, prothioconazole, tebuconazole, triadimenol, triticonazole, triazoxide, cyprodinil, carboxin and silthiofam; especially pyraclostrobin, fluoxastrobin, fluquinconazole, prothioconazole, tebuconazole, carboxin, prochloraz, difenoconazole, mefenoxam.

It has been found that the properties of the combinations (e.g. (I) and (II)) are improved further if anthraquinone is also present in the treatment of the plant propagation material. Anthraquinone can be present as a mixing partner with one of the active ingredients before
they are combined, or can be present in the combination, or can be mixed together with the combination before treating the plant propagation material (e.g. slurry composition), or can be treated separately on to the plant propagation material.

Suitable examples of mixtures of fungicides (II) are cyproconazole and difenoconazole; flutriafol, prochloraz and pyrimethanil; fluquinconazole and prochloraz; copper hydroxide and ipconazole; fludioxonil and tebuconazole; tebuconazole and thiram; azoxystrobin, fludioxonil and metalaxyl-M; anthraquinone, difenoconazole and fludioxonil; cabendazim, thiram and triadimefon; fuberidazole, imazalil and triadimenol; bitertanol and fuberidazole; diniconazole and thiabendazole; defenoconazole, metalaxyl-M and tebuconazole; antraquinone, prochloraz and triticonazole; fuberidazole and triadimenol; difenoconazole and fludioxonil; azoxystrobin and metalaxyl; azoxystrobin, metalaxyl and thiram; antraquinone, bitertanol and fuberidazole; tebuconazole and thiabendazole; tebuconazole and triazoxide; cyprodinil, fludioxonil and tebuconazole; copper oxychloride, fludioxonil and pefurazoate; iprodione and triticonazole; cymoxanil, mancozeb and thiophanate-methyl; imazalil and tebuconazole; fluoxastrobin and prothioconazole; prothioconazole, tebuconazole and triazoxide; antraquinone, cyprodinil, fludioxonil and tebuconazole; carbenazim, carboxin, thiram and triadimefon; imazalil and triticonazole; carboxin, tebuconazole and triadimenol; cyprodinil, fludioxonil and flutriafol; fluquinconazole and prothioconazole; fludioxonil and metalaxyl-M; carboxin and thiram; cymoxanil, fludioxonil and metalaxyl-M; difenoconazole and metalaxyl-M; and metalaxyl and tebuconazole.

Suitable examples of mixtures of (I) are beta-cyfluthrin and imidacloprid; imidacloprid and metaldehyde; thiamethoxam and metaldehyde; thiamethoxam and imidacloprid; tefluthrin and thiamethoxam; and beta-cyfluthrin and clothianidin.

The present invention accordingly also envisages each combination of the mixtures (I) and (II) described above.

Particularly preferred combinations of (I) and (II) are difenoconazole, fludioxonil, metalaxyl-M and thiamethoxam; imidacloprid, tebuconazole and triazoxide; anthraquinone, fludioxonil and tefluthrin; anthraquinone, bitertanol and imidacloprid; azoxystrobin, fludioxonil, metalaxyl-M and thiamethoxam; cypermethrin and triticonazole; fludioxonil, mefenoxam and thiamethoxam; bitertanol, fuberidazole and imidacloprid; defenoconazole, metalaxyl-M and thiamethoxam; imidacloprid and pencycuron; carboxin, chlorothianidin, metalaxyl and thiram; cypermethrin and tebuconazole; clothianidin and prothioconazole; clothianidin, fluoxastrobin
and prothioconazole; prothioconazole, tebuconazole, triazoxide and clothianidin; imidacloprid and triticonazole; defenoconazole; imidacloprid and tebuconazole; deltamethrin and triticonazole; cyprodinil, fludioxonil, flutriafol and thiamethoxam; difenoconazole, fludioxonil, tefluthrin and thiamethoxam; and fipronil, iminoactadine and triticonazole.

Further, the growing characteristics of a plant can be further improved by incorporating in the treatment on the propagation material one or more other further active compounds. These further compounds can be other pesticidal active ingredients (e.g., a fungicide, insecticide or nematicide), fertilizers or micronutrient donors or other preparations that influence plant growth, such as inoculants.

A single pesticide may have activity in more than area of pest control, for example, a pesticide may have fungicide, insecticide and nematicide activity. Specifically, aldicarb is known for insecticide, acaricide and nematicide activity, while metam is known for insecticide, herbicide, fungicide and nematicide activity, and thiabendazole and captan can provide nematicide and fungicide activity.

Accordingly, the active ingredients indicated in the combinations herein as having molluscicide activity can also be used as co-pesticides.

Specific examples are abamectin (1), acephate (2), acetamiprid (4), alpha-cypermethrin (202), azinphos-methyl (45), bifenthrin (76), carbaryl (115), carboxin (120), carbofuran (118), carbosulfan (119), chlorpyrifos (145), clothianidin (165), cyromazine (209), deltamethrin (223), dimethoate (262), emamectin benzoate (291), endosulfan (294), fipronil (354), furathiocarb (412), gamma-HCH (430), imidacloprid (458), Isofenphos, methiocarb (530), omethoate (594), tefluthrin (769), thiamethoxam (792), thiacloprid (791), thiodicarb (799), azoxystrobin (47), pyraclostrobin (690), benomyl (62), bitertanol (84), captan (114), carbendazim (116), carboxin (120), chlorothalonil (142), copper salts (such as copper sulfate (172), cuprous oxide (181), Bordeaux mixture (87), copper hydroxide (169), copper sulfate (tribasic) (173), copper oxychloride (171) and copper octanoate (170), cymoxanil (200), cyproconazole (207), cyprodinil (208), difenoconazole (247), diniconazole (267), ethirimol, famoxadone (322), fenamidone (325), fenhexamid (334), fenpiclonil (341), fluazinam (363), fludioxonil (368), fluquinconazole (385), flutolanil (396), flutriafol (397), fosetyl-aluminium (407), fuberidazole (409), guazatine (422), hexaconazole (435), hymexazol (447), imazalil (449), iprodione (470), isofenphos, mancozeb (496), maneb (497), metalaxyl (516), metalaxyl-M (517), metconazole (525), myclobutanil (564), silthiofam (729), nuarimol (587), oxadixyl (601), oxine-copper (605),
-17-
oxolinic acid (606), pencycuron (620), prochloraz (659), procymidone (660), pyrimethanil (705), pyroquilon (710), quintozene (716), tebuconazole (761), tetraconazole (778), thiabendazole (790), thiophanate-methyl (802), thiram (804), triadimenol (815), triazoxide (821), triticonazole (842), trifloxystrobin (832), picocystrobin (647), ipconazole (468), and 3-Difluoromethyl-1-methyl-1Hpyrazole-4-carboxylic acid (2-bicyclopropyl-2-yl-phenyl)-amide.

It has been found that a combination of (a) clothianidin and prothioconazole, (b) clothianidin, fluoxastrobin and prothioconazole, (c) clothianidin, tebuconazole, triazoxide and prothioconazole, (d) imdicloprid and prothioconazole, (e) thiamethoxam, tebuconazole and fludioxonil, (f) imdicloprid and carboxin, (g) thiamethoxam, tefluthrin, azoxystrobin and tebuconazole, or (h) imdicloprid and tebuconazole, demonstrates particularly good activity against mollusc, as well as other pesticidal activity.

Whereas commercial products will preferably be formulated as concentrates (known as a pre-mix composition (or concentrate, formulated compound (or product)), the end user will normally employ dilute formulations (known as a tank mix composition (or ready-to-apply, spray broth, or slurry)), optionally also containing one or more other pesticide pre-mix formulations for treatment of the propagation material, but can also use appropriately formulated pre-mix compositions.

The pesticide formulation for the treatment can take a variety of forms including, suspensions, emulsions, solutions or dusts, optionally with the use of polymeric carriers or stickers.

The formulation can be applied to the seeds using conventional treating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed treaters, and drum coaters. Other methods, such as spouted beds may also be useful. The seeds may be presized before coating. After coating, the seeds are typically dried and then transferred to a sizing machine for sizing. Such procedures are known in the art.

The formulation (pre-mix or tank-mix), therefore, can comprise as well as active ingredients (e.g. (I) and (II)), at least one of the auxiliary (also known as adjuvants) customary in formulation technology, such as extenders, e.g., solvents (e.g., water) or solid carriers, or surface-active compounds (surfactants), and optionally other pesticides. Accordingly, a composition of the third aspect generally also comprises one or more auxiliary customary in formulation technology.
Examples of seed treatment pre-mix formulations types are:

WS: wettable powders for seed treatment slurry
LS: solution for seed treatment
ES: emulsions for seed treatment
FS: suspension concentrate for seed treatment
WG: water dispersible granules, and
CS: aqueous capsule suspension.

Examples of formulation types suitable for tank-mix compositions are solutions, dilute emulsions, suspensions, or a mixture thereof, and dusts.

The tank-mix compositions are generally prepared by diluting with a solvent (for example, water) the one or more pre-mix compositions containing different pesticides, and optionally further auxiliaries. Generally, an aqueous tank-mix is preferred.

Normally, a tank-mix formulation for seed treatment application comprises 0.25 to 80%, especially 1 to 75 %, of a pesticide, and 99.75 to 20 %, especially 99 to 25 %, of a solid or liquid auxiliaries (including, for example, a solvent such as water), where the auxiliaries can be a surfactant in an amount of 0 to 40 %, especially 0.5 to 30 %, based on the tank-mix formulation.

Typically, a pre-mix formulation for seed treatment application comprises 0.5 to 99.9 %, especially 1 to 95 %, of a pesticide, and 99.5 to 0.1 %, especially 99 to 5 %, of a solid or liquid adjuvant (including, for example, a solvent such as water), where the auxiliaries can be a surfactant in an amount of 0 to 50 %, especially 0.5 to 40 %, based on the pre-mix formulation. Preferred seed treatment pre-mix formulations are aqueous suspension concentrates.

The Examples, which follow serve to illustrate the suitable formulations.

30  **Formulation Examples**

<table>
<thead>
<tr>
<th>Wettable powders</th>
<th>a)</th>
<th>b)</th>
<th>c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>active ingredients</td>
<td>25 %</td>
<td>50 %</td>
<td>75 %</td>
</tr>
<tr>
<td>sodium lignosulfonate</td>
<td>5 %</td>
<td>5 %</td>
<td>-</td>
</tr>
<tr>
<td>sodium lauryl sulfate</td>
<td>3 %</td>
<td>-</td>
<td>5 %</td>
</tr>
<tr>
<td>sodium diisobutyl naphthalenesulfonate</td>
<td>-</td>
<td>6 %</td>
<td>10 %</td>
</tr>
<tr>
<td>phenol polyethylene glycol ether</td>
<td>-</td>
<td>2 %</td>
<td>-</td>
</tr>
</tbody>
</table>
(7-8 mol of ethylene oxide)

highly dispersed silicic acid  5 %  10 %  10 %

Kaolin  62 %  27 %  -

The active ingredients are thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

<table>
<thead>
<tr>
<th>Dusts</th>
<th>a)</th>
<th>b)</th>
<th>c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>active ingredients</td>
<td>5 %</td>
<td>6 %</td>
<td>4 %</td>
</tr>
<tr>
<td>Talcum</td>
<td>95 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kaolin</td>
<td>-</td>
<td>94 %</td>
<td>-</td>
</tr>
<tr>
<td>mineral filler</td>
<td>-</td>
<td>-</td>
<td>96 %</td>
</tr>
</tbody>
</table>

Ready-for-use dusts are obtained by mixing the active ingredients with the carrier and grinding the mixture in a suitable mill. Such powders can be used for dry dressings for seed.

Suspension concentrates (a) (b)

| active ingredients | 5% | 30 % |
| propylene glycol    | 10%| 10 % |
| Tristyrylphenol ethoxylates | 5 % | 6 % |
| sodium lignosulfonate | -  | 10 % |
| carboxymethylcellulose | -  | 1 % |
| silicone oil (in the form of a 75 % emulsion in water) | 1 % | 1 % |
| Colour pigment      | 5 % | 5 % |
| water               | 74 %| 37 % |

The finely ground active ingredients are intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Alternatively, a suspension of the active ingredients and auxiliaries (including water) is wet milled with a bead-mill to achieve a stable formulation and with the appropriate treatment characteristics.

In an embodiment, the composition of the third aspect is in the form of an aqueous suspension, and, in the instance it is a pre-mix formulation, it is in the form of a suspension concentrate.

The treated plant propagation material of the present invention can be treated in the same manner as conventional plant propagation material.
The treated seeds can be stored, handled, sowed and tilled in the same manner as any other pesticide treated seed.

In an embodiment of the present invention, the action of the seed treatment molluscicide can be significantly improved and adapted to the given circumstances by the use of a molluscicide compounds used in agriculture, for example, by use of slug baits.

The present invention is especially suitable for agronomically important plants, which refers to a plant that is harvested or cultivated on a commercial scale.

Examples of such agronomic plants (or crops) are cereals, such as wheat, barley, rye, oats, rice, maize or sorghum; beet, such as sugar or fodder beet; fruit, for example pome fruit, stone fruit and soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries, raspberries or blackberries; legumes, such as beans, lentils, peas or soya beans; oil crops such as oil seed rape, mustard, poppies, olives, sunflowers, coconuts, castor, cacao or peanuts; the marrow family, such as pumpkins, cucumbers or melons; fibre plants such as cotton, flax, hemp or jute; citrus fruits such as oranges, lemons, grapefruits or tangerines; vegetables such as spinach, lettuce, asparagus, cabbage species, carrots, onions, chillis, tomatoes, potatoes, or capsicums; the laurel family such as avocado, Cinnamonium or camphor; and tobacco, nuts, coffee, egg plants, sugar cane, tea, pepper, grapevines, hops, the banana family, latex plants and ornamentals. Also important are forage crops such as grassed and legumes. In an embodiment, invention is suitable for wheat, barley, oats and oil seed rape.

Suitable target crops also include transgenic crop plants of the foregoing types. The transgenic crop plants used according to the invention are plants, or propagation material thereof, which are transformed by means of recombinant DNA technology in such a way that they are - for instance - capable of synthesizing selectively acting toxins as are known, for example, from toxin-producing invertebrates, especially of the phylum Arthropoda, as can be obtained from Bacillus thuringiensis strains; or as are known from plants, such as lectins; or in the alternative capable of expressing a herbicidal or fungicidal resistance. Examples of such toxins, or transgenic plants which are capable of synthesizing such toxins, have been disclosed, for example, in EP-A-0 374 753, WO 93/07278, WO 95/34656, EP-A-0 427 529 and EP-A-451 878 and are incorporated by reference in the present application.
-21-
The invention is especially suitable for wheat, barley, oil seed rape plants, sugar beets and vegetables.

In each aspect and embodiment of the invention, “consisting essentially” and inflections thereof are a preferred embodiment of “comprising” and its inflections, and “consisting of” and inflections thereof are a preferred embodiment of “consisting essentially of” and its inflections.


The following Examples are given by way of illustration and not by way of limitation of the invention.

Examples

Example 1
Wheat seeds are sown to a depth of approximately 2 cm in plastic seed trays (55 cm length, 31 cm width, 5 cm high) with the soil flush with the top of the trays. 100 seeds are sown per tray, and three trays are placed in an arena. Trays are placed in an arena so that the top of the tray is flush with soil in the arena. The arena contains a mix of composting soil and top soil (compost : top soil in a 2 : 1 ratio) to a depth of approximately 5 cm. A 2 cm wide copper tape barrier is applied to inner wall of the arena to contain the slugs. Netting to stop feeding on the seeds by birds covers the arenas. During dry weather arenas are watered regularly to ensure they do not dry out.

Each tray is sown with seeds by different treatment. Then 30 slugs (*D. reticulatum* (Muller) – average weight range 400-600 mg) are added to each arena.

The combinations according to the present invention show good action compared to the individual active ingredients alone.

Example 2
50 wheat seeds are sown in 0.2 m² tray on moist filter paper and kept under controlled conditions (17°C and 90% humidity). Five slugs are introduced into each tray, a number equivalent to a “heavy infestation”. In terms of crop protection the wheat grains are examined for signs of seed hollowing and germination.
The combinations according to the present invention show good action compared to the individual active ingredients alone.
CLAIMS

1. A method of controlling mollusc damage to plants in horticulture or agriculture comprises treating the plant's propagation material with a combination of, as active ingredients, at least (a) clothianidin and prothioconazole, (b) clothianidin, fluoxastrobin and prothioconazole, (c) clothianidin, tebuconazole, triazoxide and prothioconazole, (d) imidacloprid and prothioconazole, (e) thiamethoxam, tebuconazole and fludioxonil, (f) imidacloprid and carboxin, (g) thiamethoxam, tefluthrin, azoxystrobin and tebuconazole, or (h) imidacloprid and tebuconazole.

2. The method according to claim 1 wherein the plant is selected from cereals; beet; fruit; legumes; oil crops; the marrow family; citrus fruits; vegetables; the laurel family; and tobacco, nuts, coffee, egg plants, sugar cane, tea, pepper, grapevines, hops, the banana family, latex plants, ornamentals and forage crops.

3. The method according to either claim 1 or claim 2 wherein one or more further pesticides are also used in the treatment.

4. The method according to claim 3 wherein the pesticide is a fungicide, insecticide or nematicide.

5. The method according to any one of claims 1 to 4 wherein the treatment protects the plant propagation material and organs that grow at a later point in time against damage by molluscs.

6. A method of protecting plant propagation material and organs that grow at a later point in time against damage by molluscs, which method comprises treating the propagation material with a combination of, as active ingredients, as defined in any one of claims 1 to 4.