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(54) Title: FUNGICIDAL ACTIVE COMPOUND COMPOSITIONS FOR TURF TREATMENT

(57) Abstract: The present invention relates to novel compositions comprising a fungicide that inhibits mitochondrial respiration at the QoI site, (QoI inhibitor), a contact fungicide, a demethylation inhibitor and pigments, which are highly suitable for controlling unwanted phytopathogenic fungi. Moreover, the fungicidal compositions are able to control mold and fungus infection in glasses, in particular turf grasses.

Fungicidal active compound compositions for turf treatment

The present invention relates to novel compositions comprising a fungicide that inhibits mitochondrial respiration at the QoI site, (QoI inhibitor), a contact fungicide, a demethylation inhibitor and pigments, which are highly suitable for controlling unwanted phytopathogenic fungi. Moreover, the fungicidal compositions are able to control mold and fungus infection in grasses, in particular turf grasses.

Fine turf grass species are grown on golf course greens, fairways and tee boxes, as well as turf farms and many other locations. In northern regions, such as Canada and the northern United States, which are subject to temperate climates in the late summer and early fall and snow conditions in late fall and early winter certain moulds such as dollar spot, *Sclerotinia homeocarpa*, and snow molds, such as *Microdochium nivale*, *Typhula incarnata* and *Typhula ishikariensis*, represent a chronic problem for turf grass growers.

If left untreated in the late summer and fall, turf grass is predisposed to damage caused by *Sclerotinia homeocarpa* in the late summer and fall and the snow molds in late fall and over winter to spring. *S. homeocarpa* attacks most turf grasses grown in the South. Bent grass, common and hybrid bermuda grass and zoysia are most susceptible to *S. homeocarpa* attacks. The dollar spot disease occurs from spring through fall, and is most active during moist periods of warm days (about 70°F to about 85°F) and cool nights (about 60°F) in the spring, early summer and fall.

Where the mold infection is extensive, the recovery of the turf grass can be delayed well into the growing season and seriously affect the ability of the turf grass to recover, leaving areas of dead patches. Further, turf grasses weakened or damaged by these molds are extremely slow to recover in the spring and are often invaded by undesirable opportunistic weedy grass species such as creeping bent grass (*Agrostis palustris*) and annual bluegrass (*Poa annua*).

A typical snow mold prevention program requires a mold inhibiting fungicide to be applied to turf grass prior to permanent winter snow cover. Typical programs consist of three applications prior to permanent snow cover and an additional application after the snow cover is gone in the spring. Several commercial fungicide products have been approved for use against dollar spot and snow mould species.

COMPASS™ (trifloxystrobin; (αE)- α(methoxyimino)-2-[[[(E)-[1-[3-(trifluoromethylphenyl]ethylidine]-amino]oxy]methyl]benzenacetic acid methyl ester) is an aromatic dioxime fungicide which has been approved for the control of leaf spot, *Fusarium* patch and brown patch diseases in turf grass. Trifloxystrobin is a quinone outside inhibitor (QoI) and a member of the class of aromatic dioxime fungicides described in U.S. Pat. No. 5,238,956.

ROVRAL GREEN GT™ (iprodione; 3-(3,5-dichlorophenyl)-*N*-(1-methylethyl)-2,4-dioxo-1-imidazolidinecaboximide) is a dicarboximide fungicide for pink snow mold control at a rate of 250 ml/100m^2 and for gray snow mould control at a rate of 375 ml/100m^2. Iprodione is a member of the class of 3-phenyl hydantoin compounds described in U.S. Pat. No. 3,755,350.

The effectiveness of iprodione to control the spread of snow mold in turf grasses (especially the gray snow molds *T. incarnata* and *T. ishikariensis*) is highly variable due to the varying amounts of fungus inoculums, the varying length of snow cover under which snow mould inoculums thrive and the varying winter temperatures that exist across the country from year to year. Thus, in order to effectively control against a spectrum of snow moulds a relatively high dose may be required as well as multiple applications.

Phthalocyanines are known pigments having many applications, such as pigments for inks and coatings and even for turf grass paints. See, for example, DE 2,511,077 and JP 03/221576. Copper phthalocyanine has been used, but only in combination with certain other active ingredients, for enhancing turf quality. For example, U.S. Pat. No. 5,599,804 describes a method of combating fungi and enhancing turf quality in turf grass by applying in specific ratios certain phthalocyanines in combination with phosphorous acid or an alkaline earth metal salt thereof or with certain monoester salts of phosphorous acid. U.S. Pat. No. 5,643,852 describes a method of enhancing turf quality in turf grass by applying in specific ratios certain phthalocyanines in combination with (i) phosphorous acid or an alkaline earth metal salt thereof or certain monoester salts of phosphorous acid and (ii) certain ethylene bisdithiocarbamate contact fungicides. U.S. Pat. No. 5,336,661 describes a method of treating bent grass and enhancing turf quality by applying in specific ratios (i) certain monoester salts of phosphorous acid and (ii) a metallic ethylene bisdithiocarbamate contact fungicide. This patent also describes a specific composition containing a combination of aluminum tris(*O*-ethylphosphonate) (fosetyl-al) and a manganese-zinc ethylene bisdithiocarbamate complex (mancozeb) used in a form (FORE fungicide) believed to have contained an unknown amount of the phthalocyanine compound Pigment Blue 15.

Since the ecological and economical demands made on modern fungicides are increasing constantly, for example with respect to activity spectrum, toxicity, selectivity, application rate, formation of residues and favourable manufacture, and there can furthermore be problems, for example, with resistance, there is a constant need to develop novel fungicides which, at least in some areas, help to overcome the disadvantages mentioned.

The present invention provides active compound combinations or compositions which achieve the object at least in some aspects.

Surprisingly, it has now been found that the active compound combinations or compositions according to the invention do not only exhibit an additive effect of the activity of the individual components, but a synergistic effect. Therefore, firstly, the customary application rate of the individual substances can be reduced. Secondly, the active compound combinations according to the invention offer a high degree of activity against phytopathogens even in cases where the individual compounds are employed in amounts where, for their part, they no longer show (sufficient) activity. In principle, this allows, firstly, the activity spectrum to be broadened and, secondly, better safety during handling.

In addition to the fungicidal synergistic activity, the active compound combinations according to the invention have further surprising properties which, in a wider sense, may also be called synergistic, such as, for example: broadening of the activity spectrum, for example to resistant pathogens of plant diseases; lower application rates of the active compounds; sufficient control of pests with the aid of the active compound combinations according to the invention even at application rates where the individual compounds show no or virtually no activity; advantageous behaviour during formulation or during use, for example during grinding, sieving, emulsifying, dissolving or application; improved storage stability and light stability; advantageous residue formation; improved toxicological or ecotoxicological behaviour; improved properties of the plant, for example better growth, increased harvest yields, a better developed root system, a larger leaf area, greener leaves, stronger shoots, less seed required, lower phytotoxicity, mobilization of the defence system of the plant, good compatibility with plants. Thus, the use of the active compound combinations or compositions according to the invention contributes considerably to keeping young plant stems healthy, which increases, for example, the winter survival of the cereal seed treated, and also safeguards quality and yield. Moreover, the active compound combinations according to the invention may contribute to enhanced systemic action. Even if the individual compounds of the combination have no sufficient systemic properties, the active compound combinations according to the invention may still have this property. In a similar manner, the active compound combinations according to the invention may result in higher persistency of the fungicidal action.

It has now been found that active compound combinations comprising

A) at least one phthalocyanine pigment and

B) i) at least one QoI inhibitor fungicide and

at least one fungicide selected fron the group consisting of

ii) a contact fungicide and

iii) a DMI-fungicide,

show superior mold control abilities than compositions with similar fungicides but without the pigments.

QoI inhibitor fungicides (i) include azoxystrobin, enestrobin, picoxystrobin, pyraclostrobin, kresoxim-methyl, trifloxystrobin, dimoxystrobin, metominostrobin, orysastrobin, famoxadone, fluoxastrobin, fenamidone, pyribencarb, preferred are azoxystrobin, pyraclostrobin, trifloxystrobin and fluoxastrobin, particular preferred is trifloxystrobin.

Contact fungicides (ii) include PP-fungicides such as fludioxinil, dicarboimides such as iprodione, chlozolinate, procymidone, vinclozolin, AH-fungicides such as biphenyl, chloroneb, dicloran, quintozene (PCNB), tecnazene (TCNB), tolclofos-methyl, dithiocarbamates such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb and ziram, phthalimides such as captan, captafol and folpet, chloronitriles such as chlorothalonil, sulfamides such as dichlofluanid and tolyfluanid, guanidines, such as dodine, guazatine and iminooctadine, triazine such as anilazine and quinones such as dithianon; pencyuron, validamycin, inorganic fungicides, such as copper and sulphur products. Preferred contact fungicides are iprodione, fludioxinil and chlorothalonil, particular preferred are iprodione and fludioxinil which involve signal transduction in their mode of action.

DMI-fungicides (demethylation inhibitors) include triazoles such as azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol and triticonazole, preferred are prothioconazole, tebuconazole, propiconazole and triticonazole, particular preferred are propiconazole and triticonazole.

Prefarably the composition according to the invention comprises as compound B) i) trifloxystrobin as QoI inhibitor fungicide, ii) iprodione as contact fungicide and iii) tritriconazole as DMI-fungicide. Most preferably the composition according to the invention comprises i) trifloxystrobin as QoI inhibitor fungicide and ii) iprodione as contact fungicide.

Suitable pigments A) include phthalocyanines.

Suitable phthalocyanines are substituted copper phthalocyanines which may be substituted from 1 to 4 times on each isoindole group independently. Examples of suitable substituents for the isoindole groups of copper phthalocyanine dyes include but are not limited to halogen, unsubstituted or substituted lower alkyl, lower alkoxy, alkylamino, alkylthio, ammonium,

sulfonato, sulfonato alkyl, sulfate, phosphate, phosphonate, and carboxylate. The ionic or ionizable substituents can have as counterions the alkali metals, preferably lithium, sodium, or potassium, the alkaline earth metals, preferably beryllium, magnesium, calcium, strontium, and barium, and various ammonium ions. By the terms lower alkyl and lower alkoxy are generally meant alkyl groups of from 1 to 6 carbon atoms and alkoxy groups of from 1 to 6 carbon atoms.

Suitable copper phthalocyanines are commercially available and include but are not limited to Pigment Blue 16, Vat Blue 29, Pigment Blue 15, Heliogen Green GG, Ingrain Blue 14, Ingrain Blue 5, Ingrain Blue 1, Pigment Green 37, and Pigment Green 7. In one preferred embodiment, the copper phthalocyanine is Pigment Blue 15, also known as phthalocyanine blue and Green pigment (Green 7).

Preferably the composition according to the invention comprises as compound A) a green pigment (Green 7).

According to the invention, the term "active compound combination" means various possible combinations of the active compounds mentioned above, such as, for example, readymixes, tank mixes (which is to be understood as meaning spray mixtures prepared prior to application from the formulations of the individual active compounds by mixing and diluting) or combinations thereof (for example, a binary readymix of two of the active compounds mentioned above is converted with a formulation of the third individual substance into a tank mix). According to the invention, the individual active compounds may also be used successively, i.e. one after the other, within a reasonable interval of a few hours or days, and, in the treatment of seed, also, for example, by applying a plurality of layers comprising different active compounds. Preferably, it is immaterial in which order the individual active compounds may be employed.

The present invention furthermore relates to compositions comprising the active compound combinations according to the invention. Preferably, the compositions are fungicidal compositions comprising agriculturally suitable carriers or extenders.

According to the invention, carrier is to be understood as meaning a natural or synthetic, organic or inorganic substance which is mixed or combined with the active compounds for better applicability, in particular for application to plants or plant parts or seeds. The carrier, which may be solid or liquid, is generally inert and should be suitable for use in agriculture.

Suitable solid carriers are: for example ammonium salts and natural ground minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and natural or synthetic silicates, resins, waxes, solid fertilizers, water, alcohols, especially butanol, organic solvents, mineral oils and vegetable oils, and also derivatives thereof. It is also possible to use mixtures of such carriers. Solid carriers suitable for granules

are: for example crushed and fractionated natural minerals, such as calcite, marble, pumice, sepiolite, dolomite, and also synthetic granules of inorganic and organic meals and also granules of organic material, such as sawdust, coconut shells, maize cobs and tobacco stalks. Suitable emulsifiers and/or foam-formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, and also protein hydrolysates. Suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

Suitable liquefied gaseous extenders or carriers are liquids which are gaseous at ambient temperture and under atmospheric pressure, for example aerosol propellants, such as butane, propane, nitrogen and carbon dioxide.

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

If the extender used is water, it is also possible for example, to use organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatic compounds, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatic compounds or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols, such as butanol or glycol, and also ethers and esters thereof, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

The compositions according to the invention may comprise additional further components, such as, for example, surfactants. Suitable surfactants are emulsifiers, dispersants or wetting agents having ionic or nonionic properties, or mixtures of these surfactants. Examples of these are salts of polyacrylic acid, salts of lignosulphonic acid, salts of phenolsulphonic acid or naphthalenesulphonic acid, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, substituted phenols (preferably alkylphenols or arylphenols), salts of sulphosuccinic esters, taurine derivatives (preferably alkyl taurates), phosphoric esters of polyethoxylated alcohols or phenols, fatty esters of polyols, and derivatives of the compounds containing sulphates, sulphonates and phosphates. The presence of a surfactant is required if one of the active compounds and/or one of the inert carriers is insoluble in water and when the application takes place in water. The proportion of surfactants is between 5 and 40 per cent by weight of the composition according to the invention.

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

If appropriate, other additional components may also be present, for example protective colloids, binders, adhesives, thickeners, thixotropic substances, penetrants, stabilizers, sequestring agents, complex formers. In general, the active compounds can be combined with any solid or liquid additive customarily used for formulation purposes.

In general, the compositions according to the invention comprise between 0,05 and 99 per cent by weight of the active compound combination according to the invention, preferably between 5 and 60 per cent by weight, particularly preferably between 10 and 40 per cent by weight, very particularly preferably 20 and 30 per cent by weight.

According to another aspect, the composition according to the invention comprises between 2 and 10 per cent by weight, preferably between 4 and 9 per cent by weight, particularly preferably between 5 and 7 per cent by weight compound A), between 1 and 3,3 per cent by weight, preferably between 1,0 and 2,5 per cent by weight, particularly preferably between 1,2 and 2,0 per cent by weight compound Bi) and between 20 and 50 per cent by weight, preferably between 20 and 40 per cent by weight, particularly preferably between 20 and 30 per cent by weight compound Bii) and/or Biii), the sum of the compounds adding up to 100 per cent by weight.

The fungicidal compositions according to the invention can be used for the curative or protective control of phytopathogenic fungi. The compositions according to the invention may be applied to healthy or diseased turfs. Prophylactic application to healthy turf may be helpful in preventing turf diseases. Application to turf containing one or more turf diseases is helpful in treating the one or more turf diseases. Some pathogens of fungal diseases which can be treated according to the invention may be mentioned by way of example, but not by way of limitation:

Spring, summer and fall diseases: Dollar Spot (*Lanzia spp. and Moellerodiscus spp.*), Brown Patch *(Rhizoctonia solanii)*, Large Patch *(Rhizoctonia solani*), Rapid Blight, Rust (*Puccinia spp.*), Fusarium Blight *(Fusarium spp.)* Pink Patch, Curvularia (*Curvularia* sp.*)* and Necrotic Ring Spot *(Leptosphaeria korrae)*, Leaf Spots such as Helminthosporium Leaf Spot caused by *Drechslera* spp. pathogens, Corticum Red Thread *(Laetisaria fuciformis)* and Anthracnose *(Colletotrichum)*.

Winter diseases: Fusarium Patch (Pink Snow Mold *(Microdochium nivalis)*) and Gray Snow Mold *(Typhula* spp.*)*, Pink Snow Mold *(Fusarium nivale)*.

The described compositions are also helpful in improving turf quality after snow cover release in spring.

The fungicidal compositions according to the invention can be used for turfgrass disease control on golf courses, sod farms, and institutional areas where fine turf is grown.

The active compound combinations or compositions according to the invention can be used as such or, depending on their respective physical and/or chemical properties, in the form of their formulations or the use forms prepared therefrom, such as aerosols, capsule suspensions, cold-fogging concentrates, warm-fogging concentrates, encapsulated granules, fine granules, flowable concentrates for the treatment of seed, ready-to-use solutions, dustable powders, emulsifiable concentrates, oil-in-water emulsions, water-in-oil emulsions, macrogranules, microgranules, oil-dispersible powders, oil-miscible flowable concentrates, oil-miscible liquids, foams, pastes, pesticide-coated seed, suspension concentrates, suspoemulsion concentrates, soluble concentrates, suspensions, wettable powders, soluble powders, dusts and granules, water-soluble granules or tablets, water-soluble powders for the treatment of seed, wettable powders, natural products and synthetic substances impregnated with active compound, and also microencapsulations in polymeric substances and in coating materials for seed, and also ULV cold-fogging and warm-fogging formulations.

The formulations mentioned can be prepared in a manner known per se, for example by mixing the active compounds or the active compound combinations with at least one solvent or diluent, emulsifier, dispersant and/or binder or fixing agent, water repellant, appropriate siccatives and UV stabilizers and, if appropriate, dyes and pigments, and also further processing auxiliaries.

The treatment according to the invention of the plants and plant parts with the active compound combinations or compositions is carried out directly or by action on their surroundings, habitat or storage space using customary treatment methods, for example by dipping, spraying, atomizing, irrigating, evaporating, dusting, fogging, broadcasting, foaming, painting, spreading-on, watering (drenching), drip irrigating and, in the case of propagation material, in particular in the case of seeds, furthermore as a powder for dry seed treatment, a solution for seed treatment, a water-soluble powder for slurry treatment, by incrusting, by coating with one or more coats, etc.

The compositions according to the invention do not only comprise ready-to-use compositions which can be applied with suitable apparatus to the plant or the seed, but also commercial concentrates which have to be diluted with water prior to use.

The active compound combinations according to the invention can be present in commercial formulations and in the use forms prepared from these formulations as a mixture with other active

compounds, such as insecticides, attractants, sterilants, bactericides, acaricides, nematicides, fungicides, growth regulators or herbicides.

The present invention can be practiced with all turfgrasses, including cool season turfgrasses and warm season turfgrasses. Examples of cool season turfgrasses are bluegrasses (*Poa spp.*), such as Kentucky bluegrass (*Poa pratensis* L.), rough bluegrass (*Poa trivialis* L.), Canada bluegrass (*Poa compressa* L.), annual bluegrass (*Poa annua* L.), upland bluegrass (Poa *glaucantha Gaudin*), wood bluegrass (*Poa nemoralis* L.), and bulbous bluegrass (*Poa bulbosa* L.); the bentgrasses and redtop (*Agrostis spp.*), such as creeping bentgrass (*Agrostis palustris* Huds.), colonial bentgrass (*Agrostis tenuis* Sibth.), velvet bentgrass (*Agrostis canina* L.), South German Mixed Bentgrass (*Agrostis spp.* including *Agrostis tenius* Sibth., *Agrostis canina* L., and *Agrostis palustris* Huds.), and redtop (*Agrostis alba* L.); the fescues (*Festucu spp.*), such as red fescue (*Festuca rubra* L. spp. *rubra*), creeping fescue (*Festuca rubra* L.), chewings fescue (*Festuca rubra commutata* Gaud.), sheep fescue (*Festuca ovina* L.), hard fescue (*Festuca longifolia* Thuill.), hair fescue (*Festucu capillata* Lam.), tall fescue (*Festuca arundinacea* Schreb.), meadow fescue (*Festuca elanor* L.); the ryegrasses (*Lolium* spp.), such as annual ryegrass (*Lolium multiflorum* Lam.), perennial ryegrass (*Lolium perenne* L.), italian ryegrass (*Lolium multiflorum* Lam.); and the wheatgrasses (*Agropyron* spp.), such as fairway wheatgrass (*Agropyron cristatum* (L.) Gaertn.), crested wheatgrass (*Agropyron desertorum* (Fisch.) Schult.), and western wheatgrass (*Agropyron smithii* Rydb.). Other cool season turfgrasses include beachgrass (*Ammophila breviligulata* Fern.), smooth bromegrass (*Bromus inermis* Leyss.), cattails such as Timothy (*Phleum pratense* L.), sand cattail (*Phleum subulatum* L.), orchardgrass (*Dactylis glomerata* L.), weeping alkaligrass (*Puccinellia distans* (L.) Parl.) and crested dog's-tail (*Cynosurus cristatus* L.).

Examples of warm season turfgrasses include Bermudagrass (*Cynodon spp.* L. C. Rich), zoysiagrass (*Zoysia spp.* Willd.), St. Augustine grass (*Stenotaphrum secundatum* Walt Kuntze), centipedegrass (*Eremochloa ophiuroides* Munro Hack.), carpetgrass (*Axonopus affinis* Chase), Bahia grass (*Paspalum notatum* Flugge), Kikuyugrass (*Pennisetum clandestinum* Hochst. ex Chiov.), buffalo grass (*Buchloe dactyloids* (Nutt.) Engelm.), Blue gramma (*Bouteloua gracilis* (H.B.K.) Lag. ex Griffiths), seashore paspalum (*Paspalum vaginatum* Swartz) and sideoats grama (*Bouteloua curtipendula* (Michx. Torr.). Cool season turfgrasses are generally preferred for treatment according to the invention. More preferred is bluegrass, bentgrass and redtop, fescue, and ryegrass. Bentgrass is most preferred.

The application rate of the active compound combinations according to the invention is

- when treating leaves: from 100 to 10 000 g/ha, preferably from 1000 to 5 500 g/ha, particularly preferably from 1000 to 3 500 g/ha (when the application is carried out by watering or dripping, it may even be possible to reduce the application rate, in particular when inert substrates such as rock wool or perlite are used).

These application rates are mentioned only by way of example and not by way of limitation in the sense of the invention.

The active compound combinations or compositions according to the invention can thus be employed for protecting plants for a certain period of time after treatment against attack by the pathogens mentioned. The period for which protection is provided extends generally for 1 to 28 days, preferably 1 to 14 days, after the treatment of the plants with the active compounds, or for up to 200 days after seed treatment.

The good fungicidal activity of the active compound combinations according to the invention is demonstrated by the example below. Whereas the individual active compounds have weaknesses in the fungicidal activity, the combinations exhibit an activity which exceeds a simple addition of activity.

In fungicides, a synergistic effect is always present when the fungicidal activity of the active compound combinations is greater than the expected activity which, for a given combination of 2 or 3 active compounds, is calculated as follows according to S.R. Colby ("Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", Weeds 1967, 15, 20-22):

If

X is the efficacy when active compound A is applied at an application rate of m g/ha,

Y is the efficacy when active compound B is applied at an application rate of n g/ha,

E_1 is the efficacy when the active compounds A and B are applied at application rates of m and n g/ha, respectively, and

E_2 is the efficacy when the active compounds A and B and C are applied at application rates of m and n and r g/ha, respectively,

then

$$E_1 = X + Y - \frac{X \cdot Y}{100}$$

or $$E_2 = X + Y + Z - \frac{(X \times Y + X \times Z + Y \times Z)}{100} + \frac{X \times Y \times Z}{10\,000}$$

Here, the efficacy is determined in %. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

If the actual fungicidal activity is greater than calculated, the activity of the combination is superadditive, i.e. a synergistic effect is present. In this case, the efficacy actually observed must be greater than the value, calculated using the formula given above, for the expected efficacy E_1.

The invention is illustrated by the example below. (However, the invention is not limited to the example.)

Examples

To determine the superiority of various compositions comprise a QoI inhibitor fungicide, a contact fungicide, and a demethylation inhibitor with pigments over a composition containing three classes of fungicides but without pigments, trials were conducted at the following sites: 1. University of Massachusetts, Vermont Site; 2. University of Wisconsin, Sentry Site; 3. University of Wisconsin, Iron Mountain Site; 4. University of Wisconsin, Champion MI Site; 5. University of Wisconsin, Edina MN Site; 6. Oregon State University, Sun River Site; 7. Washington State University, McCall Site; 8. Washington State University, Chewelah Site; and 9. Washington State University Pullman Site.

A general procedure for the application of the compositions described is as follows. Treatment plots were, for example, 6 feet x 7 (3,8 m^2) feet with three replications in a randomized complete-block design. Treatments were applied from late-October to mid-November. In several instances, the compositions were applied at 80 GPA with a bicycle-wheeled CO_2 pressurized (40 psi = 2,8 bar) sprayer with 11008 flat fan TeeJet nozzles.

Several sites have intermittent snow cover throughout the winter with periods of continuous snow cover. Once the snow melted, or is mechanically removed, individual plots were evaluated for pink (*M. nivale*) and/or gray (*Typhula spp.*) snow mold disease severity (% area infected) and turf grass quality (rated on a scale of 1 to 9, with 9 being excellent).

Table 1 shows the effect of a composition containing differing amounts of a QoI inhibitor fungicide (trifloxystrobin), a contact fungicide (iprodione), a demethylation inhibitor (triticonazole) and a pigment (phthalocyanine Green pigment) in comparison with a standard combination of three classes of fungicides combined for snow mold control that does not contain any pigments (INSTRATA®, manufactured by SYNGENTA) on Turf Quality (TQ) or Turf Color (TC). The scale is from 1 to 9 with 1 = poor and 9 = excellent. INSTRATA® was used as a control because it is a snow mold product that has three classes of fungicides but does not have any pigments.

Table 1:

	Pink and Gray snow mold sites[a]									Mean of all Sites
Treatment[b]	1	2	3	4	5	6	7	8	9[d]	
Untreated	5,7	4,5	6	3,3	6,3	1,5	2,3	1	1,7	4
(A + B + C): 123 g/100 m^2 + (C + D): 25 g/100 m^2	7	8	7,8	7,8	8,3	6,5	5,7	5	4,7[e]	7
(A + B + C): 151 g/100 m^2 + (C + D): 25 g/100 m^2	7	8	7,8	7,8	8	7,3	5,7	6,3	4,7[f]	7
INSTRATA[®][c]: 280 g/100 m^2	5,7	6,8	6	6,3	7	4,3	5,7	5,7	4	6

[a] Sites: 1. University of Massachusetts, Vermont site; 2. University of Wisconsin, Sentry Site; 3. University of Wisconsin, Iron Mountain Site; 4. University of Wisconsin, Champion MI Site; 5. University of Wisconsin, Edina MN Site; 6. OSU, Sun River Site; 7. Washington State University McCall Site; 8. Washington State University Chewelah Site; 9. Washington State University Pullman Site.

[b] A = trifloxystrobin; B = iprodione; C = Phthalocyanine Green pigment (Green 7); D = triticonazole (3 lb ai/gal = 358 g/L).

[c] INSTRATA® = commercial standard without pigment (propiconazole + fludioxinil + chlorothalonil).

[d] Pink snow mold site.

[e] (A + B + C): 123 g/100 m^2.

[f] (A + B + C): 151 g/100 m^2.

A composition comprising A + B + C + D is the equivalent of INSTRATA® + a pigment. In other words, using such a composition, a direct comparison can be made to demonstrate the superior effects of a composition containing the three classes of fungicides with a pigment vs. a composition

containing only the three classes of fungicides (*i.e.*, without a pigment). The results show that in every site where the composition containing the three classes of fungicides with a pigment is used, the TQ and TC are superior to INSTRATA®. This means that the turf recovers better and looks better using the composition containing the three classes of fungicides with a pigment vs. INSTRATA®.

The results from site 9, in which a composition comprising two fungicides (A + B) and C show that the composition of two fungicides and a pigment is at least as good as INSTRATA®, if not slightly better. This is surprising because INSTRATA® has three fungicides (but no pigment). In other words, an effect similar to using three fungicides can be achieved by the use of two fungicides and a pigment.

Table 2 shows the effect of a composition containing differing amounts of a QoI inhibitor fungicide (trifloxystrobin), a contact fungicide (iprodione), a demethylation inhibitor (triticonazole) and a pigment (phthalocyanine Green pigment) in comparison with INSTRATA® on percentage disease infestation by site.

Table 2:

	Pink and Gray snow mold sites									Mean of all Sites
Treatment	1	2	3	4	5	6	7	8	9[d]	
Untreated	56,7	76,3	43,8	96,3	17,5	73,8	28,3	73,3	51,7	58
(A + B + C): 123 g/100 m^2 + (C + D): 25 g/100 m^2	11,7	0	0	3	0	6,3	5,3	6,7	0[e]	4
(A + B + C): 151 g/100 m^2 + (C + D): 25 g/100 m^2	8,7	0	0	1,3	5	8,8	2	1,7	2,7[f]	3
INSTRATA®: 280 g/100 m^2	2,3	0,5	0	13,8	0	21,3	0	0	1,7	4

[d] Pink snow mold site.

[e] (A + B + C): 123 g/100 m^2.

[f](A + B + C): 151 g/100 m^2.

The results in Table 2 show that the composition containing the three classes of fungicides with a pigment cures about the same percentage of disease infestation as INSTRATA®. In other words, the composition disclosed is as effective as INSTRATA® in killing mold. The superior benefits of a composition additionally comprising a pigment, such as a phthalocyanine, include better recovery of the turf after the winter, during the spring green up; better health of the turf; and better aesthetics (the turf looks visual better).

The QoI inhibitor fungicide, contact fungicide, the demethylation inhibitor; and the pigment may be in any ratio within the composition. Examples of suitable ratios are shown in Table 3.

Table 3:

Component (g/L)	Lower end end									Higher
QoI inhibitor fungicide	1	2	3	4	5	6	7	8	9	10
Contact fungicide[g]	50	50	50	50	50	50	50	50	50	50
Demethylation inhibitor	12	16	20	25	29	33	37	41	45	50
Pigment	20	22	24	26	29	32	34	36	38	40

[g] the amount of the contact fungicide is kept constant as a reference point

Other exemplary compositions of trifloxystrobin, iprodione, and phthalocyanine Green pigment include those shown in Table 4, suspended in water.

Table 4:

Component (wght-%)	Lower end									Higher end
Trifloxystrobin	1,30	1,34	1,37	1,40	1,44	1,47	1,50	1,54	1,57	1,60
Iprodione	21,2	21,6	22,2	22,6	23,2	23,6	24,2	24,6	25,2	25,6

Phthalocyanine	5,5	5,6	5,7	5,8	5,9	6,0	6,1	6,2	6,3	6,4

Table 5 shows the superior effects of a composition containing 1,47 g/L of trifloxystrobin, 29,41 g/L of iprodione, 3,14 g/L of triticonazole, and 6 g/L of phthalocyanine over a commercially available solution of INSTRATA®. The four-component composition and INSTRATA® were applied to a bent grass/*Poa* plot at Westmount Golf & Country Club in Kitchener, Ontario, Canada.

Table 5:

Composition applied	Amount applied (mL/m^2)	Total disease area (%)	TQ
None (untreated)	0	83	1
Trifloxystrobin: 1,47 g/L + Iprodione: 29,41 g/L + Triticonazole: 3,14 g/L + Phthalocyanine: 6 g/L	100	0	8,7
	133	0	9
	177,5	0	9
INSTRATA®	300	2	6,6

As the results show, application of the four-component composition of trifloxystrobin, iprodione, triticonazole, and phthalocyanine is superior to INSTRATA®. Not only does the four-component composition provide better disease control than INSTRATA® (as measured by the % area affected) – 0% vs. 2% but the TQ is better 8,7 to 9 vs. 6,6. Additionally, excellent results can be achieved by using significantly lower amounts of the composition (100 mL/100 m^2 to 177,5 mL/m^2) vs. INSTRATA® (300 mL/m^2). This is significant not only from an environmental perspective in that fewer chemicals are applied to the soil but also from an economic perspective in lower costs.

Without being bound by theory, it is believed that the various fungicides act in synergy with the pigment, thereby resulting in the superior effects observed.

Further trials were carried out in Europe, data displayed in the following.

Trials were set up to investigate the efficacy and effect on turf qualitiy of the combination of two active ingredients (Trifloxystrobin, QoI inhibitor fungicide and Iprodione, contact fungicide) and the pigment (Phthalocyanine). The fungicidal compounds were applied individually, in combination

(without the pigment) and in combination including the pigment at two different concentrations. These treatments were compared to commercial standard products.

Trials were conducted in various places in UK and Germany in 2008 and were between end of July to early December depending on the individual disease. Trial design was a randomized complete-block with 4 replications and a plot area of 4 to 6,25 m^2. Products were applied as spray application with 400 to 500 L water volume / ha. For application air pressurized sprayers with a teejet or flatfan noozle were used, operated at 2,2 to 3,0 bar. Two applications were carried out at 28 day interval.

Trials were evaluated in 14 to 28 day intervals up to 72 days after the first application. Turf diseases: Pink snow mold (*Microdochium nivale*), Rust (*Puccinia spp*), Red thread (*Laetisaria fuciformis*) were assessed as % infected canopy area per plot. Turf quality (color and / or density) was judged on an ordinal scale. Data is displayed as average over all assessments.

Table 6 shows the effect of a composition containing differing amounts of a QoI inhibitor fungicide (trifloxystrobin), a contact fungicide (iprodione), and a pigment (phthalocyanine Green pigment) in comparison with commercial standards which do not contain any pigments (DACONIL, and AMISTAR, both manufactured by SYNGENTA) on Turf Quality (TQ) and/or Turf Color (TC). Data is displayed on a scale from 1 to 9 with 1 = poor and 9 = excellent.

Table 6: Turf Quality, Scale 1 to 9 with 1 = poor and 9 = excellent

	Sites[n]				Mean
Treatment	1	2	3	4	of all sites
Untreated	5,2	5,4	5,8	5,2	5,4
(A): 1,59 g/100 m^2	5,8	5,4	5,6	5,8	5,6
(B): 25,50 g/100 m^2	5,9	5,2	6,7	5,9	5,9
(A): 1,59 g/100 m^2 + (B): 25,50 g/100 m^2	5,9	5,4	6,7	5,9	6,0
(A + B + C): 20,32 g/100 m^2	6,7	5,4	6,7	6,7	6,3
(A + B + C): 27,09 g/100 m^2	6,3	5,2	7,6	6,3	6,3

DACONIL[c]: 150 g/100 m^2	5,6	5,4	5,9	5,6	5,6
AMISTAR[d]: 4,6 g/100 m^2	5,9	5,4	5,9	5,9	5,8

[a] Sites: 1. UK, East Lothian; 2. UK, Middle Lothian; 3. Germany, south; 4. UK, Essex

A = trifloxystrobin; B = iprodione; C = Phthalocyanine Green pigment (Green 7)

[c] DACONIL® = commercial standard without pigment (chlorothalonil).

[d] AMISTAR ®= commercial standard without pigment (azoxystrobin).

The data of table 6 shows an improvement of turf quality in those plots where the the compounds A and B were combined with compound C. The treatment with compounds A and B alone and the combination A + B achieved a lower quality score than for A + B + C. The results are supported by the scores for the commercial standard, which do not contain compound C and achieved lower scores as well.

Table 7 shows the effect of a composition containing differing amounts of a QoI inhibitor fungicide (trifloxystrobin), a contact fungicide (iprodione) and a pigment (phthalocyanine Green pigment) in comparison with DACONIL® or AMISTAR® on percentage disease infestation by site.

Table 7: % diseased area, Indication *Puccinia spp.* on turf

	Sites[a]				Mean
Treatment	1	2	3	4	of all sites
Untreated	5,2	5,4	5,8	5,2	5,4
(A): 1,59 g/100 m^2	5,8	5,4	5,6	5,8	5,6
(B): 25,50 g/100 m^2	5,9	5,2	6,7	5,9	5,9
(A): 1,59 g/100 m^2 + (B): 25,50 g/100 m^2	5,9	5,4	6,7	5,9	6,0
(A + B + C): 20,32 g/100 m^2	6,7	5,4	6,7	6,7	6,3

(A + B + C): 27,09 g/100 m^2	6,3	5,2	7,6	6,3	6,3
DACONIL[c]: 150 g/100 m^2	5,6	5,4	5,9	5,6	5,6
AMISTAR[d]: 4, 60 g/100 m^2	5,9	5,4	5,9	5,9	5,8

[a] Sites: 1. Germany, east; 2. UK, Essex

The data in Table 7 shows that the combination of the compounds A + B + C achieved a better control of the turf pathogen *Puccinia spp.* than the combination of the compounds A + B only (without the pigment C). This effect was emphasized by the finding that the combination of compounds A + B + C outperformed the combination A + B even at reduced ai concentration.

Patent Claims:

1. Active compound combinations comprising

A) at least one phthalocyanine pigment and

B) i) at least one QoI inhibitor fungicide and

at least one fungicide selected fron the group consisting of

ii) a contact fungicide and

iii) a DMI-fungicide.

2. Active compound combinations according to Claim 1, where compound B) comprises i) trifloxystrobin as QoI inhibitor fungicide, ii) iprodine as contact fungicide and iii) triticonazole as DMI-fungicide.

3. Active compound combinations according to Claims1, where compound B) comprises i) trifloxystrobin as QoI inhibitor fungicide and ii) iprodione as contact fungicide.

4. Active compound combinations according to any of Claims 1 to 3, where compound A) is a green pigment (Green 7).

5. Active compound combinations according to any of Claims 1 to 4 which are fungicidally active.

6. Compositions comprising active compound combinations according to any of Claims 1 to 5.

7. Compositions according to Claim 6, comprising further auxiliaries, solvents, carriers, surfactants or extenders.

8. Method for contolling phytopathogenic fungi in turf grass protection, characterized in that active compound combinations according to any of Claims 1 to 5 or compositions according to Claim 6 or 7 are applied to turf grass.

9. Method for improving turf quality after snow cover release in spring, characterized in that active compound combinations according to any of Claims 1 to 5 or compositions according to Claim 6 or 7 are applied to turf grass.

10. Method according to Claim 8 or 9, characterized in that the active compounds A), Bi), Bii) and Biii) are applied simultaneously or in succession.

11. Method according to any of Claims 8 to 10, characterized in that in the treatment of turf grass from 100 to 10 000 g/ha are used.

12. Use of active compound combinations according to any of Claims 1 to 5 or of compositions according to Claim 6 or 7 for controlling unwanted phytopathogenic fungi in turf grass protection.

13. Use of active compound combinations according to any of Claims 1 to 5 or of compositions according to Claim 6 or 7 for for improving turf quality after snow cover release in spring.

14. Turf grass treated with active compound combinations according to any of Claims 1 to 5 or with compositions according to Claim 6 or 7.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/31239

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A01N 25/34 (2010.01)
USPC - 424/404
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)
USPC - 424/404

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 424/1.17; 424/93.5; 424/195.15; 424/195.16; 424/274.1 (see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
USPTO-WEST - PGPB,USPT,USOC,EPAB,JPAB keywords: fungicides, composition, synergistic activities, triticonazole, iprodine, trifloxystrobin, turfgrass, creeping bentgrass, Penncross, phthalocyanines, grass quality, Pigment Green 7, iprodione.
INTERNET search - Google - same

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/031631 A1 (LEE et al.) 23 March 2006 (23.03.2006) pg 2 - pg 4; pg 6 - pg 7; pg 23 - pg 25; pg 40 - pg 41	1-4
Y	US 2006/0293188 A1 (NORTON et al.) 28 December 2006 (28.12.2006) Abstract; para [0023], [0029]-[0030]; Claim 17	1-4
Y	WO 2008/119439 A2 (GUYON et al.) 09 October 2008 (09.10.2008) pg 1, ln 1-14; pg 9, ln 32 - pg 10, ln 15	3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 May 2010 (21.05.2010)	17 JUN 2010
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/31239

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.