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(54) Title: NOVEL AGROCHEMICAL COMBINATIONS

(57) Abstract: Disclosed herein is a seed treatment combination of fipronil; azoxystrobin; at least one benzimidazole fungicide; and either a multi-site fungicide or a neonicotinoid insecticide.

NOVEL AGROCHEMICAL COMBINATIONS

Field of the invention:

The present invention relates to agrochemical combinations for the control of plant
5 pests. More particularly, the present invention relates to novel combinations,
compositions comprising these combinations and methods of using the
combinations for the treatment of plant propagation material.

Background and Prior art:

10 Combination of insecticides and fungicides are used to broaden the spectrum of
control of insect and fungal pests, reduce dosage, thereby reducing environmental
impact, and decrease chances of development of resistance. The combination of
insecticides and fungicides at times demonstrate an additive or synergistic effect
that results in an improved control on the pests.

15 Damage to seeds from insect and fungal pests is another major concern for
agriculturalist. There are various diseases such as seed rot etc. which reduce
germination rates and cause considerable decrease in yield. Treating the seed with
insecticidal and fungicidal combinations helps reduce damage from such soil pests.
20 Another advantage of treating seeds or other plant propagation material is the
improvement in germination rates, increased yield and improved plant health.

There are many combinations of insecticide and fungicide known in the art for the
control of soil borne pests. For example, **US5877194A** teaches combinations of
25 fipronil and triticonazole for seed treatment. **US7732374B2** teaches combinations
of prothioconazole and insecticides for the control of pests in seeds, soils etc.

There is however a need for improvement of these combinations. Single active
combinations used over a long period of time has resulted in resistance. With the
30 onset of resistance to certain pests, there is a need in the art for a combination of
actives that decreases chances of resistance and improves the spectrum of
disease and pest control.

Objects of the invention:

Therefore, one object of the present invention is to provide improved combinations of insecticides and fungicides for the control of soil borne pests.

- 5 Another object of the present invention is to provide a method and a composition for controlling insect pests and fungal diseases around plant propagation material.

Yet another object of the present invention is to provide improved combinations of insecticides and fungicides that promote plant health.

10

Embodiment of the present invention can ameliorate one or more of the above mentioned problems.

Summary of the Invention:

- 15 Therefore an aspect of the present invention can provide combinations of fipronil; azoxystrobin; at least one benzimidazole fungicide; and either a multi-site fungicide or a neonicotinoid insecticide.

- 20 Another aspect of the present invention can provide a method of improving yield in crops, the method comprising applying, to a plant propagation material of said crop, a combination comprising fipronil, azoxystrobin, at least one benzimidazole fungicide and either a multi-site fungicide or a neonicotinoid insecticide.

- 25 Yet another aspect of the present invention can provide a method of improving plant health, the method comprising applying, to a plant propagation material of said crop, a combination comprising fipronil, azoxystrobin, a benzimidazole fungicide and either a multi-site fungicide or a neonicotinoid insecticide.

- 30 Another aspect of the present invention can provide a composition for treating plant propagation material, the composition comprising fipronil, azoxystrobin, at least one benzimidazole fungicide and either a multi-site fungicide or a neonicotinoid insecticide.

In another aspect, the present invention can provide a method of controlling pests by treating a plant propagation material with a composition comprising fipronil, azoxystrobin, at least one benzimidazole fungicide and either a multi-site fungicide
5 or a neonicotinoid insecticide.

In yet another aspect, the present invention can provide a composition for improving plant health, the method comprising applying to a plant propagation material of said crop, a combination comprising fipronil, azoxystrobin, a
10 benzimidazole fungicide and either a multi-site fungicide or a neonicotinoid insecticide.

Detailed Description of the Invention:

The term "plant propagation material" refers to the parts of the plant, such as
15 seeds, which can be used for the propagation 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 or young plants, which may be transplanted after germination or after emergence from the soil. "Insecticidal" refers
20 to the ability of a substance to increase mortality or inhibit, growth rate of insects. "Fungicidal" refers to the ability of a substance to decrease or inhibit growth of fungi. The term "agriculturally acceptable amount of active" refers to an amount of an active that kills or inhibits the plant disease for which control is desired, in an amount not significantly toxic to the plant being treated. To "control" or "controlling"
25 insects means to inhibit, through a toxic effect, the ability of insect pests to survive, grow, feed, and/or reproduce, or to limit insect-related damage or loss in crop plants or denotes control and prevention of a disease. Controlling effects include all deviation from natural development, for example: killing, retardation, decrease of the fungal disease or insect pest. To "control" insects may or may not mean killing
30 the insects, although it preferably means killing the insects. The term "agriculturally acceptable amount of active" refers to an amount of an active that kills or inhibits

the plant disease for which control is desired, in an amount not significantly toxic to the plant being treated.

The term "improved seed vigour" refers to seed properties that determines potential for fast and uniform emergence, and development of seedlings under a wide range of field conditions, when compared with the same trait in a control plant which has been grown under the same conditions in the absence of the method of the invention. Such traits may include, early and/or improved germination, improved emergence, increased root growth, a developed root system, increased root nodulation, increased shoot growth, improvement in plant height, an increase in plant weight (fresh or dry), bigger leaf blades, greener leaf colour, increased pigment content, increased photosynthetic activity, earlier flowering, longer panicles, early grain maturity, increased seed, fruit or pod size, increased pod or ear number, increased seed number per pod or ear, increased seed mass, enhanced seed filling, delay of senescence, and improved vitality of the plant.

The present inventors found unexpected synergy when fipronil and azoxystrobin was combined with a benzimidazole fungicide and either a multi-site fungicide or a neonicotinoid insecticide. More specifically, the present inventors found unexpected synergy when fipronil and azoxystrobin was combined with either carbendazim or thiophanate methyl and either imidacloprid or a multi-site fungicide or both.

Fipronil is a phenylpyrazole insecticide which acts on the insects' central nervous system by blocking GABA-gated chloride channels and glutamate-gated chloride channels. Its chemical name is (RS)-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)-1H-pyrazole-3-carbonitrile.

Azoxystrobin is a systemic fungicide belonging to the strobilurin class of compounds. Its mode of action is brought about by attaching to the Qo site of Complex III of the mitochondrial electron transport chain, thereby preventing

production of ATP. Its chemical name is methyl (E)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate.

5 Benzimidazole fungicides inhibit mitosis and cell division in fungi. They are broad spectrum fungicides that are known to control a wide variety of fungi.

Neonicotinoid insecticides are systemic with contact and stomach action. Acetylcholine receptor (nAChR) agonist. These insecticides are known to control a broad spectrum of insect pests.

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Multi-site fungicides are known to attack fungi at multiple sites. These fungicides are used for broad-spectrum disease control. Known multi-site fungicides include but are not limited to dithiocarbamates, phthalimides, chloronitriles, inorganic fungicides, sulfamides, bis-guanidines, triazines, quinones, quinoxalines, 15 dicoarboxamides etc.

The present inventors believe that the combination of the present invention surprisingly results in a synergistic action. The combinations of the present invention allow for a broad spectrum of pest control and has surprisingly improved 20 plant vigour and yield. The broad spectrum of the present combination also provides a solution for preventing the development of resistance.

Therefore, an aspect of the present invention can provide combinations comprising:

- 25 i) fipronil;
ii) azoxystrobin;
iii) a benzimidazole fungicide; and
iv) at least one active agent selected from a neonicotinoid insecticide or a multi-site fungicide or both.

30

In an embodiment, the benzimidazole fungicide is selected from at least one of albendazole, benomyl, carbendazim, chlorfenazole, cypendazole, debacarb,

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fuveridazole, mecarbinzid, rabenzazole, thiabendazole, furophanate, thiophanate, thiophanate-methyl.

In an embodiment, the benzimidazole fungicide is selected from benomyl,
5 carbendazim and thiophanate or thiophanate-methyl.

In an embodiment, the benzimidazole fungicide is carbendazim.

In an embodiment, the benzimidazole fungicide is thiophanate methyl.

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In an embodiment, the multi-site fungicide is a fungicide selected from the group consisting of dithiocarbamates, phthalimides, chloronitriles, inorganic fungicides, sulfamides, bis-guanidines, triazines, quinones, quinoxalines, and dicarboxamides.

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In an embodiment, the dithiocarbamate fungicide is selected from asamobam, asomate, azithiram, carbamorph, cufraneb, cuprobam, disulfiram, ferbam, metam, nabam, tecoram, thiram, urbacide, ziram, dazomet, etem, milneb, mancopper, mancozeb, maneb, metiram, polycarbamate, propineb and zineb.

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In a preferred embodiment, the dithiocarbamate fungicide is selected from maneb, mancozeb and zineb.

In another embodiment, the dithiocarbamate fungicide is mancozeb.

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In an embodiment, the multi-site fungicide is a phthalimide fungicide selected from captan, captafol and folpet.

In an embodiment, the multi-site fungicide is a chloronitrile fungicide such as
30 chlorothalonil.

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In an embodiment, the multi-site fungicide is a sulfamide fungicide selected from dichlofluanid and tolylfluanid.

5 In an embodiment, the multi-site fungicide is a bis-guanidine fungicide selected from guazatine and iminoctadine.

In an embodiment, the multi-site fungicide is a triazine fungicide selected from anilazine.

10 In an embodiment, the multi-site fungicide is a quinone fungicide dithianon.

In an embodiment, the multi-site fungicide is a quinoxaline fungicide selected from quinomethionate and chlorquinox.

15 In an embodiment, the multi-site fungicide is a dicarboxamide fungicide selected from fluoroimide.

In an embodiment, the multi-site fungicide is an inorganic fungicide selected from copper fungicides including copper (II) hydroxide, copper oxychloride, copper (II) sulfate, basic copper sulfate, Bordeaux mixture, copper salicylate $C_7H_4O_3^*Cu$, cuprous oxide CU_2O ; or sulphur.

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In an embodiment, the neonicotinoid insecticide may be selected from the group consisting of acetamiprid, clothianidin, imidacloprid, nitenpyram, nithiazine, thiacloprid and thiamethoxam.

25

In a preferred embodiment, the neonicotinoid insecticide is selected from the group consisting of acetamiprid, thiamethoxam and imidacloprid.

30 Thus, an embodiment of the present invention can provide combinations for treatment of plant propagation material comprising:

- i) fipronil;

- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate-methyl; and
- iv) at least one active agent selected from imidacloprid, acetamiprid, thiamethoxam, mancozeb, maneb, zineb, folpet, chlorothalonil, and tribasic copper sulfate.

Another embodiment of the present invention may provide combinations for treatment of plant propagation material comprising:

- i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl; and
- iv) imidacloprid.

Another embodiment of the present invention may provide combinations comprising:

- i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl; and
- iv) mancozeb.

Another embodiment of the present invention may provide combinations comprising:

- i) fipronil;
- ii) azoxystrobin
- iii) carbendazim; and
- iv) imidacloprid.

Another embodiment of the present invention may provide combinations comprising:

- i) fipronil;
- ii) azoxystrobin;
- iii) carbendazim; and
- iv) mancozeb.

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Another embodiment of the present invention may provide combinations comprising

- i) fipronil;
- ii) azoxystrobin;
- 10 iii) thiophanate methyl; and
- iv) mancozeb.

Another embodiment of the present invention may provide combinations comprising:

- 15 i) fipronil;
- ii) azoxystrobin;
- iii) thiophanate methyl; and
- iv) imidacloprid.

20 Another embodiment of the present invention can provide combinations for treatment of plant propagation material comprising:

- i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate-
- 25 methyl; and
- iv) acetamiprid.

Another embodiment of the present invention can provide combinations for treatment of plant propagation material comprising:

- 30 i) fipronil;
- ii) azoxystrobin;

- iii) a benzimidazole fungicide selected from carbendazim or thiophanate-methyl; and
- iv) thiamethoxam.

5 Yet another embodiment of the present invention can provide combinations for treatment of plant propagation material comprising:

- i) fipronil;
- ii) azoxystrobin;
- 10 iii) a benzimidazole fungicide selected from carbendazim or thiophanate-methyl; and
- iv) chlorothalonil.

Yet another embodiment of the present invention can provide combinations for treatment of plant propagation material comprising:

- 15 i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate-methyl; and
- iv) tribasic copper sulfate.

20

In an embodiment, the constituent fungicides of the combination of the present invention may be admixed in ratio of (1-80): (1-80): (1-80): (1-80) of the fipronil, azoxystrobin, benzimidazole fungicide, neonicotinoid or multi-site fungicide respectively.

25

The combinations of the present invention may be admixed with suitable agrochemical adjuvants to form compositions.

Thus, an aspect of the present invention may provide a seed treatment composition
30 comprising:

- i) fipronil;
- ii) azoxystrobin;

- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl;
- iv) an active selected from neonicotinoid or a multi-site fungicide or both; and
- 5 v) agrochemcially acceptable adjuvants.

Another aspect of the present invention may provide a seed treatment composition comprising:

- i) fipronil;
- 10 ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl;
- iv) at least one active agent selected from imidacloprid, acetamiprid, thiamethoxam, mancozeb, maneb, zineb, folpet, chlorothalonil, and
- 15 tribasic copper sulfate; and
- v) agrochemcially acceptable adjuvants.

In an embodiment, the total amount of fipronil in the composition may typically be in the range of 0.1 to 99% by weight, preferably 0.2 to 90% by weight. The total
20 amount of azoxystrobin in the composition may be in the range of 0.1 to 99% by weight. The total amount of benzimidazole inhibitor in the composition may be in the range of 0.1 to 99% by weight. The total amount of neonicotinoid in the composition may be in the range of 0.1 to 99% by weight or the total amount of multi-site fungicide in the composition may be in the range of 0.1 to 99% by weight.

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In an embodiment, the constituent fungicides and insecticides of the composition of the present invention may be admixed in ratio of (1-80): (1-80): (1-80): (1-80) of the fipronil, azoxystrobin, benzimidazole fungicide and either neonicotinoid or multi-site fungicide respectively.

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In an embodiment, the constituents of the composition of the present invention may be applied as per known methods of application to seeds and other plant propagation material or transplanted saplings.

- 5 In an embodiment of the present invention, the compositions can be formulated into either solid or liquid formulations that are suitable for application to plant propagation material. The formulation may be made as known formulation types such as wettable powders (WP), solutions (LS), emulsions (ES), suspension concentrates (FS), water dispersible granule (WG), or aqueous suspension
10 concentrate (CS).

The formulation may be applied by various methods such methods using conventional treating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed treaters, and drum coaters, spouted beds
15 etc. Pre and post coating procedures such as sizing etc., may also be carried out. Such procedures are known in the art. It is readily understood that plant propagation material will be treated only once it is removed from the plant and is ready to be re-sown.

- 20 In an embodiment, the treatment may occur before sowing of the plant propagation material so that the sown material 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
25 for pest and/or disease control.

The formulations may contain standard agriculturally acceptable adjuvants, carriers, diluents, emulsifiers, fillers, anti-foaming agents, thickening agents, anti-freezing agents, biocides, pigments etc.

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Suitable agricultural adjuvants and carriers may include, but are not limited to, crop oil concentrates; methylated seed oils, emulsified methylated seed oil, nonylphenol

ethoxylate; benzylcocoalkyldimethyl quaternary ammonium salt; blend of petroleum hydrocarbon, alkyl esters, organic acid, and anionic surfactant; C₉-C₁₁ alkylpolyglycoside; phosphated alcohol ethoxylate; natural primary alcohol (C₁₂-C₁₆) ethoxylate; di-sec-butylphenol EO-PO block copolymer; polysiloxane-methyl cap; nonylphenol ethoxylate, urea ammonium nitrate; tridecyl alcohol (synthetic) ethoxylate (8EO); tallow amine ethoxylate; PEG(400) dioleate-99, alkyl sulfates, such as diethanolammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkylphenol-alkylene oxide addition products, such as nonylphenol-C₁₈ ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol-C₁₆ ethoxylate; soaps, such as sodium stearate; alkyl-naphthalene-sulfonate salts, such as sodium dibutyl-naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride; polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; salts of mono and dialkyl phosphate esters; vegetable or seed oils such as soybean oil, rapeseed/canola oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; and esters of the above vegetable oils, and in certain embodiments, methyl esters.

Suitable liquid carriers that may be employed in a composition of the present invention may include water or organic solvents. The organic solvents include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, aromatic solvents, paraffinic oils, and the like; vegetable oils such as soybean oil, rapeseed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cottonseed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above vegetable oils; esters of monoalcohols or dihydric, trihydric, or other lower polyalcohols (4-6 hydroxy containing), such as 2-ethyl hexyl stearate, n-butyl oleate, isopropyl myristate, propylene glycol dioleate, di-octyl succinate, di-butyl adipate, di-octyl phthalate and the like; esters of mono, di and polycarboxylic acids and the like. Organic solvents include, but are not limited to toluene, xylene,

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petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol monomethyl ether and diethylene glycol monomethyl ether, methyl alcohol, ethyl alcohol, isopropyl alcohol, amyl alcohol, ethylene glycol, 5 propylene glycol, glycerine, N-methyl-2-pyrrolidinone, N,N-dimethyl alkylamides, dimethyl sulfoxide.

Solid carriers that may be employed in the compositions of the present invention may include but are not limited to attapulgite, pyrophyllite clay, silica, kaolin clay, 10 kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's earth, talc, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, walnut shell flour, lignin, cellulose etc.

Thickeners such as silicates such meal silicates, sodium carboxymethyl cellulose, 15 methyl cellulose, ethyl cellulose, polyvinylalcohol, sodium alginate, Sodium poly acrylate, xanthan gum, welan gum, gum arabic, montmorillonite, lignosulfonates, hydroxy methyl cellulose, dextrin, starch and mixtures thereof;

Anti-freezing agents such as glycerin, ethylene glycol, propylene glycol, preferably 20 propylene glycol and the like. Anti-foaming agents such as silicone oils, mineral oils, Fatty acid ester; biocides such as sodium benzoate, 1,2-benzisothiazoline - 3-one, 2-methyl-4-isothiazolin-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one, potassium sorbate, parahydroxy benzoates and the like. Pigments may also be included in the formulation and may include but are not limited to pigment blue 25 15:4, pigment blue 15:3, pigment blue 15:2, pigment blue 15:1, pigment blue 80, pigment yellow 1, pigment yellow 13, pigment red 112, pigment red 48:2, pigment red 48:1, pigment red 57:1, pigment red 53:1, pigment orange 43, pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6, pigment brown 25, basic violet 10, basic violet 49, violet 23, acid red 51, acid red 30 52, acid red 14, acid blue 9, acid yellow 23, basic red 10, basic red 108.

Polymers such as such polyvinyl alcohols, polyvinylpyrrolidone, gel-forming carraagheenans, water-soluble gelatine and casein, superabsorbent polymers such polyacrylamides and polyacrylates based polymers, Semi-synthetic or fully-synthetic peptide/protein-based superabsorbent polymers such as collagen-based
 5 synthetic polymers, elastin-like polypeptides, polyaspartic acid, polyaspartates, polyglutamic acid, polyglutamate, Semi-synthetic or fully-synthetic polysaccharide: carboxymethyl starch , sulfoethyl starch, carboxymethyl cellulose, sulfoethyl cellulos, hydroxypropyl cellulose, hydroxyethyl cellulose, methylcellulose, chitosan; cross-linked polysaccharides such as CMS cross-linked with multi-
 10 functional carboxylic acids or multi-functional epoxides and the like. Polysaccharide graft copolymer: Polysaccharides obtained by graft polymerizing a monomer onto a polysaccharide, wherein the monomer is selected from acrylonitrile, acrylic acid, methacrylic acid, acrylamide, methacrylamide, 2-acrylamido-2-methyl- propanesulfonic acid (AMPS), vinyl sulfonic acid, ethyl
 15 acrylate, and potassium acrylate and the like.

The combination of the present invention are effective against phytopathogenic fungi, especially occurring in plants, including seed borne fungi and belong to the following classes such as those selected from Ascomycetes (e.g. *Penicillium*,
 20 *Gaeumannomyces graminis*); Basidiomycetes (e.g. the genus *Hemileia*, *Rhizoctonia*, *Puccinia*); Fungi imperfecti (e. g. *Botrytis*, *Helminthosporium*, *Rhynchosporium*, *Fusarium*, *Septoria*, *Cercospora*, *Alternaria*, *Pyricularia* and *Pseudocercospora herpotrichoides*); Oomycetes (e. g. *Phytophthora*, *Peronospora*, *Bremia*, *Pythium*, *Plasmopara*); Zygomycetes (e.g., *Rhizopus* spp.).
 25 The combination of the present invention is especially effective against *Alternaria* spp., *Ascochyta* spp., *Aspergillus* spp., *Claviceps purpurea*, *Cochliobolus* spp., *Colletotrichum* spp., *Diplodia maydis*, *Erysiphe graminis*, *Fusarium* spp. (such as *Fusarium culmorum*, *Fusarium oxysporum*, *Fusarium solani*, *Fusarium graminearum* and *Fusarium moniliforme*, *Fusarium subglutinans*),
 30 *Gaeumannomyces graminis*, *Giberella fujikuroi*, *Giberella zeae*, *Helminthosporium* spp. (such as *Helminthosporium graminearum*, *Helminthosporium oryzae*, *Helminthosporium solani*), *Monographella nivalis*, *Penicillium* spp., *Puccinia* spp.,

Pyrenophora spp. (such as *Pyrenophora graminea*), *Peronosclerospora* spp., *Peronospora* spp., *Phakopsora pachyrhizi*, *Phythium* spp., *Phoma* spp., *Phomopsis* spp., *Rhizoctonia* spp. (such as *Rhizoctonia cerealis*, *Rhizoctonia solani*), *Septoria* spp., *Pseudocercospora* spp., *Tilletia* spp., *Rhizopus* spp., *Thielaviopsis* spp., *basicola*, *Typhula* spp., *Ustilago* spp., *Sphacelotheca* spp. (e.g. *Spacelotheca reilliani*), *Thanatephorus cucumeris*, and *Verticillium* spp.

The present combinations may be used to control insect pests such as those from the order Lepidoptera, for example, *Acleris* spp., *Adoxophyes* spp., *Aegeria* spp., *Agrotis* spp., *Alabama argillaceae*, *Amylois* spp., *Anticarsia gemmatilis*, *Archips* spp., *Argyrotaenia* spp., *Autographa* spp., *Busseola fusca*, *Cadra cautella*, *Carposina nipponensis*, *Chilo* spp., *Choristoneura* spp., *Clysia ambiguella*, *Cnaphalocrocis* spp., *Cnephasia* spp., *Cochylis* spp., *Coleophora* spp., *Crocidolomia* spp., *Cryptophlebia leucotreta*, *Crysodeixis includens*, *Cydia* spp., *Diatraea* spp., *Diparopsis castanea*, *Earias* spp., *Elasmopalpus* spp., *Ephestia* spp., *Eucosma* spp., *Eupoecilia ambiguella*, *Euproctis* spp., *Euxoa* spp., *Grapholita* spp., *Hedya nubiferana*, *Heliothis* spp., *Hellula undalis*, *Hyphantria cunea*, *Keiferia lycopersicella*, *Leucoptera scitella*, *Lithocolletis* spp., *Lobesia botrana*, *Lymantria* spp., *Lyonetia* spp., *Malacosoma* spp., *Mamestra brassicae*, *Manduca sexta*, *Operophtera* spp., *Ostrinia nubilalis*, *Pammene* spp., *Pandemis* spp., *Panolis flammea*, *Pectinophora gossypiella*, *Phthorimaea operculella*, *Pieris rapae*, *Pieris* spp., *Plutella xylostella*, *Prays* spp., *Scirpophaga* spp., *Sesamia* spp., *Sparganothis* spp., *Spodoptera* spp., *Synanthedon* spp., *Thaumetopoea* spp., *Tortrix* spp., *Trichoplusia ni* and *Yponomeuta* spp.; from the order Coleoptera, for example, *Agriotes* spp., *Anthonomus* spp., *Atomaria linearis*, *Ceutorhynchus* spp., *Chaetocnema tibialis*, *Cosmopolites* spp., *Curculio* spp., *Dermestes* spp., *Diabrotica* spp., *Epilachna* spp., *Eremnus* spp., *Gonocephalum* spp., *Heteronychus* spp., *Leptinotarsa decemlineata*, *Lissorhoptrus* spp., *Melolontha* spp., *Orycaephilus* spp., *Otiorhynchus* spp., *Phlyctinus* spp., *Phyllotreta* spp., *Popillia* spp., *Protostrophus* spp., *Psylliodes* spp., *Rhizopertha* spp., *Scarabeidae*, *Sitophilus* spp., *Sitotroga* spp., *Tenebrio* spp., *Tribolium* spp. and *Trogoderma* spp.; from the order Orthoptera, for example, *Blatta* spp., *Blattella* spp., *Gryllotalpa*

spp., *Leucophaea maderae*, *Locusta* spp., *Periplaneta* spp. and *Schistocerca* spp.; from the order Isoptera, for example, *Reticulitermes* spp.; from the order Psocoptera, for example, *Üposcelis* spp.; from the order Anoplura, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Pemphigus* spp. and

5 *Phylloxera* spp.; from the order Mallophaga, for example, *Damalinea* spp. and *Trichodectes* spp.; from the order Thysanoptera, for example, *Frankliniella* spp., *Hercinothrips* spp., *Taeniothrips* spp., *Thrips palmi*, *Thrips tabaci* and *Scirtothrips aurantii*; from the order Heteroptera, for example, *Dichelops melacanthus*, *Distantiella theobroma*, *Dysdercus* spp., *Euchistus* spp., *Eurygaster* spp.,

10 *Leptocoris* spp., *Nezara* spp., *Piesma* spp., *Rhodnius* spp., *Sahlbergella singularis*, *Scotinophara* spp. and *Triatoma* spp.; from the order Homoptera, for example, *Aleurothrixus floccosus*, *Aleyrodes brassicae*, *Aonidiella* spp., *Aphididae*, *Aphis* spp., *Aspidiotus* spp., *Bemisia tabaci*, *Ceroplaster* spp., *Chrysomphalus aonidium*, *Chrysomphalus dictyospermi*, *Coccus hesperidum*, *Empoasca* spp.,

15 *Eriosoma larigerum*, *Erythroneura* spp., *Gascardia* spp., *Laodelphax* spp., *Lecanium corni*, *Lepidosaphes* spp., *Macrosiphus* spp., *Myzus* spp., *Nephotettix* spp., *Nilaparvata* spp., *Paratoria* spp., *Pemphigus* spp., *Planococcus* spp., *Pseudaulacaspis* spp., *Pseudococcus* spp., *Psylla* spp., *Pulvinaria aethiopica*, *Quadraspidotus* spp., *Rhopalosiphum* spp., *Saissetia* spp., *Scaphoideus* spp.,

20 *Schizaphis* spp., *Sitobion* spp., *Trialeurodes vaporariorum*, *Trioza erytrae* and *Unaspis citri*; from the order Hymenoptera, for example, *Acromyrmex*, *Athalia rosae*, *Atta* spp., *Cephus* spp., *Diprion* spp., *Diprionidae*, *Gilpinia polytoma*, *Hoplocampa* spp., *Lasius* spp., *Monomorium pharaonis*, *Neodiprion* spp., *Solenopsis* spp. and *Vespa* spp.; from the order Diptera, for example, *Antherigona soccata*, *Bibio hortulanus*, , *Ceratitis* spp., *Chrysomyia* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Delia* spp., *Drosophila melanogaster*, , *Liriomyza* spp., ,

25 *Melanagromyza* spp., , *Orseolia* spp., *Oscinella frit*, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp.; from the order Acarina, for example, *Acarus siro*, *Aceria sheldoni*, *Aculus schlehtendali*, *Amblyomma* spp., *Argas* spp.,

30 , *Brevipalpus* spp., *Bryobia praetiosa*, *Calipitimerus* spp., *Chorioptes* spp., *Dermanyssus gallinae*, *Eotetranychus carpini*, *Eriophyes* spp., *Hyalomma* spp.,

Olygonychus pratensis, Ornithodoros spp., Panonychus spp., Phyllocoptruta oleivora, Polyphagotarsonemus latus, Psoroptes spp., Rhipicephalus spp., Rhizoglyphus spp., Sarcoptes spp., Tarsonemus spp. and Tetranychus spp.; and from the class Nematoda, for example, the species of Meloidogyne spp. (for example, Meloidogyne incognita and Meloidogyne javanica), Heterodera spp. (for example, Heterodera glycines, Heterodera schachtii, Heterodora avenae and Heterodora trifolii), Globodera spp. (for example, Globodera rostochiensis), Radopholus spp. (for example, Radopholus similis), Rotylenchulus spp., Pratylenchus spp. (for example, Pratylenchus neglectans and Pratylenchus penetrans), Aphelenchoides spp., Helicotylenchus spp., Hoplolaimus spp., Paratrichodorus spp., Longidorus spp., Nacobbus spp., Subanguina spp. Belonlaimus spp., Criconemella spp., Criconemoides spp. Ditylenchus spp., Dolichodorus spp., Hemicriconemoides spp., Hemicyclophora spp., Hirschmaniella spp., Hypsoperine spp., Macroposthonia spp., Melinius spp., Punctodera spp., Quinisulcius spp., Scutellonema spp., Xiphinema spp., and Tylenchorhynchus spp.

In an embodiment, the combination of the present invention may be used for treatment of plant propagation material of crops such as cereals such as wheat, barley, rye, oats, corn, rice, sorghum, triticale and related crops; beets such as sugar beet and fodder beet; leguminous plants such as beans, lentils, peas, soybean; oil plants such as rape, mustard, sunflowers; cucurbits such as marrows, cucumbers, melons; fibre plants such as cotton, flax, hemp, jute; vegetables such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika as well as ornamentals such as flowers, shrubs, broad-leaved trees and evergreens, such as conifers. The plant propagation material may also be used on varieties of plant propagation material such as conventional, hybrid or transgenic plants.

In an embodiment, the combinations of the present invention may further contain herbicide, fungicides, insecticides, fertilizers, biologicals, other plant growth additives such as mycorrhiza, silicic acid, plant derived growth promoters etc.

In an aspect, the present invention may provide methods of improving vigour or yield of the plant comprising, applying to a plant propagation material before sowing, a combination comprising:

- 5 i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl; and
- 10 iv) an active agent selected from imidacloprid, acetamiprid, thiamethoxam, or a multi-site fungicide or both.

In an embodiment, the multi-site fungicide is a dithiocarbamate fungicide.

In an embodiment, the dithiocarbamate fungicide is mancozeb.

15

In an embodiment, the multi-site fungicide is a phthalimide fungicide selected from captan, captafol and folpet.

In an embodiment, the multi-site fungicide is a chloronitrile fungicide such as chlorothalonil.

20

In an embodiment, the multi-site fungicide is a sulfamide fungicide selected from dichlofluanid and tolylfluanid.

25 In an embodiment, the multi-site fungicide is a bis-guanidine fungicide selected from guazatine and iminoctadine.

In an embodiment, the multi-site fungicide is a triazine fungicide selected from anilazine.

30

In an embodiment, the multi-site fungicide is a quinone fungicide selected from dithianon.

In an embodiment, the multi-site fungicide is a quinoxaline fungicide selected from quinomethionate and chlorquinox.

- 5 In an embodiment, the multi-site fungicide is a dicarboxamide fungicide selected from fluoroimide.

- In an embodiment, the multi-site fungicide is an inorganic fungicide selected from copper fungicides including copper (II) hydroxide, copper oxychloride, copper (II) sulfate, basic copper sulfate, Bordeaux mixture, copper salicylate $C_7H_4O_3 \cdot Cu$, cuprous oxide CU_2O ; or sulphur.
- 10

- In another aspect, the present invention may provide methods of controlling soil borne fungi and insect pests, the method comprising, applying to a plant propagation material before sowing, a combination comprising:
- 15

- i) fipronil;
- ii) azoxystrobin;
- iii) a benzimidazole fungicide selected from carbendazim or thiophanate methyl; and
- 20 iv) an active selected from imidacloprid, acetamiprid, thiamethoxam, mancozeb, maneb, zineb, folpet, chlorothalonil, and tribasic copper sulfate or a multi-site fungicide or both.

- In an embodiment, the multi-site fungicide is a dithiocarbamate fungicide.
- 25

In an embodiment, the dithiocarbamate fungicide is mancozeb.

- In an embodiment, the multi-site fungicide is a phthalimide fungicide selected from captan, captafol and folpet.
- 30

In an embodiment, the multi-site fungicide is a chloronitrile fungicide such as chlorothalonil.

In an embodiment, the multi-site fungicide is a sulfamide fungicide selected from dichlofluanid and tolylfluanid.

- 5 In an embodiment, the multi-site fungicide is a bis-guanidine fungicide selected from guazatine and iminoctadine.

In an embodiment, the multi-site fungicide is a triazine fungicide selected from anilazine.

10

In an embodiment, the multi-site fungicide is a quinone fungicide selected from dithianon.

- 15 In an embodiment, the multi-site fungicide is a quinoxaline fungicide selected from quinomethionate and chlorquinox.

In an embodiment, the multi-site fungicide is a dicarboxamide fungicide selected from fluoroimide.

- 20 In an embodiment, the multi-site fungicide is an inorganic fungicide selected from copper fungicides including copper (II) hydroxide, copper oxychloride, copper (II) sulfate, basic copper sulfate, Bordeaux mixture, copper salicylate $C_7H_4O_3 \cdot Cu$, cuprous oxide CU_2O ; or sulphur.

- 25 In an aspect, the combination of the present invention may be presented as a kit of parts, or as a ready mix formulation that may be readily applied to the plant propagation material or may be applied to plant propagation material before being commercially vended.

- 30 Surprisingly, it has been found by the present inventors that combinations of fipronil, azoxystrobin, a benzimidazole fungicide and at least one of Imidacloprid or a multi-site fungicide when applied individually, was ineffective in the control of soil

borne fungi and insect pests, but demonstrated excellent synergistic control on weeds when applied together. The combination controlled the soil borne fungi and insect pests. The combination of fipronil, azoxystrobin, a benzimidazole fungicide and at least one of Imidacloprid or a multi-site fungicide controlled seed borne diseases such as seed rot among others. The current invention therefore provides advantageous methods of soil borne fungal and insect pests. The present method also provides a broader spectrum of controlling such pests and helps in resistance management, thus improving germination rate and producing plants with improved vigour and a broader spectrum of control at lower use rates.

Advantages of the present invention:

The combinations of the present invention exert at least one of the following advantages:

These combinations prevent mycelial development, spore germination and the formation of apressories and haustoria, controlling the main soil and seed pathogens such as *Rhizoctonia solani* and *Sclerotinia sclerotiorum*. The combinations were found to be totally selective for the cultures and not interfering in the organisms responsible for nodulation in legumes, containing the first multisite fungicide for seed treatment that has multiple action in relation to the cellular functions of the pathogens, forms a barrier on the surface of the seeds. The combinations of the invention thus eliminated the fungi present on the surface of the seeds and prevented germination of the spores that come after the treatment, presenting synergistic effect among the three fungicides, potentiated by mancozeb.

The storage time of the thus treated seeds was found to be greater than 120 days without interfering with the germination and vigor patterns.

The combination of the invention could be adapted to a violet color associated to the "optical brightness" providing nighttime brightness through black light, making it difficult to falsify the product and aiding the differentiation of grain for treated seed.

The combinations displayed improvement of the plant defense mechanism against pathogens. It promoted the growth of the seedlings through the increment of the root system, with greater depth of roots and better utilization of nutrients. Increased photosynthetic, consequently lower energy consumption of the seedling providing
 5 vigorous growth, conditioning the plant to achieve superior productivity even under stress conditions

The combinations of the invention facilitated better coverage of seeds due to adherence products through a differentiated and specific formulation for the
 10 treatment of seeds, consequently less loss of active ingredient.

Example:

Experiments were carried out to study the combinations of the present invention for seed treatment in corn. These studies were aimed at verifying the efficacy of
 15 doses of the combinations of the inventions, when compared to the standard products. The following combinations were tank-mixed and used for treating corn seeds.

S No.	Composition	Combination components
1	UPL1	Fipronil 150 g/L + Imidacloprid 150 g/L + Azoxystrobin 30 g/L + Cabendazim 90 g/L
2	UPL2	Fipronil 150 g/L + Imidacloprid 150 g/L + Azoxystrobin 30 g/L + Thiophanate-methyl 120 g/L
3	UPL3	Fipronil 160 g/L + Mancozeb 160 g/L + Azoxystrobin 23 g/L + Thiophanate-methyl 90 g/L
4	Comparative P1	Metalaxyl 20 g/L + Thiabendazol 150 g/L + Fludioxonil 25 g/L
5	Comparative P2	Thiamethoxam 350 g/L
6	Comparative P3	Thiodicarb 450 g/L + Imidacloprid 150 g/L

7	Comparative P4	Clothianidin 600 g/L

These combinations were used to treat corn seeds before sowing, and the treated seeds were tested for plant strength after emergence. The plant strength was tested by measuring the percentage of plants found laid (fallen) at 70 days after emergence in the field. The following results were tabulated:

Table 1:

S No.	Treatment	Plants laid (percentage %) at 70 DAE
1	Untreated	77.5
2	UPL1 @ 0.30 kg/Ha	7.6
3	UPL1 @ 0.50 kg/Ha	6.6
4	UPL2 @ 0.40 kg/Ha	1.2
5	UPL3 @ 0.30 kg/Ha	0.0
6	UPL3 @ 0.40 g/Ha	10.0
7	UPL3 @ 0.50 kg/Ha	7.5
8	P3 + Carbendazim 150 g/L + Thiram 350 g/L	42.5
9	P1 + P2 + Fipronil @ 250 g/L	61.2
10	Pyroclostrobin 25 g/L + Thiophanate-methyl 225 g/L + Fipronil 250 g/L	12.5

It was thus concluded that the plants emerging from the seeds treated with the combinations according to the present invention displayed surprisingly improved plant strength.

Example 2:

The combination UPL2 according to the present invention was tested for seed treatment advantages in dry bean, and compared vis-à-vis the industry standard of thiadcarb 225 g/L and imidacloprid 75 g/L. The dry bean seeds were treated with the following regimen, and the percentage control of *Bemisia tabaci* nymphs was calculated using Abbott's formula. The following results were tabulated:

Table 2:

S No.	Treatment [/per 100 kg of seeds]	<i>Bemisia tabaci</i> Control (%) of nymphs Abbott's formula				
		7 DAE	15 DAE	21 DAE	30 DAE	45 DAE
1	Untreated	0.0	0.0	0.0	0.0	0.0
2	UPL2 @ 0.40 kg	80.2	66.3	39.4	68.8	38.1
3	UPL2 @ 0.50 kg	81.0	73.6	33.3	25.0	33.3
4	UPL2 @ 0.60 kg	94.3	89.6	42.4	62.5	23.8
5	UPL2 @ 0.70 kg	89.1	82.8	27.3	72.5	66.7
6	Thiadicarb 225 g/L and Imidacloprid 75 g/L [@ 0.50 kg]	54.9	54.7	15.2	37.5	4.7

The percentage control (%) for adults + nymphs of *Bemisia tabaci* was also calculated using Abbott's formula and tabulated as below:

Table 3:

S No.	Treatment [/per 100 kg of seeds]	<i>Bemisia tabaci</i> Control (%) of nymphs + adults Abbott's formula				
		7 DAE	15 DAE	21 DAE	30 DAE	45 DAE
1	Untreated	0.0	0.0	0.0	0.0	0.0
2	UPL2 @ 0.40 kg	80.2	66.3	84.4	49.7	0.0
3	UPL2 @ 0.50 kg	81.0	73.6	30.5	21.7	15.4
4	UPL2 @ 0.60 kg	94.3	89.6	77.3	63.7	40.0
5	UPL2 @ 0.70 kg	89.1	82.8	81.3	70.1	44.6
6	Thiadicarb 225 g/L and Imidacloprid 75 g/L [@ 0.50 kg]	54.9	54.7	11.7	0.6	0.0

It was thus concluded that the combinations of the present invention were surprisingly efficacious for the control of *Bemisia tabaci* nymphs and adults during the treatment of dry bean seeds.

While the foregoing written description of the invention enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The invention should therefore not be limited by the above described embodiment, method, and examples, but by all embodiments and methods within the scope and spirit of the invention.

CLAIMS

1. A seed treatment combination comprising:
 - a. fipronil;
 - 5 b. azoxystrobin;
 - c. a benzimidazole fungicide; and
 - d. at least one active agent selected from a neonicotinoid insecticide or a multi-site fungicide or both.
- 10 2. The combination as claimed in claim 1 wherein benzimidazole fungicide is selected from albendazole, benomyl, carbendazim, chlorfenazole, cypendazole, debacarb, fuberidazole, mecarbinzid, rabenzazole, thiabendazole, furophanate, thiophanate, thiophanate-methyl.
- 15 3. The combination as claimed in claim 1 wherein multi-site fungicide is a fungicide selected from the group consisting of dithiocarbamates, phthalimides, chloronitriles, inorganic fungicides, sulfamides, bis-guanidines, triazines, quinones, quinoxalines, and dicarboxamides.
- 20 4. The combination as claimed in claim 1 wherein the dithiocarbamate fungicide is selected from asamobam, asomate, azithiram, carbamorph, cufraneb, cuprobam, disulfiram, ferbam, metam, nabam, tecoram, thiram, urbacide, ziram, dazomet, etem, milneb, mancopper, mancozeb, maneb, metiram, polycarbamate, propineb and zineb;
phthalimide fungicide is selected from captan, captafol and folpet;
chloronitrile fungicide is chlorothalonil;
sulfamide fungicide is selected from dichlofluanid and tolylfluanid;
25 bis-guanidine fungicide is selected from guazatine and iminoctadine;
multi-site fungicide is a triazine fungicide selected from anilazine;
the multi-site fungicide is a quinone fungicide dithianon;
the multi-site fungicide is a quinoxaline fungicide selected from quinomethionate and chlorquinox is a dicarboxamide fungicide selected
30 from fluoroimide;
inorganic fungicide selected from copper fungicides including copper (II) hydroxide, copper oxychloride, copper (II) sulfate, basic copper sulfate,

Bordeaux mixture, copper salicylate $C_7H_4O_3 \cdot Cu$, cuprous oxide CU_2O ; or sulphur.

5. The combination as claimed in claim 1 wherein neonicotinoid insecticide may be selected from the group consisting of acetamiprid, clothianidin, imidacloprid,
5 nitenpyram, nithiazine, thiacloprid and thiamethoxam.
6. A combination as claimed in claim 1 wherein the said combination comprises:
 - a. Fipronil, azoxystrobin, carbendazim; and mancozeb
 - b. Fipronil, azoxystrobin, carbendazim; and Imidacloprid
 - 10 c. Fipronil, azoxystrobin, thiophanate methyl; and mancozeb
 - d. Fipronil, azoxystrobin, thiophanate methyl; and Imidacloprid
 - e. Fipronil, azoxystrobin, carbendazim; and acetamiprid
 - f. Fipronil, azoxystrobin, thiophanate methyl; and acetamiprid
 - g. Fipronil, azoxystrobin, carbendazim; and thiamethoxam
 - 15 h. Fipronil, azoxystrobin, thiophanate methyl; and thiamethoxam
 - i. Fipronil, azoxystrobin, carbendazim; and chlorothalonil
 - j. Fipronil, azoxystrobin, thiophanate methyl; and chlorothalonil
 - k. Fipronil, azoxystrobin, carbendazim; and tribasic copper sulfate
 - 20 l. Fipronil, azoxystrobin, thiophanate methyl; and tribasic copper sulfate
7. A combination as claimed in claim 1 wherein the said combination is admixed in the ratio of (1-80): (1-80): (1-80): (1-80).
8. A composition comprising a combination as claimed in claims 1 – 7.
9. A composition as claimed in claim 8, wherein fipronil is present in the range
25 of 0.1 to 99% by weight; azoxystrobin is present in the range of 0.1 to 99% by weight; benzimidazole inhibitor is present in the range of 0.1 to 99% by weight; neonicotinoid is present in the range of 0.1 to 99% by weight or multi-site fungicide is present in the range of 0.1 to 99% by weight.
10. A method of improving vigour or yield of the plant comprising, applying to a
30 plant propagation material before sowing, a combination as claimed in claim 1-8

11. A method of controlling soil borne fungi and insect pests, the method comprising, applying to a plant propagation material before sowing, a combination comprising a combination as claimed in claim 1-8
- 5 12. A kit comprising a kit of parts, or as a ready mix formulation that may be readily applied to the plant propagation material or may be applied to plant propagation material seed treatment combination as claimed in claims 1-8

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

A01N 51/00 (2006.01) **A01N 47/34 (2006.01)** **A01N 43/54 (2006.01)** **A01N 47/02 (2006.01)** **A01N 47/18 (2006.01)**
A01N 47/14 (2006.01) **A01P 3/00 (2006.01)** **A01P 7/04 (2006.01)**

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)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPOQUE 5.2 (PATENW): Applicant/Inventor names (UPL Ltd, S Wagner, G A H Oliveira, S P Vaidyalingam, M D Borane, A F Queiroz, N Gonçalves, S M Bharambe, P D Wagh, J R Shroff, V R Shroff and abbreviations thereof), CPC/IPC symbols (A01N --, 47/02, 43/54, 51/00, 47/18, 47/34, 47/14), Keywords (fipronil, azoxystrobin, carbendazim, thiophanate-methyl, mancozeb, imidacloprid, and like terms and alternatives). **NEW STN (CAPlus, DWPI, BIOSIS, CABA, Registry, CN/DE/FR/IN/JP/KRFULL):** Applicant/Inventor names (*as above*), CAS Numbers (120068-37-3, 131860-33-8, 138261-41-3, 105827-78-9, 10605-21-7, 37953-07-4, 23564-05-8, 8018-01-7), Keywords (*as above*). **ONLINE DATABASES (Espacenet, Google Scholar/Patents/Search):** Applicant/Inventor names (*as above*), Keywords (*as above*). **INTERNAL DATABASES:** Applicant/Inventor names (*as above*).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 28 February 2019		Date of mailing of the international search report 28 February 2019	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Austin Smith AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832381	

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/IB2018/060686
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/095913 A2 (BASF SE) 14 August 2008 p15 ln 21-25, pp 75-81, p82 ln 22-30, Table 2 (Table Q: M-664, M-670, M-864, M-895)	1-4 & 6-12
X	WO 2009/098225 A2 (BASF SE) 13 August 2009 Abstract, p5 ln 21-23, pp 11-12 & 25-32, p35 ln 31 to p36 ln 18, Table 1 (R-21, R-49, R-77, R-105, R-133, R-161, R-189, R-217 & R-245)	1-2 & 5-12
A	WO 2010/043553 A1 (BASF SE) 22 April 2010 Table 1 (R-25, R-54, R-83 & R-112)	
A	WO 2016/197457 A1 (ROTAM AGROCHEM INTERNATIONAL COMPANY LIMITED) 15 December 2016 Abstract	
A	WO 2010/092032 A1 (BASF SE) 19 August 2010 Table 1 (S-56 to S-59)	
A	WO 2011/154494 A2 (SYNGENTA PARTICIPATIONS AG) 15 December 2011 pp 1-2 & 13-30)	
A	WO 2011/151261 A2 (BASF SE) 08 December 2011 Abstract, Table 1	
A	WO 2011/110583 A2 (BASF SE) 15 September 2011 Table QII (1-19 to 1-21, 1-46 to 1-48, 1-73 to 1-75, 1-100 to 1-102)	
P,X	WO 2018/112563 A1 (HELM DO BRASIL MERCANTIL LTDA) 28 June 2018 Abstract, Examples, Claims (based on English machine translation, Espacenet, 18 FEB 2019)	1-2 & 5-12
Form PCT/ISA/210 (fifth sheet) (revised January 2019)		

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