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(54) Title: FUNGICIDE COMPOSITION COMPRISING MANDELAMIDE TYPE COMPOUND, STROBILURIN AND DITHIOCARBAMATE

(57) Abstract: The present invention relates to novel fungicidal composition for protecting crops against fungal diseases, and the corresponding methods of protection by application of the said composition. More, particularly, the present invention relates to fungicidal composition comprising mandelamide compounds particularly mandipropamid, pyraclostrobin which is a strobilurin fungicide and propineb, a dithiocarbamate fungicide.

FUNGICIDE COMPOSITION COMPRISING MANDELAMIDE TYPE COMPOUND, STROBILURIN AND DITHIOCARBAMATE

FIELD OF THE INVENTION

[001] The present invention relates to novel fungicidal composition for protecting crops against fungal diseases, and the corresponding methods of protection by application of the said composition. More, particularly, the present invention relates to fungicidal composition comprising mandelamide type compounds particularly mandipropamid, pyraclostrobin which is a strobilurin fungicide and propineb, a dithiocarbamate fungicide.

BACKGROUND OF THE INVENTION

[002] Diseases are a common occurrence on plants, often having a significant economic impact on yield and quality, thus managing diseases is an essential component of production for most crops. Broadly, there are three main reasons as to why fungicides are used: (a) to control a disease during the establishment and development of a crop, (b) to increase productivity of a crop and to reduce blemishes, (c) to improve the storage life and quality of harvested plants and its products. Fungi often spoil (render unusable) stored fruits, vegetables, tubers, and seeds. Attempts have been made to control the fungal attack on plants by using different fungicides.

[003] Fungicides are compounds, of natural or synthetic origin, which act to protect plants against damage caused by fungi. Current methods of agriculture rely heavily on the use of fungicides. In fact, some crops cannot be grown usefully without the use of fungicides. Using fungicides allows a grower to increase the yield and the quality of the crop, and consequently, increase the value of the crop. In most situations, the increase in value of the crop is worth at least three times the cost of the use of the fungicide.

[004] However, no one fungicide is useful in all situations and repeated usage of a single fungicide frequently leads to the development of resistance to that and related fungicides. Actual experiences of fungicide have shown that

repeat application of one specific active compound to prevent and treat fungi will results in quick selectivity of fungal strains in many cases, in order to lower risk of selectivity of fungal strains, a mixture of compounds of different activities are commonly used to prevent and treat harmful fungi presently. Active compounds having different mechanisms of action are combined to delay the generation of resistance, and reduce the application amount and prevention and treatment costs. Consequently, research is being conducted to produce fungicides and combinations of fungicides that are safer, that have better performance, that require lower dosages, that are easier to use, and that cost less.

SUMMARY OF THE INVENTION

[005] The present invention provides a fungicidal composition comprising as its active ingredient a mandelamide fungicide Mandipropamid, a strobilurin fungicide Pyraclostrobin, a dithiocarbamate fungicide Propineb and adjuvants.

[006] In an embodiment of the present invention the fungicidal composition comprises 2 to 6% (w/w) of Mandipropamid; 2 to 6% (w/w) of Pyraclostrobin; and 50 to 55% (w/w) of Propineb.

[007] In an embodiment of the present invention the adjuvants are selected from the group comprising wetting agent, dispersing agent, rheology modifiers, and filler.

[008] In an embodiment of the present invention the wetting agent is selected from the group comprising non-ionic surfactants, anionic surfactants, cationic surfactants, Alkylnaphthalene sulfonate (ANS) condensate blend, Linear Alcohol Derivative, and Polyethyleneglycol Nonylphenyl ether ammonium sulfate, Dialkyl naphthalene sulphonate sodium salt, alcohol alkoxylate, fatty alcohol ethoxylates, sodium dodecyl benzene sulfonate, alcohol alkoxylate, fatty alcohol ethoxylates and alkyl naphthalene sulfonate condensate or sodium lauryl sulfonate present in an amount of 2 to 6% (w/w).

[009] In an embodiment of the present invention the dispersing agent is selected from the group comprising phenol sulfonic acid-formaldehyde polycondensation as sodium salt, Sodium polyalkylnaphthalene sulphonate,

Acrylate polymer, sodium polycarboxylate, sodium methyl oleoyl taurate, Sodium Ligno sulphonate, and Sodium lauryl sulphate or combination thereof present in an amount of 3 to 6% (w/w).

[010] In an embodiment of the present invention the adjuvant is selected from amino acids and Polydimethylsiloxane present in an amount of 1 to 5% (w/w).

[011] In an embodiment of the present invention the rheology modifiers is selected from the group comprising of guar gum, locust bean gum, xanthan gum, carrageenan, alginates, methyl cellulose, carboxymethyl sodium carboxymethylcellulose, hydroxyethylcellulose, modified starches; other polysaccharides and modified polysaccharides, polyethylene alcohol, glycerol alkyl resins and cellulose derivatives, natural oils, mineral oils such as kyros oil, vegetable oil derivatives, the organoclays, silicon dioxide and fumed silicas present in an amount of 1 to 5% (w/w).

[012] In an embodiment of the present invention the filler is selected from the group comprising of aluminium silicate, silica sand, silicon carbide, aluminium trioxide, barium sulfate, calcium carbonate, calcium sulfate, carbon black, copper, kaolin clay present in an amount of 10 to 25% (w/w).

[012] In an embodiment of the present invention the composition is formulated as a Wettable powder.

DETAILED DESCRIPTION OF THE INVENTION

[013] It is to be noted that, as used in the specification, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing “a compound” includes a mixture of two or more compounds. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[014] Similarly, the words "comprise," "comprises," and "comprising" are to be interpreted inclusively rather than exclusively. Likewise, the terms

"include," "including" and "or" should all be construed to be inclusive, unless such a construction is clearly prohibited from the context. However, the embodiments provided by the present disclosure may lack any element that is not specifically disclosed herein. Thus, a disclosure of an embodiment defined using the term "comprising" is also a disclosure of embodiments "consisting essentially of" and "consisting of" the disclosed components. Where used herein, the term "example," particularly when followed by a listing of terms, is merely exemplary and illustrative, and should not be deemed to be exclusive or comprehensive. Any embodiment disclosed herein can be combined with any other embodiment disclosed herein unless explicitly indicated otherwise.

[015] The expression of various quantities in terms of "% w/w" or "%" means the percentage by weight, relative to the weight of the total solution or composition unless otherwise specified.

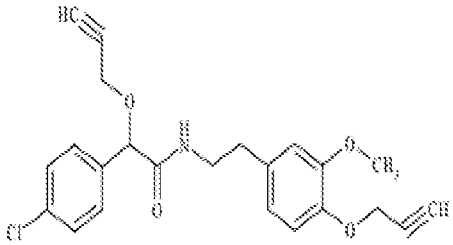
[016] The term "active ingredient" (a.i.) or "active agent" used herein refers to that component of the composition responsible for control of fungi, insects-pests or disease.

[017] As used herein, the term "effective amount" means the amount of the active substances in the compositions to achieve an observable effect on growth, including the effects of necrosis, death, retardation, prevention, and removal, destruction, or otherwise diminishing the occurrence and activity of the target organism. An effective amount of the compositions will also vary according to the prevailing conditions such as desired pesticidal effect and duration, weather, target species, locus, mode of application, and the like.

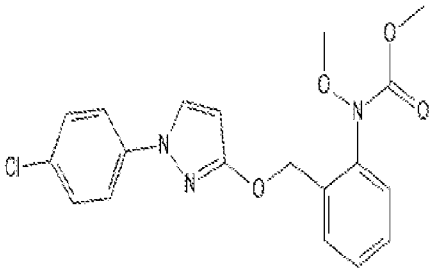
[018] This invention relates to a novel fungicidal composition comprising mandipropamid, pyraclostrobin and propineb. The present invention also relates to use of such compositions in preventing fungal diseases in plants.

[019] Mandipropamid [4-chloro-N-[2-[3-methoxy-4-(2-propynyloxy)phenyl]ethyl]a-(2-propynyloxyl)- benzeneacetamide], is a new fungicide in the mandelamide class developed by Syngenta Crop Protection, Inc. for the control of foliar oomycete pathogens in a range of crops including *Plasmopara viticola* in grapes, *Phytophthora infestans* in potatoes and tomatoes,

and *Pseudoperonospora cubensis* in cucurbits. Mandipropamid is also proposed for uses on leafy vegetables to control downy mildew (*Bremia lactucae*) and blue mold (*Peronospora effuse*). Mandipropamid inhibits steps in the biosynthesis of phospholipids. The structure of mandipropamid is

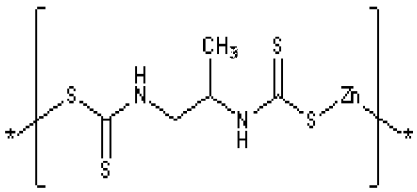


[020] Pyraclostrobin (Methyl *N*-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]phenyl]-*N*-methoxycarbamate) is a quinone outside inhibitor belonging to the strobilurin chemical class. Pyraclostrobin is a broad-spectrum fungicide, controlling major plant pathogens from the ascomycete, basidiomycete, deutromycete and oomycetes classes of fungi. Pyraclostrobin is taken up rapidly by the plant and is largely retained by the waxes in the leaf cuticle. It demonstrates good translaminar movement through leaf, resulting in disease control on both leaf surfaces. Pyraclostrobin is effective against wheat leaf blotch (*Septoria tritici),* wheat stripe rust (*Puccinia striiformis),* brown rust *(Precondite),* leaf blotch *(Rhynocsporium secalis)* and net blotch *(Pyrenophora teres).* The structure of Pyraclostrobin is



[021] Propineb, ([[(1-Methyl-1,2-ethanediyl)bis[carbamodithioato]](2-)]zinc)) is a contact fungicide with broad spectrum activity. It is used to control a wide range of fungal diseases, including downy mildew, brown rot, black rot, red fire, leaf spot, and blight in crops such as grapes, tomatoes, potatoes, berries,

citrus, rice and tea. Propineb is a polymeric zinc-containing dithiocarbamate. Due to the release of zinc, the application of propineb results in greening effect on the crop and subsequent improvement in quality of product. The structure of Propineb is



[022] Compositions comprising a single fungicidally active component suffer from numerous drawbacks such as development of resistant fungal species, requirement of high amount and concentration of the active ingredient, environmental damage, seepage of the active component into ground water, phytotoxicity and harmful effects on the health of animals and humans.

[023] Accordingly, the present invention provides a novel fungicidal composition comprising:

a mandelamide type fungicide;

a strobilurin fungicide;

a dithiocarbamate fungicide, in effective amounts and suitable adjuvants.

[024] According to the present invention the mandelamide type fungicide is mandipropamid, strobilurin fungicide is selected from azoxystrobin, picoxystrobin, pyraclostrabin, trifloxystrobin and dithiocarbamate fungicide is selected from mancozeb, propineb, maneb, metiram, thiram, ziram.

[025] Another embodiment of the present invention provides a novel fungicidal composition, comprising:

a Mandipropamid;

a Pyraclostrobin;

a Propineb in effective amounts, and suitable adjuvants.

[026] Another embodiment of the present invention provides a novel fungicidal composition, comprising:

2 to 6% (w/w) of Mandipropamid,

2 to 6% (w/w) of Pyraclostrobin,

50 to 55% (w/w) of Propineb, and suitable adjuvants.

[027] The novel fungicidal composition of the present invention may be formulated as Capsule suspension (CS), Dispersible concentrate (DC), Dustable powder (DP), Powder for dry seed treatment (DS), Emulsifiable concentrate (EC), Emulsifiable granule (EG), Emulsion water-in-oil (EO), Emulsifiable powder (EP), Emulsion for seed treatment (ES), Emulsion oil-in-water (EW), Flowable concentrate for seed treatment (FS), Granules (GR), Micro-emulsion (ME), Oil-dispersion (OD), Oil miscible flowable concentrate (OF), Oil miscible liquid (OL), Oil dispersible powder (OP), Suspension concentrate (SC), Suspension concentrate for direct application (SD), Suspo-emulsion (SE), Water soluble granule (SG), Soluble concentrate (SL), Spreading oil (SO), Water soluble powder (SP), Water soluble tablet (ST), Ultra-low volume (ULV) suspension, Tablet (TB), Ultra-low volume (ULV) liquid, Water dispersible granules (WG), Wettable powder (WP), Water dispersible powder for slurry seed treatment (WS), Water dispersible tablet (WT), a mixed formulation of CS and SC (ZC), a mixed formulation of CS and SE (ZE), a mixed formulation of CS and EW (ZW). Preferably, the composition of the present invention is formulated as Wettable powder.

[028] The composition further contains a support, an adjuvant and/or a surfactant. During application, a common adjuvant can be mixed with the composition.

[029] Suitable adjuvants may be a solid or liquid, and are generally a substance commonly used in formulation processing process, for example, natural or regenerated minerals, solvents, dispersing agents, wetting agents, adhesives, thickeners, binders or fertilizers.

[030] A method for applying the composition of the present invention includes: applying the composition of the present invention on the seed, bulbs, roots of transplants, and other propagative organs and aboveground part of plants, especially the leaves or foliage. The frequency of application and

application amount depend on the biological characteristics and the climate survival conditions of the fungal pathogen. A liquid formulation containing the composition may be used to wet the plant growing place such as rice field, or the composition may be applied in the soil in the solid form, such as in the granular form (soil application), so that the composition can get into the plant body (systemic action) through the plant roots from the soil.

[031] For the purpose of the present invention, the suitable adjuvants are selected from the group comprising of wetting agent, dispersing agent, adjuvant, rheology modifier, filler and other suitable adjuvants as required.

[032] The wetting agent is a compound that facilitates rapid wetting of the powder when added to the water. The wetting agent employed in the formulation composition is selected from the group consisting of non-ionic surfactants, anionic surfactant and a mixture of anionic and non-ionic surfactant and polymeric surfactant.

[033] Suitable wetting agent useful in accordance with the invention are Alkylnaphthalene sulfonate (ANS) condensate blend, Linear Alcohol Derivative, and Polyethyleneglycol Nonylphenyl ether ammonium sulfate, Dialkyl naphthalene sulphonate sodium salt, alcohol alkoxylate, fatty alcohol ethoxylates and sodium dodecyl benzene sulfonate. The wetting agent employed in the wettable powder formulation may be non-ionic surfactants belonging to the class of alcohol alkoxylate and fatty alcohol ethoxylates. Wetting agent may also be an anionic surfactant belonging to alkyl naphthalene sulfonate condensate or sodium lauryl sulfonate. The wetting agent used in the present invention is in amount of 2 to 6% (w/w).

[034] The dispersing agent is a compound which ensures that the particles remain suspended in water. The dispersing agent can be ionic or non-ionic or a mixture of such surface-active agents or graft co-polymer dispersant.

[035] Suitable dispersing agent useful in accordance with the invention are phenol sulfonic acid-formaldehyde polycondensation as sodium salt, Sodium polyalkylnaphthalene sulphonate, Acrylate polymer, sodium polycarboxylate, sodium methyl oleoyl taurate, Sodium Ligno sulphonate, and Sodium lauryl

sulphate. The dispersing agent used in the present invention is in an amount of 3 to 6% (w/w).

[036] Adjuvants are used in the present invention for increasing biological efficacy of agrochemicals. Suitable adjuvants for the purpose of the present invention are amino acids (Active 30.1x) and Polydimethylsiloxane (Silwet 408). The adjuvants are present in an amount of 1 to 5% (w/w).

[037] The rheology modifier is any material that alters the rheology of a composition to which it is added. Suitable rheology modifier useful in accordance with the invention are natural polymers selected from the group guar gum, locust bean gum, xanthan gum, carrageenan, alginates, methyl cellulose, carboxymethyl sodium carboxymethylcellulose, hydroxyethylcellulose, modified starches; other polysaccharides and modified polysaccharides, polyethylene alcohol, glycerol alkyl resins and cellulose derivatives, natural oils, mineral oils such as kyros oil, vegetable oil derivatives such as SURFOM® ESP 8105, the organoclays such as Bentone, Bentone SD and Benathix Plus and the fumed silicas such as Aerosil R974, Aerosil 200 and Aerosil 972, Aerosil R816 (silanehexadecyltrimethoxy hydrolysis product with silica), silicon dioxide and equivalent products thereof, preferably used is aerosilR816 (silanehexadecyltrimethoxy hydrolysis product with silica). The rheology modifier is present in an amount of 1 to 5% (w/w).

[038] Suitable filler useful in accordance with the invention are aluminium silicate, silica sand, silicon carbide, aluminium trioxide, barium sulfate, calcium carbonate, calcium sulfate, carbon black, copper, kaolin clay. The filler is present in an amount of 10-25% (w/w).

[039] The active compounds within the composition according to the invention have potent microbicide activity and can be employed for controlling undesired micro-organisms, such as fungi or bacteria, in crop protection or in the protection of materials.

[040] These compositions may merely contain the active components in effective amount and be applied, and may also mixed with additives for use, so the composition of the present invention may be formulated into various

formulations, for example, wettable powder, a suspension, an oil suspension, a water dispersible granule, an emulsion in water and a microemulsion. Preferably, the composition of the present invention is in wettable powder form.

[041] According to the properties of these compositions and the purpose to be achieved by applying the composition as well as the environmental conditions, the method for applying the composition may be selected to be spraying, atomizing, dusting, scattering or pouring and the like.

[042] It has been surprisingly found that the novel fungicidal composition of the present invention delays the appearance of the resistant strains of fungi and achieves effective and economical control of undesired fungicide infection. The composition achieves improved biological activity by enhancing overall control of diseases caused by fungi over a shorter period of time. Additional benefits of using the fungicidal composition of the present invention includes reduced risk of occupational hazard, lower cost of application, better cost: benefit ratio to the end user, reduced fuel and labour cost, saving in applicator's time and loss caused by mechanical damage to the crop and soil.

[043] The composition of the present invention can also be applied in conjunction with one or more herbicides, fungicides, insecticides, nematicides, growth factor enhancers and/or one or more fertilizers. The composition when used in conjunction may comprise other actives like one or more herbicides, fungicides, insecticides, nematicides, growth factor enhancers and/or one or more fertilizers.

[044] The composition can be applied in conjunction with one or more other fungicides to control a wider variety of fungi. The composition comprising the other fungicide can be formulated with the other fungicide by tank mixing with other fungicides or applied sequentially with other herbicides.

[045] The present invention is further illustrated by the following examples which are provided merely to be exemplary of the inventions and is not intended to limit the scope of the invention. Certain modifications and equivalents will be apparent to those skilled in the art and are intended to be included within the scope of the present invention.

Examples:

[046] Example 1: Preparation of composition of Mandipropamid + Pyraclostrobin + Propineb in wettable powder form

The composition of the present invention is prepared in following steps:

Step 1: weighing the raw materials according to batch size and mixing it for one hour. For illustration purpose the raw material may be china clay, Sodium ligno sulfonate, Supragil WP, mandipropamid, pyraclostrobin, propineb, ppt silica and active 30. 1 X.

Step 2: Milling the sample through air jet mill instrument at inlet pressure 2-3 kg/cm^2 and grinding pressure 6 kg/cm^2 and checking for the particle size < 15 micron.

Step 3: Collecting the milled material, and post blending the sample for 1 hour.

Step 4: Sending the sample to the quality analysis.

Step 5: Packing the formulated material in a suitable package.

[047] Example 2: Compositions of the present invention

The illustrative embodiments show the composition of Mandipropamid, Pyraclostrobin and Propineb in wettable powder form in different amount as follows:

Table 1: Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50 WP

Compositions	Function	Chemical Name	% (w/w)
Mandipropamid@96.7 % (b) 3.5 %	Fungicide	(*RS*)-2-(4-chlorophenyl)-*N*-[3-methoxy-4-(prop-2-ynyloxy)phenethyl]-2-(prop-2-ynyloxy) acetamide	3.619
Pyraclostrobin @97% (b) 3.5%	Fungicide	Methyl *N*-{2-[1-(4-chlorophenyl)pyrazol-3-yl	3.608

		oxymethyl]phenyl}(*N*-methoxy) carbamate	
Propineb @ 81% (b) 50%	Fungicide	Polymeric zinc 1,2-propylenebis (dithiocarbamate)	61.728
Supragil WP	Wetting agent	Dialkyl naphthalene sulphonate sodium salt	2.5
Sodium Ligno sulphonate	Dispersing agent	Sodium Ligno sulphonate	6.0
Active 30.1X	Adjuvant	Amino acids	3.0
PPT silica	Rheology modifier	Amorphous form of silica	1.0
China clay	Filler	Aluminium silicate	18.545
Total			100

Table 2: Mandipropamid 4% + Pyraclostrobin 4% + Propineb 50.5 WP

Compositions	**Function**	**Chemical Name**	**% (w/w)**
Mandipropamid @96.7 % (b) 4.0 %	Fungicide	(*RS*)-2-(4-chlorophenyl)-*N*-[3-methoxy-4-(prop-2-ynyloxy)phenethyl]-2-(prop-2-ynyloxy) acetamide	4.13
Pyraclostrobin @97% (b) 4.0%	Fungicide	Methyl *N*-{2-[1-(4-chlorophenyl) pyrazol-3-yl oxymethyl]phenyl}(*N*-methoxy)carbamate	4.12
Propineb @ 81% (b) 50.5%	Fungicide	Polymeric zinc 1,2-propylenebis (dithiocarbamate)	62.34

Morwet 3028	Wetting agent	Alkylnaphthalene sulfonate (ANS) condensate blend	5.0
Tamol FBPP	Dispersing agent	Phenol sulfonic acid-formaldehyde-polycondensation as sodium salt.	3.0
Agrilan 789	Dispersing agent	Acrylate copolymer	1.0
Ppt Silica	Rheology modifier	Silicon dioxide	2.0
Silwet 408	Adjuvent	Polydimethylsiloxane	3.0
China clay	Filler	Aluminium silicate	15.41
Total			100

Table 3: Mandipropamid 4.2% + Pyraclostrobin 4.2% + Propineb 51.5 WP

Compositions	Function	Chemical Name	% (w/w)
Mandipropamid@96.7 % (b) 4.2 %	Fungicide	(*RS*)-2-(4-chlorophenyl)-*N*-[3-methoxy-4-(prop-2-ynyloxy)phenethyl]-2-(prop-2-ynyloxy) acetamide.	4.34
Pyraclostrobin @97% (b) 4.2%	Fungicide	Methyl *N*-{2-[1-(4-chlorophenyl) pyrazol-3-yl oxymethyl] phenyl}(*N*-methoxy) carbamate.	4.32
Propineb @ 81% (b) 51.5%	Fungicide	Polymeric zinc 1,2-propylenebis (dithiocarbamate)	63.58
Supragil WP	Wetting agent	Dialkyl naphthalene sulphonate sodium salt	4.5

Supragil MNS 90	Dispersing agent	Sodium salt of methyl naphthalene sulfonate	2.5
Dispersol PSR19	Dispersing agent	Phenol sulfonic acid-formaldehyde-polycondensation as sodium salt	2.5
Ppt Silica	Rheology modifier	Silicon dioxide,	1.8
Silwet 408	Adjuvant	Polydimethylsiloxane	3.0
China clay	Filler	Aluminium silicate	13.46
Total			100

Table 4: Mandipropamid 4.5% + Pyraclostrobin 4.5% + Propineb 52 WP

Compositions	**Function**	**Chemical Name**	**% (w/w)**
Mandipropamid @96.7 % (b) 4.5 %	Fungicide	(*RS*)-2-(4-chlorophenyl)-*N*-[3-methoxy-4-(prop-2-ynyloxy)phenethyl]-2-(prop-2-ynyloxy) acetamide.	4.65
Pyraclostrobin @97% (b) 4.5%	Fungicide	Methyl *N*-{2-[1-(4-chlorophenyl)pyrazol-3-yl oxymethyl]phenyl}(*N*-methoxy)carbamate	4.63
Propineb @ 81% (b) 52%	Fungicide	Polymeric zinc 1,2-propylenebis (dithiocarbamate)	64.19
Geropon L wet	Wetting agent	Linear Alcohol Derivative	4.5
Geropon T 36	Dispersing agent	Sodium polycarboxylate	2.5

Geropon T 77	Dispersing agent	Sodium methyl oleoyl taurate	3.0
Ppt Silica	Rheology modifier	Silicon dioxide,	2.5
Silwet 408	Adjuvant	Polydimethylsiloxane	3.0
China clay	Filler	Aluminium silicate	11.03
Total			100

Table 5: Mandipropamid 5% + Pyraclostrobin 5% + Propineb 53 WP

Compositions	**Function**	**Chemical Name**	**% (w/w)**
Mandipropamid @96.7 % (b) 5.0 %	Fungicide	(*RS*)-2-(4-chlorophenyl)-*N*-[3-methoxy-4-(prop-2-ynyloxy)phenethyl]-2-(prop-2-ynyloxy) acetamide.	5.17
Pyraclostrobin @97% (b) 5.0%	Fungicide	Methyl *N*-{2-[1-(4-chlorophenyl)pyrazol-3-yloxymethyl]phenyl}(*N*-methoxy)carbamate.	5.15
Propineb@ 81% (b) 53%	Fungicide	Polymeric zinc 1,2-propylenebis (dithiocarbamate)	65.43
Dispersol PS	Wetting agent	Polyethylene glycol nonyl phenyl ether ammonium sulfate.	5.0
Sodium Ligno sulphonate	Dispersing agent	Sodium ligno sulphonate	3.0
Sodium lauryl sulphate	Dispersing agent	Sodium lauryl sulphate	1.0

Ppt Silica	Rheology modifier	Silicon dioxide,	2.5
Silwet 408	Adjuvant	Polydimethylsiloxane	3.0
China clay	Filler	Aluminium silicate	9.75
Total			100

[048] Example 3: Efficacy study for combination of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP

Field Bio-efficacy trials: Grape downy mildew.

[049] Trial 1: Bio-efficacy against grapes downy mildew

[050] The Downy mildew is caused by the Oomycete group of fungal pathogens *Plasmopara viticola*. This is potentially devasting disease can infect grapes foliage and berries at any stage of crop development. The pathogen overwinters as thick-walled spores (oospores) in leaf debris from the previous growing season on the soil surface under vines. Oospores at or near the soil surface will germinate in spring by producing sporangia that are rain-splashed or wind-blown to susceptible grape tissues. Sporangia release swimming zoospores in a film of water (rain or dew) which infect the leaves by penetrating the leaf stomata within several hours. Light green or yellow lesions, called "oil spots," on leaves appear within 5 to 17 days after infection, depending on the temperature.

[051] Disease development required cool, moist weather under the favourable condition foliar symptoms appear as yellow circular spot with an oily appearance (oily spots). Young oily spots on young leaves surrounded by a brownish yellow halo. The halo fades the oil spots matures. Under favourable weather conditions, large numbers of oil spots may develop and coalesce to cover most of leaf surface.

[052] The field trial was conducted to evaluate the efficacy of innovative mixtures of Mandipropamid, Pyraclostrobin and Propineb against grapes downy mildew. Trial was conducted with randomized block design with net plot size of

5m x 10m. Grape crop was raised with all standard agronomic practices. Spraying was done with manual operated backpack knapsack sprayer with 1000 L of water spray volume per hectare at 8 to 10 days after pruning.

[053] The visual observations were recorded for % disease control from ten plants per plot. The observations were recorded at before spraying, 5 DAA (Days after application) and 10 DAA (Days after application).

Table 6: Downy mildew disease control in grapes:

Compositions	**Dose (g AI/ha)**	**Percent disease control – Grapes Downy mildew.**	
		05 DAA	**10 DAA**
Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	95	85
Mandipropamid	70	50	40
Pyraclostrobin	70	40	25
Propineb	1000	35	15

WP – Wettable powder and DAA - Days after application.

[054] The trial results in table 6 show excellent efficacy of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP combinations against downy mildew disease of grape. The solo application of three active ingredients tested here, were also not able to provide satisfactory control of downy mildew disease. The combination of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP found very promising against grapes downy mildew in terms of efficacy as well as residual control.

[055] **Synergy Studies:**

[056] After calculating % disease control, the synergism was calculated by below formula:

[057] The synergistic pesticidal action of the inventive mixtures calculated by Colby's formula as follows:

Appropriate analysis of plant response to pesticide combination is critical in determining the type of activity observed. The most widely used model is one Gowing* derived and Colby** modified. Gowing described a mathematical formula for calculating the predicting response values for pesticide mixtures. He suggested the expected (E) percent inhibition of growth induced by pesticide A plus pesticide B and plus pesticide C is as follows, *(Jerry Flint et al, 1988)***

$$\text{Expected (E)} = A + B + C - \frac{(AB + AC + BC)}{100} + \frac{ABC}{10000}$$

Where,

A = observed efficacy of active ingredient A at the same concentration as used in the mixture.

B = observed efficacy of active ingredient B at the same concentration as used in the mixture.

C = observed efficacy of active ingredient C at the same concentration as used in the mixture.

[058] When the percentage of pesticidal control observed for the combination is greater than the expected percentage, there is a synergistic effect. (Ratio of O/E > 1, means synergism observed.)

Reference:

Gowing, D. P. 1960. Comments on tests of herbicide mixtures. Weeds 8:379–391.

***Colby, S. R. 1967. Calculating synergistic and antagonistic responses of herbicide combinations. Weeds 15:20–22*

**** Jerry Flint et al, 1988. Analyzing Herbicide Interactions: A Statistical Treatment of Colby's Method. Weed Technology 2: 304-309*

Table 7: Percent downy mildew disease control at 10 DAA

Compositions	Dose (g or ml/ha)	% Downy mildew disease control	
		Expected	Actual
Mandipropamid	70		40
Pyraclostrobin	70		25
Propineb	1000		15
Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	61.75	85
Ratio of O/E	1.38		

WP – Wettable powder and DAA - Days after application.

[059] The results in table 7 clearly demonstrates synergy between Mandipropamid, Pyraclostrobin and Propineb in controlling grapes downy mildew disease. The large difference between the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

Field Bio-efficacy trials: Potato Early and Late blight.

[060] Trial 1: Bio-efficacy against Potato Early blight

The Early blight of Potato is caused by the fungal pathogen *Alternaria solani*. This is potentially devasting disease can infect Potato foliage at any stage of crop development. Symptoms of early blight occur on fruit, stem and foliage of potatoes and stem, foliage, and tubers of potatoes. Initial symptoms on leaves appear as small 1-2 mm black or brown lesions and under conducive environmental conditions the lesions will enlarge and are often surrounded by a yellow halo. Lesions greater than 10 mm in diameter often have dark pigmented concentric rings. As lesions expand and new lesions develop entire leaves may turn chlorotic and dehisce, leading to significant defoliation. Lesions occurring on stems are often sunken and lens-shaped with a light centre and have the

typical concentric rings. On young potato seedlings lesions may completely girdle the stem, a phase of the disease known as "collar rot," which may lead to reduced plant vigor or death. Warm, humid (24-29°C/ 75-84°F) environmental conditions are conducive to infection. In the presence of free moisture and at an optimum of 28-30°C (82-86°F), conidia will germinate in approximately 40 min. Desiccated germ tubes are able to renew growth when re-wetted, and, hence, infection can occur under conditions of alternating wet and dry periods.

[061] The field trial was conducted to evaluate the efficacy of innovative mixtures of Mandipropamid + Pyraclostrobin + Propineb against *Alternaria solani* fungus in Potato. Trial was conducted with randomized block design with net plot size of 5m x 6m. Rice crop was raised with all standard agronomic practices. Spraying was done with manual operated backpack knapsack sprayer with 500 L of water spray volume per hectare at 45 days after transplanting.

[062] The visual observations were recorded for % disease control from ten leaf per plot. The observations were recorded at before spraying, 7 DAA (Days after application) and 14 DAA (Days after application).

Table 8: Early blight disease control in Potato:

Compositions	**Dose (g AI/ha)**	**Percent disease control – Potato Early blight.**	
		07 DAA	**14 DAA**
Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	90	80
Mandipropamid	70	10	5
Pyraclostrobin	70	40	30
Propineb	1000	35	30

WP – Wettable powder and DAA - Days after application.

[063] The trial results in table 8 show excellent efficacy of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP combinations against Early blight disease of Potato. The solo application of three active ingredients tested here, were also not able to provide satisfactory control of Early blight disease. The combination of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP was found very promising against Potato Early blight in terms of efficacy as well as residual control.

[064] **Synergy Studies:**

[065] After calculating % disease control, the synergism was calculated by below formula:

$$\text{Expected (E)} = A + B + C - \frac{(AB + AC + BC)}{100} + \frac{ABC}{10000}$$

Where,

A = observed efficacy of active ingredient A at the same concentration as used in the mixture.

B = observed efficacy of active ingredient B at the same concentration as used in the mixture.

C = observed efficacy of active ingredient C at the same concentration as used in the mixture.

[066] When the percentage of pesticidal control observed for the combination is greater than the expected percentage, there is a synergistic effect. (Ratio of O/E > 1, means synergism observed.)

Table 9: Percent Early blight disease control at 14 DAA

Compositions	**Dose (g or ml/ha)**	**% Early blight disease control**	
		Expected	**Actual**
Mandipropamid	70		5
Pyraclostrobin	70		30
Propineb	1000		30

Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	53.45	80
Ratio of O/E		1.5	

WP – Wettable powder and DAA - Days after application.

[067] The results in table 9 clearly demonstrates synergy between Mandipropamid, Pyraclostrobin and Propineb in controlling Potato Early blight disease. The large difference between the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

[068] **Trial 2: Bio-efficacy against Potato Late blight**

[069] The late blight is caused by the Oomycete group of fungal pathogen *Phytophthora infestans*. This is potentially devasting disease can infect potato foliage and tuber at any stage of crop development. The first symptoms of late blight in the field are small, light to dark green, circular to irregular-shaped water-soaked spots. These lesions usually appear first on the lower leaves. Lesions often begin to develop near the leaf tips or edges, where dew is retained the longest. During cool, moist weather, these lesions expand rapidly into large, dark brown or black lesions, often appearing greasy. The lesions are not limited by leaf veins, and as new infections occur and existing infections coalesce, entire leaves can become blighted and killed within just a few days. The lesions also may be present on petioles and stems of the plant. Maximum and minimum temperatures in the range of 16-20°C and 1-6°C were found favourable for potato blight disease. Similarly, relative humidity, rainfall, and wind speed in the range of 63-71%, 1.5-3.75 mm and 1-5.5 Km/h, respectively, were conducive for PLB disease which are helpful in disease development.

[070] The field trial was conducted to evaluate the efficacy of innovative mixtures of Mandipropamid, Pyraclostrobin and Propineb against *Phytophthora infestans* fungus in potato crop. Trial was conducted with randomized block design with net plot size of 5m x 6m. Potato crop was raised with all standard agronomic practices. Spraying was done with manual operated backpack

knapsack sprayer with 500 L of water spray volume per hectare at 45 days after planting.

[071] The visual observations were recorded for % disease control from ten plants per plot. The observations were recorded at before spraying, 7 DAA (Days after application) and 14 DAA (Days after application).

Table 10: Late blight disease control in potato:

Compositions	**Dose (g AI/ha)**	**Percent disease control – Potato late blight.**	
		07 DAA	**14 DAA**
Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	90	75
Mandipropamid	70	65	50
Pyraclostrobin	70	25	15
Propineb	1000	40	20

WP - Wettable Powder and DAA - Days after application.

[072] The trial results in table 10 show excellent efficacy of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP combinations against late blight disease of potato. The solo application of two active ingredients tested here, were also not able to provide satisfactory control of late blight disease. The combination of Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP was found very promising against potato late blight in terms of efficacy as well as residual control.

[073] **Synergy Studies:**

[074] After calculating % disease control, the synergism was calculated by below formula:

$$\text{Expected (E)} = A + B + C \cdot \frac{(AB + AC + BC)}{100} + \frac{ABC}{10000}$$

Where,

A = observed efficacy of active ingredient A at the same concentration as used in the mixture.

B = observed efficacy of active ingredient B at the same concentration as used in the mixture.

C = observed efficacy of active ingredient C at the same concentration as used in the mixture.

When the percentage of pesticidal control observed for the combination is greater than the expected percentage, there is a synergistic effect. (Ratio of O/E > 1, means synergism observed.)

Table 11: Percent late blight disease control at 14 DAA:

Compositions	**Dose (g or ml/ha)**	**% late blight disease control**	
		Expected	**Actual**
Mandipropamid	70		50
Pyraclostrobin	70		15
Propineb	1000		20
Mandipropamid 3.5% + Pyraclostrobin 3.5% + Propineb 50% WP	1140	66.00	75
Ratio of O/E	1.14		

WP – Wettable powder and DAA - Days after application.

[075] The results in table 11 clearly demonstrates synergy between Mandipropamid, Pyraclostrobin and Propineb in controlling late blight disease in potato. The large difference between the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

[076] The composition of the present invention shows synergistic effect and hence resulting in lower disease infestation, lower rates of application, a longer duration of action and altogether higher crop yields. Other advantages include reduce application frequency, slow the evolution of fungicide resistance, broaden the fungi control spectrum and efficacy, and contribute to the environmental sustainability of fungicides.

[077] Although the present invention has been described and illustrated with respect to preferred embodiments and a preferred user thereof, it is not to be so limited since modifications and changes can be made therein which are within the full scope of the invention.

We Claim:

1. A fungicidal composition comprising as its active ingredient a mandelamide fungicide Mandipropamid, a strobilurin fungicide Pyraclostrobin, a dithiocarbamate fungicide Propineb and adjuvants.
2. The fungicidal composition as claimed in claim 1, comprising:
    i. 2 to 6% (w/w) of Mandipropamid,
    ii. 2 to 6% (w/w) of Pyraclostrobin, and
    iii. 50 to 55% (w/w) of Propineb.
3. The fungicidal composition as claimed in claim 1, wherein adjuvants are selected from the group comprising wetting agent, dispersing agent, adjuvants, rheology modifiers, and filler.
4. The fungicidal composition as claimed in claim 3, wherein the wetting agent is selected from the group comprising non-ionic surfactants, anionic surfactants, cationic surfactants, Alkylnaphthalene sulfonate (ANS) condensate blend, Linear Alcohol Derivative, and Polyethyleneglycol Nonylphenyl ether ammonium sulfate, Dialkyl naphthalene sulphonate sodium salt, alcohol alkoxylate, fatty alcohol ethoxylates, sodium dodecyl benzene sulfonate, alcohol alkoxylate, fatty alcohol ethoxylates and alkyl naphthalene sulfonate condensate or sodium lauryl sulfonate present in an amount of 2 to 6% (w/w).
5. The fungicidal composition as claimed in claim 3, wherein the dispersing agent is selected from the group comprising phenol sulfonic acid-formaldehyde polycondensation as sodium salt, Sodium polyalkylnaphthalene sulphonate, Acrylate polymer, sodium polycarboxylate, sodium methyl oleoyl taurate, Sodium Ligno sulphonate, and Sodium lauryl sulphate or combination thereof present in an amount of 3 to 6% (w/w).
6. The fungicidal composition as claimed in claim 3, wherein the adjuvant is selected from amino acids and Polydimethylsiloxane present in an amount of 1 to 5% (w/w).

7. The fungicidal composition as claimed in claim 3, wherein the rheology modifiers is selected from the group comprising of guar gum, locust bean gum, xanthan gum, carrageenan, alginates, methyl cellulose, carboxymethyl sodium carboxymethylcellulose, hydroxyethylcellulose, modified starches; other polysaccharides and modified polysaccharides, polyethylene alcohol, glycerol alkyl resins and cellulose derivatives, natural oils, mineral oils such as kyros oil, vegetable oil derivatives, the organoclays, silicon dioxide and fumed silicas present in an amount of 1 to 5% (w/w).
8. The fungicidal composition as claimed in claim 3, wherein the filler is selected from the group comprising of aluminium silicate, silica sand, silicon carbide, aluminium trioxide, barium sulfate, calcium carbonate, calcium sulfate, carbon black, copper, kaolin clay present in an amount of 10 to 25% (w/w).
9. The fungicidal composition as claimed in claim 1, wherein the composition is formulated as a Wettable powder.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2022/050739

A. CLASSIFICATION OF SUBJECT MATTER
A01N37/18,A01N43/54,A01N37/34,A01N37/50,A01N47/14,A01P3/00
Version=2022.01
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)

A01N, A01P

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

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

PatSeer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2019186359 A1 (UPL LTD. [IN]), 3 October 2019 (03-10-2019) Abstract, Claims 1-6	1-9
A	EP 2815649 A1 (BASF SE [DE]), 24 December 2014 (24-12-2014) Abstract, Claims 1-2	1-9
A	WO 2006136551 A1 (BAYER CROPSCIENCE SA [FR]), 28 December 2006 (28-12-2006) Abstract, Claims 1-4	1-9

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"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
17-11-2022	17-11-2022
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Subhankar Panda Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2022/050739

Citation	Pub.Date	Family	Pub.Date
WO 2019186359 A1	03-10-2019	BR 102019005881 A2	11-08-2020
		CN 111988995 A	24-11-2020
		EA 202092287 A1	12-01-2021
		US 20210022343 A1	28-01-2021
EP 2815649 A1	24-12-2014	PL 2815650 T3	28-02-2017
		ES 2604152 T3	03-03-2017
WO 2006136551 A1	28-12-2006	CA 2612106 A1	28-12-2006
		EP 1898709 A1	19-03-2008
		KR 20080026174 A	24-03-2008
		CN 101198254 A	11-06-2008
		JP 2008546735 A	25-12-2008
		US 20090117200 A1	07-05-2009