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(54) Title: SYNERGISTIC FUNGICIDAL COMPOSITION COMPRISING PICOXYSTROBIN AND THIOPHANATE METHYL AND METHOD RELATED THERETO

(57) Abstract: The present invention relates to a fungicidal composition comprising fungicidal active ingredients. In particular, the present invention relates to novel a synergistic pesticidal composition(s) comprising picoxystrobin and thiophanate methyl including agriculturally acceptable salts and non-ionic superspreader surfactant for the treatment and selective comprehensive control of fungal diseases in crops of useful plants and method(s) related thereto.

SYNERGISTIC FUNGICIDAL COMPOSITION COMPRISING PICOXYSTROBIN AND THIOPHANATE METHYL AND METHOD RELATED THERETO

FIELD OF THE INVENTION

The present invention generally relates to fungicidal composition for the treatment of fungal pathogens diseases of useful plants and methods of preparation of said combination and use thereof for the control of a wide variety of undesired insect pests and mites. More particularly, the present invention relates to novel synergistic fungicidal composition comprising picoxystrobin and thiophanate methyl along with inert silicone-based superspreader for the treatment and control of a broad range of fungal diseases of useful crops. In particularly, the present invention relates to novel synergistic fungicidal composition comprising picoxystrobin and thiophanate methyl for the treatment and control of the brown spot, sheath blight, blast, and grain discoloration causing fungal pathogens in paddy crop and to a method of controlling fungal pathogens diseases in paddy crop.

BACKGROUND OF THE INVENTION

Paddy crop is one of the most important staple food worlds over including India. India stands second largest producer in the world. Fungal pathogens cause 15-30% reduction in paddy yield depending upon the severity of the disease. Paddy is infected by different fungal pathogens from its nursery to maturity stage and therefore, require multiple type of fungicides and sprays. Most of the available fungicides have limited spectra to control fungal pathogens. Various fungicidal compounds of different chemical classes are widely known as plant fungicides for application in various crops of cultivated plants. However, crop tolerance and activity against phytopathogenic plant fungi do not always satisfy the needs of agricultural practice in many incidents and aspects. This increases the production cost of the farmers.

Picoxystrobin is an enoate ester that is the methyl ester of (2E)-3-methoxy-2-[2-({[6-(trifluoromethyl)pyridin-2-yl]oxy}methyl)phenyl]prop-2-enoic acid. A cereal fungicide

used to control a wide range of diseases including brown rust, tan spot, powdery mildew and net blotch. It has a role as a mitochondrial cytochrome-bc1 complex inhibitor and an antifungal agrochemical.

The fungicide thiophanate methyl widely used to control some of the most common fungal diseases in crops is metabolized in animals into benzimidazole compounds, including the reproductive toxicant carbendazim.

Surprisingly, it has been found now that composition thereof of the present invention have the potential of overcoming drawbacks of the prior art and are suitable for crop protection against phytopathogenic micro-organisms causing plant diseases in particularly fungal pathogens diseases in paddy crop.

Various patent applications disclose the mixture of Picoxystrobin or ethion along with the different insecticides. However, there is no specific disclosure for the combination of Picoxystrobin and thiophanate methyl in suitable dosage in the prior art. Further, there is no effective combination available that can act simultaneously on a wide variety of insect pests and mites.

The present invention, therefore, intends to provide novel synergistic fungicidal composition and method related thereto for effective treatment and control of multiple fungal diseases having long duration control and improvement of yield quality. It has been found that the use of picoxystrobin in combination with thiophanate methyl and with an inert silicone superspreader in a certain weight percentage ratio being disclosed hereinafter surprisingly and substantially enhances the effectiveness of the composition against controlling fungal pathogens diseases in paddy crop. Additionally, the methods of the invention are effective against a wider spectrum of such fungal pathogens diseases in paddy crop that can be combated with the active ingredients of this method, when used solely.

The inert silicone-based superspreader helps in getting better coverage on the plant surface, which helps in obtaining better efficacy at lower dose of the combination. Thus,

the composition of the present invention is effective to manage and combat a diverse array of fungal diseases in crops.

Surprisingly, the fungicidal activity of the active compound combination according to the invention comprising the combination of two active compounds i.e. picoxystrobin and thiophanate methyl and the inert silicone spreader are considerably higher than the sum of the activities of the individual active compounds or the activity of the prior-art mixtures comprising in each case two active compounds. Thus, an unforeseeable true synergistic effect is present, and not just an addition of activities.

SUMMARY AND OBJECTS OF THE INVENTION

A primary object and advantage of the present invention is to provide a novel synergistic fungicidal composition for the treatment of a broad range of fungal diseases of useful crops.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition for the treatment of the brown spot, sheath blight, blast, and grain discoloration causing fungal pathogens in paddy crops.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition comprising picoxystrobin and thiophanate methyl with a non-ionic organosilicone superspreading surfactant.

It is another object and advantage of the present invention to provide, said another novel synergistic fungicidal composition comprising picoxystrobin in an amount of 5 to 30% w/w.

It is another object and advantage of the present invention to provide said novel synergistic fungicidal composition comprising thiophanate methyl in an amount of 25 to 50% w/w.

It is another object and advantage of the present invention to provide the novel synergistic composition comprising an inbuilt non-ionic organosilicone superspreading surfactant in an amount of 1 to 5% w/w.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition formulated as a dry flowable (DF) or a wettable powder (WP) or Water Dispersible Granule (WG) or Suspension Concentrate (SC) or Suspo Emulsion (SE) or the like.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition further comprising wetting agent, an anti-caking agent, a dispersing agent, an anti-foaming agent, stabilising agent, preservative, suspending agent, a filler or the like. Such composition may be produced in conventional manner, e.g. by mixing the active ingredients with at least one appropriate inert formulation adjuvant (for example, diluents, solvents, fillers and optionally other formulating ingredients such as surfactants, anti-freeze, stickers, thickeners and compounds that provide adjuvancy effects).

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition which is also suitable for increasing the harvest yield.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition which is non phytotoxic.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition which provides phytotonic effect increasing the yield production.

It is another object and advantage of the present invention to provide composition comprising non-ionic organosilicone superspreading surfactant which lowers the surface tension, which helps in better absorption of the chemical by plants with more effective wetting and uniform coverage on foliar surface.

It is another object and advantage of the present invention to provide a novel synergistic fungicidal composition which provides superior control and treatment of fungal pathogen growth compared to individual picoxystrobin active and thiophanate methyl active.

It is a further object and advantage of the present invention to provide a novel synergistic fungicidal composition which provides longer duration control of fungal pathogen in different useful crop including paddy crop, which will reduce the multiple fungicide application cost of farmers.

In accordance with one aspect of the present invention, there is provided a novel synergistic fungicidal composition comprising picoxystrobin in an amount of 5 to 30% w/w and thiophanate methyl in an amount of 30 to 60% w/w.

In one embodiment of the invention, the composition according to the invention has a systemic action and can be used as foliar and soil application fungicides.

With the use of composition according to the invention it is possible to inhibit or destroy the phytopathogenic microorganisms which occur in plants or in parts of plants (fruit, blossoms, leaves, stems, tubers, roots) in different useful plants including paddy crop, while at the same time the parts of plants which grow later are also protected from attack by phytopathogenic microorganisms.

The composition according to the invention can be applied to the phytopathogenic microorganisms, before or after infection of the useful plants including paddy crop.

In accordance with another aspect of the present invention, there is provided a process for preparing fungicidal composition, the process comprising the step of mixing the active compound combination of picoxystrobin and thiophanate methyl with extenders and/or surfactants or other formulating ingredients. The method for preparation of the synergistic water dispersible granule pesticidal composition as claimed in claim 1 comprising the steps of:

(a) mixing a compound of formula (I), a compound of formula (II) and agriculturally accepted excipient/acceptable carrier to obtain a free-flowing fine powder;

(b) adding simultaneously a water and non-ionic organosilicone superspreading surfactant into the free-flowing powder to obtain a wet powder;

(c) extruding a wet powder in a screw to get needle shaped wet granules;

(d) sieving and drying the mixture.

In accordance with another aspect of the present invention, there is provided method(s) for effectively controlling fungal pathogens diseases at a locus of useful crops, in particularly of a paddy crop, comprising the step of treating a locus with a composition comprising picoxystrobin and thiophanate methyl.

DETAILED DESCRIPTION OF THE INVENTION

The following definitions provided herein for the terminologies used in the present invention are for illustrative purposes only and in no manner limit the scope of the present claimed invention.

As used herein, the terms “comprises”, “comprising”, “includes”, “including”, “has”, “having”, “contains”, “containing”, “characterized by” or any other variation thereof, are intended to cover a non-exclusive inclusion, subject to any limitation explicitly indicated. For example, a composition, mixture, process or method that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, mixture, process or method.

Further, unless expressly stated to the contrary, “or” refers to an inclusive “or” and not to an exclusive “or”. For example, a condition A “or” B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present). It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

It will be understood that the terminology used herein is for the purpose of describing embodiments only, and is not intended to be limiting. As used in this specification, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, the reference to "a surfactant" includes one or more of such surfactants.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one ordinary skilled in the art to which the invention pertains. Although other methods and materials similar, or equivalent, to those described herein can be used in the practice of the present invention, the preferred materials and methods are described herein.

Furthermore, the indefinite articles “a” and “an” preceding an element or component of the present invention are intended to be nonrestrictive regarding the number of instances (i.e., occurrences) of the element or component. Therefore “a” or “an” should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular. The singular forms “a” and “an”, “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition comprising “a compound includes a mixture of two or more compounds.

As used herein, the term “composition” or "formulation" can be used interchangeably, unless stated otherwise, is meant to encompass, and are not limited to, compositions or formulations containing the combination of picoxystrobin and thiophanate methyl.

The term “pathogenic diseases” or “plant diseases” or “diseases” used herein refers to the diseases which caused by a pathogenic organism such as a fungus, bacterium, mycoplasma, virus, viroid, nematode, or parasitic flowering plant which can cause severe damage to crop plants or even cause death eventually.

The term “pathogen” or “pathogenic” used herein refers to an organism or microorganism that has potential to cause infectious diseases in its host (for example plant).

The term “resistance” or “cross resistance” refers to the event that occurs where pathogen or insect is being resistance to the pesticides or a group of pesticides and becomes resistant after a period of time, to one or more other pesticide on a later stage.

The expression of various quantities in the terms of “% w/w” means the percentage by weight, relative to the weight of the total composition unless otherwise specified.

The expression of various quantities in the terms of “g.a.i/ha” means the gram active ingredient per hectare.

The term “pesticide” is used herein to describe the active ingredients that kills, controls or otherwise adversely modifies the growth of pathogens and/or insect attach and/or undesired plants in crops or may surrounds the crop. A pesticidally effective dose or controlling dose is an amount of active ingredient(s) which causes an adversely modifying effect in the pathogens/weeds/insects such as deviations from natural development, killing, regulation, desiccation, retardation and the like.

The terms “plants and vegetation” are used herein include germinant seeds, emerging seedlings, plants emerging from vegetative propagules and established vegetation.

The terms like “protecting a plant from disease” or “control of a plant disease” includes preventative action (interruption of the fungal cycle of infection, colonization, symptom development and spore production) and/or curative action (inhibition of colonization of plant host tissues).

The term “mode” or “mode of action” or “action” are used herein refers to the overall manner in which any pesticidal active ingredient or in combination thereof, affects an organism at the tissue or cellular level.

The term “crop plant” and “crops of useful plants” used herein refers to the plant or plant product that can be grown and harvested on a large scale for profit or subsistence.

Parts of plants of organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes.

As used herein, the term “additive(s)” or "auxiliary agent(s)" or “agriculturally acceptable carrier(s)” can be used interchangeably and refers to inert substances which are commonly used as diluent, to provide stability or to increase the activity profile of the composition or formulation with or without having agrochemical activity or direct effect on the undesired insect pests and mites.

As used herein, the term “surfactant(s)” means a compound that, when dissolved in a liquid, reduces the surface tension of the liquid, which reduces the interfacial tension between two liquids or which reduces surface tension between a liquid and a solid.

As used herein, the term “stabilizer(s)” refers to a substance capable of imparting resistance against physical or chemical deterioration or deformulation.

As used herein, the term “biocide(s)” refers to a substance used to protect against unwanted plants, animals, or microorganisms.

As used herein, the term “defoaming agent(s)” refers to a chemical additive that reduces and hinders the formation of foam in the industrial process liquids, semi-solids, or solids. The terms defoaming agent and anti-foaming agent can be used interchangeably.

As used herein, the term “thickener(s)” refers to a polymeric material, which at a low concentration increases the viscosity of an aqueous solution and helps to stabilize the composition.

Unless otherwise specified, % refers to % weight; and % weight refers to % of the weight of the respective component with respect to the total weight of the composition.

As used herein, the term “locus" means a plant, plant parts, plant propagation material (preferably seed), soil, area, material or environment in which a pest is growing or may grow.

As used herein, the term “plant parts” are understood to mean all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples including leaves, needles, stems, stalks, flowers, fruit-bodies, fruits and seeds, and also roots, tubers and rhizomes. The plant parts also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

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

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. The effective amount can vary for the various compositions used in the present invention. 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.

The formulation "Water dispersible granules" used herein refers to solid, non-dusty granular formulation of agricultural chemicals that disperses or dissolves quickly in water. These granules create a finely suspended particle mixture suitable for application to soil or plants, facilitating the efficient delivery of active ingredients to a specific target organism.

Parts of plants also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings, and seeds.

According to the invention, it is possible to treat all plants and parts of plants. Plants are to be understood here as meaning all plants including useful plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combination of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by plant breeders' certificates. Parts of plants are to be understood as meaning all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes. Parts of plants also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

In a preferred embodiment, the active compound combination according to the invention can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and micro-

encapsulations in polymeric substances and in coating compositions for seeds, and ULV formulations.

The treatment of the plants and parts of plants according to the invention with the active compounds is carried out directly or by activity on their environment, habitat or storage area according to customary treatment methods, for example by dipping, spraying, evaporating, atomizing, broadcasting, brushing-on and, in the case of propagation material, in particular in the case of seeds, furthermore by one- or multi-layer coating.

The active compound combination according to the invention can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and microencapsulations in polymeric substances and in coating compositions for seeds, and ULV formulations.

The composition of the present invention comprises non-ionic organosilicone superspreading surfactant which lowers the surface tension which facilitates enhanced absorption of the chemical by promoting more effective wetting and ensuring uniform coverage on the plant's foliar surface. In addition, the silicone-based surfactant also contributes to the mechanical strength in plants. Besides structural role, silicone may protect plants from insect attack, disease, and environmental stress by improving the plant's defense response. It also confers protection against both biotic and abiotic stressors.

The formulations of the present invention are produced in a known manner, for example by mixing the active compounds or active compound combination with extenders, that is liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants, and/or foam formers. If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents.

In one embodiment, suitable surfactants are selected from the group consisting of siloxane polyalkyeneoxide copolymer and polyalkyleneoxide, and monoglyceride of

long-chain fatty acids, polyoxyethylenated alkylphenol, and polyoxyethylenated alcohol.

In another embodiment, liquefied gaseous extenders or carriers are to be understood as meaning liquids which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants such as butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example, ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates. Suitable solid carriers for granules are: for example, crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

In an embodiment, suitable emulsifiers and/or foam formers are: for example, nonionic and anionic emulsifiers, such as nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl sulfates, arylsulfonates, or else protein hydrolyzates.

In an embodiment, suitable dispersants are: for example, lignin-sulfite waste liquors and methylcellulose. Suitable formulating agents include (alkaryl sulphonate) mixture of salt of naphthelene sulphonic acid and phenol sulphonic acid condensate product, (alkylated naphthalene sulphonate formaldehyde polymer, sodium salt 1,2 benzisothiazoline-3-one, 1,2- propylene glycol, 3 EO alkyl (C12 ±C15) ether sulfate, alkyl aryl sulphonate, alpha-alkyl (C10-C16) omega hydroxypoly (oxyethylene), condensed alkylnaphthalene sulphonate, sodim salt, ethoxylated fatty alcohol, ethoxylated polymethacrylate in propylene glycol, lignosulfonate, magnesium aluminium silicate, methyl methacrylate graft copolymer, napthalene sulfonate sodium salt condensed with formaldehyde, polyoxyethylene nonylphenyl ether, polyvinyl pyrrolidone copolymer, potassium carboxylate, potassium dihydrogen phosphate, sodium alkylnaphthalene sulfonate formaldehyde condensate, sodium dialkyl naphathalene sulfonate, sodium dioctyl sulfosuccinate, sodium lignosulfonate

sulfomethylated, sodium naphthalene sulfonate, sodium polycarboxylate, sodium salt of alcohol ether sulfate, sodium salt of poly carboxylic acid, soluble starch, ethylene oxide-propylene oxide, tallow soap.

In an embodiment, suitable wetting agent may be employed in the present invention including sodium alkylnaphthalene sulfonate formaldehyde, polyalkoxylated butyl ether, polyoxyethylene fatty alcohol ethers, alkylated naphthalene sulphonate formaldehyde polymer, alkyl aryl sulphonate.

In an embodiment, suitable anti-caking agent may be used in the present invention which may include soluble starch, talc, precipitated silica.

In an embodiment, suitable anti-foaming agent may be used in the present invention which may include polydimethyl Siloxane, dimethyl polysiloxane, dimethyl siloxane, dimethylpolysiloxane.

In an embodiment, suitable stabilizing agent may be employed in the present invention which may include salt of naphthalene sulphonic acid, Xanthane gum, sodium dioctyl sulfosuccinate, polyoxyethylene nonylphenyl ether.

In an embodiment, suitable suspending agent may be employed in the present invention including methylcellulose.

In an embodiment, suitable thickener may be employed in the present invention which may include hetero polysaccharide, heteropolysaccharide 2% solution, Xanthan gum.

A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components. The action to be expected E for a given active ingredient combination obeys the so-called COLBY formula and can be calculated as follows (COLBY, S.R. "Calculating synergistic and antagonistic responses of herbicide combination". Weeds, Vol. 15, pages 20-22; 1967):

ppm = milligrams of active ingredient (= a.i.) per liter of spray mixture

X = % action by active ingredient (A) using p ppm of active ingredient
Y = % action by active ingredients (B+C) using q ppm of active ingredient.

Or:

X = % action by active ingredient (A+B) using p ppm of active ingredient
Y = % action by active ingredient (C) using q ppm of active ingredient.

Or:

X = % action by active ingredient (A+C) using p ppm of active ingredient
Y = % action by active ingredient (B) using q ppm of active ingredient.

According to COLBY, the expected (additive) action of active ingredients (A)+(B+C) or (A+B) + (C) or (A+C) + (B) using + m of active ingredient is:

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

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is super-additive, i.e., there is a synergistic effect. In mathematical terms, synergism corresponds to a positive value for the difference of (O-E). In the case of purely complementary addition of activities (expected activity), said difference (O-E) is zero. A negative value of said difference (O-E) signals a loss of activity compared to the expected activity.

Synergism can also be calculated by using the following formula:

$$E \text{ (expected value)} = X + Y + Z - [\,(X\,Y) + (X\,Z) + (Y\,Z)/100\,] + [\,X\,Y\,Z/10000\,]$$

X, Y, Z = % action by active ingredient (A), (B) and (C) alone using p ppm of active ingredient.

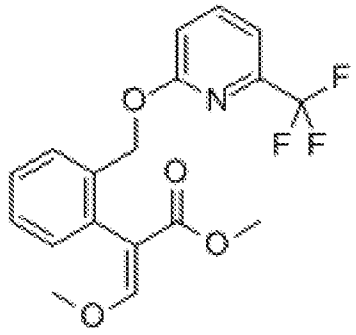
In an embodiment, the composition claimed in the present invention can control a broad range of fungal pathogens include, but not limited to, genus *Phytophthora* plant-damaging oomycetes such as *Phytophtora infestans*, *Phytophthora capsici*, and Phythium genus which causes rot such as *Pythium irregulare*, *Pythium ultimum*, and *ythium aphanidermatum* and genus Rhizoctonia which is also responsible for causing root rot such as *Rhizoctonia solani,* along with *Pyricularia oryzae*, *Phakopsora euvitis* *Cercospora personatum, Colletotrichum capsica, Albugo candida*, *Alternaria solani* etc., which are responsible to cause various other diseases in different crops.

Besides the actual synergistic action with respect to fungicidal activity, the composition according to the invention can also have further surprising advantageous properties which can also be described, in a wider sense, as synergistic activity. Examples of such advantageous properties that may be mentioned are: more advantageous degradability; or improved characteristics of the useful plants, in particularly of paddy crop including: emergence, crop yields, more developed root system, tillering increase, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, less fertilizers needed, less seeds needed, more productive tillers, earlier flowering, early grain maturity, less plant verse (lodging), increased shoot growth, improved plant vigor, and early germination.

Throughout this document the expression "composition" means the various mixtures or combination or formulations of picoxystrobin and thiophanate methyl, for example in a single "ready-mix" form, "pre-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix", and in a combined use of the single active ingredients when applied in a sequential manner, i.e. one after the other with a reasonably short period, such as a few hours or days. The order of applying the individual components of the combination of picoxystrobin and thiophanate methyl is not essential for working the present invention.

Thus, there is provided a novel synergistic fungicidal composition comprising picoxystrobin and thiophanate methyl.

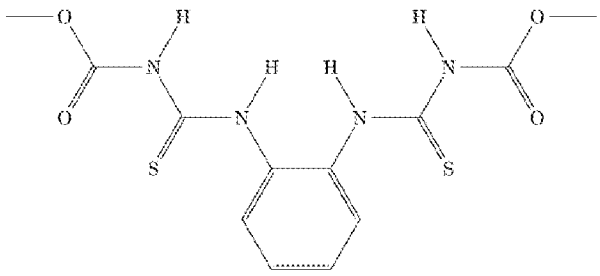
Wherein picoxystrobin being a compound of formula (I)



(I) (picoxystrobin)

is an enoate ester with the formula $C_{18}H_{16}F_3NO_4$ that is the methyl ester of (2E)-3-methoxy-2-[2-({[6-(trifluoromethyl)pyridin-2-yl]oxy}methyl)phenyl]prop-2-enoic acid. A cereal fungicide used to control a wide range of diseases including brown rust, tan spot, powdery mildew and net blotch. It has a role as a mitochondrial cytochrome-bc1 complex inhibitor and an antifungal agrochemical. It is an aromatic ether, an enoate ester, an enol ether, an organofluorine compound, a member of pyridines and a methoxyacrylate strobilurin antifungal agent. Preferred IUPAC name of component picoxystrobin is methyl (*E*)-3-methoxy-2-[2-[[6-(trifluoromethyl)pyridin-2-yl]oxymethyl]phenyl]prop-2-enoate.

Wherein thiophanate methyl being a compound of formula (II)



(II) (thiophanate methyl)

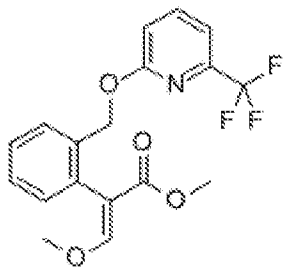
is a known organic compound with the formula $C_6H_4(NHC(S)NH(CO)OCH_3)_2$. Preferred IUPAC name of component thiophanate methyl is Dimethyl N,N′-[1,2-phenylenebis(azanediylcarbonothioyl)]dicarbamate.

In general, the weight ratio of compound of formula (I) in the novel synergistic fungicidal composition is in an amount of amount of 5 to 30% w/w and compound of formula (II) is in an amount of 30 to 60% w/w along with the non-ionic silicone superspreader is in an amount of 1 to 5% w/w.

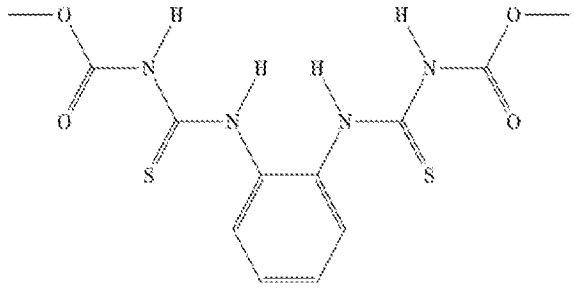
In an embodiment, the synergistic fungicidal composition comprising:

a. a compound of formula (I) in a range of 5 to 30% w/w;
b. a compound of formula (II) in a range of 25 to 60% w/w;
c. a non-ionic silicone surfactant in a range of 1 to 5% w/w;
d. an agriculturally accepted excipient/acceptable carrier in a range of 1 to 25% w/w.

wherein



Formula (I) is
(picoxystrobin)



Formula (II) is
(thiophanate methyl)

In another embodiment composition is selected from a suspo-emulsion (SE), an emulsion-in-water (EW), an emulsifiable concentrate (EC), a water dispersible granule (WDG), a water dispersible tablet (WT), an ultra-low volume (ULV) liquid (UL), an ultra-low volume (ULV) suspension (SU), a wettable granules (WG), a water soluble powder (SP), wettable powder (WP), granule (GR), an emulsifiable granule (EG), a micro-

emulsion (ME), an oil dispersion (OD), a suspension concentrate (SC), a capsule suspension (CS), a dustable powder (DP) or an aerosol (AE).

In another embodiment, the composition is formulated as a WDG formulation comprising a. a compound of formula (I) in a range of 5 to 30% w/w; a compound of formula (II) in a range of 25 to 60% w/w; c. a non-ionic silicone surfactant in a range of 1 to 5% w/w; an agriculturally accepted excipient/acceptable carrier in a range of 1 to 25% w/w; emulsifier; dispersant; wetting agent; thickener, anti-foaming agent; suspending agent; formulating agent and other ingredients which is suitable for the formulation.

In an embodiment, the non-ionic silicone surfactant is siloxane polyalkyeneoxide copolymer and polyalkyleneoxide.

In an embodiment, the agriculturally acceptable carrier is selected from the group consisting of kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina, silicates, fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

In a embodiment, the emulsifier is selected from the group consisting of nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl sulfates, arylsulfonates, or else protein hydrolyzates.

In an embodiment, the dispersant is selected from the group consisting of lignin-sulfite waste liquors and methylcellulose. Suitable formulating agents include (alkaryl sulphonate) mixture of salt of naphthelene sulphonic acid and phenol sulphonic acid condensate product, (alkylated naphthalene sulphonate formaldehyde polymer, sodium salt 1,2 benzisothiazoline-3-one, 1,2- propylene glycol, 3 EO alkyl (C12 ±C15) ether sulfate, alkyl aryl sulphonate, alpha-alkyl (C10-C16) omega hydroxypoly (oxyethylene), condensed alkylnaphthalene sulphonate, sodim salt, ethoxylated fatty

alcohol, ethoxylated polymethacrylate in propylene glycol, lignosulfonate, magnesium aluminium silicate, methyl methacrylate graft copolymer, napthalene sulfonate sodium salt condensed with formaldehyde, polyoxyethylene nonylphenyl ether, polyvinyl pyrrolidone copolymer, potassium carboxylate, potassium dihydrogen phosphate, sodium alkylnaphthalene sulfonate formaldehyde condensate, sodium dialkyl naphathalene sulfonate, sodium dioctyl sulfosuccinate, sodium lignosulfonate sulfomethylated, sodium naphthalene sulfonate, sodium polycarboxylate, sodium salt of alcohol ether sulfate, sodium salt of poly carboxylic acid, soluble starch, ethylene oxide-propylene oxide, tallow soap.

In an embodiment, the wetting agent is selected from the group consisting of sodium alkylnaphthalene sulfonate formaldehyde, polyalkoxylated butyl ether, polyoxyethylene fatty alcohol ethers, alkylated naphthalene sulphonate formaldehyde polymer, alkyl aryl sulphonate.

In an embodiment, the thickener is selected from the group consisting of hetero polysaccharide, heteropolysaccharide 2% solution, Xanthan gum.

In an embodiment, the anti-foaming agent is selected from the group consisting of polydimethyl Siloxane, dimethyl polysiloxane, dimethyl siloxane, dimethylpolysiloxane.

In an embodiment, the suspending agent is selected from the group consisting of methylcellulose.

In an embodiment, the formulating agent is selected from the group consisting of propylene glycol, silica acid, silicone, sodium alkylnaphthalene sulfonate formaldehyde condensate, sodium dialkyl naphathalene sulfonate, sodium dioctyl sulfosuccinate, sodium lignosulfonate sulfomethylated, sodium naphthalene sulfonate, sodium polycarboxylate, sodium salt of alcohol ether sulfate, sodium salt of poly carboxylic acid, soluble starch, ethylene oxide-propylene oxide, tallow soap, xanthan gum.

It has been found, surprisingly, that specific weight ratios between the compound of formula (I) and the compound of formula (II) can result in synergistic activity when

combined with an inert non-ionic silicone superspreader in the composition. Therefore, a further aspect of the invention is composition, wherein compound of formula (I) and compound of formula (II) are present in the composition in amounts producing a synergistic effect. This synergistic activity is apparent from the fact that the fungicidal activity of the composition comprising compound of formula (I) and compound of formula (II) is greater than the sum of the fungicidal activities of compound of formula (I) and of compound of formula (II). This synergistic activity extends the range of action of compound of formula (I) and compound of formula (II) in two ways. Firstly, the rates of application of compound of formula (I) and compound of formula (II) are lowered whilst the action remains equally good, meaning that the active ingredient mixture still achieves a high degree of phytopathogen control even where the two individual components have become totally ineffective in such a low application rate range. Secondly, there is a substantial broadening of the spectrum of phytopathogens that can be controlled.

The composition comprising organic or inorganic carrier material, including agriculturally acceptable additive(s) are selected from the group comprising of solid carrier(s), liquid carrier(s), gaseous carrier(s), surfactant(s), binder(s), biocide(s), disintegrating agent(s), pH adjuster(s), thickener(s), preservative(s), anti-caking agent(s), anti-freezing agent(s), defoaming agent(s), extender(s), stabilizer(s) and/or coloring agent(s) or a combination thereof. The composition may also contain if desired, one or more auxiliaries customary for crop protection compositions.

Solid carrier(s) is selected from the group comprising of, but not limited to, natural minerals such as quartz, talc, kaolin, pyrophyllite, montmorillonite, attapulgite, bentonite, chalk, zeolite, calcite, sericite, clay, acid clay, diatomaceous earth, Fuller's earth, meerschaum, gibbsite, dolomite or pumice; synthetic minerals such as precipitated silica, fumed silica, sodium silicate, alumina, aluminum hydroxide; inorganic salts such as calcium carbonate, ammonium sulfate, sodium sulfate, potassium chloride, organic materials such as urea, solid polyoxyethylene, solid polyoxypropylene, polyethylene, polypropylene, lactose, starch, lignin, cellulose, cottonseeds hulls, wheat flour, soyabean flour, wood flour, walnut shell flour, plant

powders, sawdust, coconut shellflower, corn cob, tobacco stem. These solid carriers may be used alone or in combination.

In an embodiment, the present invention also relates to a method for controlling fungi by the composition comprising the compound of formula (I) and the compound of formula (II) and which are applied simultaneously, that is jointly or separately, or in succession to act on the fungi, their habitat or the plants, parts of plants, seeds, soils, areas, materials or spaces to be kept free from those pathogens and pests or in order to inhibit them.

In order to facilitate a further understanding of the invention, the following example(s) are presented primarily for the purpose of illustrating more specific details thereof. The scope of the invention should not be deemed limited by the examples and should not be construed as limiting embodiment for the invention. Thus, the invention is not, however, limited to the example(s) provided herein.

Example 1: Preparation of fungicidal composition:

In an embodiment, the composition of the present fungicidal composition is given below:

Table 1: WDG fungicidal composition:

S. No.	Ingredient	Percentage (w/w)
1.	Thiophanate methyl (a.i.)	50.00%
2.	Picoxystrobin (a.i)	10.00%
3.	Sodium naphthalene sulfonate	02.00%
4.	Lauryl alcohol sulfate	02.00%
5.	Naphthalene sulfonate condensate sodium salt	08.00%
6.	Polydimethyl siloxane	03.00%

7.	Siloxane Polyalkyeneoxide Copolymer and Polyalkyleneoxide	02.00%
8.	Lavigated micronized china clay	QS to make 100 %
	Total	**100%**

Preparation method steps:

Studies were conducted for optimization of various ingredients and processes. The following method is finalized for preparation of Thiophanate Methyl 50% + Picoxystrobin 10% Water Dispersible Granules (WDG) formulation in the lab. The ingredients in the process are mentioned in Table 1 while the lab process consisting of five steps for preparing formulation is given below.

STEP -I: PREPARATION OF MIXTURE OF INGREDIENTS

Ingredients mentioned at Sl. No. 1 to 6 & 8 are taken in a kitchen mixer and grinding is done to get 'a free-flowing fine powder.

STEP-II: ADDITION OF WATER & SUPERSPREADING SURFACTANT

The powder obtained from step I is taken in a beaker/ vessel of kitchen mixer and D.M. Water is slowly added into it. Approximately 9-10 grams. water is sufficient to properly wet 100 grams. powder suitable for extrusion. The requirement of water may sometimes change. The quantity of water may be optimized for wetting of the powder suitable for extrusion. The non-ionic organosilicone superspreading surfactant was added at this point to the mixture.

STEP-III: EXTRUSION

The wet powder obtained from step II is extruded in a Screw Extruded to get needle shaped wet granules.

STEP-IV: DRYING OF GRANULES

The granules obtained from step III are dried for 27-28 hours in a hot air oven maintained at 54° - 55°C.

Note: Precaution should be taken in the drying step for maintaining the drying temperature.

STEP-V: SIEVING

The dried granules obtained from step IV are sieved between 12 mesh and 45 mesh sieves to remove coarse granules and fine powder to get the final product.

FIELD AND SYNERGY STUDIES

The fungicidal activity of the fungicides of the present invention and the combination thereof were evaluated on fungal infections such as *Blast, Sheath Blight and Grain discoloration.*

Bio efficacy trials were carried out at various locations across India to generate independent data. Total 8 trails were taken up in the year 2021-22 at Haryana (Karnal), Chhattisgarh (Dhamtari/Raipur), West Bengal (Burdhwan) & Andhra Pradesh (Warangal). The trials were conducted in Randomized Block Design with 3 replicates per treatment under GAP (Good Agricultural Practice) practice. Spraying was done with battery operated backpack knapsack sprayer with 500 Litre of water per hectare as spray volume. Total 2 applications of the combination were taken up with 10 days of interval. Paddy sheath blight & Blast data was taken up from 10 hills per replication i.e., 30 hills per treatment collected on 5^{th} & 10^{th} DAA (Day after application). Grain discoloration data was taken at the time of harvest by taking 1000 grain per replication and counting the infected grains.

The synergy of the composition has been calculated by using S.R. Colby method.

If the action actually observed (O) is greater than the expected action (E), then the action of the combination is super-additive, i.e., there is a synergistic effect. In mathematical terms, synergism corresponds to a positive value for the difference of (O-E). In the case of purely complementary addition of activities (expected activity), said difference (O-E) is zero. A negative value of said difference (O-E) signals a loss of activity compared to the expected activity.

Synergism can also be calculated by using the following formula:

$$E \text{ (expected value)} = X + Y + Z - [(X Y) + (X Z) + (Y Z)/100] + [X Y Z/10000]$$

X, Y, Z = % action by active ingredient (A), (B) and (C) alone using p ppm of active ingredient.

Table 2: Synergistic control of Blast, Sheath blight, Brown leaf spot and Grain discolouration diseases of Paddy following application of Picoxystrobin (A), Thiophanate methyl i.e., TPM (B) <u>without</u> Surfactant siloxane polyalkyeneoxide copolymer and polyalkyleneoxide:

Bio-efficacy of TPM and Picoxystrobin combination on different Rice disease (% control over treated) <u>without</u> Surfactant Siloxane Polyalkyeneoxide Copolymer and Polyalkyleneoxide										
Trt No.	**AI**		**Application Rate g a.i./ha**		**Blast**		**Sheath Blight**		**Grain Discoloration**	
			(A)	**(B)**	**Observed Value %**	**Expected value %**	**Observed Value %**	**Expected value %**	**Observed Value %**	**Expected value %**
1	TPM		500		38.34		30.84		32.64	
2	TPM		450		35.11		25.61		29.61	
3	Picoxystrobin		150		58.28		39.88		59.08	
4	Picoxystrobin		100		46.25		34.25		54.25	
5	Picoxystrobin		90		36.66		32.46		44.86	
6	TPM	Picoxystrobin	500	150	77.06	74.28 (+2.78)	66.20	58.42 (+7.78)	80.09	72.44 (+7.65)
7	TPM	Picoxystrobin	500	100	68.11	66.86 (+1.25)	60.78	54.53 (+6.25)	71.43	69.18 (+2.25)
8	TPM	Picoxystrobin	450	90	59.75	58.90 (+0.85)	53.61	49.76 (+3.85)	64.04	61.19 (+2.85)

Figures in ( ) are difference in Observed value vs Expected value; g a.i./ha - grams of active ingredient per hectare.

Table 3: Synergistic control of Blast, Sheath blight, Brown leaf spot and Grain discolouration diseases of Paddy following application of Picoxystrobin (A), Thiophanate methyl i.e., TPM (B) with Surfactant siloxane polyalkyeneoxide copolymer and polyalkyleneoxide:

Bio-efficacy of TPM combination on different Rice disease (% control over treated) with Surfactant Siloxane Polyalkyeneoxide Copolymer and Polyalkyleneoxide										
Trt No.	AI		Application Rate g a.i./ha		Blast		Sheath Blight		Grain Discoloration	
			(A)	(B)	Observed Value %	Expected value %	Observed Value %	Expected value %	Observed Value %	Expected value %
1	TPM		500		38.34		30.84		32.64	
2	TPM		450		35.11		25.61		29.61	
3	Picoxystrobin		150		58.28		39.88		59.08	
4	Picoxystrobin		100		46.25		34.25		54.25	
5	Picoxystrobin		90		36.66		32.46		44.86	
6	TPM	Picoxystrobin	500	150	89.95	74.28 (+15.67)	80.00	58.42 (+21.58)	92.45	72.44 (+20.01)
7	TPM	Picoxystrobin	500	100	79.46	66.86 (+12.6)	74.66	54.53 (+20.13)	83.31	69.18 (+14.13)
8	TPM	Picoxystrobin	450	90	70.60	58.90 (+11.7)	66.00	49.76 (+16.24)	74.45	61.19 (+13.26)

Figures in ( ) are difference in Observed value vs Expected value; g a.i./ha - grams of active ingredient per hectare.

The results in Tables 2 and 3 clearly demonstrates synergy between TPM and Picoxystrobin with or without the Surfactant siloxane polyalkyeneoxide copolymer and polyalkyleneoxide. The higher ratio of the observed and the expected efficacy in Table 2 clearly demonstrates the synergistic effect of the composition with silicone super spreader surfactant.

Besides the actual synergistic action with respect to fungicidal activity, the fungicidal composition according to the invention also has further surprising advantageous properties which can also be described, in a wider sense, as synergistic activity.

Examples of the advantageous properties of the composition disclosed herein that may be mentioned are a broadening of the spectrum of fungicidal activity to other phytopathogens, for example a reduction in the rate of application of the active ingredients; adequate pest control with the aid of the composition according to the invention, even at a rate of application at which the individual compounds are totally ineffective; advantageous behaviour during formulation and/or upon application, for example upon grinding, sieving, emulsifying, dissolving or dispensing; increased storage stability; improved stability to light; more advantageous degradability; improved characteristics of the useful plants including: crop yields, increase in plant height, bigger leaf blade, less dead basal leaves, stronger tillers, greener leaf color, less fertilizers needed, more productive tillers, earlier flowering, less plant verse (lodging), increased shoot growth and improved plant vigor.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Any discussion of documents, acts, materials, devices, articles and the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

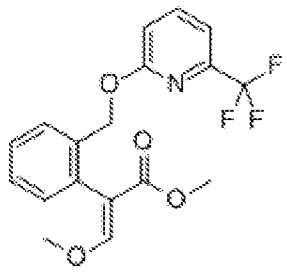
The numerical values mentioned in the description and the foregoing claims though might form a critical part of the invention of the present disclosure, any deviation from such numerical values shall still fall within the scope of the present disclosure if that deviation follows the same scientific principle as that of the invention disclosed in the present disclosure.

Although the present invention has been described and illustrated with respect to preferred embodiments and a preferred use 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.

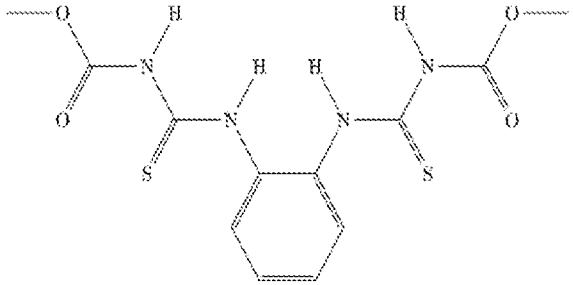
CLAIMS:

1. A synergistic fungicidal composition comprising:
   a. a compound of formula (I) in a range of 5 to 30% w/w;
   b. a compound of formula (II) in a range of 25 to 60% w/w;
   c. a non-ionic silicone surfactant in a range of 1 to 5% w/w;
   d. an agriculturally accepted excipient/acceptable carrier in a range of 1 to 25% w/w.

wherein



Formula (I) is
(picoxystrobin)



Formula (II) is
(thiophanate methyl)

2. The composition as claimed in claim 1, wherein the composition formulated as a dry flowable (DF) or a wettable powder (WP) or Water Dispersible Granule (WG) or Suspension Concentrate (SC) or Suspo Emulsion (SE) or the like.

3. The composition as claimed in claim 1, wherein the non-ionic silicone surfactant is siloxane polyalkyeneoxide copolymer and polyalkyleneoxide.

4. The composition as claimed in claim 1, wherein the agriculturally acceptable carrier is selected from the group consisting of kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina, silicates, fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and

organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks.

5. The composition as claimed in claim 1, comprising an emulsifier selected from the group consisting of nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl sulfates, arylsulfonates, or else protein hydrolyzates.

6. The composition as claimed in claim 1, comprising a dispersant selected from the group consisting of lignin-sulfite waste liquors and methylcellulose, formulating agents include (alkaryl sulphonate) mixture of salt of naphthelene sulphonic acid and phenol sulphonic acid condensate product, (alkylated naphthalene sulphonate formaldehyde polymer, sodium salt 1,2 benzisothiazoline-3-one, 1,2- propylene glycol, 3 EO alkyl (C12 ±C15) ether sulfate, alkyl aryl sulphonate, alpha-alkyl (C10-C16) omega hydroxypoly (oxyethylene), condensed alkylnaphthalene sulphonate, sodim salt, ethoxylated fatty alcohol, ethoxylated polymethacrylate in propylene glycol, lignosulfonate, magnesium aluminium silicate, methyl methacrylate graft copolymer, napthalene sulfonate sodium salt condensed with formaldehyde, polyoxyethylene nonylphenyl ether, polyvinyl pyrrolidone copolymer, potassium carboxylate, potassium dihydrogen phosphate, sodium alkylnaphthalene sulfonate formaldehyde condensate, sodium dialkyl naphathalene sulfonate, sodium dioctyl sulfosuccinate, sodium lignosulfonate sulfomethylated, sodium naphthalene sulfonate, sodium polycarboxylate, sodium salt of alcohol ether sulfate, sodium salt of poly carboxylic acid, soluble starch, ethylene oxide-propylene oxide, tallow soap.

7. The composition as claimed in claim 1, comprising a wetting agent selected from the group consisting of sodium alkylnaphthalene sulfonate formaldehyde, polyalkoxylated butyl ether, polyoxyethylene fatty alcohol ethers, alkylated naphthalene sulphonate formaldehyde polymer, alkyl aryl sulphonate.

8. The composition as claimed in claim 1, comprising a thickener selected from the group consisting of hetero polysaccharide, heteropolysaccharide 2% solution, Xanthan gum.

9. The composition as claimed in claim 1, comprising an anti-foaming agent selected from the group consisting of polydimethyl Siloxane, dimethyl polysiloxane, dimethyl siloxane, dimethylpolysiloxane.

10. The composition as claimed in claim 1, comprising a suspending agent selected from the group consisting of methylcellulose.

11. The composition as claimed in claim 1, comprising a formulating agent selected from the group consisting of propylene glycol, silica acid, silicone, sodium alkylnaphthalene sulfonate formaldehyde condensate, sodium dialkyl naphathalene sulfonate, sodium dioctyl sulfosuccinate, sodium lignosulfonate sulfomethylated, sodium naphthalene sulfonate, sodium polycarboxylate, sodium salt of alcohol ether sulfate, sodium salt of poly carboxylic acid, soluble starch, ethylene oxide-propylene oxide, tallow soap, xanthan gum.

12. A method for preparation of the synergistic water dispersible granule pesticidal composition as claimed in claim 1 comprising the steps of:
    (e) mixing a compound of formula (I), a compound of formula (II) and agriculturally accepted excipient/acceptable carrier to obtain a free-flowing fine powder;
    (f) adding simultaneously a water and non-ionic organosilicone superspreading surfactant into the free-flowing powder to obtain a wet powder;
    (g) extruding a wet powder in a screw to get needle shaped wet granules;
    (h) sieving and drying the mixture.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2023/061628

A. CLASSIFICATION OF SUBJECT MATTER
A01N43/40,A01N47/34 Version=2024.01

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

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	IN202011005829A (KRISHI RASAYAN EXPORTS PVT LTD), 27 August 2021 the whole document	1-12
A	US5104647A (UNION CARBIDE CHEMICALS AND PLASTICS TECHNOLOGY CORPORATION), 14 April 1992 abstract; claims 1-5	1-12

☐ 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

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29-02-2024	29-02-2024

Name and mailing address of the ISA/	Authorized officer
Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Kiran Yadav Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2023/061628

Citation	Pub.Date	Family	Pub.Date
US 5104647 A	14-04-1992	CA 2045223 C	01-04-1997