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(54) Title: COMPOSITION COMPRISING EUTECTIC MIXTURE OF BOSCALID AND A STROBILURIN FUNGICIDE

(57) Abstract: The present invention relates to a eutectic mixture of boscalid and strobilurin fungicide. Agrochemical compositions comprising a eutectic mixture of boscalid and a strobilurin fungicide and a method of controlling phytopathogenic fungi using said compositions are also provided.



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**COMPOSITION COMPRISING EUTECTIC MIXTURE OF BOSCALID AND A
STROBILURIN FUNGICIDE**

Technical field of the invention:

5 The present invention relates to a composition comprising eutectic mixture of boscalid and a strobilurin fungicide. The invention further relates to a process for formulating a composition comprising eutectic mixture of boscalid and a strobilurin fungicide and to a method of controlling phytopathogenic fungi using said compositions.

10 **Background:**

Boscalid is a fungicide known to be a succinate dehydrogenase inhibitor. It is a fungicide, with translaminar and acropetal movement within the plant leaf, providing preventive and in some cases, curative action. It inhibits spore germination, germ tube elongation and is also effective on all other stages of fungal development. Boscalid is used to control Alternaria blight, Botrytis, Powdery mildew, Purple blotch, Rust, Leaf spot, Target spot, Grey mould, and Stem rot.

In order to widen the spectrum of activity as well as to enhance the effectiveness of fungicidal control, it is a common practice to combine succinate dehydrogenase Inhibitor such as boscalid with fungicidal active ingredients of other classes. One such important class of fungicide is Quinone outside inhibitor (QoI).

Strobilurins are QoI inhibiting fungicides and inhibit fungal respiration by binding to the cytochrome bc₁ complex at the QoI site in mitochondrial respiration. These fungicides work by inhibiting the fungi's ability to undergo normal respiration. The strobilurin chemistries have a very specific target site, or mode-of-action (MOA).

25 Strobilurins are known to control fungi such as Erysiphe graminis, Puccinia spp., Leptosphaeria nodorum, Septoria tritici and Pyrenophora teres on temperate cereals, Pyricularia oryzae and Rhizoctonia solani on rice; Plasmopara viticola and Uncinula necator on vines; Sphaerotheca fuliginea and Pseudoperonospora cubensis on cucurbitaceae; Phytophthora infestans and Alternaria solani on potato

and tomato; *Mycosphaerella arachidis*, *Rhizoctonia solani* and *Sclerotium rolfsii* on peanut; *Monilinia* spp. and *Cladosporium carpophilum* on peach; *Pythium* spp. and *Rhizoctonia solani* on turf; *Mycosphaerella* spp. on banana; *Cladosporium caryigenum* on pecan; *Elsinoë fawcettii*, *Colletotrichum* spp. and *Guignardia citricarpa* on citrus; *Colletotrichum* spp. and *Hemileia vastatrix* on coffee.

In view of the improvements that can be expected to effectively control phytopathogenic fungi by combining succinate dehydrogenase inhibitor with strobilurin fungicides there exist a requirement for exploring and developing stable compositions of the active ingredients from such groups.

It is noted that boscalid undergoes irrepressible morphological changes when brought in contact with water or solvents. It is further observed that specific techniques, tedious and costly procedures are often required to make formulations of boscalid suitable for commercial production as well as for the intended application. Such formulations on long time storage develops stability issues as well.

Thus, it is a need to develop stable compositions of boscalid together with a strobilurin fungicide which eliminates the drawbacks of the known formulations.

Surprisingly inventors of the present invention found out that compositions comprising eutectic mixture of boscalid and a strobilurin fungicide can be prepared which do not undergo any morphological changes, stable and highly suitable for the intended application of controlling phytopathogenic fungi.

Object of the invention:

It is an object of the present invention to provide compositions comprising eutectic mixture of boscalid and a strobilurin fungicide.

It is another object of the present invention to provide compositions comprising eutectic mixture of boscalid and azoxystrobin.

It is another object of the present invention to provide compositions comprising eutectic mixture of boscalid and fluoxastrobin.

It is yet another object of the present invention to provide a process for preparing a eutectic mixture of boscalid and a strobilurin fungicide.

It is another object of the present invention to provide a process for preparing fungicidal compositions comprising eutectic mixture of boscalid and a strobilurin
5 fungicide.

Summary of the invention:

A eutectic mixture comprising boscalid and a strobilurin fungicide.

The present invention provides an agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

10 The present invention provides an agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide wherein said composition comprises between 10-90% of boscalid and 90-10% of strobilurin fungicide by weight.

A eutectic mixture comprising boscalid and azoxystrobin.

The present invention further provides an agrochemical composition comprising
15 eutectic mixture of boscalid and azoxystrobin.

The present invention further provides an agrochemical composition comprising eutectic mixture of boscalid and azoxystrobin wherein said composition comprises between 10-90% of boscalid and 90-10% of azoxystrobin by weight.

A eutectic mixture of boscalid and azoxystrobin wherein said eutectic mixture is
20 characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103.5\pm 3^{\circ}\text{C}$.

The present invention further provides an agrochemical composition comprising eutectic mixture of boscalid and azoxystrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at
25 $103.5\pm 3^{\circ}\text{C}$.

A eutectic mixture comprising boscalid and fluoxastrobin.

The present invention further provides an agrochemical composition comprising eutectic mixture of boscalid and fluoxastrobin.

The present invention further provides an agrochemical composition comprising eutectic mixture of boscalid and fluoxastrobin wherein said composition comprises
5 between 10-90% of boscalid and 90-10% of fluoxastrobin by weight.

A eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

The present invention further provides an agrochemical composition comprising
10 eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

A eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at
15 $107\pm 3^{\circ}\text{C}$.

The present invention further provides an agrochemical composition comprising eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $107\pm 3^{\circ}\text{C}$.

20 The present invention relates to a process for formulating an agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

Further it relates to a process for preparing a eutectic mixture of boscalid and a strobilurin fungicide.

The present invention further provides a method of controlling phytopathogenic
25 fungi said method comprising applying to a plant, or its habitat, plant seed or soil, a fungicidally effective amount of a composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

Brief Description to the Drawings:

The present invention can be understood by reference to the following figures:

Figure 1: DSC thermogram of Boscalid.

Figure 2: DSC thermogram of Azoxystrobin.

5 Figure 3: DSC thermogram of Boscalid and Azoxystrobin in % ratio of 60: 40.

Figure 4: Phase diagram of eutectic mixture of Boscalid and Azoxystrobin

Figure 5: DSC thermogram for Example 2.

Figure 6: DSC thermogram for Example 3.

Figure 7: DSC thermogram for Example 8.

10 Figure 8: DSC thermogram for Example 2 after 9 months storage.

Figure 9: DSC thermogram of Fluoxastrobin.

Figure 10: DSC thermogram of Boscalid and Fluoxastrobin mixture in 30:70 ratio
(Example 9)

15 Figure 11: DSC thermogram of Boscalid and Fluoxastrobin mixture in 25:75 ratio
(Example 10)

Detailed Description of the Invention

The inventors of the present invention surprisingly found out that eutectic mixture of boscalid and strobilurin compound can be successfully prepared which is stable as well as highly suitable for the intended use of controlling phytopathogenic fungi.

20 Further it has been observed by the inventors of the present invention that the composition comprising eutectic mixture of boscalid and strobilurin compound does not suffer from uncontrolled morphological changes while preparing such composition and further noted that the said compositions remain stable during longtime storage.

With respect to the present invention, boscalid refers to 2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide, its salts and derivatives and polymorphs. Throughout the specification, the term 'boscalid' includes the known polymorphic forms of the molecule namely boscalid anhydrate modification I, boscalid
5 anhydrate modification II and boscalid hydrate form.

The term 'eutectic mixture' is defined as a mixture of two or more components which usually do not interact to form a new chemical compound but, which at certain ratios, inhibit the crystallization process of one another resulting in a system having a lower melting point than either of the components. A phase diagram
10 depicting the onset melting temperature (using Differential Scanning Calorimetry - DSC thermograms) of the eutectic mixture and the excess components at various % of both components illustrates the melting pattern of compositions according to the present invention. The point at which all the components in the mixture exist at equilibrium is called the eutectic point.

15 The term eutectic mixture shall also be understood to include a mixture according to the invention in a ratio of two components at which the melting point is lowered to the minimum value. However, it shall also include other ratios which have a higher melting point than the melting point of the eutectic mixture although lower than the melting points of the individual components, wherein at least a portion of
20 the mixed active ingredients are at the eutectic point.

In an embodiment, the present invention provides a eutectic mixture comprising boscalid and a strobilurin fungicide.

In an embodiment, the present invention provides an agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

25 In an embodiment of the present invention, there is provided an agrochemical composition comprising a eutectic mixture of boscalid and a strobilurin fungicide; and at least one agrochemically acceptable excipient, wherein formation of said eutectic mixture inhibits the crystallization process of boscalid and the strobilurin fungicide.

In an embodiment, the composition comprises boscalid in a form selected from the group comprising boscalid anhydrate modification I, boscalid anhydrate modification II, and boscalid hydrate form.

5 In an embodiment, compositions according to the present invention comprise a strobilurin fungicide selected from the group comprising azoxystrobin, pyraclostrobin, trifloxystrobin, picoxystrobin, fluoxastrobin, mandestrobin, pyribencarb, coumoxystrobin, enoxastrobin, flufenoxystrobin, pyraoxystrobin, pyrametostrobin, triclopyricarb, dimoxystrobin, fenaminstrobin, metominostrobin, orysastrobin, and kresoxim-methyl.

10 In a preferred embodiment, compositions according to the present invention comprise a strobilurin fungicide selected from the group comprising azoxystrobin, pyraclostrobin, trifloxystrobin, fluoxastrobin and picoxystrobin.

In an embodiment of the present invention, the composition comprises between 10-90% of boscalid and 90-10% of strobilurin fungicide by weight.

15 In an embodiment of the present invention, the composition comprises between 50-80% of boscalid and 50-20% of strobilurin fungicide by weight.

In an embodiment of the present invention, the composition comprises between 50-80% of boscalid and 50-20% of strobilurin fungicide by weight of the active ingredients.

20 In an embodiment, the present invention provides a eutectic mixture of boscalid and azoxystrobin.

In an embodiment, the present invention provides a eutectic mixture comprising boscalid and azoxystrobin in a molar ratio of 1.5:1.

25 In an embodiment of the present invention, there is provided an agrochemical composition comprising a eutectic mixture of boscalid and azoxystrobin.

In an embodiment of the present invention, the composition comprises between 10-90% of boscalid and 90-10% of azoxystrobin by weight.

In certain embodiments of the present invention, the composition comprises between 50-80% of boscalid and 50-20% of azoxystrobin by weight.

In certain embodiments of the present invention, the composition comprises between 50-80% of boscalid and 50-20% of azoxystrobin by weight of the active ingredients.

In an embodiment, the present invention provides a eutectic mixture comprising about 60% boscalid and about 40% azoxystrobin by weight of the active ingredients.

In an embodiment, the composition comprises about 60% of boscalid and about 40% of azoxystrobin by weight of the active ingredients.

In an embodiment, the composition comprises boscalid and azoxystrobin in a molar ratio of 1: 9 to 9: 1.

In an embodiment, the composition comprises boscalid and azoxystrobin in a molar ratio of 1:5 to 5: 1.

In an embodiment, the composition comprises boscalid and azoxystrobin in a molar ratio of 1:3 to 3: 1.

In a preferred embodiment, the composition comprises boscalid and azoxystrobin in a molar ratio of 1.5: 1.

In an embodiment, the present invention provides a eutectic mixture comprising boscalid and azoxystrobin in a molar ratio of 1.5:1.

In an embodiment, the composition comprising a eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103^{\circ}\text{C} \pm 3^{\circ}\text{C}$.

In an embodiment, the present invention provides a eutectic mixture comprising boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103^{\circ}\text{C} \pm 3^{\circ}\text{C}$.

In an embodiment, the composition comprising a eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak between 103°C and 106°C .

In an embodiment, the present invention provides a eutectic mixture comprising
5 boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak between 103°C and 106°C .

In a preferred embodiment, the composition comprising the eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at 103.5°C .

10 In an embodiment, the present invention provides a eutectic mixture comprising boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at 103.5°C .

In an embodiment, the present invention provides a eutectic mixture of boscalid and fluoxastrobin.

15 In an embodiment of the present invention, there is provided an agrochemical composition comprising a eutectic mixture of boscalid and fluoxastrobin.

In an embodiment of the present invention, the composition comprises between 10-90% of boscalid and 90-10% of fluoxastrobin by weight.

In certain embodiments of the present invention, the composition comprises
20 between 50-80% of boscalid and 50-20% of fluoxastrobin by weight.

In certain embodiments of the present invention, the composition comprises between 50-80% of boscalid and 50-20% of fluoxastrobin by weight of the active ingredients.

In an embodiment, the present invention provides a eutectic mixture comprising
25 about 60% boscalid and about 40% fluoxastrobin by weight of the active ingredients.

In an embodiment, the composition comprises about 60% of boscalid and about 40% of fluoxastrobin by weight of the active ingredients.

In an embodiment, the composition comprises boscalid and fluoxastrobin in a molar ratio of 1: 9 to 9: 1.

In an embodiment, the composition comprises boscalid and fluoxastrobin in a molar ratio of 1:5 to 5: 1.

- 5 In an embodiment, the composition comprises boscalid and fluoxastrobin in a molar ratio of 1:3 to 3: 1.

In an embodiment, the composition comprises boscalid and fluoxastrobin in a molar ratio of 1.5: 1.

- 10 In an embodiment, the present invention provides a eutectic mixture comprising boscalid and fluoxastrobin in a molar ratio of 1:3.

In an embodiment, the composition comprising a eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

- 15 In an embodiment, the present invention provides a eutectic mixture comprising boscalid and fluoxastrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $107^{\circ}\text{C} \pm 3^{\circ}\text{C}$.

In a preferred embodiment, the composition comprising the eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at 97 to 100°C .

- 20 In a preferred embodiment, the composition comprising the eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at 107 to 109°C .

In an embodiment, the present invention provides a process to prepare eutectic mixture of boscalid and a strobilurin fungicide.

- 25 In an embodiment, the present invention provides a process to prepare eutectic mixture of boscalid and a strobilurin fungicide said process comprising subjecting boscalid and a strobilurin fungicide to solution crystallization, dry grinding, solvent drop grinding technique, or spray drying technique.

In an embodiment, the present invention provides a process for preparation of eutectic mixture of boscalid and strobilurin said process comprising following steps:

- a. preparing a concentrated solution of boscalid and a strobilurin fungicide in one or more solvents;
- 5 b. optionally evaporating said solvent; and
- c. triturating or precipitating with an anti-solvent to obtain eutectic mixture.

In an embodiment, the present invention provides a process for preparation of eutectic mixture of boscalid and strobilurin said process comprising following steps:

- a. preparing a concentrated solution of boscalid and a strobilurin fungicide in
10 one or more solvents;
- b. evaporating said solvent to effect crystallisation to obtain eutectic mixture.

In an embodiment the solvent in step a) is selected from aliphatic alcohols, ketones, esters, ethers, polar protic solvents, polar aprotic solvents, halogenated solvents, aliphatic hydrocarbon or aromatic hydrocarbon.

- 15 In an embodiment of the present invention the anti-solvent can be aliphatic or aromatic hydrocarbon.

In an embodiment in step (b) the solvent is partially evaporated.

In an embodiment in step (b) the solvent is completely evaporated.

- 20 In an embodiment of the present invention, the anti-solvent in step c) is selected from aliphatic or aromatic hydrocarbon solvents.

In an embodiment, the present invention provides a process to prepare eutectic mixture of boscalid and strobilurin fungicide said process comprising following steps:

- a. admixing boscalid and a strobilurin fungicide;
- 25 b. optionally admixing solvent to said admixture; and
- c. grinding or crushing or milling said admixture to obtain said eutectic mixture.

In an embodiment, the temperature at which step (a), step (b) or step (c) of the process is carried out is not limiting.

In another embodiment, step (a), step (b) or step (c) of the process is carried out at a temperature below the melting point of boscalid and a strobilurin fungicide.

- 5 The present invention further provides a process for preparing a composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

In an embodiment there is provided a process for preparing a composition comprising a eutectic mixture of boscalid and a strobilurin fungicide, said process comprises preparing a eutectic mixture of boscalid and a strobilurin fungicide with
10 or without the addition of agrochemically acceptable excipient and further processing the mixture into a suitable form.

In an embodiment there is provided a process for preparing a granular composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

In an embodiment of the present invention, the granular composition comprising a
15 eutectic mixture of boscalid and a strobilurin fungicide is prepared by a process comprising:

- (a) preparing a eutectic mixture of boscalid and a strobilurin fungicide optionally with an agrochemically acceptable excipient;
- (b) optionally adding one or more other agrochemicals;
- 20 (c) optionally grinding and pulverizing; and
- (d) granulating said mixture to obtain granular composition.

In an embodiment of the present invention, the granular composition comprising a eutectic mixture of boscalid and a strobilurin fungicide is prepared by a process comprising:

- 25 (a) preparing a eutectic mixture of boscalid and a strobilurin fungicide with at least one agrochemically acceptable excipient;
- (b) optionally adding one or more other agrochemicals;
- (c) grinding and pulverizing; and

(d) granulating said mixture to obtain granular composition.

The step of granulating the mixture is not particularly limiting. Appropriate granulating processes are conventional processes described in granulating technology for example spray drying, fluidized bed granulation, agglomeration, pan
5 granulation and in particular extrusion granulation.

In an embodiment of the present invention, the granular composition comprising a eutectic mixture of boscalid and a strobilurin fungicide is prepared by a process comprising:

- 10 (a) mixing boscalid and a strobilurin fungicide with at least one agrochemically acceptable excipient;
- (b) grinding and pulverizing; and
- (c) granulating said mixture to obtain granular composition.

In an embodiment, mixing of step (a) includes grinding.

In an embodiment of the present invention the eutectic mixture is prepared by
15 grinding boscalid with a strobilurin fungicide.

In an embodiment, the eutectic mixture is prepared by milling boscalid with a strobilurin fungicide.

In an embodiment, the eutectic mixture is prepared by melting of boscalid with a strobilurin fungicide.

20 In an embodiment, the eutectic mixture is prepared by crystallizing boscalid and a strobilurin fungicide from one or more suitable solvent.

In an embodiment, suitable solvent for preparation of eutectic mixture of boscalid and a strobilurin fungicide is selected from alcohols, esters, ethers, ketones, aldehydes, halogenated hydrocarbon, aromatic hydrocarbons, aliphatic
25 hydrocarbons, amides and water or mixtures thereof.

In an embodiment, the eutectic mixture is prepared by granulation of a mixture of boscalid and a strobilurin fungicide.

In an embodiment the process of granulation is not particularly limiting and can be performed by spray drying, fluidized bed granulation, agglomeration, pan granulation and extrusion granulation.

In an embodiment, the eutectic mixture is prepared by granulation of a mixture of
5 boscalid and a strobilurin fungicide wherein the strobilurin fungicide is selected from azoxystrobin, pyraclostrobin, trifloxystrobin, picoxystrobin, fluoxastrobin, mandestrobin, pyribencarb, coumoxystrobin, enoxastrobin, flufenoxystrobin, pyraoxystrobin, pyrametostrobin, triclopyricarb, dimoxystrobin, fenaminstrobin, metominostrobin, orysastrobin or kresoxim-methyl.

10 In an embodiment, the eutectic mixture is prepared by granulation of a mixture of boscalid and azoxystrobin.

The fungicidal composition according to the present invention may further comprise other agrochemical suitable excipients such as auxiliary
15 adjuvants/surfactants such as wetting agents spreading agents, penetration aids, dispersing agents, carriers, sticking and binding agents, inert ingredients, pH modifiers, suspending agents, spray droplet modifiers, pigments, antioxidants, UV protectants, compatibilizing agents, antifoam agents, sequestering agents, neutralizing agents, corrosion inhibitors, dyes, odorants, fertilizers, micronutrients, emollients, lubricants, and the like.

20 The agrochemical compositions comprising the eutectic mixture of boscalid and a strobilurin fungicide can be prepared as dispersible granule, wettable powder, dry flowable, emulsion, dispersion, suspension concentrate, encapsulation in polymeric materials, oil dispersion, emulsifiable concentrate, micro emulsion, flowable concentrate, or suspo-emulsion.

25 The compositions according to the present invention can further comprise one or more other active ingredients. Other active ingredients may be selected from fungicides, insecticides or herbicides.

In an embodiment, the additional active ingredient is a fungicide. In this
30 embodiment, the composition of the invention comprises a third fungicide.

In an embodiment, the additional fungicide may be a combination of two or more additional fungicides. In this embodiment, the composition of the invention comprises a third and a fourth fungicide.

5

In an embodiment the composition of the invention comprises a third and a fourth fungicide selected from a multisite contact fungicide, a conazole fungicide and a succinate dehydrogenase inhibitor.

10 In an embodiment, the third fungicide may be a multisite contact fungicide.

In an embodiment, the multisite contact fungicide may be selected from the group consisting of

- 15 (i) copper fungicides selected from copper oxychloride, copper sulfate, copper hydroxide and tribasic copper sulfate (Bordeaux mixture);
- (ii) elemental sulfur;
- (iii) dithiocarbamate fungicides selected from amobam, asomate, azithiram, carbamorph, cufraneb, cuprobam, disulfiram, ferbam, metam, nabam, tecoram, thiram, urbacide, ziram, dazomet, etem, milneb, mancopper, 20 mancozeb, maneb, metiram, polycarbamate, propineb and zineb;
- (iv) phthalimide fungicides selected from folpet, captan and captafol;
- (v) chlorothalonil;
- (vi) sulfamide fungicides selected from dichlofluanid and tolylfluanid;
- (vii) guanidine fungicides selected from dodine, guazantime and 25 iminoctadine;
- (viii) anilazine;
- (ix) dithianon; and
- (x) combinations thereof;

30 In an embodiment, the third fungicide is mancozeb.

In an embodiment, the third fungicide mancozeb is used in an amount that provides 0.5 kg/ha to 5.0 kg/ha to the field.

In an embodiment, the third fungicide mancozeb is used in an amount that provides
5 1.0 kg/ha to 3.0 kg/ha to the field.

In an embodiment, the multisite fungicide is chlorothalonil.

In an embodiment, the third fungicide may be a conazole fungicide selected from the group consisting of climbazole, clotrimazole, imazalil, oxpoconazole,
10 prochloraz, prochloraz-manganese, triflumizole, azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluotrimazole, fluquinconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole,
15 propiconazole, prothioconazole, quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, perfurazoate and uniconazole-P.

In an embodiment, the third fungicide may be a second succinate dehydrogenase
20 inhibitor selected from the group consisting of benodanil, flutolanil, mepronil, fluopyram, fenfuram, carboxin, oxycarboxin, thifluzamide, bixafen, fluxapyroxad, furametpyr, isopyrazam, penflufen, penthiopyrad, and sedaxane.

In an embodiment, the third fungicide is a multisite contact fungicide and the fourth
25 fungicide may be a conazole fungicide selected from the group consisting of climbazole, clotrimazole, imazalil, oxpoconazole, prochloraz, prochloraz-manganese, triflumizole, azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluotrimazole, fluquinconazole, flusilazole, flutriafol,
30 furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole,

quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, perfurazoate and uniconazole-P.

In an embodiment, the third fungicide is mancozeb and the fourth fungicide may
5 be a conazole fungicide selected from the group consisting of climbazole, clotrimazole, imazalil, oxpoconazole, prochloraz, prochloraz-manganese, triflumizole, azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazol, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluotrimazole, fluquinconazole, flusilazole, flutriafol, furconazole,
10 furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, quinconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, perfurazoate and uniconazole-P.

15 In an embodiment, the third fungicide may be a multisite contact fungicide and the fourth fungicide may be a second succinate dehydrogenase inhibitor selected from the group consisting of benodanil, flutolanil, mepronil, fluopyram, fenfuram, carboxin, oxycarboxin, thifluzamide, bixafen, fluxapyroxad, furametpyr, isopyrazam, penflufen, penthiopyrad, and sedaxane.

20 In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be a second succinate dehydrogenase inhibitor selected from the group consisting of benodanil, flutolanil, mepronil, fluopyram, fenfuram, carboxin, oxycarboxin, thifluzamide, bixafen, fluxapyroxad, furametpyr, isopyrazam,
25 penflufen, penthiopyrad, and sedaxane.

In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be fluopyram.

30 In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be thifluzamide.

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In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be bixafen.

5 In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be fluxapyroxad.

In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be isopyrazam.

10 In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be penthiopyrad.

In an embodiment, the third fungicide may be mancozeb and the fourth fungicide may be sedaxane.

15 In an embodiment, the third fungicide is a multisite contact fungicide and the fourth fungicide is a conazole fungicide selected from prothioconazole, tebuconazole, cyproconazole, epoxiconazole, metconazole and tebuconazole.

20 In an embodiment, the third fungicide is mancozeb and the fourth fungicide is prothioconazole.

In an embodiment, the third fungicide is mancozeb and the fourth fungicide is tebuconazole.

25 In an embodiment, the third fungicide is mancozeb and the fourth fungicide is cyproconazole.

30 In an embodiment, the third fungicide is mancozeb and the fourth fungicide is epoxiconazole.

In an embodiment, the third fungicide is mancozeb and the fourth fungicide is metconazole.

The compositions according to the present invention can be prepared as pre-mix,
5 or by tank-mixing with other actives or alternatively may be sold as a kit of parts containing the eutectic mixture of boscalid and a strobilurin fungicide and other ingredients that may be mixed prior to spraying or a ready mix kit of parts containing the eutectic mixture of boscalid and a strobilurin fungicide in one part and other actives or suitable agrochemical excipients in another part.

10

The composition comprising eutectic mixture of boscalid and a strobilurin fungicide of the present invention is suitable for combating or controlling fungi.

The present invention provides a method of controlling phytopathogenic fungi, said method comprising applying to a plant, or its habitat, plant seed or soil, a
15 fungicidally effective amount of a composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

Accordingly there is provided a method of combating or controlling fungi, said method comprising applying to a plant, or its habitat, plant seed or soil, a fungicidally effective amount of a composition comprising a eutectic mixture of
20 boscalid and a strobilurin fungicide.

In an embodiment there is provided a method of combating or controlling fungi, said method comprising applying to a plant, or its habitat, plant seed or soil, a fungicidally effective amount of a composition comprising a eutectic mixture of boscalid and a strobilurin fungicide wherein said strobilurin fungicide is selected
25 from azoxystrobin, pyraclostrobin, trifloxystrobin, picoxystrobin, fluoxastrobin, mandestrobin, pyribencarb, coumoxystrobin, enoxastrobin, flufenoxystrobin, pyraoxystrobin, pyrametostrobin, triclopyricarb, dimoxystrobin, fenaminstrobin, metominostrobin, orysastrobin or kresoxim-methyl.

In an embodiment there is provided a method of combating or controlling fungi,
30 said method comprising applying to a plant, or its habitat, plant seed or soil, a

fungicidally effective amount of a composition comprising a eutectic mixture of boscalid and azoxystrobin.

In an embodiment there is provided a method of combating or controlling fungi, said method comprising applying to a plant, or its habitat, plant seed or soil, a

- 5 fungicidally effective amount of a composition comprising a eutectic mixture of boscalid and fluoxastrobin.

Following are the preferred embodiments of the present invention, which are exemplary and non-limiting:

A eutectic mixture comprising boscalid and a strobilurin fungicide.

- 10 An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide wherein said composition comprises between 10-90% of boscalid and 90-10% of strobilurin fungicide by weight.

- 15 A eutectic mixture comprising boscalid and azoxystrobin.

An agrochemical composition comprising eutectic mixture of boscalid and azoxystrobin.

An agrochemical composition comprising eutectic mixture of boscalid and azoxystrobin wherein said composition comprises between 10-90% of boscalid and

- 20 90-10% of azoxystrobin by weight.

A eutectic mixture of boscalid and azoxystrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103.5\pm 3^{\circ}\text{C}$.

A composition comprising eutectic mixture of boscalid and azoxystrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an

- 25 endothermic peak at $103.5\pm 3^{\circ}\text{C}$.

A eutectic mixture comprising boscalid and fluoxastrobin.

An agrochemical composition comprising eutectic mixture of boscalid and fluoxastrobin.

An agrochemical composition comprising eutectic mixture of boscalid and fluoxastrobin wherein said composition comprises between 10-90% of boscalid
5 and 90-10% of fluoxastrobin by weight.

A eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

A composition comprising eutectic mixture of boscalid and fluoxastrobin wherein
10 said eutectic mixture is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and has an endothermic peak at $97\pm 3^{\circ}\text{C}$.

A eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and has an endothermic peak at $107\pm 3^{\circ}\text{C}$.

15 A composition comprising eutectic mixture of boscalid and fluoxastrobin wherein said eutectic mixture is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and has an endothermic peak at $107\pm 3^{\circ}\text{C}$.

A process for formulating an agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

20 A process for preparing a eutectic mixture of boscalid and a strobilurin fungicide comprising processing boscalid and the strobilurin fungicide together in a predetermined ratio.

A method of controlling phytopathogenic fungi said method comprising applying to a plant, or its habitat, plant seed or soil, a fungicidally effective amount of a
25 composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

A eutectic mixture comprising boscalid and a strobilurin fungicide.

An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.

An agrochemical composition comprising a eutectic mixture of boscalid and a strobilurin fungicide; and at least one agrochemically acceptable excipient, wherein formation of said eutectic mixture inhibits the crystallization process of boscalid and the strobilurin fungicide.

- 5 A composition comprising between 10-90% of boscalid and 90-10% of strobilurin fungicide by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising between 50-80% of boscalid and 50-20% of strobilurin fungicide by weight, wherein at least a portion of the fungicide mixture is in the form
10 of a eutectic mixture.

A composition comprising between 50-80% of boscalid and 50-20% of strobilurin fungicide by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture of boscalid and azoxystrobin.

- 15 An agrochemical composition comprising a eutectic mixture of boscalid and azoxystrobin.

A composition comprising between 10-90% of boscalid and 90-10% of azoxystrobin by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

- 20 A composition comprising between 50-80% of boscalid and 50-20% of azoxystrobin by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising between 50-80% of boscalid and 50-20% of azoxystrobin by weight of the active ingredients, wherein at least a portion of the
25 fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture comprising about 60% boscalid and about 40% azoxystrobin by weight of the active ingredients.

A composition comprising about 60% of boscalid and about 40% of azoxystrobin by weight of the active ingredients, wherein the fungicide mixture is in the form of a eutectic mixture.

5 A eutectic mixture comprising about 37.5% boscalid and about 25% azoxystrobin by weight of the active ingredients.

A composition comprising about 37.5% of boscalid and about 25% of azoxystrobin by weight of the active ingredients, wherein the fungicide mixture is in the form of a eutectic mixture.

10 A composition comprising boscalid and azoxystrobin in a molar ratio of 1: 9 to 9: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising boscalid and azoxystrobin in a molar ratio of 1:5 to 5: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

15 A composition comprising boscalid and azoxystrobin in a molar ratio of 1:3 to 3: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising boscalid and azoxystrobin in a molar ratio of 1.5: 1, wherein the fungicide mixture is in the form of a eutectic mixture.

20 A eutectic mixture comprising boscalid and azoxystrobin in a molar ratio of 1.5:1.

A composition comprising a eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103\pm 3^{\circ}\text{C}$.

25 A eutectic mixture comprising boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at $103\pm 3^{\circ}\text{C}$.

A composition comprising a eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak between 102°C and 106°C .

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A eutectic mixture comprising boscalid and azoxystrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak between 102°C and 106°C .

A composition comprising the eutectic mixture of boscalid and azoxystrobin is characterized by DSC having an onset at 100.07°C and an endothermic peak at
5 103.5°C .

A eutectic mixture comprising boscalid and azoxystrobin is characterized by DSC having an onset at 100.07°C and an endothermic peak at 103.5°C .

A eutectic mixture comprising boscalid and azoxystrobin characterized by having a DSC thermogram as illustrated in figure 3.

10 A composition comprising boscalid and azoxystrobin characterized by having a DSC thermogram as illustrated in figure 3.

A eutectic mixture comprising boscalid and azoxystrobin characterized by having a phase diagram as illustrated in figure 4.

A composition comprising boscalid and azoxystrobin characterized by having a
15 phase diagram as illustrated in figure 4.

A eutectic mixture of boscalid and fluoxastrobin.

An agrochemical composition comprising a eutectic mixture of boscalid and fluoxastrobin.

A composition comprising between 10-90% of boscalid and 90-10% of
20 fluoxastrobin by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising between 50-80% of boscalid and 20-50% of fluoxastrobin by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

25 A composition comprising between 20-50% of boscalid and 50-80% of fluoxastrobin by weight, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

25

A composition comprising between 50-80% of boscalid and 50-20% of fluoxastrobin by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

5 A composition comprising between 20-50% of boscalid and 50-80% of fluoxastrobin by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture

A eutectic mixture comprising about 25% boscalid and about 75% fluoxastrobin by weight of the active ingredients.

10 A composition comprising about 25% of boscalid and about 75% of fluoxastrobin by weight of the active ingredients, wherein the fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture comprising about 50% boscalid and about 50% fluoxastrobin by weight of the active ingredients.

15 A composition comprising about 50% of boscalid and about 50% of fluoxastrobin by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture comprising about 60% boscalid and about 40% fluoxastrobin by weight of the active ingredients.

20 A composition comprising about 60% of boscalid and about 40% of fluoxastrobin by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture comprising about 75% boscalid and about 25% fluoxastrobin by weight of the active ingredients.

25 A composition comprising about 75% of boscalid and about 25% of fluoxastrobin by weight of the active ingredients, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising boscalid and fluoxastrobin in a molar ratio of 1: 9 to 9: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

5 A composition comprising boscalid and fluoxastrobin in a molar ratio of 1:5 to 5: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A composition comprising boscalid and fluoxastrobin in a molar ratio of 1:3 to 3: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

10 A composition comprising boscalid and fluoxastrobin in a molar ratio of 1.5: 1, wherein at least a portion of the fungicide mixture is in the form of a eutectic mixture.

A eutectic mixture comprising boscalid and fluoxastrobin in a molar ratio of 1: 3.

15 A composition comprising a eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

A eutectic mixture comprising boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at $97\pm 3^{\circ}\text{C}$.

20 A composition comprising a eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak between 94°C and 100°C .

A composition comprising the eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $92\pm 3^{\circ}\text{C}$ and an endothermic peak at 97 to 99°C .

25 A composition comprising a eutectic mixture of boscalid and fluoxastrobin is characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak between 104°C and 110°C .

A composition comprising the eutectic mixture of boscalid and fluoxastrobin characterized by DSC having an onset at $100\pm 3^{\circ}\text{C}$ and an endothermic peak at 107 to 108 $^{\circ}\text{C}$.

5 A eutectic mixture comprising boscalid and fluoxastrobin characterized by having a DSC thermogram as illustrated in figure 10 and figure 11.

A composition comprising boscalid and fluoxastrobin characterized by having a DSC thermogram as illustrated in figure 10 and figure 11.

A eutectic mixture comprising boscalid, a strobilurin fungicide and a third fungicide.

10 A eutectic mixture comprising boscalid, a strobilurin fungicide, at least one third fungicide, and at least one fourth fungicide.

An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide, and a third fungicide.

An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide, at least one third fungicide, and at least one fourth fungicide.

15 The invention shall now be described with reference to the following specific examples. It should be noted that the examples appended below illustrate rather than limit the invention and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the present invention.

20 **Example 1:** A eutectic mixture of boscalid and azoxystrobin according to the present invention was prepared as follows:

Boscalid and azoxystrobin were grinded in different ratios as shown in table 1 in an agate mortar and the mixture was ground thoroughly. The resulting mixture was analyzed by DSC.

25 Table 1: Boscalid-Azoxystrobin mixture in different ratios.

Sr. No.	Boscalid (%)	Azoxystrobin (%)	Melting point - 1 (°C)	Melting point-2 (°C)
1	0	100	116.5	
2	20	80	104.12	128
3	30	70	103.39	124.9
4	40	60	103.57	119.19
5	50	50	103.56	118.55
6	60	40	103.52	103.52
7	70	30	103.55	120
8	80	20	103.49	135.71
9	100	0	145	

Method of detecting a eutectic mixture:

The eutectic mixture was detected by recording DSC.

The endothermic peak of boscalid was recorded between 144 to 148°C (onset at 144.71, $\Delta H = 83.65$ J/g) [Fig. 1]. The endothermic peak of azoxystrobin was recorded between 112 to 118°C (onset at 114.34.2°C, $\Delta H = 86.19$ J/g) [Fig. 2]. The DSC was carried out for mixtures of boscalid: azoxystrobin in various ratios. The results showed that boscalid: azoxystrobin in a ratio of 60:40, eutectic mixture was formed showing a single endothermic peak (eutectic point) at 103.5 °C (Fig. 3). In all other ratios, two distinct endotherms were observed, one from the melting of eutectic mixture and the other from the melting of excess component which is depicted in phase diagram (Fig.4)

Example 2: A composition comprising a eutectic mixture of boscalid (anhydrate modification I) and azoxystrobin according to the present invention has been prepared as follows:

Table 2: Boscalid-Azoxystrobin WDG composition:

Sr. No.	Ingredients	% w/w
1.	Boscalid	35
2.	Azoxystrobin	25
3.	Dispersing agent	10
4.	Wetting agent	3
5.	Inert	23.5
6.	Polymeric surfactant	3.5
	Total	100.00

Boscalid and azoxystrobin were weighed, grinded in an agate mortar and the mixture was ground thoroughly. The mixture was then milled together with the listed ingredients in an Air Jet mill to obtain required particle size. To this powdered mixture was added water to prepare dough. Granules were prepared by subjecting the dough to granulator. The granules were dried using dryer and then screened. The granules were analyzed by DSC. DSC endothermic peak was observed at: 104.5 °C. (Fig. 5).

Example 3: A composition comprising a eutectic mixture of boscalid (anhydrate modification II) and azoxystrobin according to the present invention has been prepared as follows:

Table 4: Boscalid-Azoxystrobin WDG composition:

Sr. No.	Ingredients	% w/w
1.	Boscalid	35
2.	Azoxystrobin	25
3.	Dispersing agent	10
4.	Wetting agent	3
5.	Inert	23.5
6.	Polymeric surfactant	3.5
	Total	100.00

Boscalid and Azoxystrobin were weighed and then milled together with the listed ingredients in an Air Jet mill to obtain required particle size and the compositions were prepared following the procedure of Example 2. The granules were analyzed by DSC. DSC endothermic peak was observed at: 105.89°C. (Fig. 6).

- 5 Details of various inventive compositions according to the present invention comprising eutectic mixture of boscalid and azoxystrobin are given in Table 4. The compositions were prepared following the procedure of Example 2.

Varied ratios of boscalid and azoxystrobin were used to prepare different formulations. The details of weight ratio of various components are listed in the below table 4:

Table 3 : Inventive compositions according to the present invention comprising a eutectic mixture of boscalid and azoxystrobin.

Example Number	Boscalid % w/w	Azoxystrobin % w/w	dispersing agent % w/w	wetting agent % w/w	Inert % w/w	polymeric surfactant % w/w	Total
4	30	30	7	3	26	4	100
5	40	20	15	5	15	5	100
6	25	35	10	3	23.50	3.5	100
7	20	40	12	5	18	5	100
8	37.5	25	10	3.0	21	3.5	100

Stability of the formulations according to the present invention

- 15 The Boscalid-Azoxystrobin compositions prepared according to the present invention were tested for stability on storage as per BIS specifications. Samples were kept at room temperature (27±2°C) for carrying out real time stability of the formulations. It has been observed by the present inventors that the compositions prepared according to the present invention were stable and no morphological changes were observed for the compositions. DSC of Example 2, after storage for 20 a period of 9 months showed an endothermic peak at 105.3°C corresponding to the eutectic mixture (Figure 8) demonstrating the stability of the composition.

Example 9: A eutectic mixture of Boscalid and Fluoxastrobin according to the present invention was prepared as follows (dry grinding method):

Boscalid and Fluoxastrobin were grinded in different ratios as shown in table 5 in an agate mortar and the mixture was ground thoroughly. The resulting mixture was analyzed by DSC.

Table 5: Boscalid-Fluoxastrobin mixture in different ratios.

Sr. No.	Boscalid mole (%)	Fluoxastrobin mole (%)	Endothermic peak-1 (°C)	Endothermic peak-2 (°C)
1	0	100	110.72	-
2	10	90	99.78	-
3	20	80	98.68	-
4	30	70	97.73	-
5	40	60	98.02	125.35
6	50	50	97.23	127.37
7	60	40	97.81	131.91
8	70	30	97.5	135.2
9	80	20	97.5	138.96
10	90	10	97.2	142.76
11	100	0	145.26	-

Method of detecting a eutectic mixture:

The eutectic mixture was detected by recording DSC.

- 10 The endothermic peak of boscalid was recorded between 144 to 148°C (onset at 144.71, $\Delta H = 83.65$ J/g) [Fig. 1]. The endothermic peak of fluoxastrobin was recorded between 104 to 114°C (onset at 105.82°C, $\Delta H = 72.04$ J/g) [Fig. 9]. The DSC was carried out for mixtures of boscalid: fluoxastrobin in various ratios. The results showed that boscalid: fluoxastrobin in a ratio of 30:70, eutectic mixture was formed showing a single endothermic peak (eutectic point) at 97.7 °C (Fig. 10).

Example 10: A eutectic mixture of Boscalid and Fluoxastrobin according to the present invention was prepared as follows (solvent evaporation method):

Boscalid (1.005 g, 1.02 moles) and Fluoxastrobin (4.029 g, 3.0 moles) are stirred in acetone (20 ml) till dissolution at 50-55 °C and the solution is maintained at this

temperature for 15 min. Solvent is partially evaporated and the concentrated solution is kept aside for 18 h to facilitate crystallization. The crystalline solid was dried under vacuum to obtain 4.9 g of eutectic mixture (Boscalid: Fluoxastrobin:: 25: 75). The crystals were analyzed by DSC. DSC endothermic peak was observed at: 107.5°C. (Fig. 11).

Example 11: A composition comprising a eutectic mixture of boscalid (anhydrate modification II) and Fluoxastrobin according to the present invention has been prepared as follows:

Table 6: Boscalid-Fluoxastrobin WDG composition:

Sr. No.	Ingredients	% w/w
1.	Boscalid	15
2.	Fluoxastrobin	45
3.	Dispersing agent	10
4.	Wetting agent	3
5.	Inert	23.5
6.	Polymeric surfactant	3.5
	Total	100.00

The Boscalid and fluoxastrobin were taken and the compositions were prepared following the procedure of Example 2.

Details of various inventive compositions according to the present invention comprising eutectic mixture of boscalid and fluoxastrobin are given in Table 7. The compositions were prepared following the procedure of Example 2.

Varied ratios of boscalid and fluoxastrobin were used to prepare different formulations. The details of weight ratio of various components are listed in the below table 7:

Table 7: Inventive compositions according to the present invention comprising a eutectic mixture of boscalid and fluoxastrobin

Example Number.	Boscalid % w/w	fluoxastrobin % w/w	dispersing agent % w/w	wetting agent % w/w	Inert % w/w	polymeric surfactant % w/w	Total
12	30	30	7	3	26	4	100
13	10	40	15	5	25	5	100
14	15	35	10	3	32	5	100
15	20	40	12	5	18	5	100
16	25	37.5	10	3	21	3.5	100
17	15	45	10	3	22	5	100
18	45	15	10	3	23.5	3.5	100

Field trial study:

Protocol: Field trials were carried out using the compositions of the eutectic mixture of boscalid and Azoxystrobin prepared according to the present invention as fungicide. The compositions were optionally mixed with other tank mix auxiliaries and applied at an application rate of 500-600 kg/ha to tomato (early blight), Chilli (powdery mildew), Onion (blight), and Grape (Powdery mildew). Dose of commercial conventional formulation of Pyraclostrobin 12.8% + Boscalid 25.2% WG- Visma is 600 ml/h. Dose of commercial conventional formulation of Azoxystrobin 250 SC-Amistar is 562.5 ml/h. Observations after 10 days and 14 days after treatment have been summarized in below tables demonstrating the bio-efficacy of the compositions.

Field Trial: Fungi control study in Tomato (early blight), Chilli (powdery mildew), Onion (blight), and Grape (Powdery mildew).

A formulation comprising eutectic mixture of Boscalid and Azoxystrobin, (Example 2) as well as market sample of Pyraclostrobin+ Boscalid WG (VISMA) and market sample of Azoxystrobin (AMISTAR) for the various dosages were tested for fungus control in Tomato, Chilli, Onion, and Grape. The fungus includes *Alternaria solani* for Tomato, *Leveillula taurica* for Chilli, *Stemphylium vesicarium* for Onion, and *Leveillula taurica* for Grape.

Table 8: % fungi control after application

Treatment	Formulation Rate g, ml/ha	14 days after 3 applications		10 days after 3 applications	
Product		Tomato (early blight)	Chilli (powdery mildew)	Onion (blight)	Grape Powdery mildew
Ex. 2	400	81.6	81.6	83.4	78.0
Ex. 2	500	82.1	84.6	86.0	87.0
Ex. 2	600	88.3	87.0	88.5	89.0
VISMA	600	81.3	81.0	77.9	81.0
AMISTAR	562.5	74.8	77.6	72.2	71.0

From the above results it has been observed that formulations comprising the eutectic mixture of Boscalid and Azoxystrobin prepared according to Example 2 showed good fungus control at lower application rate of 400 kg/ha. It has been noted that at any given rate of application, formulations comprising the eutectic mixture of Boscalid and Azoxystrobin showed higher bio-efficacy and higher consistency compared to VISMA (Pyraclostrobin 12.8% + Boscalid 25.2% WG, commercial sample) and AMISTAR (Azoxystrobin 250 SC, commercial sample). More particularly, it has been observed that formulations comprising the eutectic mixture of Boscalid and Azoxystrobin exhibited better bio-efficacy at a lower application rate of 500.0 kg/ha than VISMA at an application rate of 600 kg/ha and AMISTAR at an application rate of 562.5 kg/ha. Thus, it was concluded that formulations comprising the eutectic mixture Boscalid and Azoxystrobin can be effectively employed as a fungicide at a lower dosage with better bio-efficacy compared to other conventional boscalid and/or strobilurin based formulations.

CLAIMS

1. A Eutectic mixture of boscalid and strobilurin fungicide.
2. The eutectic mixture of claim 1 wherein said strobilurin fungicide is selected
5 from the group comprising azoxystrobin, picoxystrobin, trifloxystrobin and fluoxastrobin.
3. An agrochemical composition comprising eutectic mixture of boscalid and a strobilurin fungicide.
4. An agrochemical composition of claim 3, wherein said composition
10 comprises between 10-90% of boscalid and 90-10% of strobilurin fungicide by weight.
5. An agrochemical composition of claim 3 where the strobilurin fungicide is selected from the group comprising azoxystrobin, picoxystrobin, trifloxystrobin and fluoxastrobin.
- 15 6. A process to prepare a eutectic mixture of boscalid and a strobilurin fungicide said process comprising subjecting boscalid and a strobilurin fungicide to solution crystallization, dry grinding, solvent drop grinding technique, or spray drying technique.
7. A process of claim 6 wherein said process comprising:
20 a. preparing a concentrated solution of boscalid and a strobilurin fungicide in one or more solvents;
b. optionally evaporating said solvent; and
c. triturating or precipitating with an anti-solvent to obtain eutectic mixture.
- 25 8. A process of claim 6 wherein said process comprising:
a. preparing a concentrated solution of boscalid and a strobilurin fungicide in one or more solvents;
b. evaporating said solvent.
9. A process of claim 7 and 8 wherein said solvent is selected from aliphatic
30 alcohols, ketones, esters, ethers, polar protic solvents, polar aprotic

solvents, halogenated solvents, aliphatic hydrocarbon or aromatic hydrocarbon.

10. A process of claim 7 and 8 wherein said anti-solvent is selected from aliphatic or aromatic hydrocarbon solvents.

5 11. A process of claim 6 wherein said process comprising:

- a. admixing boscalid and a strobilurin fungicide;
- b. optionally admixing solvent to said admixture; and
- c. grinding or crushing or milling said admixture to obtain said eutectic mixture.

10 12. A eutectic mixture of boscalid and azoxystrobin.

13. A eutectic mixture of claim 12, wherein said eutectic mixture has an endothermic peak at $103.5 \pm 3^\circ\text{C}$.

14. An agrochemical composition comprising eutectic mixture of boscalid and azoxystrobin.

15 15. An agrochemical composition of claim 14, wherein said composition comprises between 10-90% of boscalid and 90-10% of azoxystrobin by weight.

16. An agrochemical composition of claim 14, wherein said eutectic mixture has an endothermic peak at $103.5 \pm 3^\circ\text{C}$.

20 17. A eutectic mixture of boscalid and fluoxastrobin.

18. A eutectic mixture of claim 17, wherein said eutectic mixture has an endothermic peak at $97 \pm 3^\circ\text{C}$.

19. An agrochemical composition comprising a eutectic mixture of boscalid and fluoxastrobin.

25 20. An agrochemical composition of claim 19, wherein said composition comprises between 10-90% of boscalid and 90-10% of fluoxastrobin by weight.

21. An agrochemical composition of claim 19, wherein said eutectic mixture has an endothermic peak at $97 \pm 3^\circ\text{C}$.

30 22. A process for formulating an agrochemical composition comprising eutectic mixture of boscalid and strobilurin fungicide said process comprising preparing a eutectic mixture of boscalid and a strobilurin fungicide with or

without the addition of agrochemically acceptable excipient and further processing the mixture into a suitable form.

23. A process of claim 22, wherein said agrochemical composition is formulated as a granular composition.

5 24. An agrochemical composition of claim 3, wherein said composition further comprises one or more other active ingredients.

25. An agrochemical composition of claim 24 wherein said active ingredient is a fungicide

10 26. An agrochemical composition of claim 24 wherein said active ingredient is a combination of two or more additional fungicides.

27. An agrochemical composition of claim 25 wherein said fungicide is selected from a multisite contact fungicide, a conazole fungicide and a succinate dehydrogenase inhibitor.

15 28. A method of combating or controlling fungi, said method comprising contacting fungi or their locus with a fungicidally effective amount of composition comprising a eutectic mixture of boscalid and a strobilurin fungicide.

20 29. The method of claim 28 wherein said strobilurin fungicide is selected from the group comprising azoxystrobin, picoxystrobin, trifloxystrobin and fluoxastrobin.

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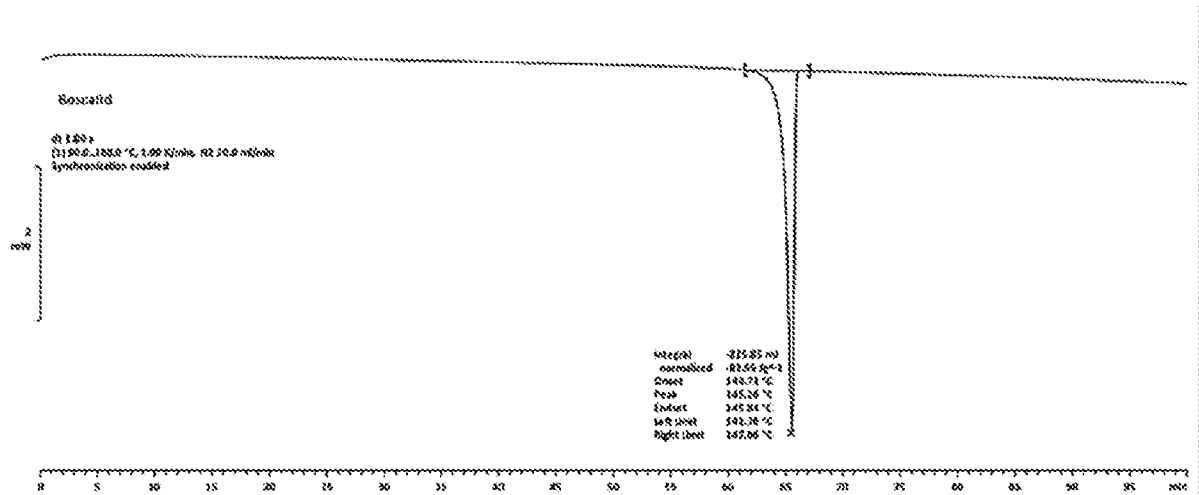


Fig. 1

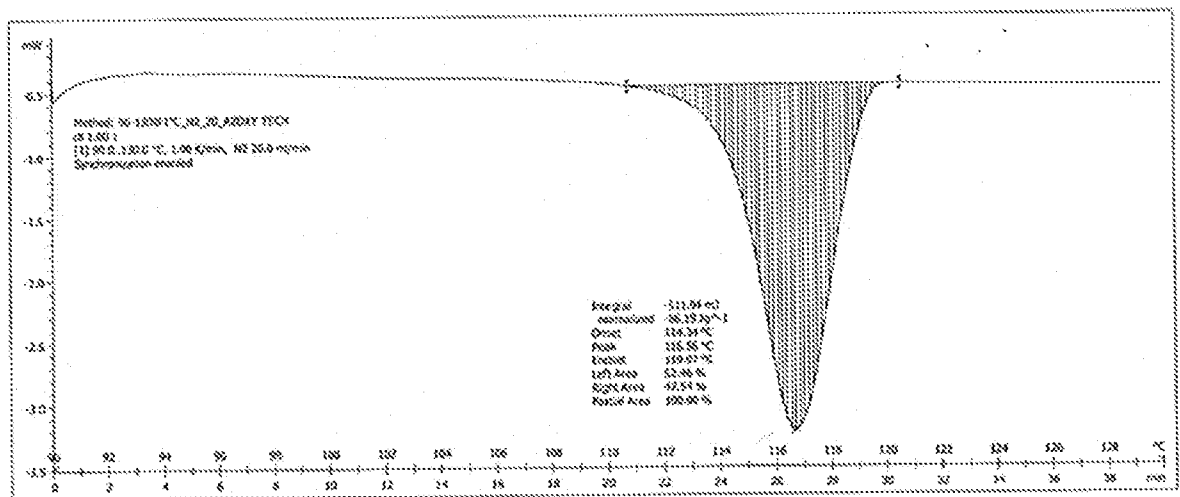


Fig. 2

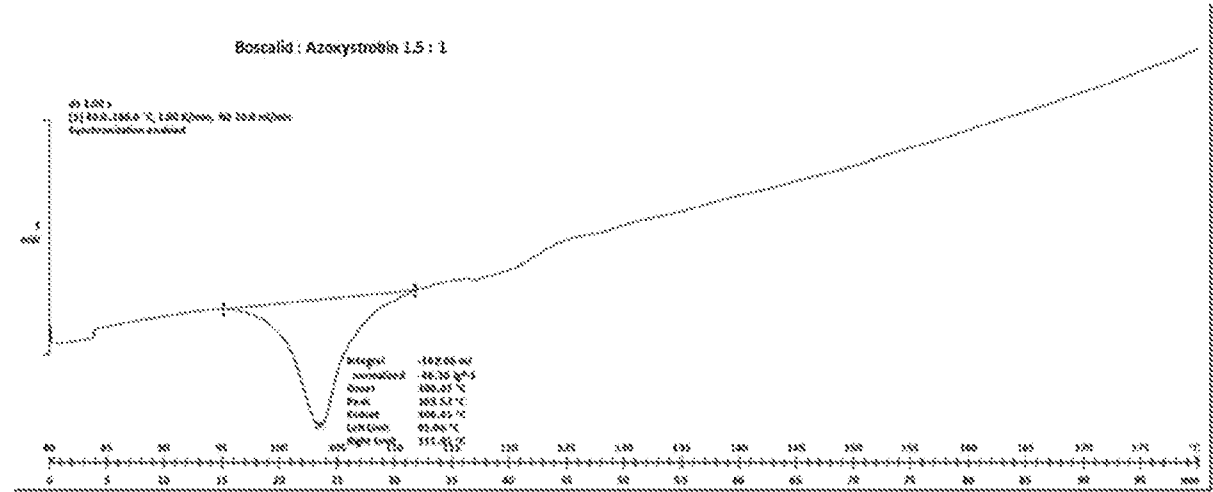


Fig. 3

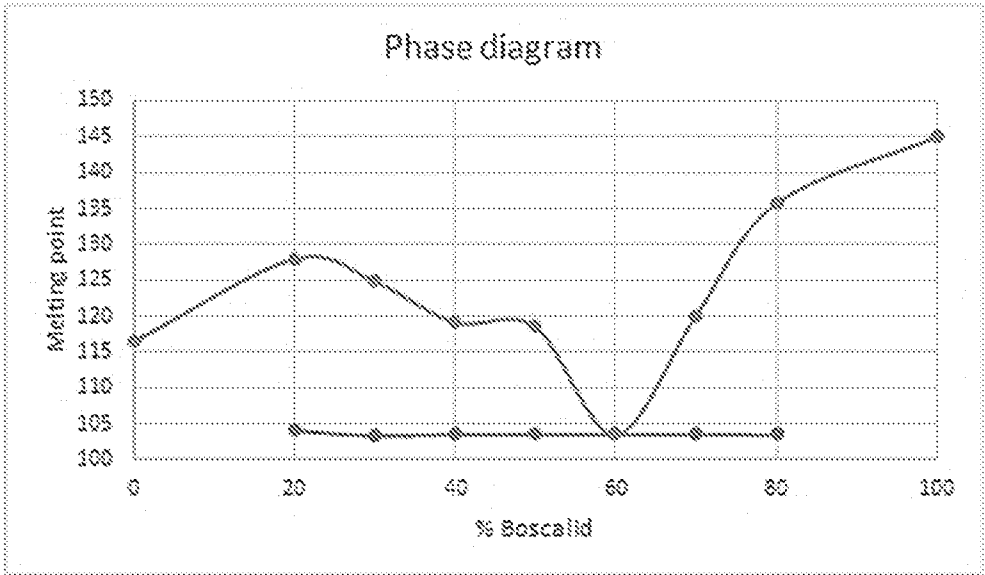


Fig. 4

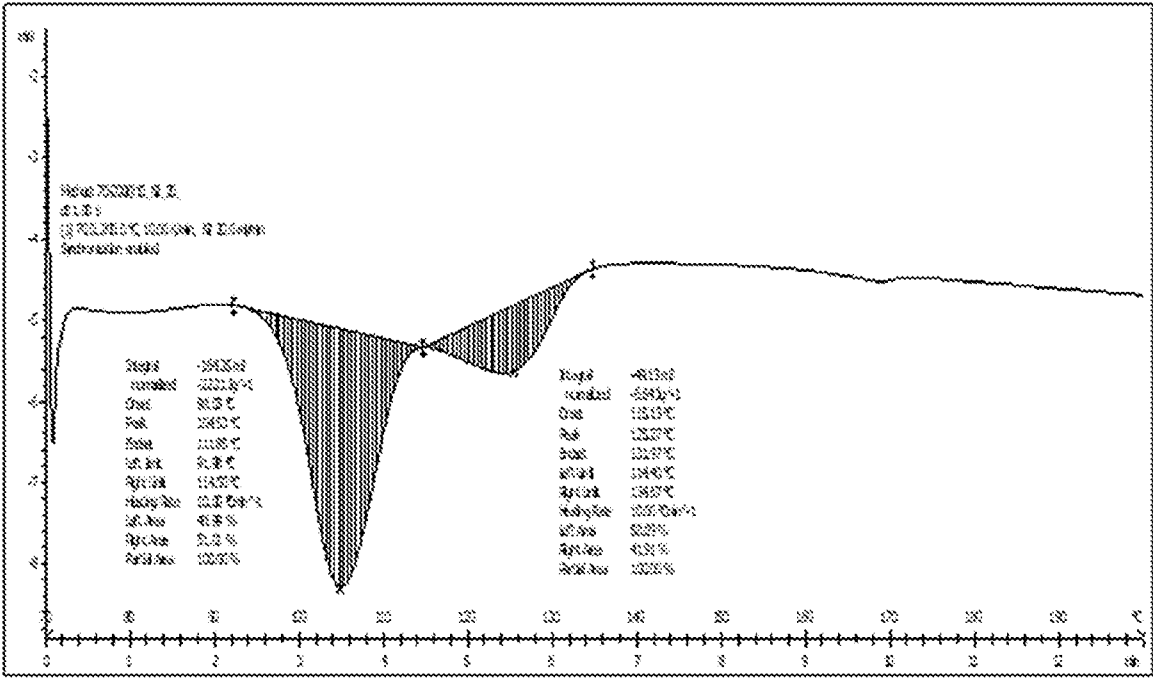


Fig. 5

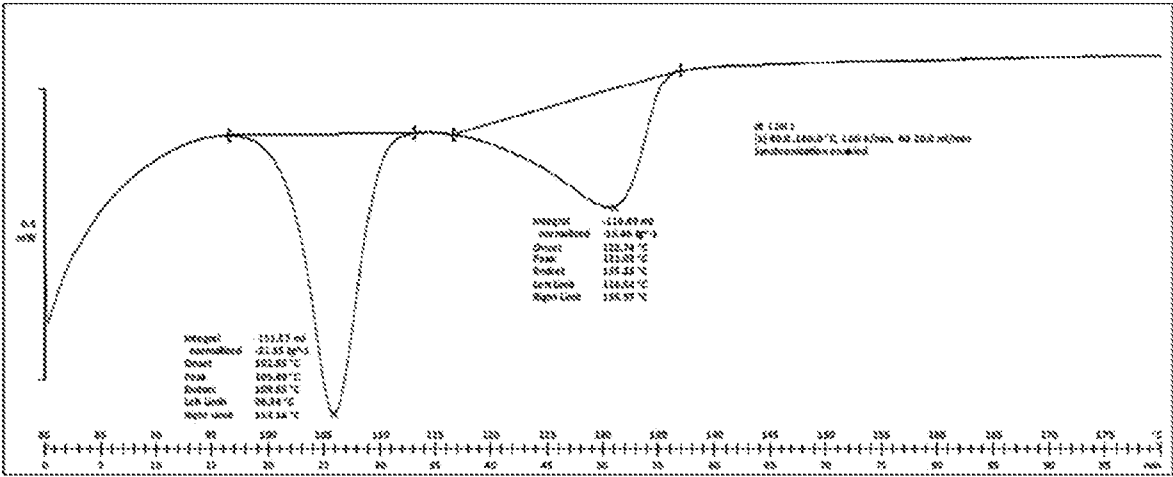


Fig. 6

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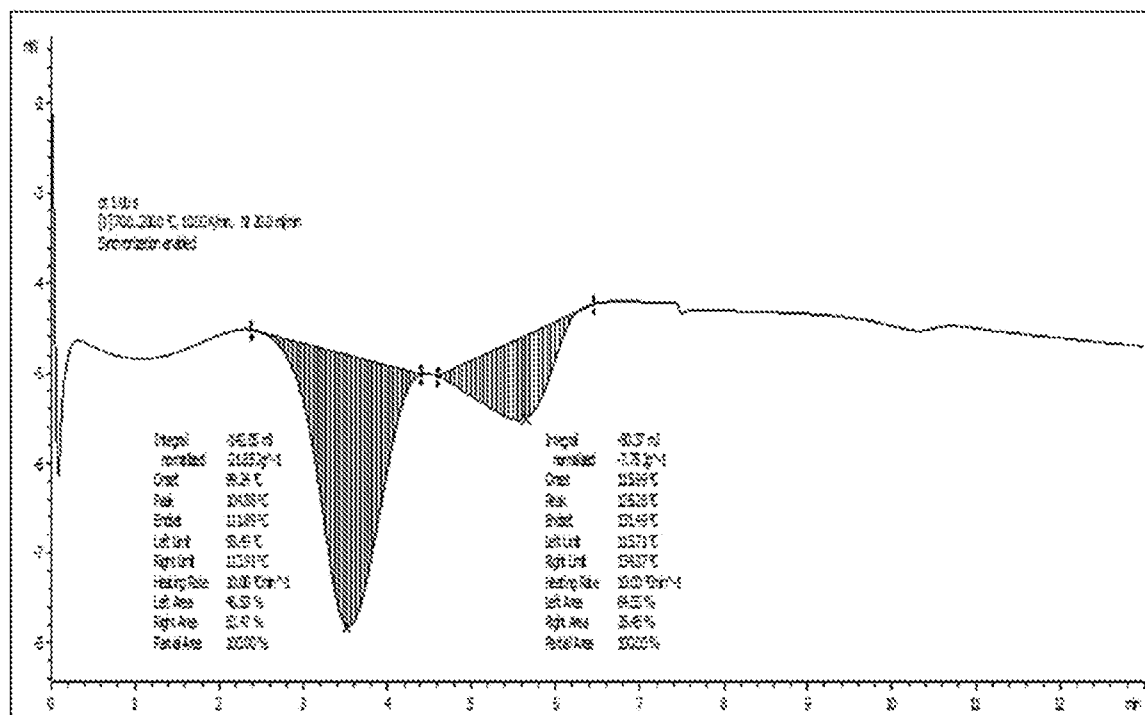


Fig. 7

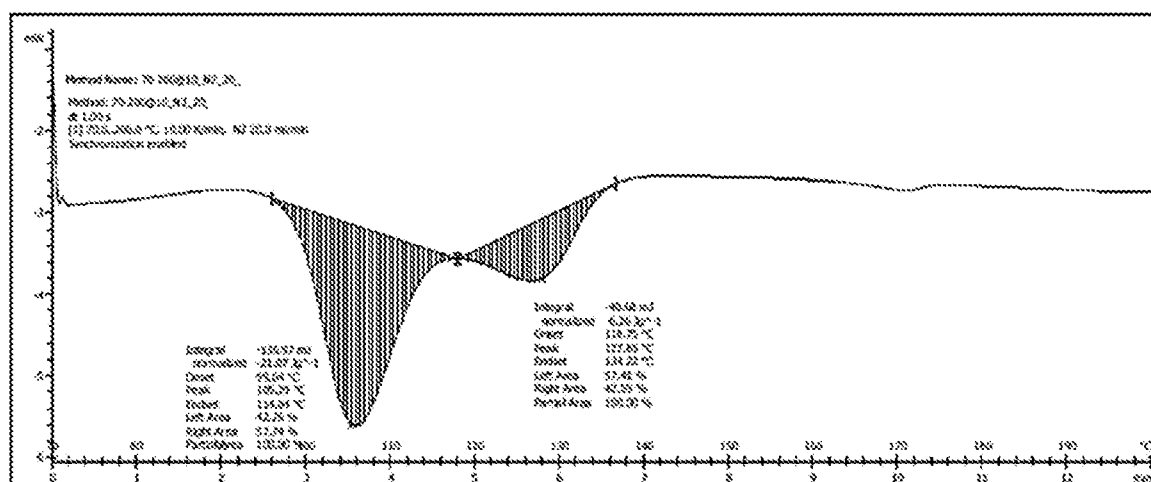


Fig. 8

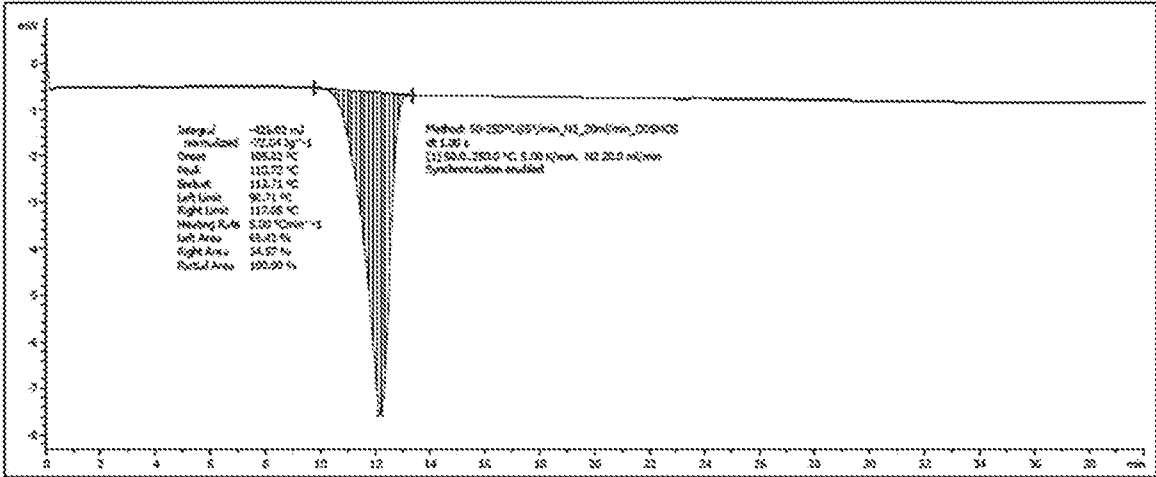


Fig. 9

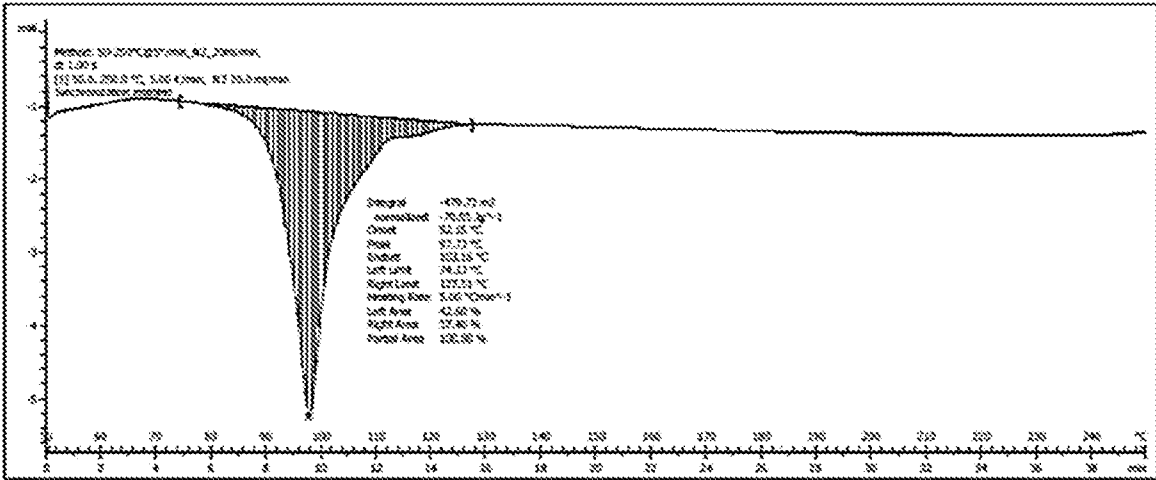


Fig. 10

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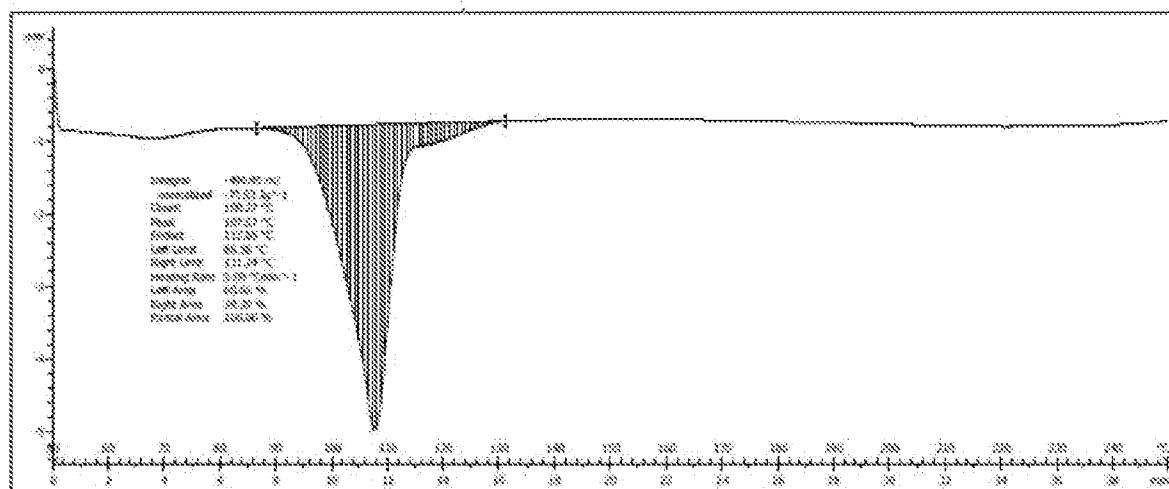


Fig. 11

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/IB2019/055989

A. CLASSIFICATION OF SUBJECT MATTER

A01N 43/54 (2006.01) A01N 43/88 (2006.01) A01N 43/40 (2006.01) A01N 37/50 (2006.01) A01N 25/12 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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

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

Databases: Espacenet, Google Scholar/Patents/Search, PATENW, CAplus, Registry, CABA, CN/JP/KR FULL.

IPC/CPC symbols: A01N (A01N43/54, A01N43/88, A01N43/40, A01N25/12, A01N37/50, A01N23/0000)

Keywords: boscalid, strobilurin, eutectic, azoxystrobin, fluoxastrobin, picoxystrobin, trifloxystrobin, fungicide, agrochemical, melting point, differential scanning calorimetry.

Applicant/Inventor: UPL LTD, Sujata Dhondiram DESAI, Paresh Vithaldas TALATI, Jaidev Rajnikant SHROFF and Vikram Rajnikant SHROFF.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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



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Date of the actual completion of the international search 23 September 2019	Date of mailing of the international search report 23 September 2019
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Stefanie-Ann Zavras, PhD AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832069

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/IB2019/055989
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			

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INTERNATIONAL SEARCH REPORT		International application No.	
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