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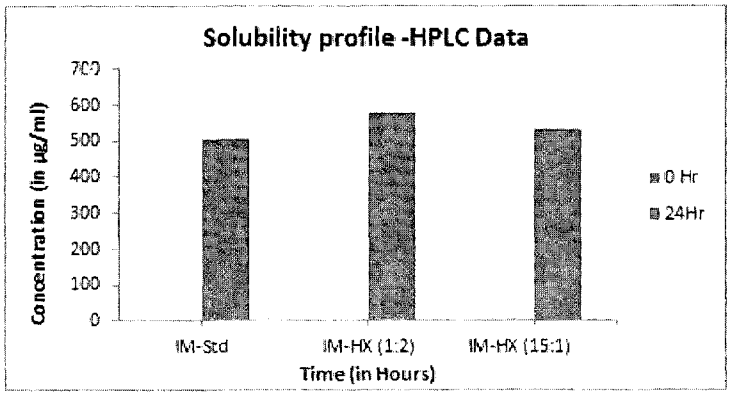

Figure 4

(57) Abstract: A pesticidal formulation comprising a molecular complex of hexaconazole and imidacloprid, having a melting point of around 105 °C measured as a single melting endotherm by differential scanning calorimetry is disclosed. A process for the preparation of a molecular complex of hexaconazole and imidacloprid, is also disclosed.

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A MOLECULAR COMPLEX OF HEXACONAZOLE AND IMIDACLOPRID AND A PROCESS FOR PRODUCTION THEREOF

The present disclosure relates to a molecular complex of hexaconazole and imidacloprid and a process for production thereof.

BACKGROUND

Hexaconazole is a white to off-white crystalline powder having a broad-spectrum fungicidal activity. It is a systemic fungicide that particularly controls ascomycetes and basidiomycetes by inhibiting ergosterol biosynthesis. Hexaconazole rapidly degrades in soil.

Imidacloprid is a systemic insecticide which serves as an insect neurotoxin. This insecticide is effective for controlling aphids, whiteflies, thrips, scales, psyllids, plant bugs and various other harmful pest species in a variety of different crops.

Imidacloprid is colorless crystalline solid with a weak characteristic odor and high water solubility.

Due to its high water solubility imidacloprid rapidly leaches from soil thereby limiting its use for long duration control of soil insects.

Additionally, during storage as water based formulations imidacloprid goes through a series of cycles of solubilization and re-crystallization leading to the generation of large and undesirable particles. These particles cause problems such as blockage of spray nozzles during application of the product. In addition, due to the solubilization and recrystallisation it is difficult to maintain imidacloprid products as a homogeneous

formulation that leads to issues during transfer to dilution tanks and in ensuring correct concentration of imidacloprid on dilution.

In agriculture there is a need for a single formulation that when applied can effectively control both the insect and fungal pests for long durations. Such formulations should be stable, have better hydrolytic stability and reduced water solubility.

SUMMARY

A pesticidal formulation is disclosed. The pesticidal formulation comprises a molecular complex of hexaconazole and imidacloprid, having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

A process for preparing a molecular complex of hexaconazole and imidacloprid is disclosed. The process comprises mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture; melting the dry mixture; and cooling the melted mixture followed by grinding to obtain a molecular complex of hexaconazole and imidacloprid having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

A process for preparing a molecular complex of hexaconazole and imidacloprid is also disclosed in accordance with another embodiment. The process comprises mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture; adding a solvent to the dry mixture followed by grinding to obtain a wet mixture; and air drying the wet mixture to obtain the molecular complex having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

BRIEF DESCRIPTION OF ACCOMPANYING FIGURES

Figure 1 illustrates a comparison Powder X-ray Diffraction (PXRD) profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid.

Figure 2 illustrates the comparison Differential Scanning Calorimetric (DSC) profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid.

Figure 3 illustrates the comparison Fourier Transformed Infrared Spectra (FT-IR) profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid.

Figure 4 illustrates the solubility profile HPLC data of samples of imidacloprid, and molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid.

Figure 5 illustrates the degradation profile – HPLC data of samples of imidacloprid, and molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid.

DETAILED DESCRIPTION

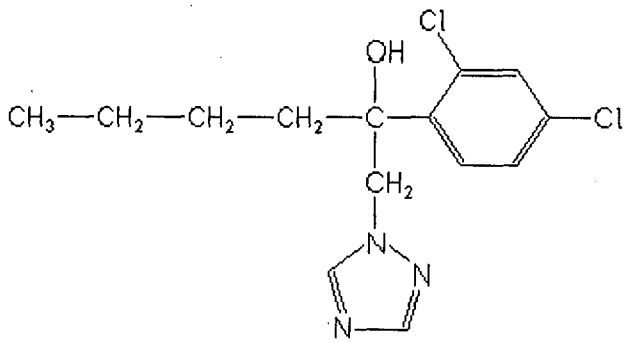
For the purpose of promoting an understanding of the principles of the invention, reference will now be made to embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the disclosed process, and such further applications of the principles of the invention therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

It will be understood by those skilled in the art that the foregoing general description and the following detailed description are exemplary and explanatory of the invention and are not intended to be restrictive thereof.

Reference throughout this specification to "one embodiment" "an embodiment" or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrase "in one embodiment", "in an embodiment" and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

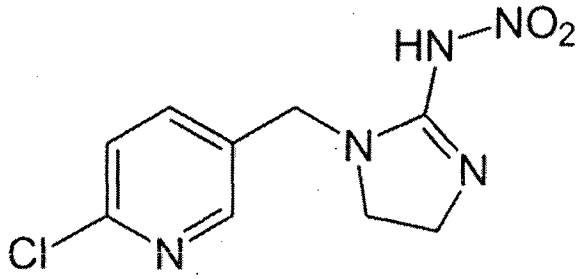
The disclosure relates to a pesticidal formulation. The pesticidal formulation comprises a molecular complex of hexaconazole and imidacloprid. "Molecular complex" herein refers to a substance in a solid form or solid formulations, which comprises at least two pure substances which interact with each other through hydrogen bonding or any other non covalent interactions to form molecular complex including co-crystals, solvates, hydrates or eutectic combinations or solid solutions, in which at least one of the pure substance is present in the solid form.

Hexaconazole refers to all polymorphs, solvates, and hydrates of the substance having the formula (I):



(I)

Imidacloprid refers to all polymorphs, solvates, and hydrates of the substance having the formula (II):



(II)

The melting point of the molecular complex of hexaconazole and imidacloprid measured as a single melting endotherm by differential scanning calorimetry is around 105 °C.

In accordance with an aspect, the molar ratio of imidacloprid to hexaconazole in the molecular complex of hexaconazole and imidacloprid is in a range of 1:20 to 20:1 and preferably in a range of 2:1 to 8:1.

In accordance with an aspect, suitable amounts of hexaconazole and imidacloprid may be added to the pesticidal formulation.

The present disclosure also provides a method for producing the molecular complex of hexaconazole and imidacloprid.

The process comprises of preparing a mixture of hexaconazole and imidacloprid in required stoichiometric ratios, grinding the mixture, melting the ground mixture by heating, cooling the melted mixture and grinding it to obtain molecular complex of hexaconazole and imidacloprid. In accordance with an embodiment the ground mixture is melted by heating it at 100 to 110°C. The melting may be carried out under an inert atmosphere.

In accordance with an alternate embodiment, the process comprises of admixing hexaconazole and imidacloprid to form a dry mixture, grinding said dry mixture for a predetermined period of time, adding to the ground dry mixture a solvent to obtain a wet mixture, grinding the wet mixture and air drying the same to obtain the molecular complex of hexaconazole with imidacloprid. The grinding of the dry mixture may be carried out for 15 to 20 minutes.

By way of an alternate embodiment, the process comprises of admixing hexaconazole and imidacloprid to form a dry mixture, grinding said dry mixture for a predetermined period of time, adding to the ground dry mixture a solvent and grinding the same to obtain a wet mixture, heating the wet mixture, transferring the heated wet mixture to a glass vessel and air drying to obtain molecular complex of hexaconazole with imidacloprid. The heating may be carried out at a temperature around 100°C for 10 minutes. The heating may be carried out under nitrogen atmosphere.

The grinding of the dry mixture may be carried out for 15 to 20 minutes. The grinding of the wet mixture may be carried out for 30 minutes.

The grinding may be carried out in any suitable apparatus for grinding solids. Such apparatus includes but is not limited to mortar mills, vibrator mills or ball mills.

In accordance with an embodiment the solvent is any suitable solvent including but not limited to acetonitrile, ethanol, methanol, ethyl acetate, acetone or their mixture. The amount of solvent added is in a range of 0.1 ml to 5 ml per 1 gram of combined weight of hexaconazole and imidacloprid.

In accordance with an aspect, hexaconazole and imidacloprid are mixed in a molar ratio of 1:20 to 20:1 and preferably in a ratio of 2:1 to 8:1.

EXAMPLES

Example 1

Hexaconazole and imidacloprid are weighed in a 2:1 to 8:1 molar ratios for different experiments and ground using mortar pestle for 15 minutes followed melting under inert atmosphere at around 100 to 110°C and subsequently cooled to room temperature and ground to finer particles to obtain molecular complex of hexaconazole and imidacloprid.

Example 2: Powder X-ray Diffraction

Technical Details:

Powder X-ray Diffraction (PXRD) profiles were obtained from 5 to 10 mg of lightly ground samples obtained from Example 1 placed over Zero background silica flat sample stage. X-ray diffraction data was collected on a PANalytical "X"pertPRO diffractometer on a Copper source (Kα – 1.5418) powered by 40kV and 30mA with a proportional counter radiation detector. Samples include molecular complex of hexaconazole and imidacloprid having hexaconazole and imidacloprid in molar ratios of 2:1, 4:1, 6:1 and 8: 1. Data collection was done with step size 0.020°, 0.50 second per step over 5-70 ° 2θ. Data was analyzed using Xpert Viewer software. PXRD profile data presented for the region where significant peaks were observed.

Analysis:

Molecular complexes of hexaconazole and imidacloprid gave different PXRD profile than pure hexaconazole and imidacloprid. Overall pattern shows molecular complexes adopt similar profile as hexaconazole with some shifting in diffraction peaks. Figure 1, illustrates a comparison PXRD profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid along with pure hexaconazole and imidacloprid.

Example 3: Differential Scanning Calorimetry

Technical Details:

Differential Scanning Calorimetric (DSC) thermograms of samples from Example 1 were recorded on a Mettler DSC1 instrument. Samples include molecular complexes of hexaconazole and imidacloprid having hexaconazole and imidacloprid in molar ratios of 2:1, 4:1, 6:1 and 8: 1. The thermal behavior of the samples, placed in vented aluminum pans, was studied under nitrogen purge with a heating rate of 10 °C per minute covering the temperature range 30 °C to 300 °C.

Analysis:

Molecular complexes of hexaconazole with imidacloprid gave completely different DSC profile with a melting endotherm at approximately 105 °C than hexaconazole (having melting point of 111 °C) and imidacloprid (having melting point of 142 °C). Figure 2, illustrates the comparison DSC profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and imidacloprid along with pure hexaconazole and imidacloprid.

Example 3: Infrared Spectroscopy

Technical Details:

Fourier transformed infrared spectra (FT-IR) were collected on a Bruker Vertex 70 model. The samples were mixed with potassium bromide (KBr) and data was collected in the spectral range 400-4000 cm^{-1} with an average of 512 scan of 2 cm^{-1} resolution. Samples include molecular complexes of hexaconazole and imidacloprid having hexaconazole and imidacloprid in molar ratios of 2:1, 4:1, 6:1 and 8: 1. **Figure 3** illustrates the comparison IR profile of various samples of molecular complex of hexaconazole and imidacloprid having different molar ratios of hexaconazole and

imidacloprid along with pure hexaconazole and imidacloprid. H denotes Hexaconazole and I denotes Imidacloprid in figure 3.

Analysis:

FT-IR spectra of various molecular complex obtained from examples 1 were compared with hexaconazole and imidacloprid individually and it was found that there are significant changes in IR spectral band of functional group regions to confirm the formation novel molecular complex.

Solubility study

Solubility study was conducted on following molecular complexes.

- Imidacloprid Standard. (IM)
- Molecular complex of Imidacloprid and Hexaconazole -1:2 [IM:HX (1:2)]
- Molecular complex of imidacloprid and Hexaconazole - 15:1 [IM:HX (15:1)]

Pouch of approximately 1gm of each molecular complex was prepared and these samples were immersed into the glass beakers containing 150ml of distilled water (DW). All samples were continuous stirring for 24 hours. After specified time intervals, the samples were withdrawn and filtered through 0.45μ filters. Filtrate was then diluted 10 times with distilled water and injected to HPLC. Solubility was determined by calculating Area under curve (AUC) obtained by HPLC at λmax 270nm. Figure 4 illustrates the HPLC data obtained.

HPLC method: A Waters 717plus autosampler with UV-2487 detector system was used. Experimental conditions used were Column: C-18 (30X2.1 mm); particle size: 1.5μm; (Merck, Purospher); flow rate: 1ml per minute; mobile phase: Water: Acetonitrile (60:40), injection volume: 10μL. A binary gradient system was used as the elution for imidacloprid was obtained on time gradient method. A UV-Vis detector was used on dual wavelength at

270nm and 230nm. Samples were run for 10 minutes as Imidacloprid has retention time in the time window of 5.6-5.9 minutes.

The HPLC profile of solubility of Imidacloprid of individual molecular complexes is as follows-

The Area under the curve data at λmax 270nm

Sr. no.	Sample name	0 hr	24 hr
1	IM	0	2985463
2	IM:HX (1:2)	0	3414035
3	IM:HX (15:1)	0	3159192

Amount of Imidacloprid (µg/ml)

Sr. no.	Sample name	0 hr	24 hr
1	IM	0	506.3
2	IM:HX (1:2)	0	577.7
3	IM:HX (15:1)	0	535.2

Degradation profile

Solubility study was conducted for the following molecular complexes.

- Imidacloprid Standard. (IM)
- Molecular complex of Imidacloprid and Hexaconazole -1:2 [IM:HX (1:2)]
- Molecular complex of imidacloprid and Hexaconazole - 15:1 [IM:HX (15:1)]

Approximately 1mg of each molecular complex was dissolved in 10ml of water, and filtered through 0.45µ filters. The filtrate was then diluted by adding 10 ml of water. These samples were then incubated at 40°C for 10 minutes in a water bath. All samples were

made completely soluble in water and used to determine degradation kinetics study up to 24 hours. The samples were withdrawn immediately for initial reading (0 hour reading) and after 24 hours of UV exposure and analysed by HPLC. Degradation was determined by calculating Area under curve (AUC) obtained by HPLC at λmax 270nm using the following formula:

%degradation = [(AUC at 0hour-AUC at 24hour)/AUC at 0hr]*100

A waters 717plus autosampler with UV-2487 detector system was used. Experimental conditions used were – Column: C-18 (30X2.1 mm); particle size: 1.5µm; (Merck, Purospher); flow rate: 1ml/min; mobile phase: Water:Acetonitrile (60:40), injection volume: 10µL. Binary gradient system was used as the elution for imidacloprid was obtained on time gradient method. A UV-Vis detector was used on dual wavelength at 270nm and 230nm. Samples were run for 10 minutes as Imidacloprid has a retention time in the time window of 5.6-5.9 minutes.

The HPLC profile of solubility of Imidacloprid from individual molecular complexes is as follows-

AUC at λmax 270nm

Sr. no.	Sample name	0 hr	24 hr
1	Imidacloprid Std	13017467	12797698
2	Imidacloprid and Hexaconazole complex (1:2)	13148026	13030977
3	Imidacloprid and Hexaconazole complex (15:1)	12623959	12377634

Degradation of Imidacloprid

Sr. no.	Sample name	%degradation
1	Imidacloprid Std	1.69
2	Imidacloprid and Hexaconazole complex (1:2)	0.89
3	Imidacloprid and Hexaconazole complex (15:1)	1.95

It is observed that molecular complex of Imidacloprid and Hexaconazole in a 1:2 ratio has better stability than pure Imidacloprid.

Specific Embodiments are disclosed below:

A pesticidal formulation comprising a molecular complex of hexaconazole and imidacloprid, having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

Such pesticidal formulation(s), wherein hexaconazole and imidacloprid in the molecular complex are in a stoichiometric ratio in a range of 1:20 to 20:1.

Such pesticidal formulation(s), wherein hexaconazole and imidacloprid in the molecular complex are in a stoichiometric ratio in a range of 2:1 to 8:1.

Further specific embodiments are disclosed below:

A process for preparing a molecular complex of hexaconazole and imidacloprid, the process comprising: mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture; melting the dry

mixture; and cooling the melted mixture followed by grinding to obtain a molecular complex of hexaconazole and imidacloprid having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

Further specific embodiments are disclosed below:

A process for preparing a molecular complex of hexaconazole and imidacloprid, the process comprising mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture; adding a solvent to the dry mixture followed by grinding to obtain a wet mixture; and air drying the wet mixture to obtain the molecular complex having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

Such process(s), wherein the process further comprises heating the wet mixture at about 100°C prior to air drying.

Such process(s), wherein the wet mixture is heated under a nitrogen atmosphere.

Such process(s), wherein the solvent is added to the dry mixture in a range of 0.5 ml to 10 ml with respect to each gram of combined weight of hexaconazole and imidacloprid.

Such process(s), wherein the solvent is selected from acetonitrile, ethanol and mixtures thereof.

INDUSTRTICAL APPLICABILITY

The molecular complex of hexaconazole and imidacloprid as disclosed provide broad spectrum of control on both insect and fungal for a longer duration. Additionally, the molecular complexes of hexaconazole and imidacloprid have better hydrolytic stability as compared to commercially available versions of hexaconazole and imidacloprid.

WE CLAIM:

1. A pesticidal formulation comprising a molecular complex of hexaconazole and imidacloprid, having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

2. A pesticidal formulation as claimed in claim 1, wherein hexaconazole and imidacloprid in the molecular complex are in a stoichiometric ratio in a range of 1:20 to 20:1.

3. A pesticidal formulation as claimed in claim 1, wherein hexaconazole and imidacloprid in the molecular complex are in a stoichiometric ratio in a range of 2:1 to 8:1.

4. A process for preparing a molecular complex of hexaconazole and imidacloprid, the process comprising:

mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture;

melting the dry mixture; and

cooling the melted mixture followed by grinding to obtain a molecular complex of hexaconazole and imidacloprid having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

5. A process for preparing a molecular complex of hexaconazole and imidacloprid, the process comprising:

mixing hexaconazole and imidacloprid in a stoichiometric ratio in a range of 1:20 to 20:1, followed by grinding to obtain a dry mixture;

adding a solvent to the dry mixture followed by grinding to obtain a wet mixture; and

air drying the wet mixture to obtain the molecular complex having a melting point of around 105°C measured as a single melting endotherm by differential scanning calorimetry.

6. A process as claimed in claim 5, wherein the process further comprises heating the wet mixture at about 100°C prior to air drying.

7. A process as claimed in claim 6, wherein the wet mixture is heated under a nitrogen atmosphere.

8. A process as claimed in claim 5, wherein the solvent is added to the dry mixture in a range of 0.5 ml to 10 ml with respect to each gram of combined weight of hexaconazole and imidacloprid.

9. A process as claimed in claim 5, wherein the solvent is selected from acetonitrile, ethanol and mixtures thereof.

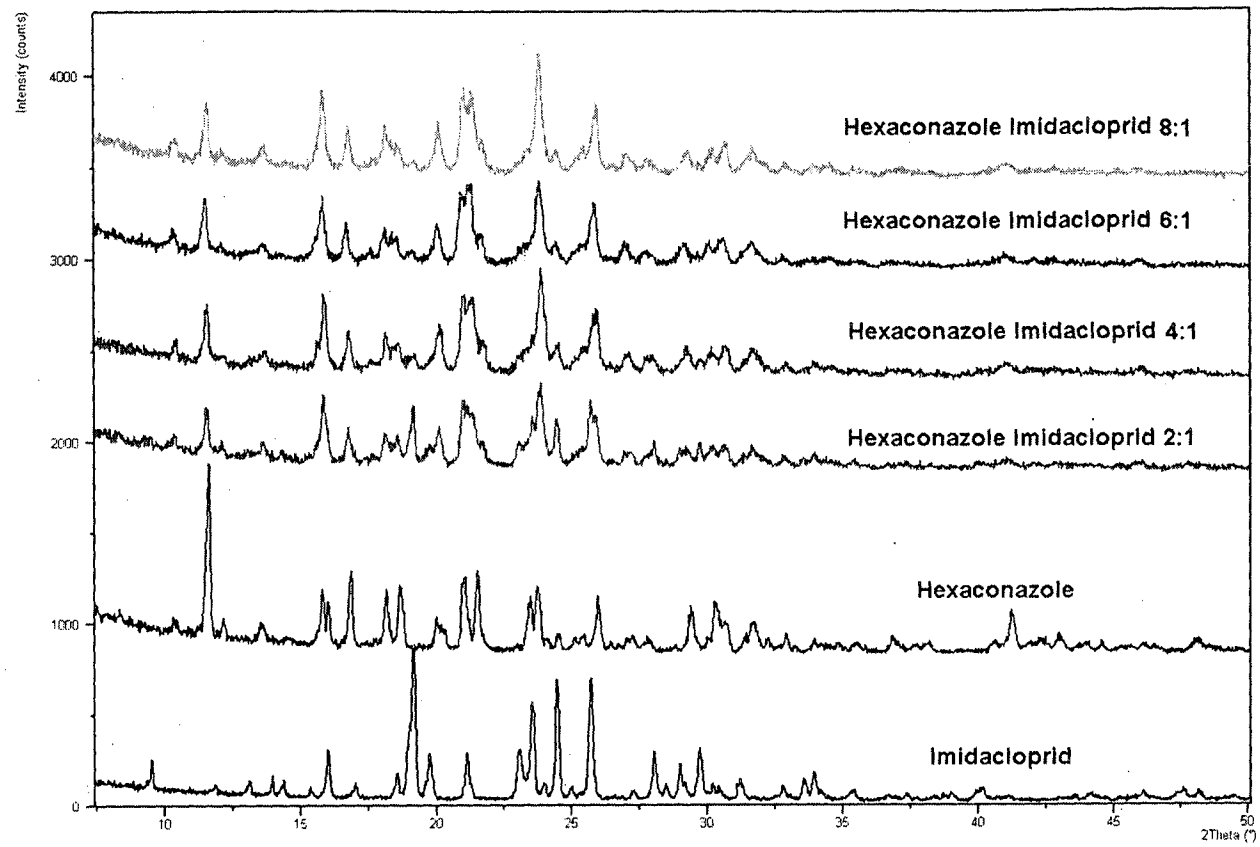

Intensity (counts)
4000
3000
2000
1000
0
Hexaconazole Imidacloprid 8:1
Hexaconazole Imidacloprid 6:1
Hexaconazole Imidacloprid 4:1
Hexaconazole Imidacloprid 2:1
Hexaconazole
Imidacloprid
10
15
20
25
30
35
40
45
50
2Theta (°)

Figure 1

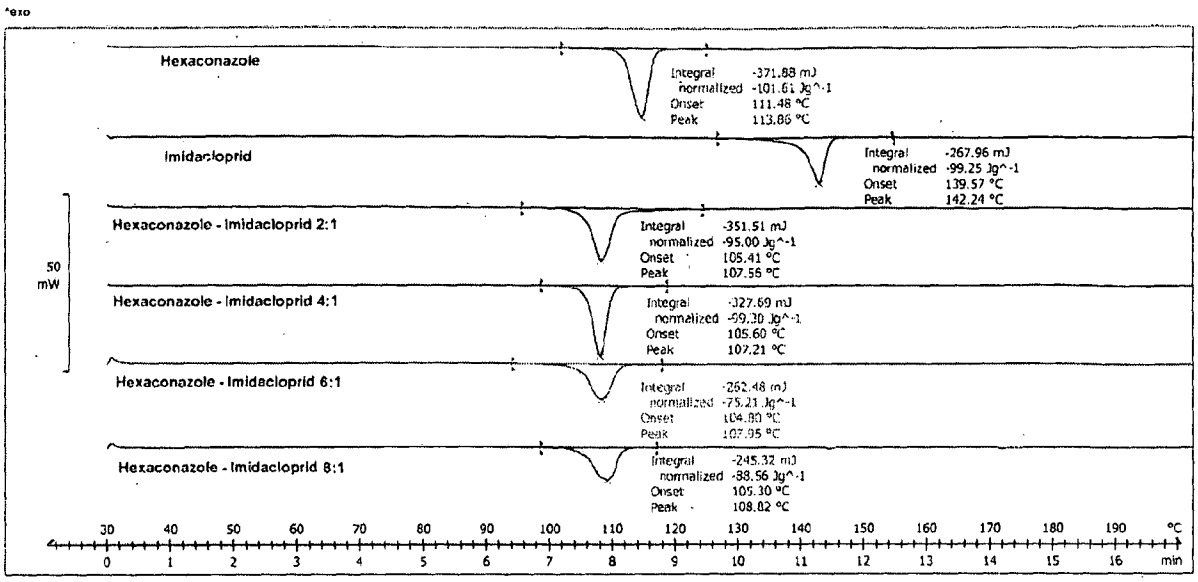

exo
Hexaconazole
Integral -371.88 mJ
normalized -101.61 Jg^-1
Onset 111.48 °C
Peak 113.86 °C
Imidacloprid
Integral -267.96 mJ
normalized -99.25 Jg^-1
Onset 139.57 °C
Peak 142.24 °C
Hexaconazole - Imidacloprid 2:1
Integral -351.51 mJ
normalized -95.00 Jg^-1
Onset 105.41 °C
Peak 107.56 °C
50 mW
Hexaconazole - Imidacloprid 4:1
Integral -327.69 mJ
normalized -99.30 Jg^-1
Onset 105.60 °C
Peak 107.21 °C
Hexaconazole - Imidacloprid 6:1
Integral -262.48 mJ
normalized -75.21 Jg^-1
Onset 104.80 °C
Peak 107.95 °C
Hexaconazole - Imidacloprid 8:1
Integral -245.32 mJ
normalized -88.56 Jg^-1
Onset 105.30 °C
Peak 108.82 °C
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 °C
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 min

Figure 2

5

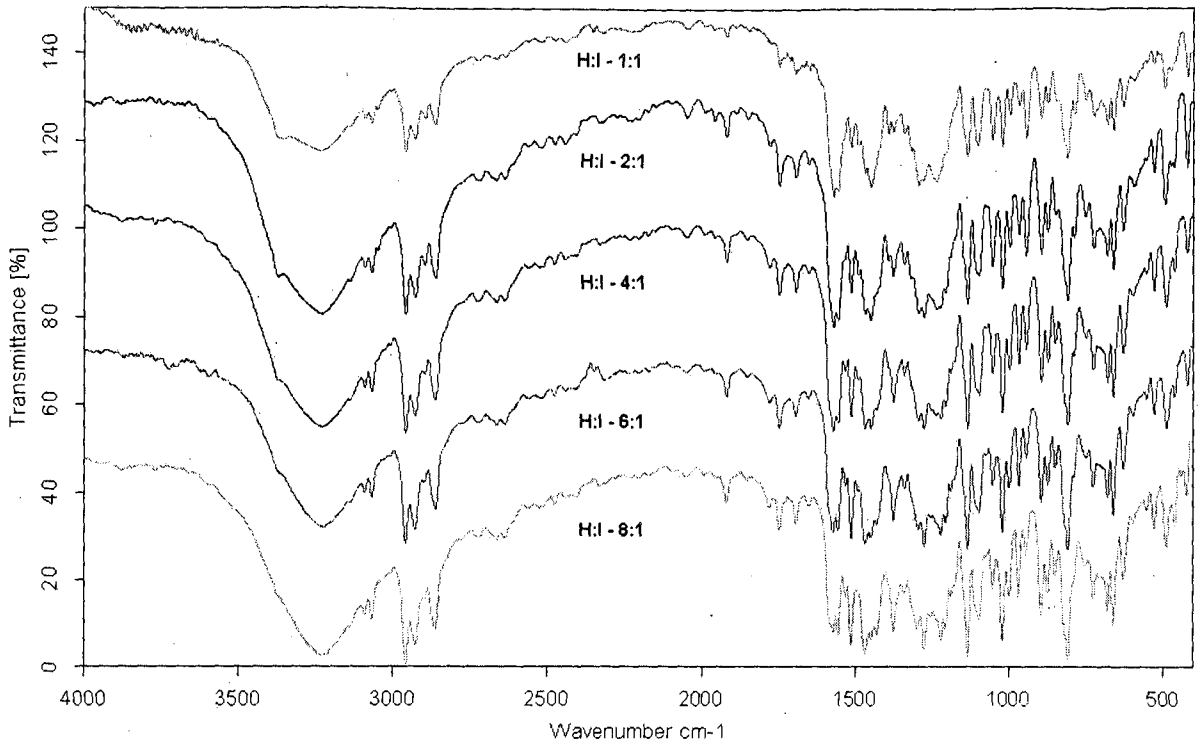


Figure 3.

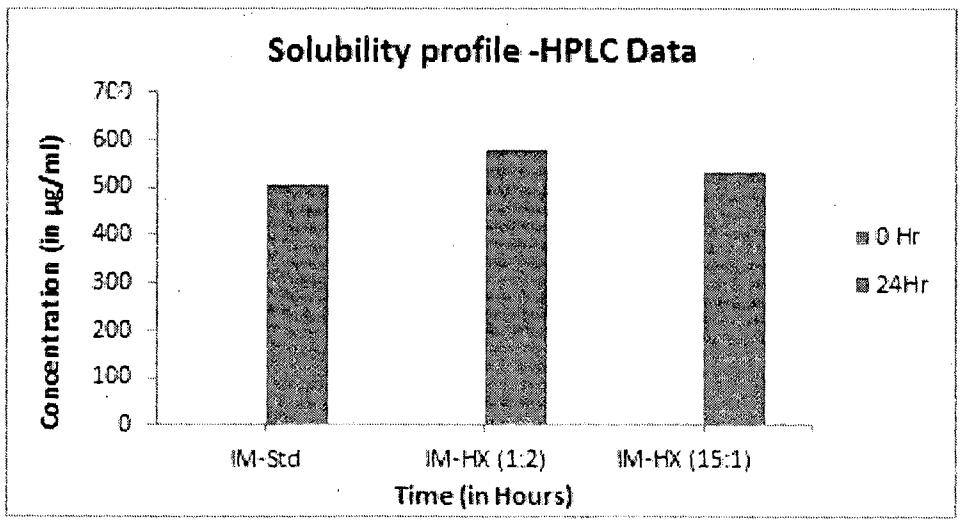


Figure 4

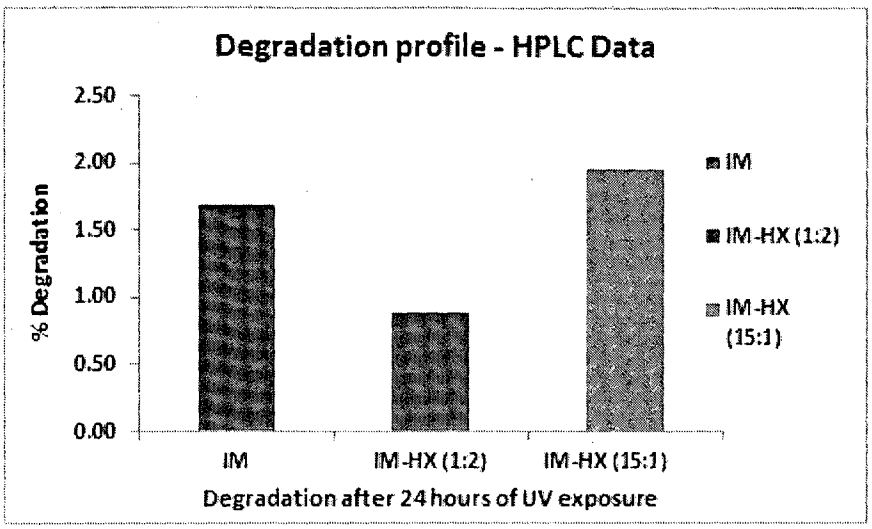

Degradation profile - HPLC Data
2.50
2.00
1.50
1.00
0.50
0.00
% Degradation
IM
IM-HX (1:2)
IM-HX (15:1)
IM-HX (1:2)
IM-HX (15:1)
Degradation after 24 hours of UV exposure

Figure 5

5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/002438

A. CLASSIFICATION OF SUBJECT MATTER
A01N37/00 Version=2014.01

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

IPO INTERNAL,PATSER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US2008274882 (A1) 2008-11-06; BAYER CROPSCIENCE AG[DE] + (BAYER CROPSCIENCE AG) Claim-1 and page: 7	1-9
Y	WO2008003738 (A1) 2008-01-10; BAYER CROPSCIENCE AG[DE]; Claims 10-12 pages: 47-49	1-9
Y	US5972971 (A) 1999-10-26; BAYER AG[DE] + (BAYER AKTIENGESELLSCHAFT) Claims 10 and 11; pages: 10	1-9

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

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Date of the actual completion of the international search	Date of mailing of the international search report
23-03-2015	23-03-2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2014/002438

Citation	Pub.Date	Family	Pub.Date
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