(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 July 2020 (30.07.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/152592 A1

(51) International Patent Classification:
C07D 401/06 (2006.01) *C07B 63/00* (2006.01)

(21) International Application Number:
PCT/IB2020/050480

(22) International Filing Date:
22 January 2020 (22.01.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201931002861 23 January 2019 (23.01.2019) IN

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

(54) **Title:** PROCESS FOR PREPARATION OF IMIDACLOPRID POLYMORPH FORM I

(57) **Abstract:** The present invention relates to process for preparation of Form I polymorph of 1-[(6- chloro-3-pyridyl) methyl]-N-nitroimidazolidin-2-ylideneamine (imidacloprid). In particular the present invention relates to process for preparation of Form I of imidacloprid containing dimer impurity ≤ 0.5%.

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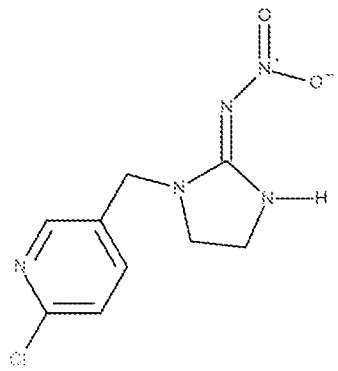
PROCESS FOR PREPARATION OF IMIDACLOPRID POLYMORPH FORM I

Field of the innovation

The present invention relates to process for preparation of polymorph of 1-[(6-chloro-3-pyridyl) methyl]-*N*-nitroimidazolidin-2-ylideneamine (imidacloprid). In particular the present invention relates to process for preparation of Form I of imidacloprid.

Background of the invention

Imidacloprid also known as 1-[(6-chloro-3-pyridyl) methyl]-*N*-nitroimidazolidin-2-ylideneamine represented by formula 1, is a neonicotinoid insecticide used to control sucking insects, termites, some soil insects, and fleas on pets.



It is a broad-spectrum insect neurotoxin with high efficiency and low residue.

US6818769 disclose a process for preparation of heterocyclic diamine single-sided condensation products. This patent also discloses a di-condensation by-product (dimer compound). The process disclosed in this patent can improve yield, minimize double-sided condensation byproduct, and produce high-quality product

It has been known that imidacloprid exists in two polymorphic forms of which Form I is thermodynamically stable form and Form II is metastable form (Org. Process Res. Dev. 2013, Vol. 17, Pg. No. 375−381).

Inventors of the present invention found that impurities affect the selective formation of desired polymorphic form. It was observed by the inventors that, the presence of impurities such as dimer compound inhibits formation of the imidacloprid polymorph Form I and leads to formation of metastable form (imidacloprid polymorph Form II) and ultimately results in formation of mixture of imidacloprid polymorph Form I and imidacloprid polymorph Form II. Hence, there is an urgent and unmet need of an efficient process for selectively preparing imidacloprid polymorph Form I.

Objects of the invention

It is an object of the present invention to reduce the content of dimer and unreacted reactants present as impurities in imidacloprid.

It is another object of the present invention to provide a process for preparation of pure a crystalline form of Imidacloprid polymorph.

Yet another object of the present invention is to provide a process for purification and selective formation of imidacloprid polymorph Form I.

Thus, the object of the present invention is to prepare Form I of Imidacloprid characterized by a melting point of 145.23 ±2°C, determined by differential scanning calorimetry (DSC) of figure 1.

Summary of the invention

In an aspect of the present invention there is provided a process for preparation of imidacloprid Form I.

In another aspect the process for preparation of imidacloprid Form I comprising

a) Refinement of imidacloprid and
b) selective crystallisation of imidacloprid polymorph Form I

The present invention provides a process for selectively preparing imidacloprid Form I by selective crystallisation of imidacloprid Form I and reducing the impurity content wherein said impurity comprise a compound represented by formula (2) referred herein as dimer impurity.

In another aspect the present invention provides a process for preparing imidacloprid Form I comprising:

step-1:

a) dissolving Imidacloprid in an organic solvent;
b) cooling the solution at a predetermined rate; and
c) effecting crystallization resulting in imidacloprid having substantially less impurities

step-2:

a) dissolving Imidacloprid obtained from the step-1, in an organic solvent;
b) cooling the solution at a predetermined rate; and
c) effecting crystallization resulting in imidacloprid polymorph Form I

Further there is provided a process for selectively preparing imidacloprid polymorph Form I said process comprising the steps of:

a) dissolving Imidacloprid having impurities ≤0.5% in an organic solvent;
b) cooling the solution at a predetermined rate; and
c) effecting crystallization resulting in imidacloprid polymorph Form I

The present invention also provides a process for preparing compositions comprising imidacloprid polymorph Form I having dimer impurity content less than or equal to about 0.5%.

The present invention also provides a process for preparing compositions comprising imidacloprid polymorph Form I having dimer impurity content less than about 0.2%.

There is also provided agrochemical combinations comprising imidacloprid crystalline polymorph Form I produced according to the present process with one or more other pesticides.

Further there is provided agrochemical compositions comprising imidacloprid polymorph Form I produced according to the present process in combination with one or more other pesticides and a process for preparing such compositions.

Brief description of the drawings

Fig.1 is a graph of a thermogram obtained by DSC of Form I of imidacloprid prepared according to the present invention.

Fig.2 is the powder X-ray diffraction pattern of the substantially pure Form I crystalline polymorph of imidacloprid prepared according to the present invention.

Detailed description of the invention

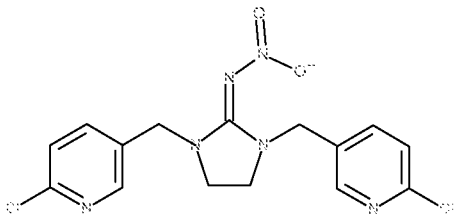
For the purposes of the following detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers expressing, for example, quantities of materials/ingredients used in the specification are to be understood as being modified in all instances by the term "about".

The term "about" shall be interpreted to mean "approximately" or "reasonably close to" and any statistically insignificant variations therefrom.

As used herein, the terms “comprising” “including,” “having,” “containing,” “involving,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. The terms “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances.

In an embodiment, the aspects and embodiments described herein shall also be interpreted to replace the clause “comprising” with either “consisting of” or with “consisting essentially of” or with “consisting substantially of”.

Inventors of the present Invention found that the compound imidacloprid synthesized as per US 6307053 or by any other known process comprises a mixture of polymorphs, di-condensation by-product represented by the Formula (2) and unreacted reactants as impurities.



Formula (2)

In the present invention, herein after, di-condensation by-product represented by formula (2) is referred to as 'dimer impurity'.

It is surprisingly found by the present inventors that imidacloprid crystalline Form I is prepared in substantially pure form by reducing the dimer impurity in the synthesized imidacloprid. Specifically, the present invention is directed to reduce the content of dimer impurity below 0.5% in the manufactured imidacloprid and/or polymorphic forms thereof in order to obtain the desired substantially pure form of imidacloprid.

With respect to the present disclosure, imidacloprid form I refers to monoclinic Imidacloprid modification I with melting point 145.23 ±2°C.

With respect to the present disclosure, imidacloprid form II refers to monoclinic Imidacloprid modification I with melting point 137.72 ±2°C.

In an embodiment the present invention provides imidacloprid Form I having dimer impurity represented by formula (2) content less than or equal to 0.5% w/w.

In an embodiment the present invention provides imidacloprid Form I having dimer impurity represented by formula (2) content less than 0.2% w/w.

In another aspect the present invention provides a process for selectively preparing crystalline polymorph Form I of imidacloprid.

The term, "substantially pure" as used herein refers to a polymorphic form of imidacloprid, Form I or Form II, which is at least about 90% pure. This means that the polymorph of imidacloprid does not contain more than about 10% of any other compound and, in particular, does not contain more than about 10% of any other form of imidacloprid. Preferably, the term "substantially pure" refers to a polymorph of imidacloprid, Form I or Form II, which is greater than about 95% pure. This means that the polymorph of imidacloprid does not contain more than about 5% of any other compound and, in particular, does not contain more than about 5% of any other form of imidacloprid. More preferably, the term "substantially pure" refers to a polymorph of imidacloprid, Form I or Form II; which is greater than about 98% pure, which means that the polymorph of imidacloprid does not contain more than about 2% of any other compound and, in particular, does not contain more than about 1% of any other form of imidacloprid.

Characteristic powder X-ray diffraction pattern peak positions are reported for polymorphs in terms of the angular positions (two theta) with an allowable variability of ±0.1°. The variability of ±0.1° is intended to be used when comparing two powder X-ray diffraction patterns.

Accordingly, the process for preparation of substantially pure polymorphs of imidacloprid are described hereinafter.

In an embodiment a process for selectively preparing imidacloprid Form I comprising the steps of:

Step 1: Refinement of imidacloprid; and

Step 2: selective crystallisation of imidacloprid Form I

In another embodiment the process for selectively preparing imidacloprid Form I comprises:

Step 1: refinement of imidacloprid from impurities; and

Step 2: selective reducing the dimer impurity (2) content to less than 0.5% and crystallising pure imidacloprid Form I.

In another embodiment the process for selectively preparing imidacloprid Form I comprises:

Step 1: refinement of imidacloprid from impurities; and

Step 2: selective crystallisation of imidacloprid Form I substantially free from dimer impurity represented by formula (2).

In an embodiment the refinement in step 1) comprises purification of imidacloprid.

In another embodiment step 1) comprises purification of imidacloprid by reducing the impurities content wherein said impurity comprise dimer impurity represented by formula (2).

In another embodiment step 1) comprises purification of imidacloprid from impurities wherein said impurities comprise dimer and starting materials and other by products.

In an embodiment step 1) comprises crystallisation of imidacloprid using suitable solvent to obtain imidacloprid Form I.

In an embodiment imidacloprid of step 1) comprises imidacloprid having mixture of polymorphs and impurities.

In another embodiment imidacloprid of step 1) comprises substantially pure imidacloprid having reduced dimer impurity content.

In yet another embodiment imidacloprid of step 1) has purity about 80% w/w.

In an embodiment imidacloprid of step 1) has purity about 95% w/w.

In another embodiment imidacloprid of step 1) has purity about 98% w/w.

In an embodiment step 2) comprises crystallisation of imidacloprid using suitable solvent to obtain substantially pure imidacloprid Form I.

In another embodiment step 2) comprises selective crystallisation of imidacloprid Form I wherein imidacloprid has purity more than 98% w/w.

The present invention further provides a process for selectively preparing imidacloprid Form I said process comprising the steps of:

step 1:

a) dissolving Imidacloprid in an organic solvent to obtain a solution;
b) cooling the solution at a predetermined rate; and
c) effecting crystallization resulting in imidacloprid having less impurities

step-2:

a) dissolving Imidacloprid obtained from the step 1 in an organic solvent to obtain a solution;
b) cooling the solution at a predetermined rate; and
c) effecting crystallization resulting in imidacloprid Form I.

In an embodiment the starting compound, imidacloprid of step 1 (a) comprises Imidacloprid having mixture of polymorphs and impurities.

In an embodiment imidacloprid of step 1 (a) comprises imidacloprid Form II and impurities.

In an embodiment imidacloprid of step 1 (a) comprises imidacloprid Form II and dimer impurity represented by formula 2 as one of the impurity.

In an embodiment of the present invention, in step 1 (a) the organic solvent is selected from, but not limited to, alcohols, ethers, aromatic hydrocarbons, ketones, chlorinated solvents, esters, aliphatic hydrocarbons, nitriles, amides, organosulfur solvents, water and mixtures thereof.

In a preferred embodiment of the present invention, organic solvent is selected from, but not limited to, following stated solvents:

alcohols may include methanol, ethanol, isopropyl alcohol, n-butanol, t-butanol, etc.
ethers may include diethyl ether, tetrahydrofuran, dioxanes, dibutyl ether, etc.;
aromatic hydrocarbons may include toluene, benzene, xylene, etc.;
ketones may include acetone, MIBK, etc.;
chlorinated solvents may include methylene chloride, dichloromethane, chloroform, dichloroethane, and carbon tetrachloride, etc.;
esters may include ethyl acetate, methyl acetate, etc.;
aliphatic hydrocarbons may include n-Hexane, petroleum ether, etc.;
nitriles may include acetonitrile, etc.;
amides may include N, N-dimethylformamide (DMF), etc.; and

organosulfur solvents may include dimethyl sulfoxide (DMSO), etc.

In a preferred embodiment, the organic solvent is selected from alcohols, aliphatic or aromatic hydrocarbons, nitriles, water and mixtures thereof.

In another preferred embodiment, the organic solvent is selected from nitriles and mixture of nitriles optionally with other organic solvents.

In an embodiment of the present invention, the step-1 (a) is carried out at temperature in the range from about 25° to about 120° C.

In an embodiment of the present invention, the step-1 (b), is carried out at temperature in the range from about 20°C to about 50° C.

In an embodiment of the present invention, the step-1 (b), cooling of Imidacloprid solution is carried out for a period of 15 minutes to 3 hours.

According to an embodiment of the present invention, the step-1 (c) is effected at a temperature in the range from about -15°C to about 30° C.

According to an embodiment of the present invention, in step-1 (c), the crystallization is effected by sudden cooling.

According to to an embodiment of the present invention, in step-1 (c), the crystallization is effected by sudden cooling in less than 15 minutes.

According to an embodiment of the present invention, in step-1 (c), the crystallization is effected by gradual cooling, keeping the solution at a temperature in the range from about -15°C to about 0° C for 15 minutes to 3 hours.

In an embodiment of the present invention, the solution is stirred at reflux temperature in organic solvent for 1 hr and then cooled to 20-22°C at a cooling rate of about 0.3-0.5°C./min.

In an embodiment the organic solvent is acetonitrile.

In an embodiment, the organic solvent is methanol.

According to one embodiment of the present invention, the step-1 (c), the crystallization is optionally initiated by seeding the solution with Imidacloprid having purity ≥98% w/w.

In an embodiment of the present invention, in step 1 (c), imidacloprid with less impurities is isolated by filtration or decantation.

In another embodiment, the step 1 (c) provides imidacloprid having dimer impurity represented by formula 2 content reduced to less than or equal to 0.5% w/w.

In another embodiment, the step 1 (c) provides imidacloprid having a mixture of imidacloprid Form I and imidacloprid Form II.

In an embodiment the present invention provides imidacloprid Form I having dimer impurity content represented by formula (2) reduced to less than or equal to 0.5% w/w.

In an embodiment, the step 2) comprises a process for selective crystallization of imidacloprid Form I.

In another embodiment, imidacloprid of step 2 (a) comprises a mixture of imidacloprid Form I and imidacloprid Form II.

In another embodiment, imidacloprid of step 2 (a) comprises a mixture of imidacloprid Form I and imidacloprid Form II optionally obtained as a product of step-1 (c).

In yet another embodiment imidacloprid of step 2 (a) comprises imidacloprid Form II.

In an embodiment of the present invention, in step 2 (a) the organic solvent is selected from, but not limited to the group consisting of alcohols, ethers, aromatic hydrocarbons, ketones, chlorinated solvents, esters, aliphatic hydrocarbons, nitriles, amides, organosulfur solvents, water and mixtures thereof.

In a preferred embodiment, the organic solvent is selected from the group consisting of:
alcohols may include methanol, ethanol, isopropyl alcohol, n-butanol, t-butanol, etc.
ethers may include diethyl ether, tetrahydrofuran, dioxanes, dibutyl ether, etc.

aromatic hydrocarbons may include toluene, benzene, xylene, etc.
ketones may include acetone, MIBK, etc.
chlorinated solvents may include methylene chloride, dichloromethane, chloroform, dichloroethane, and carbon tetrachloride, etc.
esters may include ethyl acetate, methyl acetate, etc.
aliphatic hydrocarbons may include n-Hexane, petroleum ether, etc.
nitriles may include acetonitrile, etc.
amides may include N, N-dimethylformamide (DMF), etc. and
organosulfur solvents may include dimethyl sulfoxide (DMSO), etc.

In a preferred embodiment, the organic solvent is selected from the group consisting of alcohols, aliphatic or aromatic hydrocarbons, nitriles, water and mixtures thereof.

In another preferred embodiment, the organic solvent is selected from nitriles and mixture of nitriles optionally with other organic solvents.
In an embodiment of the present invention, the step 2 (a) is carried out at temperature in the range from about 25° to about 120° C.

In an embodiment of the present invention, the step 2 (b) is carried out at temperature in the range from about 20°C to about 50° C.

In an embodiment of the present invention, the step 2 (b) is carried out for a period of about 15 minutes to 3 hours.

According to an embodiment, the step 2 (c), is performed at temperature in the range from about -15°C to about 30° C.

According to an embodiment, in step 2 (c) the crystallization is effected by gradual cooling.

In present embodiment, the step 2 (c) is carried out for a period of about 15 minutes to 3 hours.

In an embodiment the solution is stirred at reflux temperature for 1 hr, then cooled to 20-22°C to form crystals of Form 1 of imidacloprid.

According to one embodiment of the present invention, in step 2 (c), the crystallization is optionally initiated by seeding the solution with imidacloprid Form I having purity ≥98% w/w.

In an embodiment of the present invention imidacloprid Form I crystals are isolated in step 2 (c) by filtration.

In another embodiment there is provided a process for selectively preparing imidacloprid Form I comprising:

a) dissolving Imidacloprid having dimer content ≤0.5% w/w in an organic solvent to obtain a solution;

b) cooling the solution at a predetermined rate; and

c) effecting crystallization resulting in imidacloprid Form I

In an embodiment Imidacloprid of step a) comprises a mixture of imidacloprid Form I and imidacloprid Form II and having dimer impurity ≤0.5% w/w.

In an embodiment imidacloprid of step a) comprises imidacloprid Form II having impurities ≤0.5% w/w.

In an embodiment the organic solvent used in step a) is selected from, but not limited to, the group consisting of alcohols, ethers, aromatic hydrocarbons, ketones, chlorinated solvents, esters, aliphatic hydrocarbons, nitriles, amides, organosulfur solvents, water and mixtures thereof.

In a preferred embodiment of the present invention, organic solvent is selected from the group consisting of:

alcohols may include methanol, ethanol, isopropyl alcohol, n-butanol, t-butanol, etc.

ethers may include diethyl ether, tetrahydrofuran, dioxanes, dibutyl ether, etc.

aromatic hydrocarbons may include toluene, benzene, xylene, etc.

ketones may include acetone, MIBK, etc.

chlorinated solvents may include methylene chloride, dichloromethane, chloroform, dichloroethane, and carbon tetrachloride, etc.

esters may include ethyl acetate, methyl acetate,etc.
aliphatic hydrocarbons may include n-Hexane, petroleum ether, etc.
nitriles may include acetonitrile, etc.
amides may include N, N-dimethylformamide (DMF), etc.
organosulfur solvents may include dimethyl sulfoxide (DMSO), etc.

In a preferred embodiment, the organic solvent is selected from alcohols, aliphatic or aromatic hydrocarbons, nitriles, water and mixtures thereof.

In another preferred embodiment, the organic solvent is selected from nitriles and mixture of nitriles optionally with other organic solvents.

In an embodiment the step a) is carried out at temperature in the range from about 25° to about 120° C.

In an embodiment the step b) is carried out at temperature in the range from about 20°C to about 50° C.

In an embodiment, the step b) is carried out for a period of about 15 minutes to 3 hours.

According to an embodiment, the step c) is carried out at temperature in the range from about -15°C to about 30° C.

According to an embodiment, in step c), the crystallization is effected by gradual cooling for a period of about 15 minutes to 3 hours.

According to an embodiment, the crystallization in step c) is optionally initiated by seeding the solution with Imidacloprid Form I having purity more than or equal to (≥) 98% w/w.

According to the present invention, imidacloprid comprising a mixture of imidacloprid Form I and imidacloprid Form II and having dimer impurity content ≥ 0.5% undergo purification for reducing the level of dimer impurity and then polymorphic conversion to form Imidacloprid Form 1. It has been unexpectedly found that crystallization of imidacloprid having dimer impurity content ≤ 0.5%, using suitable solvent provides selective formation of desired polymorph of Imidacloprid i.e. Form I.

In the above stated embodiments, the level of dimer compound impurity is a crucial factor in the formation of desired polymorph. As shown in Table 1, mixture of imidacloprid Form I and imidacloprid Form II having dimer content ≥ 0.5% needs a two-step process for the selective formation of desired polymorphic form of imidacloprid i.e. Form I whereas, imidacloprid comprising mixture of Form I and Form II having dimer content ≤ 0.5% needs a one-step process for the selective formation of desired polymorphic form of imidacloprid i.e. Form I.

Table 1

Imidacloprid		Step 1 (First crystallization)	DSC MP (°C)	Step 2 (Second crystallization)	DSC MP (°C)
FORM	Dimer	FORM		FORM	
1 + 2	2.4%	2	136.5	1	144.8
1 + 2	1.0%	2	136.5	1	144.8
1 + 2	0.5%	1	144.8	-	-

In above stated embodiment, disclosed a method that provides, in step-2 optionally, a crystalline polymorphic form of imidacloprid is designated Form I. This polymorph is characterised, for example, by DSC.

As shown in Fig.1, Form I exhibit a differential scanning calorimetry (DSC) thermogram which is characterised by a predominant endotherm peak at 144.87 °C.

The invention will now be described further by reference to the following examples, which are intended to illustrate, but not limit, the scope of the appended claims.

Examples:

Example 1

Step 1:

10 g of imidacloprid (purity 97.6% w/w and dimer content 2.4% w/w) was heated in 30 ml of acetonitrile to reflux temperature until complete dissolution of the imidacloprid was observed. The solution was stirred at reflux temperature for 1 hr. The solution was then cooled to 20-22°C at a cooling rate of about 0.3-0.5°C./min. The crystals of pure imidacloprid formed were filtered out, washed with acetonitrile and dried at 60-65 °C in an oven.

Yield: 80%.

Purity: 98.27% w/w; Dimer content: 0.13 % w/w using HPLC.

Step 2

5 g of imidacloprid obtained from step 1 was heated in 10 ml of acetonitrile to reflux temperature until complete dissolution. The solution was stirred at reflux temperature for 1 hr. The solution was then cooled to 20-22°C. The crystals of Form 1 of imidacloprid formed were filtered and dried at 60-65°C in an oven.

Yield: 93%.

Purity by HPLC: 98.46% w/w, dimer content: 0.04%

DSC endotherm peak: 144.87°C.

Example 2

Step 1:

10 g of imidacloprid (purity 98.5% and dimer content 1.5%) was heated in 40 ml of acetonitrile to reflux temperature until complete dissolution of the imidacloprid was observed. The solution was stirred at reflux temperature for 1 hr. The solution was then cooled to 20-22°C at a cooling rate of about 0.3-0.5°C./min. The crystals of pure imidacloprid formed were filtered out, washed with acetonitrile and dried at 60-65°C in an oven.

Yield: 79%.

Purity by HPLC: 98.39% w/w; dimer content: 0.31% w/w).

Step 2:

5 g of imidacloprid obtained from step 1 was heated in 10 ml of acetonitrile to reflux temperature until complete dissolution. The solution was stirred at reflux temperature for 1 hr. The solution was then cooled to 20-22°C. The crystals of Form 1 of imidacloprid formed were filtered out and dried at 60-65°C in an oven.

Yield: 92%.

Purity by HPLC: 98.58% w/w; dimer content: 0.15% w/w; DSC endotherm peak at: 146.3°C.

Example 3

Step 1:

10 g of imidacloprid (having purity 98.2% and dimer content 1.8%) was heated in 30 ml of methanol to reflux temperature until complete dissolution of the imidacloprid was observed. The solution was stirred at reflux temperature for 1 hr. The solution was then hot filtered at 45-50°C. The crystals of pure Imidacloprid formed were filtered out and dried at 60-65°C in an oven.

Yield: 81%.

Purity by HPLC: 98.52%, dimer content: 0.18% w/w).

Step 2:

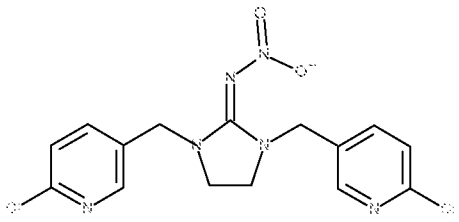
5 g of imidacloprid obtained from step 1 was heated in 10 ml of acetonitrile to reflux temperature until complete dissolution. The solution was stirred at reflux temperature for 1 hr. The solution was then cooled to 20-22°C. The crystals of Form 1 of imidacloprid formed were filtered out and dried at 75-85°C in an oven.

Yield: 93.8%.

Purity by HPLC: 99.74% w/w; dimer content: 0.11% w/w; DSC endotherm peak: 143.3°C.

CLAIMS

1. A process for preparation of imidacloprid Form I comprising:
   a) refinement of imidacloprid; and
   b) selective crystallisation of imidacloprid polymorph Form I.
2. The process according to claim 1 comprises purification of imidacloprid by reducing the impurities wherein said impurities comprise a dimer impurity represented by formula 2.



Formula (2)

3. The process according to claim 1 wherein said process provides imidacloprid Form I having an impurity of dimer represented by formula 2 reduced to less than or equal to 0.5% w/w.
4. A process for preparing imidacloprid Form I comprising

   step-1:
   a) dissolving Imidacloprid in an organic solvent;
   b) cooling the solution at a predetermined rate; and
   c) effecting crystallization resulting in imidacloprid having substantially less impurities

   step-2:
   a) dissolving Imidacloprid obtained from the step-1, in an organic solvent;
   b) cooling the solution at a predetermined rate; and
   c) effecting crystallization resulting in substantially pure imidacloprid polymorph Form I

5. The process according to claim 4 wherein said impurity comprise a dimer represented by formula 2.
6. The process according to claim 4 wherein said organic solvent is selected from alcohols, ethers, aromatic hydrocarbons, ketones, chlorinated solvents, esters, aliphatic hydrocarbons, nitriles, amides, organosulfur solvents, water or mixtures thereof.
7. The process according to claim 4 wherein said organic solvent is selected from alcohols, aliphatic or aromatic hydrocarbons, nitriles, water or mixtures thereof.
8. The process according to claim 4 wherein said organic solvent is selected from methanol, ethanol, isopropyl alcohol, n-butanol, t-butanol, acetonitrile or combinations thereof.
9. The process according to claim 4 wherein said process comprises at least one step selected from; step-1 (a) is carried out at temperature in the range from about 25° to about 120° C, step-1 (b) is carried out at temperature in the range from about 20°C to about 50° C or step-1 (c) crystallization is effected by sudden or gradual cooling.
10. The process according to claim 4 wherein step 1 (a) comprises imidacloprid Form II and dimer impurity represented by formula 2.
11. The process according to claim 4 wherein said process comprises at least one step selected from; step 2 (a) is carried out at temperature in the range from about 25° to about 120° C, step 2 (b) is carried out at temperature in the range from about 20°C to about 50° C, step 2 (c) is carried out at temperature in the range from about -15°C to about 30° C or step 2 (c) crystallization is effected by gradual cooling.
12. The process according to claim 4 wherein step 2 (a) comprises imidacloprid Form II or a mixture of imidacloprid Form I and imidacloprid Form II.
13. The process according to claim 4 wherein said process provides imidacloprid Form I having an impurity of dimer represented by formula 2 reduced to less than or equal to 0.5% w/w.
14. The process according to claim 4 wherein said process provides imidacloprid Form I having purity at least 98%.
15. A process for selectively preparing imidacloprid polymorph Form I comprising:
a) dissolving Imidacloprid having impurities less than 0.5% in an organic solvent;

b) cooling the solution at a predetermined rate; and

c) effecting crystallization resulting in imidacloprid polymorph Form I

16. The process according to claim 15 wherein said impurities comprise a dimer represented by formula 2.

17. The process according to claim 15 wherein said organic solvent is selected from alcohols, ethers, aromatic hydrocarbons, ketones, chlorinated solvents, esters, aliphatic hydrocarbons, nitriles, amides, organosulfur solvents, water or mixtures thereof.

18. The process according to claim 15 wherein said organic solvent is selected from alcohols, aliphatic or aromatic hydrocarbons, nitriles, water or mixtures thereof.

19. The process according to claim 15 wherein said process provides imidacloprid Form I having an impurity of dimer represented by formula 2 reduced to less than or equal to 0.5% w/w.

20. Substantially pure Imidacloprid Form I having purity more than 98% and a dimer impurity of formula 2 less than or equal to 0.5% w/w.

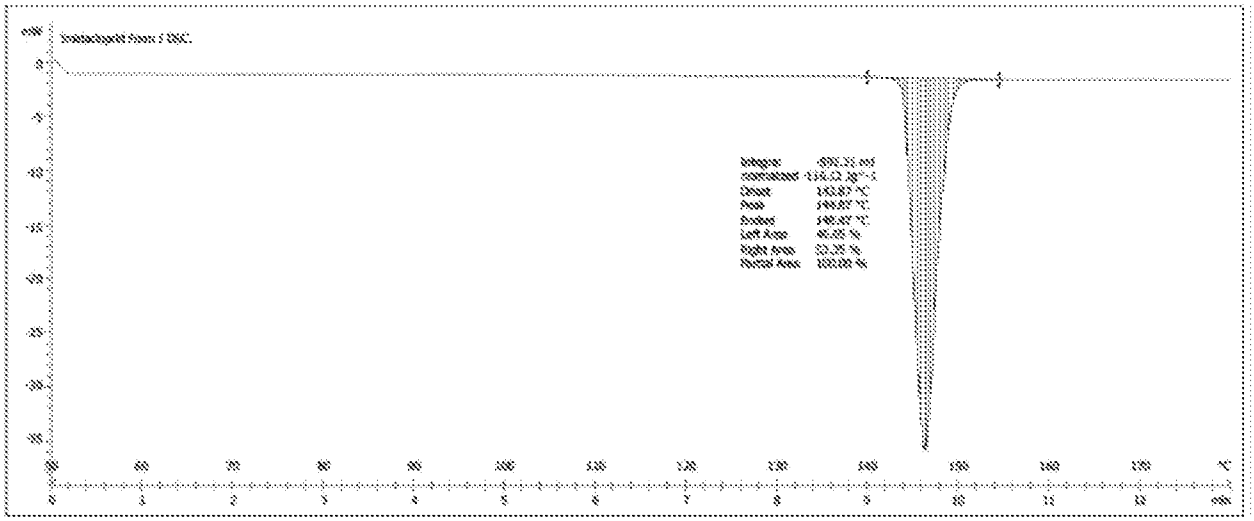


Figure 1

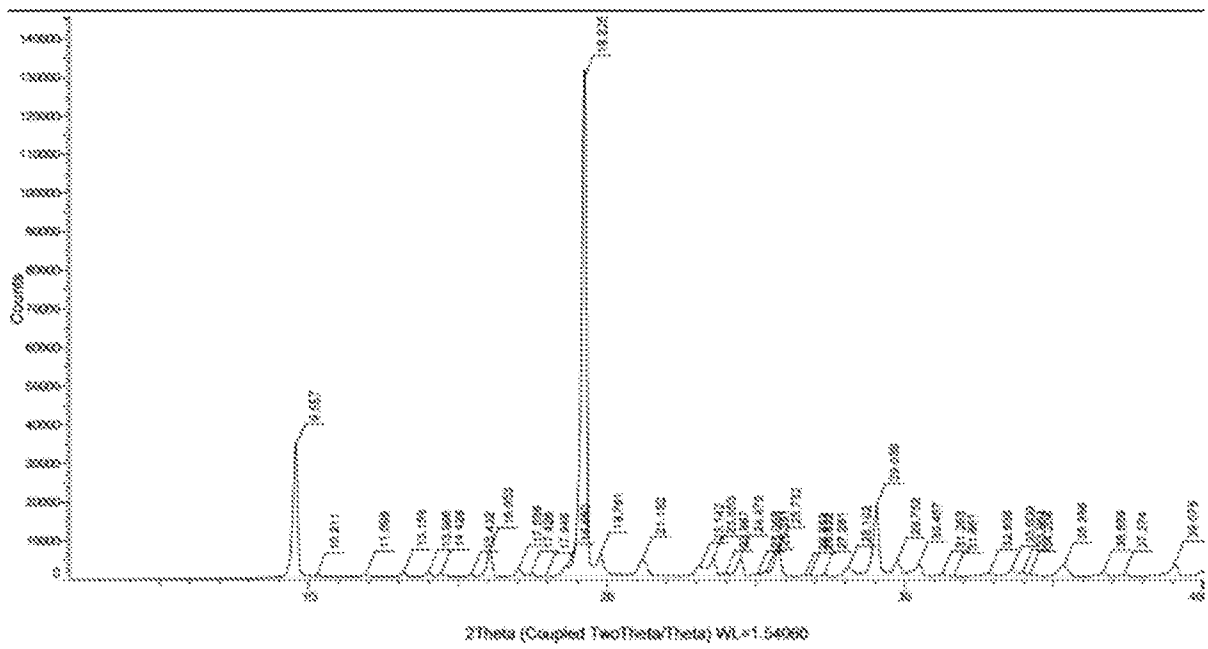


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2020/050480

A. CLASSIFICATION OF SUBJECT MATTER

C07D 401/06 (2006.01) C07B 63/00 (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)

STN: Registry and Sub-structure search based on Imidacloprid Form I and formula (2) and Applicant and Inventor search UPL LTD & KINI, Prashant, Vasant; MUKADAM, Vilas, Manikant in External Databases conducted in Espacenet and Patentscope and internal databases provided by IP Australia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 March 2020	25 March 2020

Name and mailing address of the ISA/AU	**Authorised officer**
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INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/IB2020/050480**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	IN 2016/210969916 A1 (MEGHMANI ORGANICS LTD) 09 February 2016	
X	See whole doc. especially abstract, page 6 and example 2 on page 8	1-20
Y	See whole doc. especially abstract, page 6 and example 2 on page 8	2, 3, 5, 10, 12, 13, 16, 19 and 20
	US 2015/0368227 A1 (ROTAM AGROCHEM INTERNATIONAL COMPANY LIMITED) 24 December 2015	
X	See whole doc. especially abstract, claims and paragraph [0051]	1, 4, 6, 7, 8, 9, 11, 14, 15, 17, 18,
Y	See whole doc. especially abstract, claims and paragraph [0051]	2, 3, 5, 10, 12, 13, 16, 19 and 20

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/IB2020/050480**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
IN 2016/210969916 A1	09 February 2016	None	
US 2015/0368227 A1	24 December 2015	US 9212162 B1	15 Dec 2015
		US 2015368227 A1	24 Dec 2015
		BR 112016024977 A2	15 Aug 2017
		CN 106470984 A	01 Mar 2017
		CN 110526897 A	03 Dec 2019
		TW 201625582 A	16 Jul 2016
		US 2016060246 A1	03 Mar 2016
		US 9475794 B2	25 Oct 2016
		WO 2015196926 A1	30 Dec 2015

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.