



(51) International Patent Classification:

C07D 251/52 (2006.01) A01N 39/04 (2006.01)

C07D 251/50 (2006.01) A01N 43/70 (2006.01)

C07C 59/70 (2006.01)

(21) International Application Number:

PCT/GB2019/052217

(22) International Filing Date:

07 August 2019 (07.08.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1816445.9 09 October 2018 (09.10.2018) GB

(71) Applicant: **JOHNSON MATTHEY PUBLIC LIMITED COMPANY** [GB/GB]; 5th Floor, 25 Farringdon Street, London EC4A 4AB (GB).

(72) Inventors: **BONNAUD, Thierry**; c/o Johnson Matthey Plc, Unit 250 Science Park, Milton Road, Cambridge Cambridgeshire CB4 0WE (GB). **CHORLTON, Alan**; c/o Johnson Matthey Plc, Unit 250 Science Park, Milton Road, Cambridge Cambridgeshire CB4 0WE (GB). **KENDALL, Thomas**; c/o Johnson Matthey Plc, Unit 250 Science Park, Milton Road, Cambridge Cambridgeshire CB4 0WE

(GB). **VILLORIA, Jose**; c/o Johnson Matthey Plc, Johnson Matthey Technology Centre, Blount's Court Road, Sonning Common, Reading Berkshire RG4 9NH (GB).

(74) Agent: **WHITCOMBE, Nicole**; c/o Johnson Matthey Plc, Group Intellectual Property Department, Gate 20, Orchard Road, Royston Hertfordshire SG8 5HE (GB).

(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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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,

(54) Title: MOLECULAR COMPLEXES COMPRISING MCPA AND A TRIAZINE HERBICIDE

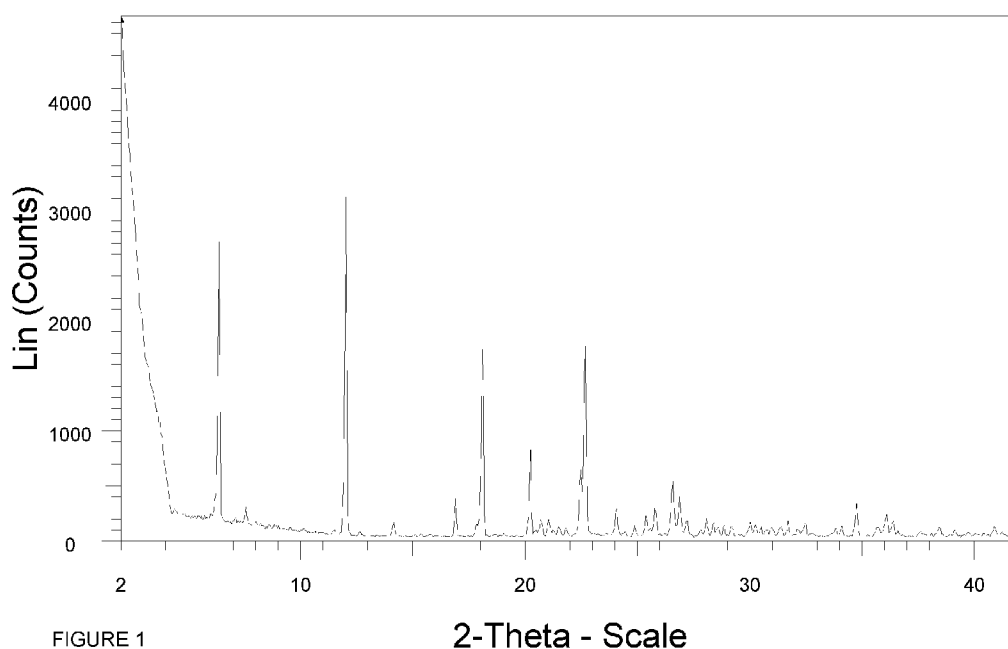


FIGURE 1

2-Theta - Scale

(57) Abstract: Molecular complexes comprising 2-methyl,4-chlorophenoxyacetic acid (MCPA) and a compound selected from the group of triazine herbicides are described, together with compositions comprising such molecular complexes, and methods of their preparation.

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))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

MOLECULAR COMPLEXES COMPRISING MCPA AND A TRIAZINE HERBICIDE

FIELD OF THE INVENTION

This invention relates to molecular complexes of herbicide compounds. In particular this invention relates to molecular complexes comprising 2-methyl-4-chlorophenoxyacetic acid and a triazine herbicide, and to herbicidal compositions comprising such molecular complexes.

BACKGROUND OF THE INVENTION

2-methyl-4-chlorophenoxyacetic acid (MCPA) is a widely used systemic herbicide which is a member of the phenoxy family of herbicides. MCPA acts as a synthetic auxin which is a plant hormone which is absorbed by the leaves of plants. MCPA is used to control broadleaf weeds, in particular for agricultural applications.

An increasing number of weed populations have been identified which show resistance to MCPA, and the spread of these resistant populations could have a significant impact on the effectiveness of this herbicide. For example, it has been found that intensive use of MCPA in Western Australia has led to the evolution of MCPA resistant wild radish populations (J. Agric. Food. Chem, 2013, 61, 12516-12521).

One strategy to overcome such issues is the use of MCPA in combination with one or more additional herbicide compounds with alternative modes of action. The development of a single formulation containing each of the herbicide compounds to be applied in combination is attractive. For example, the development of such formulations can reduce the need for multiple applications of herbicide, can help to ensure consistent delivery of the desired ratio of each herbicide compound, and can reduce delivery costs.

However, the development of such formulations incorporating MCPA is challenging. For example, a single combination formulation must provide conditions in which both MCPA and additional herbicide compounds are stable. In addition, the relatively high aqueous solubility of MCPA can lead to potential problems in the development of combination formulations with less water soluble active agents due to the relatively rapid release of MCPA after application.

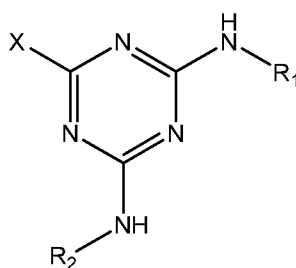
There remains a need to develop new stable herbicide formulations containing MCPA which overcome one or more of the issues identified above.

SUMMARY OF THE INVENTION

The present inventors have surprisingly found that triazine herbicides may be used to form molecular complexes with 2-methyl-4-chlorophenoxyacetic acid (MCPA). The molecular complexes formed have been found to have high stability, modified melting point, and provide MCPA in a form which has reduced solubility.

Therefore, in a first aspect of the invention there are provided molecular complexes of 2-methyl-4-chlorophenoxyacetic acid (MCPA) and a compound selected from the group of triazine herbicides.

Triazine herbicides of particular utility may be represented by formula (I):



(I)

wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.

Preferably, the triazine herbicide is selected from atrazine, simazine, cyanazine, propazine, terbutryn, prometryn or ametryn. Typically, the molar ratio of MCPA: triazine herbicide 1:1.

Typically, the molecular complexes are formed by solution or slurry crystallisation processes. Therefore, in a second aspect of the invention there is provided a method for the preparation of molecular complexes as described herein which comprises combining MCPA and a triazine herbicide in a suitable solvent.

In a third aspect of the invention there is provided a method for preparing a molecular complex as described herein, the method comprising the step of applying dual asymmetric centrifugal forces to a mixture of MCPA and the triazine herbicide to form the molecular complex.

In a fourth aspect of the invention there is provided a herbicidal composition comprising molecular complexes as described herein and at least one agriculturally acceptable carrier. Typically, such compositions may be in the form of a solid formulation, such as a

powder or granulated composition, or may be a liquid formulation, such as an aqueous suspension concentrate or a suspo-emulsion.

In a fifth aspect of the invention, there is provided the use of such herbicidal compositions for controlling undesired vegetation, for example during crop cultivation.

- 5 In a sixth aspect of the invention there is provided a method for controlling undesired vegetation comprising contacting the vegetation with a composition comprising molecular complexes as described herein and at least one agriculturally acceptable carrier.

DEFINITIONS

- 10 The term “about” or “approximately” means an acceptable error for a particular value as determined by a person of ordinary skill in the art, which depends in part on how the value is measured or determined. In certain embodiments, the term “about” or “approximately” means within 1, 2, 3 or 4 standard deviations. In certain embodiments, the term “about” or “approximately” means within 30%, 25%, 20%, 15%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or 0.5% of a given value or range. In certain
15 embodiments and with reference to X-ray powder diffraction two-theta peaks, the terms “about” or “approximately” means within $\pm 0.2^\circ 2\theta$.

The term “ambient temperature” means one or more room temperatures between about 15 °C to about 30 °C, such as about 15 °C to about 25 °C.

- 20 The term “crystalline” and related terms used herein, when used to describe a compound, substance, modification, material, component or product, unless otherwise specified, means that the compound, substance, modification, material, component or product is substantially crystalline as determined by X-ray diffraction. See, e.g., Remington: The Science and Practice of Pharmacy, 21st edition, Lippincott, Williams and Wilkins, Baltimore, Md. (2005); The United States Pharmacopeia, 23rd ed., 1843-1844
25 (1995).

The term “overnight” refers to the period of time between the end of one working day to the subsequent working day in which a time frame of about 12 to about 18 hours has elapsed between the end of one procedural step and the instigation of the following step in a procedure.

- 30 “Slurry” means a heterogeneous mixture of at least a portion of the molecular complex in one or more solvents. “Slurry” therefore includes a mixture of molecular complex which is partially present as a solid, as well as being partially dissolved in the one or more solvents.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 1.

5 Figure 2 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 1.

Figure 3 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 2.

Figure 4 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 2.

10 Figure 5 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 3.

Figure 6 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 3.

15 Figure 7 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 4.

Figure 8 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 4.

Figure 9 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 5.

20 Figure 10 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 5.

Figure 11 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 6.

25 Figure 12 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 6.

Figure 13 shows a representative x-ray powder diffraction pattern of the molecular complex of Example 7.

Figure 14 shows a representative differential scanning calorimetry (DSC) curve of the molecular complex of Example 7.

30 Figure 15A-C illustrate how centrifugal forces are applied to materials in a SpeedMixer™.

Figure 15A is a view from above showing the base plate and basket. The base plate rotates in a clockwise direction.

Figure 15B is a side view of the base plate and basket.

Figure 15C is a view from above along line A in Figure 10B. The basket rotates in an anti-clockwise direction.

DETAILED DESCRIPTION OF THE INVENTION

Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

The present invention relates to an isolated molecular complex comprising 2-methyl-4-dichlorophenoxyacetic acid (MCPA) and a compound selected from the group of triazine herbicides, and to herbicidal compositions comprising such crystalline materials.

A molecular complex is a crystalline material composed of two or more different components which has a defined single-phase crystal structure. The components are held together by non-covalent bonding, such as hydrogen bonding, ionic bonding, van der Waals interactions, π - π interactions, etc. The term molecular complex includes salts, co-crystals and salt/cocrystal hybrids. In one embodiment, the molecular complex is a salt. In another embodiment, the molecular complex is a co-crystal. In another embodiment, the molecular complex is a salt/co-crystal hybrid.

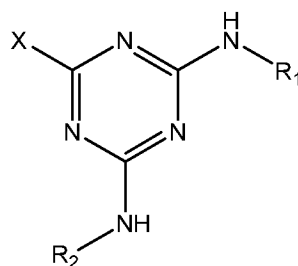
Without wishing to be bound by theory, it is believed that when the molecular complex is a co-crystal, the co-crystal demonstrates improved physiochemical properties, such as crystallinity, solubility properties and/or modified melting points. In certain embodiments, the melting point of the molecular complex may be higher than the melting point of MCPA itself and/or the triazine itself. In this instance, a higher melting point may be of benefit in the preparation of, for example, a suspension concentrate formulation of the molecular complex. In certain embodiments, the melting point of the molecular complex may be lower than the melting point of MCPA itself and/or the triazine itself. In this instance, a lower melting point may be of benefit in the preparation of, for example, an encapsulated formulation of the molecular complex or liquid formulation of the molecular complex.

The molecular complexes may be distinguished from mixtures of MCPA and the selected triazine herbicide by standard analytical means which are well known to those skilled in the art, for example x-ray powder diffraction (XRPD), single crystal x-ray diffraction, or differential scanning calorimetry (DSC). The molar ratio of the components of the molecular complex may be determined using, for example, HPLC or ^1H NMR.

The molecular complexes comprise 2-methyl-4-chlorophenoxyacetic acid (MCPA) and a triazine herbicide. Triazine herbicides are well known to those skilled in the art and comprise a 1,3,5-triazine core with -N(H)alkyl substituents at the 2- and 4- positions, and a further substituent at the 6-position, such as a chloro, -OCH₃ or -SCH₃ substituent.

Typically, the alkyl groups are unbranched, branched or cyclic C₁₋₅ alkyl groups, optionally substituted, for example with -CN.

Triazine herbicides of particular utility may be represented by formula (I):



(I)

wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.

Preferably, X = Cl or -SCH₃, more preferably X = Cl.

Further preferred compounds have X = -OCH₃, R₁ = isopropyl, and R₂ = isopropyl; or X = -SCH₃, R₁ = ethyl or iso-propyl, and R₂ = iso-propyl or tert-butyl.

Preferably, the triazine herbicide is selected from atrazine (6-chloro-4-N-ethyl-2-N-(propan-2-yl)-1,3,5-triazine-2,4-diamine), simazine (6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine), cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile), propazine (6-chloro-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine), terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine), prometryn (6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine) or ametryn (4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine).

In one embodiment, the present invention relates to a molecular complex comprising, or consisting of, MCPA and atrazine (6-chloro-4-N-ethyl-2-N-(propan-2-yl)-1,3,5-triazine-

2,4-diamine). The molar ratio of MCPA:atrazine is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: atrazine is 1:1, the current inventors have
5 identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 1. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 1. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 1 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta.
10 The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 2, in particular by the melting point temperature with an onset temperature of about 128.9 $^{\circ}$ C as determined by DSC.

In another embodiment, the present invention relates to a molecular complex comprising, or consisting of, MCPA and propazine (6-chloro-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-
15 2,4-diamine). The molar ratio of MCPA: propazine is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: propazine is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α
20 radiation) substantially as shown in Figure 3. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 2. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 2 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC)
25 curve as shown in Figure 4, in particular by the melting point temperature with an onset temperature of about 112.4 $^{\circ}$ C as determined by DSC.

In a further embodiment, the present invention relates to molecular complexes comprising, or consisting of, MCPA and cyanazine ((2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile). The molar ratio of MCPA: cyanazine is
30 generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA and cyanazine is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 5. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are

shown in Table 3. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 3 as degree 2-Theta ($^{\circ}2\theta$) values ± 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 6, in particular by the melting point temperature with an onset temperature of about 144.4 $^{\circ}\text{C}$ as determined by DSC.

In another embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, MCPA and simazine ((6-chloro-2-N,4-N-diethyl-1,3,5-triazine-2,4-diamine). The molar ratio of MCPA: simazine is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: simazine is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu $K\alpha$ radiation) substantially as shown in Figure 7. The XRPD degree 2-theta ($^{\circ}2\theta$) values are shown in Table 4. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 4 as degree 2-Theta ($^{\circ}2\theta$) values ± 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 8, in particular by the melting point temperature with an onset temperature of about 128.4 $^{\circ}\text{C}$ as determined by DSC.

In a further embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, MCPA and terbutryn (2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine). The molar ratio of MCPA: terbutryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: terbutryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu $K\alpha$ radiation) substantially as shown in Figure 9. The XRPD degree 2-theta ($^{\circ}2\theta$) values are shown in Table 5. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 5 as degree 2-Theta ($^{\circ}2\theta$) values ± 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 10, in particular by the melting point temperature with an onset temperature of about 52.5 $^{\circ}\text{C}$ as determined by DSC.

In a further embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, MCPA and prometryn (6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine). The molar ratio of MCPA: prometryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: prometryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 11. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 6. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 6 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 12, in particular by the melting point temperature with an onset temperature of about 62.3 $^{\circ}$ C as determined by DSC.

In a further embodiment, the present invention relates to a molecular complex comprising, or consisting essentially of, MCPA and ametryn (4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine). The molar ratio of MCPA: ametryn is generally in the range from 1:1 to 2:1, such as 1:1. However, variations are possible which typically do not exceed 20 mol% and preferably do not exceed 10 mol%.

In the case that the molar ratio of MCPA: ametryn is 1:1, the current inventors have identified a crystalline form which exhibits an x-ray powder diffraction pattern (Cu K α radiation) substantially as shown in Figure 13. The XRPD degree 2-theta ($^{\circ}$ 2 θ) values are shown in Table 7. Preferably, the molecular complex shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 7 as degree 2-Theta ($^{\circ}$ 2 θ) values $\pm$ 0.2 degrees 2-theta. The crystalline form may also be identified by its differential scanning calorimetry (DSC) curve as shown in Figure 14, in particular by the melting point temperature with an onset temperature of about 43.6 $^{\circ}$ C as determined by DSC.

The molecular complexes may be formulated into a herbicidal composition with at least one agriculturally acceptable carrier. The composition may be a solid formulation, for example a powder, granule, or dust, or may be a liquid formulation, such as a suspension of particles of the molecular complex.

In one embodiment, the herbicidal composition is an aqueous suspension concentrate, i.e. an aqueous composition comprising particles of the molecular complex dispersed in an aqueous medium.

5 In a further embodiment, the herbicidal composition is a suspo-emulsion, i.e. an aqueous composition comprising particles of the molecular complex dispersed in an aqueous medium and a water-immiscible organic solvent, optionally with one or more additional herbicides solubilised in the organic solvent.

10 In another embodiment, the herbicidal composition is a solid formulation, such a powder, for example a water-dispersible powder or a dustable powder, or a granulated composition, such as water-dispersible granules.

It will be understood by the skilled person that the compositions may also include further components, such as surfactants, viscosity modifiers, anti-freeze agents, agents for pH control, preservatives, stabilisers and anti-caking agents.

15 The amount of the molecular complex in the composition is generally between 0.001 and 99 wt%, such as between 1 and 99%, 5 and 95 wt% or 10 and 90 wt% based on the total weight of the composition.

20 In liquid compositions which are designed to be diluted prior to use, such as an aqueous suspension concentrate or a suspo-emulsion, the amount of molecular complex is typically in the range from 10 and 90 wt%, such as between 10 and 70 wt%, in particular in the range from 15 to 50 wt%, based on the total weight of the composition. Such compositions are then diluted, typically with water, to around 0.001 and 1 wt% of active material before application.

25 In solid formulations, the amount of molecular complex is typically in the range from 10 to 90 wt%, in particular in the range from 15 to 70 wt%, based on the total weight of the composition.

The amount of carrier varies depending on the formulation type. Typically, the carrier is in the range from 1 to 90 wt%, in particular from 30 to 90 wt%, or particularly preferably between 30 to 85 wt%, or 50 to 85 wt% based on the total weight of the composition.

30 Suitable agriculturally acceptable carriers are well known to those skilled in the art. Such carriers should not be phytotoxic to crops, in particular at the concentrations employed for the control of undesirable plants in the presence of crops, and should not react chemically with the compounds of the molecular complex or other composition

components. The compositions may be applied directly, or may be formulations or concentrates which are diluted, for example with water, prior to application.

Liquid carriers that may be employed include water, optionally including water-miscible organic solvents, and organic solvents, although it is typically preferred that water is used. If organic solvents are used, then it will be understood that the organic solvent or solvents should be selected in which the molecular complexes have low solubility, for examples solvents in which the solubility is less than 1 mg/ml at 25 °C.

Suitable solid carriers include mineral earths, such as clays, silicates, diatomaceous earths, or kaolin, fertilisers, and organic products such as woodmeal and cellulose carriers.

Generally, the solid and liquid compositions comprise the molecular complexes in finely divided particulate form. In liquid compositions, the particles of the molecular complex are suspended in a liquid medium, preferably in an aqueous medium. In water-dispersible granules or water-dispersible powders the finely divided particles are typically loosely agglomerated into larger granules that disintegrate upon dilution in water and then lead to a suspension of these finely divided particles. The size of the particles of the molecular complex, i.e. the size which is not exceeded by 90% by weight of the active compound particles, is typically not more than 30 µm, preferably not more than 20 µm, in particular not more than 10 µm, especially not more than 5 µm, as determined by dynamic light scattering.

Suspension concentrates, in particular aqueous suspension concentrates, can be prepared by suspending particles of the molecular complex in a suitable liquid carrier. The suspension concentrate may also be prepared by mixing or milling particles of MCPA and the selected triazine herbicide in the liquid medium until a molecular complex has been formed.

Suspo-emulsions can be prepared in accordance with the method as described for suspension concentrates with the addition of an organic solvent, typically containing an additional active ingredient, such as a herbicide, pesticide or fungicide, to the formed suspension concentrate or during the preparation of the suspension concentrate.

Powders, such as dustable or water-dispersible powders, can be prepared by mixing or grinding particles of the molecular complex with a solid carrier.

Granules, for example water-dispersible granules, can be prepared by binding the particles of the molecular complex to suitable solid carriers.

The compositions as described above may also comprise further active compounds. For example, insecticides, fungicides, or further herbicides can be added as required.

All embodiments of the compositions comprising at least one molecular complex described herein are referred to as a "herbicidal composition".

- 5 The herbicidal compositions as described herein may be used for controlling undesirable vegetation. Undesirable vegetation is understood to mean plants considered undesirable in a particular location, e.g. in an area of crops, and may be known as weeds.

Control may be achieved by a method comprising contacting the vegetation with the herbicidal composition. It will be understood by the skilled person that the composition at
10 the point of application should contain a herbicidally effective amount of the molecular complex. A herbicidally effective amount is an amount of the active ingredients which causes an adverse deviation of the natural development of the undesired vegetation.

In particular, the compositions have utility for controlling undesirable vegetation in a culture of crop plants, especially crop plants which are tolerant to MCPA and / or triazine
15 herbicides, for example through genetic modification of the crop plants. The compositions may also have particular utility for the control of undesirable vegetation which is resistant to either MCPA and / or the selected triazine herbicide.

The present invention also comprises a method for the preparation of molecular complexes according to the present invention, the method comprising combining MCPA
20 and the selected triazine herbicide in a suitable solvent.

In one embodiment of the process, MCPA and the triazine herbicide are dissolved in at least one solvent to form a solution, optionally with heating, and then crystallisation is induced, for example, by cooling the solution, evaporation of the solvent, or by
25 precipitation. Precipitation may be induced, for example, by the addition of an anti-solvent or by cooling.

For example, in the case that the molecular complex comprises MCPA and atrazine, crystallisation may be achieved by the formation a solution of MCPA and atrazine in a suitable solvent, such as toluene, and then cooling the solution to induce precipitation of the molecular complex, such as cooling to a temperature of around 5 °C. In the case
30 that the molecular complex comprises MCPA and cyanazine, crystallisation may be achieved by the formation a solution of MCPA and cyanazine in a suitable solvent, such as methanol, at an elevated temperature, such as between 40 and 60 °C, and then

cooling the solution to induce precipitation of the molecular complex, such as cooling to a temperature of around 5 °C.

In a further embodiment of the process, MCPA and the triazine herbicide are combined with a suitable solvent but the compounds are not fully dissolved so that solid material
5 remains. The mixture is then subjected to stirring, milling or grinding until the molecular complex is obtained. The amount of time required for crystal formation can be readily determined by one skilled in the art and depends on factors including the temperature and the level of energy input.

For example, in the case that the molecular complex comprises MCPA and propazine or
10 MCPA and simazine, crystallisation may be achieved by the combination of MCPA and propazine or MCPA and simazine with a suitable solvent, such as heptane, in an amount such that the compounds are not fully dissolved, and then stirring at an elevated temperature, such as between 40 and 60 °C, and then filtering the crystalline product.

In the case that the molecular complex comprises MCPA and terbutryn, MCPA and
15 prometryn, or MCPA and ametryn, crystallisation may be achieved by the combination of MCPA and terbutryn, MCPA and prometryn, or MCPA and ametryn with a suitable solvent, such as heptane, in an amount such that the compounds are not fully dissolved, for example at a temperature between 2 and 7 °C, and then filtering the crystalline product.

It has been advantageously found that the molecular complexes may be formed by
20 milling the active materials in an aqueous medium to form a suspension of particles of the molecular complexes. Such a method may simplify the manufacture of herbicidal compositions as described herein, in particular compositions provided in the form of a suspension concentrate. Therefore, in a further embodiment of the method, the method
25 comprises the steps of (i) preparing an aqueous suspension of MCPA and a triazine herbicide; (ii) milling the aqueous suspension.

Alternatively, the MCPA triazine herbicide molecular complex may be prepared by a method comprising the step of applying dual asymmetric centrifugal forces to a mixture of MCPA and the triazine herbicide to form the molecular complex.

30 The molecular complex of MCPA and triazine herbicide is formed using dual asymmetric centrifugal forces. By “dual asymmetric centrifugal forces” we mean that two centrifugal forces, at an angle to each other, are simultaneously applied to the particles. In order to create an efficient mixing environment, the centrifugal forces preferably rotate in opposite

directions. The Speedmixer™ by Hauschild (<http://www.speedmixer.co.uk/index.php>) utilises this dual rotation method whereby the motor of the Speedmixer™ rotates the base plate of the mixing unit in a clockwise direction (see Figure 15A) and the basket is spun in an anti-clockwise direction (see Figures 15B and 15C).

- 5 The method may be controlled by various parameters including the rotation speed at which the process takes place, the length of processing time, the level to which the mixing container is filled, the use of milling media and/or the control of the temperature of the components within the milling pot.

The dual asymmetric centrifugal forces may be applied for a continuous period of time.

- 10 By “continuous” we mean a period of time without interruption. The period of time may be from about 1 second to about 90 minutes, such as about 5 seconds to about 60 minutes, for example, about 40 minutes.

- Alternatively, the dual asymmetric centrifugal forces may be applied for an aggregate period of time. By “aggregate” we mean the sum or total of more than one periods of time (e.g. 2, 3, 4, 5 or more times). The advantage of applying the centrifugal forces in a stepwise manner is that excessive heating of the particles can be avoided. The dual asymmetric centrifugal forces may be applied for an aggregate period of about 1 second to about 30 minutes, for example about 30 seconds to about 15 minutes and such as about 10 seconds to about 10 minutes. In one embodiment, the dual asymmetric centrifugal forces are applied in a stepwise manner with periods of cooling therebetween. In another embodiment, the dual asymmetric centrifugal forces may be applied in a stepwise manner at one or more different speeds.

- The speed of the dual asymmetric centrifugal forces may be from about 200 rpm to about 4000 rpm. In one embodiment, the speed may be from about 300 rpm to about 3750 rpm, for example about 500 rpm to about 3500 rpm. In one embodiment, the speed may be about 1900 rpm.

- The level to which the mixing container is filled is determined by various factors which will be apparent to the skilled person. These factors include the apparent density of the MCPA and triazine herbicide, the volume of the mixing container and the weight restrictions imposed on the mixer itself.

Milling media as described above may be used to assist the reaction. In certain embodiments, the dual asymmetric centrifugal forces may be applied in a stepwise manner in which milling media may be used for some, but not all, periods of time.

The method may be carried out in a wet or dry environment. For example, water may be added to the mixture of MCPA and triazine herbicide. Water can act to minimise particle welding. The addition of water may be particularly helpful if the MCPA and/or triazine herbicide being reacted has agglomerated prior to use, in which case the water can assist with breaking down the agglomerates.

When the method is carried out in a dry environment, no additional solvent (such as water) is added to the mixture of MCPA and triazine herbicide.

When the dual asymmetric centrifugal forces are applied for an aggregate period of time, the wet or dry environment may be changed for each period of time. For example, the method may comprise a first period of time in which the environment is dry (i.e. MCPA and triazine herbicide are reacted together optionally with milling media in the absence of solvent), and a second period of time in which the environment is wet after the addition of solvent.

The MCPA may be present in stoichiometric or excess molar equivalents to the triazine herbicide. In one embodiment, the MCPA is present in stoichiometric quantities.

The present invention will now be described with reference to the following examples, which are provided to assist with understanding the present invention, and are not intended to limit its scope.

Examples

Example 1 - MCPA: atrazine (1:1) molecular complex

Atrazine (20 mg) (Tokyo Chemical Industry) and MCPA (18.6 mg, 1 mol eq.) (Sigma Aldrich) were dissolved in toluene (0.6 ml) at 50 °C with stirring. The clear solution was cooled to 5 °C at 0.2 °C min⁻¹ to give a slurry. This slurry was filtered, then dried under suction to yield a crystalline product.

The crystalline material was analysed by ¹H NMR which confirmed a molar ratio of MCPA: atrazine of 1:1.

The material was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 1.

The molecular complex of MCPA and atrazine shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 1 as degree 2-Theta (° 2θ) values ± 0.2 degrees 2-theta.

Table 1 – MCPA: Atrazine (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
6.4	87.2	25.4	7.0
7.5	9.6	25.8	9.1
12.0	100.0	26.6	17.2
14.1	5.9	26.9	12.5
16.9	12.0	27.2	5.6
18.1	55.5	28.1	6.3
20.2	26.7	30.0	5.3
20.7	5.7	31.7	5.6
21.0	6.6	32.5	5.0
22.5	20.8	34.8	10.5
22.7	56.8	36.1	7.5
24.1	9.2	36.4	5.5
24.9	4.1		

DSC analysis (Figure 2) indicated a melting point with an onset temperature of about 128.9 °C.

5 **Example 2 - MCPA: propazine (1:1) molecular complex**

Propazine (20 mg) (Bond Chemicals Ltd) and of MCPA (17.5 mg, 1 mol eq.) (Sigma Aldrich) were suspended in heptane (1.2 ml) at 50 °C with stirring. The slurry was filtered, then dried under suction to yield a crystalline product.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of
10 MCPA: propazine of 1:1.

The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 3.

The molecular complex of MCPA and propazine shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the
15 reflexes shown in Table 2 as degree 2-Theta (2θ) values ± 0.2 degrees 2-theta.

Table 2 - MCPA: Propazine (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
9.1	20.1	20.0	9.1
9.8	73.5	20.2	8.3
10.2	11.5	20.8	5.2

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
11.2	36.2	21.5	7.2
12.2	37.1	21.7	9.2
12.6	3.5	22.1	12.0
13.1	5.5	22.5	5.4
13.4	16.4	24.0	6.5
13.6	3.7	25.3	100.0
14.1	2.6	26.0	8.0
14.6	5.5	27.2	25.9
16.0	9.6	29.4	7.5
17.3	2.8	31.7	9.4
18.5	20.7		
19.0	4.0		

DSC analysis (Figure 4) indicated a melting point with an onset temperature of about 112.4°C.

Example 3 – MCPA: cyanazine: (1:1) molecular complex

- 5 20 mg of cyanazine (Bond Chemicals Ltd) and 16.7 mg of MCPA (1 mol eq.) (Sigma Aldrich) were dissolved in methanol (0.4 ml) at 50 °C with stirring. The clear solution was cooled to 5 °C at 0.2 °C min⁻¹ to give a slurry. This slurry was filtered, then dried in a vacuum oven for a few days.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of

- 10 MCPA: cyanazine of 1:1.

The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 5.

- This molecular complex of MCPA and cyanazine shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the
15 reflexes shown in Table 3 as degree 2-Theta (2θ) values ± 0.2 degrees 2-theta.

Table 3 - MCPA: cyanazine (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
6.1	40.6	22.9	37.4
8.9	100.0	23.1	14.7
10.2	45.6	24.5	41.2
11.4	46.8	25.4	11.9
12.2	82.3	25.8	59.5

14.1	21.4	26.3	30.9
15.3	9.8	26.8	19.7
16.5	17.9	27.3	69.7
19.6	32.6	29.6	10.5
20.3	8.6	32.1	19.3
20.7	20.9	32.3	12.6
21.0	13.9	33.4	7.5
21.2	14.9	40.0	11.1
21.4	40.5		

DSC analysis (Figure 6) indicated a melting point with an onset temperature of about 144.4 °C.

Example 4 – MCPA: simazine (1:1) molecular complex

- 5 A mixture of 20 mg of simazine (Atlantic Research Chemicals Ltd) and 19.9 mg of MCPA (1 mol eq) (Sigma Aldrich) was suspended in heptane (1.2 ml) and stirred at 50 °C for 12 hrs. The slurry was filtered and dried under suction.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of MCPA: simazine of 1:1.

- 10 The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 7.

This molecular complex of MCPA and simazine shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 4 as degree 2-Theta (2θ) values ± 0.2 degrees 2-theta.

- 15 Table 4 - MCPA: simazine (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)
6.6	95.5
9.7	12.5
11.8	100.0
12.0	33.3
13.1	32.7
19.3	38.1
19.9	18.2
20.3	13.5
22.3	27.2
23.3	55.7
24.8	21.0

25.7	9.0
26.1	13.1
27.1	22.8
27.7	24.6
29.7	10.2

DSC analysis (Figure 8) indicated a melting point with an onset temperature of about 128.4 °C.

Example 5 – MCPA: terbutryn (1:1) molecular complex

- 5 A mixture of 20 mg of terbutryn (Bond Chemicals Ltd) and 16.6 mg of MCPA (1 mol eq) (Sigma Aldrich) was placed in heptane (50 µl) and stirred at 5 °C. The slurry was filtered and dried by evaporation.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of MCPA: terbutryn of 1:1.

- 10 The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 9.

This molecular complex of MCPA and terbutryn shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 5 as degree 2-Theta (2θ) values ± 0.2 degrees 2-theta.

- 15 Table 5 - MCPA: terbutryn (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
7.5	34.5	19.6	100.0
7.9	48.0	20.4	14.1
10.9	49.7	20.9	32.9
11.2	24.4	21.3	26.6
11.8	11.8	21.5	61.8
13.2	13.1	22.5	16.4
14.0	54.9	23.0	35.2
14.7	52.8	23.3	64.3
14.9	24.5	24.1	35.5
15.5	12.2	24.5	32.6
15.9	51.6	25.7	54.1
16.2	13.7	26.3	26.0
16.6	9.6	29.0	15.8
16.9	38.5	31.8	32.5
18.5	14.5	33.3	15.5

19.0	55.9	34.2	11.4
------	------	------	------

DSC analysis (Figure 10) indicated a melting point with an onset temperature of about 52.5 °C.

Example 6 – MCPA: prometryn (1:1) molecular complex

- 5 A mixture of 20 mg of prometryn (Bond Chemicals Ltd) and 16.6 mg of MCPA (1 mol eq) (Sigma Aldrich) was placed in heptane (50 µl) and stirred at 5 °C. The slurry was filtered and dried by evaporation.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of MCPA: prometryn of 1:1.

- 10 The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 11.

This molecular complex of MCPA and prometryn shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 6 as degree 2-Theta (2θ) values ± 0.2 degrees 2-theta.

- 15 Table 6 - MCPA: prometryn (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
4.7	23.9	19.9	6.8
7.1	8.9	20.3	15.4
7.3	17.8	20.4	12.0
8.7	100.0	20.8	27.4
9.0	78.4	21.0	10.3
9.4	22.0	21.5	19.2
11.3	10.9	21.7	14.7
12.1	59.1	22.2	18.9
12.4	9.1	22.5	25.0
13.0	4.6	22.7	13.7
13.5	14.3	22.9	18.3
14.1	28.2	24.4	16.8
14.7	21.8	25.1	15.3
15.3	13.5	25.9	32.6
16.1	17.6	26.7	35.1
17.0	6.6	27.5	13.2
17.6	20.8	28.2	12.4
17.8	13.2	28.6	9.2

18.2	13.5	29.3	7.4
18.8	17.7	29.8	7.3
19.4	8.2	31.6	8.0
19.7	9.0	35.1	9.7

DSC analysis (Figure 12) indicated a melting point with an onset temperature of about 62.3 °C.

Example 7 – MCPA: ametryn (1:1) molecular complex

- 5 A mixture of 20 mg of ametryn (Bond Chemicals Ltd) and 17.7 mg of MCPA (1 mol eq) (Sigma Aldrich) was placed in heptane (50 ml) and stirred at 5 °C. The slurry was filtered and dried by evaporation.

The molecular complex was analysed by ¹H NMR which confirmed a molar ratio of MCPA: ametryn of 1:1.

- 10 The molecular complex was also analysed by XRPD which showed a crystalline material and yielded a diffractogram as provided in Figure 13.

This molecular complex of MCPA and ametryn shows at least 5, preferably at least 8 or at least 12, more preferably at least 15, even more preferably at least 20, or all of the reflexes shown in Table 7 as degrees 2-Theta (2θ) values ± 0.2 degrees 2-theta.

15

Table 7 - MCPA: ametryn (1:1) molecular complex XRPD data

Angle (2-Theta °)	Intensity (%)	Angle (2-Theta °)	Intensity (%)
7.5	28.2	21.0	20.2
7.6	31.8	21.4	19.2
9.6	100.0	21.5	20.5
10.2	43.5	22.2	37.4
13.2	29.5	22.7	30.2
13.6	19.7	23.1	54.8
15.0	60.2	23.9	43.6
15.4	43.4	24.3	28.9
16.8	23.1	24.5	30.3
18.1	19.5	25.0	91.0
19.0	20.5	26.8	37.0
20.0	20.0	29.3	16.9
20.5	45.8	31.6	19.5

DSC analysis (Figure 14) indicated a melting point with an onset temperature of about 43.6 °C.

Example 8 – Preparation of MCPA: atrazine (1:1) molecular complex in water

5 Atrazine (20 mg) (Tokyo Chemical Industry) and MCPA (19 mg) (Sigma Aldrich) was placed in a 2 ml HPLC vial with two grinding beads. The mixture was initially wetted with water (20 µl) and ground for 2 hr at 600 rpm using a Fritsch milling system with an Automaxion adapter then air dried for 5 min.

XRPD analysis provided a diffractogram which was consistent with that of Example 1

Example 9 – Preparation of MCPA: simazine (1:1) molecular complex in water

10 Simazine (20 mg) (Tokyo Chemical Industry) and MCPA (20 mg) (Sigma Aldrich) was placed in a 2 ml HPLC vial with two grinding beads. The mixture was initially wetted with water (20 µl) and ground for 2 hr at 600 rpm using a Fritsch milling system with an Automaxion adapter then air dried for 5 min.

XRPD analysis provided a diffractogram which was consistent with that of Example 4

15 **Example 10 – preparation of MCPA: cyanazine (1:1) molecular complex in water**

Cyanazine (20 mg) (Tokyo Chemical Industry) and MCPA (17 mg) (Sigma Aldrich) was placed in a 2 ml HPLC vial with two grinding beads. The mixture was initially wetted with water (20 µl) and ground for 2 hr at 600 rpm using a Fritsch milling system with an Automaxion adapter then air dried for 5 min.

20 XRPD analysis provided a diffractogram which was consistent with that of Example 3.

Example 11 – MCPA : atrazine (1:1) molecular complex

A mixture of atrazine (538 mg) (Tokyo Chemical Industry) and MCPA (500 mg, 1 mol eq.) (Tokyo Chemical Industry) was placed in a 40 ml plastic beaker with 3 mm stainless steel beads 0.5 ml of water were added. The mixture was milled at 1900 rpm for 40 min in a
25 DAC 150-FVZK Speedmixer™. Samples obtained after this milling procedure were air-dried overnight before analysis. XRPD data and DSC analysis indicated a molecular complex consistent with Example 1 and Figures 1 and 2.

The same molecular complex was prepared by milling in the absence of water or solvents. The dry sample showed an XRPD pattern consistent with that prepared with water.

30 **Example 12 – MCPA : simazine (1:1) molecular complex**

A mixture of simazine (503 mg) (Atlantic Research Chemicals) and MCPA (500 mg, 1 mol eq.) (Tokyo Chemical Industry) was placed in a 40 ml plastic beaker with 3 mm stainless steel beads. The dry mixture was milled at 1900 rpm for 40 min in a DAC 150-FVZK Speedmixer™. Samples obtained after this milling procedure were stored overnight before analysis. XRPD data and DSC analysis indicated a molecular complex consistent with Example 4 and Figures 7 and 8.

Molecular complex testing

X-Ray Powder Diffraction (XRPD)

XRPD diffractograms were collected on a Bruker D8 diffractometer.

Brucker D8 uses Cu K α radiation (40 kV, 40 mA) and a θ -2 θ goniometer fitted with a Ge monochromator. The incident beam passes through a 2.0 mm divergence slit followed by a 0.2 mm anti-scatter slit and knife edge. The diffracted beam passes through an 8.0 mm receiving slit with 2.5° Soller slits followed by the Lynxeye Detector. The software used for data collection and analysis was Diffrac Plus XRD Commander and Diffrac Plus EVA respectively.

Samples were run under ambient conditions as flat plate specimens using powder as received. The sample was prepared on a polished, zero-background (510) silicon wafer by gently pressing onto the flat surface or packed into a cut cavity. The sample was rotated in its own plane.

Data collection method is:

- Angular range: 2 to 42° 2 θ
- Step size: 0.05° 2 θ
- Collection time: 0.5 s/step (total collection time: 6.40 min)

Stability in water

The stability in water over a period of three weeks was assessed by stirring 50 mg of the molecular complex in 1 ml water for 3 weeks at 25 °C followed by XRPD analysis.

Thermodynamic solubility in water

Aqueous solubility was determined by suspending sufficient amount of compound in deionised water to give a maximum final concentration of ≥ 10 mg/ml of the compound.

The suspension was equilibrated at 25 °C, on a Heidolph plate shaker set to 750 rpm for

24 hours. The pH of the saturated solution was then measured and the suspension filtered through a glass fibre C filter (particle retention 1.2 µm) and diluted appropriately. Quantitation was by HPLC with reference to a standard solution of approximately 0.15 mg/ml in DMSO. Different volumes of the standard, diluted and undiluted sample solutions were injected. The solubility was calculated using the peak areas determined by integration of the peak found at the same retention time as the principal peak in the standard injection.

Table 8 - HPLC method for solubility measurements

Parameter	Value		
Type of method	Reverse phase with gradient elution		
Column	Phenomenex Luna, C18 (2) 5 µm 50 x 4.6 mm		
Column Temperature (°C)	25		
Standard Injections (µl)	1, 2, 3, 4, 5, 7		
Test Injections (µl)	1, 2, 3, 10, 15, 20		
Detection: Wavelength, Bandwidth (nm)	260,90		
Flow Rate (ml/min)	2		
Phase A	0.1% TFA in water		
Phase B	0.085% TFA in acetonitrile		
Timetable	Time (min)	% Phase A	% Phase B
	0	95	5
	1	80	20
	2.3	5	95
	3.3	5	95
	3.5	95	5
	4.4	95	5

Analysis was performed on an Agilent HP1100 series system equipped with a diode array detector and using ChemStation software.

Differential Scanning calorimetry (DSC)

DSC (melting point) was assessed using either a TA Instruments Q2000 or TA Instruments Discovery DSC. Typically, 0.5 - 3 mg of each sample, in a pin-holed aluminium pan, was heated at 10 °C/min from 25 °C to 300 °C. A purge of dry nitrogen at 50 ml/min was maintained over the sample.

Thermogravimetric analysis (TGA)

TGA was assessed using either a TA Instruments Q500 TGA or TA Instruments Discovery TGA. Typically, 5 - 10 mg of each sample was loaded onto a pre-tared aluminium DSC pan and heated at 10 °C/min from ambient temperature to 350 °C. A nitrogen purge at 60 ml/min was maintained over the sample.

5 Gravimetric Vapour Sorption

Hygroscopicity of a solid material may be determined by means of gravimetric vapour sorption (GVS) analysis, sometimes known by dynamic vapour sorption (DVS) analysis. The experiment subjects a sample material which is held in a fine wire basket on a microbalance within a temperature and humidity controlled environment (chamber).

10 Using the software, the collected data can then be processed to determine the isotherm points at the increment ranges specified during the experiment and show the overall water uptake of the material.

Hygroscopicity was assessed by Gravimetric vapour sorption. Sorption isotherms were
 15 obtained using a SMS DVS Intrinsic moisture sorption analyser, controlled by DVS Intrinsic Control software. The sample temperature was maintained at 25 °C by the instrument controls. The humidity was controlled by mixing streams of dry and wet nitrogen, with a total flow rate of 200 ml/min. The relative humidity was measured by a calibrated Rotronic probe (dynamic range of 1.0 – 100 %RH), located near the sample.
 20 The weight change, (mass relaxation) of the sample as a function of %RH was constantly monitored by a microbalance (accuracy ± 0.005 mg).

Typically, 5 - 30 mg of sample was placed in a tared mesh stainless steel basket under ambient conditions. The sample was loaded and unloaded at 40 %RH and 25 °C (typical room conditions). A moisture sorption isotherm was performed as outlined below (2
 25 scans per complete cycle). The standard isotherm was performed at 25 °C at 10 %RH intervals over a 0 – 90 %RH range. Typically, a double cycle (4 scans) was carried out. Data analysis was carried out within Microsoft Excel using the DVS Analysis Suite.

Table 9 - Method for SMS DVS Intrinsic experiments

Parameter	Value
Adsorption – Scan 1	40 – 90
Desorption, Adsorption – Scan 2	90 – 0, 0 – 40
Intervals (%RH)	10
Number of Scans	4

Flow rate (ml/min)	200
Temperature (°C)	25
Stability (°C/min)	0.2
Sorption Time (hours)	6 hour time out
Number of cycles	2

The sample was recovered after completion of the isotherm and re-analysed by XRPD.

Example 1

The physicochemical properties of the MCPA: atrazine molecular complex formed in Example 1 were evaluated alongside the individual compounds MCPA and atrazine. The results are provided in Table 10.

Table 10 – Results of the testing of physicochemical properties of molecular complex formed in Example 1

	Example 1	Atrazine	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.18 mg/ml Atrazine: 0.04 mg/ml (3.91)	0.03 mg/mL (8.81)	0.81 mg/ml (2.96)
DSC (melting point)	128.9 °C	176.0 °C	119.2 °C
TGA	Degradation from ca. 100 °C	Degradation from ca. 200 °C	Degradation from ca. 100 °C
GVS	Non hygroscopic up to 70 % RH, 4.1% uptake to 90% RH Small hysteresis from 80-40 % RH	Non hygroscopic. 0.16% uptake at 90% RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% RH Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

Example 2

The physicochemical properties of the MCPA: propazine molecular complex formed in Example 2 were evaluated alongside the individual compounds MCPA and propazine. The results are provided in Table 11.

Table 11 – Results of the testing of physicochemical properties of molecular complex formed in Example 2

5

	Example 2	Propazine	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.51 mg/ml Propazine: 0.01 mg/ml (3.18)	0.01 mg/ml (8.75)	0.81 mg/ml (2.96)
DSC (melting point)	112.4 °C	215.7 °C	119.2 °C
TGA	Degradation from 180 °C	Degradation from ca. 120 °C	Degradation from ca. 100 °C
GVS	Non hygroscopic up to 70% RH 6.4 % uptake between 70 and 90 % RH Hysteresis between 90 and 40% RH	Non hygroscopic up to 70% RH Hygroscopic from 70 to 90% RH with 3.6 % uptake Hysteresis between 70 and 40% RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% RH Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

Example 3

The physicochemical properties of the MCPA:cyanazine molecular complex formed in Example 3 were evaluated alongside the individual compounds MCPA and cyanazine.

10 The results are provided in Table 12.

Table 12 – Results of the testing of physicochemical properties of molecular complex formed in Example 3

	Example 3	Cyanazine	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.14 mg/ml Cyanazine: 0.16 mg/ml (4.32)	0.02 mg/ml (7.39)	0.81 mg/ml (2.96)

DSC (melting point)	144.4 °C	164.5 °C	119.2 °C
TGA	Degradation from 140 °C	Degradation from ca. 130 °C	Degradation from ca. 100 °C
GVS	Non-hygroscopic up to 70% RH 0.8% uptake between 70 and 90% RH Small hysteresis between 90 and 40% RH	Non-hygroscopic up to 70% RH 1.9% uptake from 70 to 90% RH Small hysteresis between 90 and 40% RH	Non-hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% RH Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

Example 4

The physicochemical properties of the MCPA: simazine molecular complex formed in Example 4 were evaluated alongside the individual compounds MCPA and simazine.

- 5 The results are provided in Table 13.

Table 13 – Results of the testing of physicochemical properties of molecular complex formed in Example 4.

	Example 4	Simazine	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.52 mg/ml Simazine: 0.01 mg/ml (3.11)	<0.001 mg/ml (7.27)	0.81 mg/ml (2.96)
DSC (melting point)	128.4 °C	No melt	119.2 °C
TGA	Degradation from 130 °C	Degradation from ca. 160 °C	Degradation from ca. 100 °C
GVS	Non-hygroscopic up to 70% RH, 5.5% uptake between 70 and 90% RH Hysteresis between 80 and 40% RH	Non-hygroscopic up to 70% RH, 3.2% uptake between 70% and 90% RH Hysteresis between 80 and 40% RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% RH Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

Example 5

The physicochemical properties of the MCPA: terbutryn molecular complex formed in Example 5 were evaluated alongside the individual compounds MCPA and simazine. The results are provided in Table 14.

5 Table 14 – Results of the testing of physicochemical properties of molecular complex formed in Example 5.

Sample ID	Example 5	Terbutryn	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.42 mg/ml Terbutryn: 0.13 mg/ml (3.67)	0.03 mg/ml (8.85)	0.81 mg/ml (2.96)
DSC (melting point)	52.4 °C	102.2 °C	119.2 °C
TGA	Degradation from ca. 125 °C	Degradation from ca. 140 °C	Degradation from ca. 100 °C
GVS	Non-hygroscopic up to 70% RH, Hygroscopic between 70 and 90% RH with 3.4% uptake Small hysteresis between 70 and 40 % RH	Non hygroscopic to 70% RH, Hygroscopic after 70%, 2.2% uptake from 70 to 90% RH Small hysteresis from 80 – 40 % RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No Change	No change

Example 6

The physicochemical properties of the MCPA: prometryn molecular complex formed in Example 6 were evaluated alongside the individual compounds MCPA and prometryn.

10 The results are provided in Table 15.

Table 15 – Results of the testing of physicochemical properties of molecular complex formed in Example 6.

Sample ID	Example 6	Prometryn	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MCPA: 0.34 mg/ml Prometryn: 0.14 mg/ml (3.6)	0.03 mg/ml (8.99)	0.81 mg/ml (2.96)
DSC (melting point)	62.3 °C	119.5 °C	119.2 °C
TGA	Degradation from ca. 140 °C	Degradation from ca. 120 °C	Degradation from ca. 100 °C
GVS	Non-hygroscopic up to 70% RH, 4.3% uptake between 70 and 90% RH, Small hysteresis between 80 and 40% RH	Non-hygroscopic up to 70% RH, 1.0 % uptake after 70%, Small hysteresis between 80 and 40% RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

5 **Example 7**

The physicochemical properties of the MCPA: ametryn molecular complex formed in Example 7 were tested alongside the individual compounds MCPA and ametryn. The results are provided in Table 16.

Table 16 – Results of the testing of physicochemical properties of molecular complex formed in Example 7

Sample ID	Example 7	Ametryn	MCPA
¹ H-NMR (Stoichiometry)	1:1	N/A	N/A
Thermodynamic solubility in water (25 °C) (pH)	MPCA: 0.48 mg/ml Ametryn: 0.52 mg/ml (3.88)	0.20 mg/ml (8.99)	0.81 mg/ml (2.96)

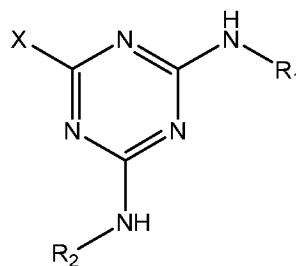
DSC (melting point)	43.6 °C	84.9 °C	119.2 °C
TGA	Degradation from ca. 120 °C	Degradation from ca. 115 °C	Degradation from ca. 100 °C
GVS	Non hygroscopic up to 70% RH 3.8% uptake from 70 to 90% RH Hysteresis from 80 to 40% RH	Non-hygroscopic, 0.38% uptake at 90% RH Small hysteresis between 80 and 40% RH	Non hygroscopic up to 70% RH Hygroscopic with 8.3% uptake from 70 to 90% Small hysteresis between 70 and 40% RH
XRPD post-GVS	No change	No change	No change

The results of the testing of the physicochemical properties testing of the molecular complexes generated in Examples 1-7 indicates that the MCPA / triazine molecular complexes show good stability and a high melting point. In addition, the solubility of

5 MCPA is reduced and is more closely matched to the triazine active agents.

Claims

1. A molecular complex comprising:
2-methyl-4-chlorophenoxyacetic acid (MCPA); and
a compound selected from the group of triazine herbicides.
2. A molecular complex according to claim 1 wherein the triazine herbicide is of formula (I):



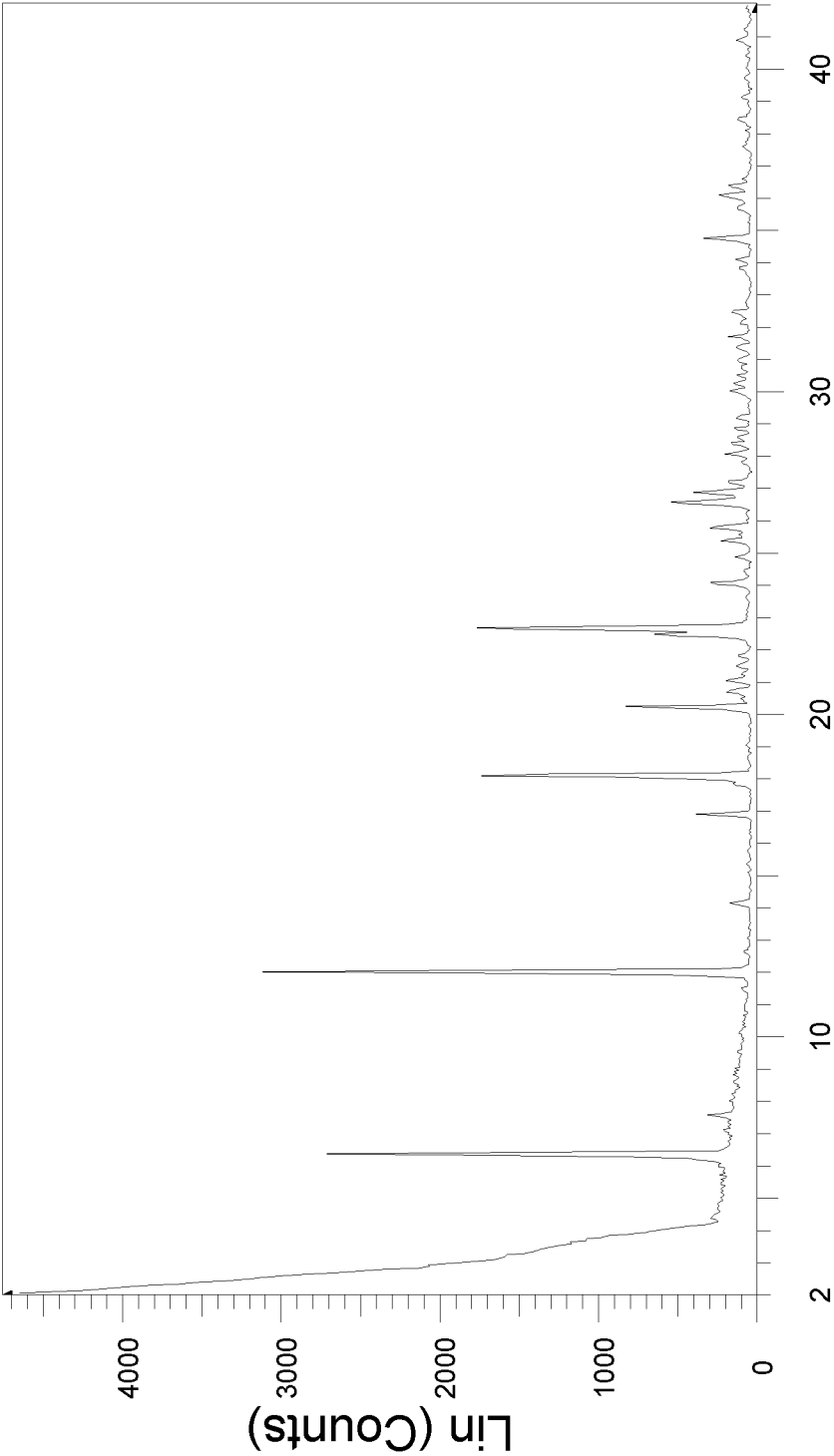
(I)

- wherein X = Cl, -OCH₃, or -SCH₃; R₁ = ethyl or isopropyl; R₂ = ethyl, iso-propyl, cyclopropyl, tert-butyl, or -C(CH₃)₂CN.
3. A molecular complex according to claim 1 or claim 2 wherein the molar ratio of MCPA to the triazine herbicide is 1:1.
 4. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is selected from atrazine, simazine, cyanazine, propazine, terbutryn, prometryn or ametryn.
 5. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is atrazine.
 6. A molecular complex according to claim 5 wherein the molar ratio of MCPA: atrazine is 1:1.
 7. A molecular complex according to claim 5 or claim 6 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 6.4, 7.5, 12.0, 14.1, 16.9, 18.1, 20.2, 20.7, 21.0, 22.5, 22.7, 24.1, 24.9, 25.4, 25.8, 26.6, 26.9, 27.2, 28.1, 30.0, 31.7, 32.5, 34.8, 36.1, 36.4 degrees two-theta $\pm$ 0.2 degrees 2-theta.
 8. A molecular complex according to claim 5 or claim 6 with a melting point with an onset temperature of about 129 °C

9. A molecular complex according to any one of the preceding claims wherein the triazine herbicide is propazine.
10. A molecular complex according to claim 9 wherein the molar ratio of MCPA: propazine is 1:1.
- 5 11. A molecular complex according to claim 9 or claim 10 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 9.1, 9.8, 10.2, 11.2, 12.2, 12.6, 13.1, 13.4, 13.6, 14.1, 14.6, 16.0, 17.3, 18.5, 19.0, 20.0, 20.2, 20.8, 21.5, 21.7, 22.1, 22.5, 24.0, 25.3, 26.0, 27.2, 29.4, 31.7 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 10 12. A molecular complex according to claim 9 or claim 10 with a melting point with an onset temperature of about 112 °C.
13. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is cyanazine.
14. A molecular complex according to claim 13 wherein the molar ratio of MCPA: cyanazine is 1:1.
- 15 15. A molecular complex according to claim 13 or claim 14 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 6.1, 8.9, 10.2, 11.4, 12.2, 14.1, 15.3, 16.5, 19.6, 20.3, 20.7, 21.0, 21.2, 21.4, 22.9, 23.1, 24.5, 25.4, 25.8, 26.3, 26.8, 27.3, 29.6, 32.1, 32.3, 33.4, 40.0 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 20 16. A molecular complex according to claim 13 or claim 14 with a melting point with an onset temperature of about 112 °C.
17. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is simazine.
18. A molecular complex according to claim 17 wherein the molar ratio of MCPA: simazine is 1:1.
- 25 19. A molecular complex according to claim 17 or claim 18 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 6.6, 9.7, 11.8, 12.0, 13.1, 19.3, 19.9, 20.3, 22.3, 23.3, 24.8, 25.7, 26.1, 27.1, 27.7, 29.7 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 30 20. A molecular complex according to claim 17 or claim 18 with a melting point with an onset temperature of about 128 °C.

21. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is terbutryn.
22. A molecular complex according to claim 21 wherein the molar ratio of MCPA: terbutryn is 1:1.
- 5 23. A molecular complex according to claim 21 or claim 22 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 7.5, 7.9, 10.9, 11.2, 11.8, 13.2, 14.0, 14.7, 14.9, 15.5, 15.9, 16.2, 16.6, 16.9, 18.5, 19.0, 19.6, 20.4, 20.9, 21.3, 21.5, 22.5, 23.0, 23.3, 24.1, 24.5, 25.7, 26.3, 29.0, 31.8, 33.3, 34.2 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 10 24. A molecular complex according to claim 21 or claim 22 with a melting point with an onset temperature of about 53 °C.
25. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is prometryn.
26. A molecular complex according to claim 25 wherein the molar ratio of MCPA: prometryn is 1:1.
- 15 27. A molecular complex according to claim 25 or claim 26 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 4.7, 7.1, 7.3, 8.7, 9.0, 9.4, 11.3, 12.1, 12.4, 13.0, 13.5, 14.1, 14.7, 15.3, 16.1, 17.0, 17.6, 17.8, 18.2, 18.8, 19.4, 19.7, 19.9, 20.3, 20.4, 20.8, 21.0, 21.5, 21.7, 22.2, 22.5, 22.7, 22.9, 24.4, 25.1, 25.9, 26.7, 27.5, 28.2, 28.6, 29.3, 29.8, 31.6, 35.1 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 20 28. A molecular complex according to claim 25 or claim 26 with a melting point with an onset temperature of about 62 °C.
29. A molecular complex according to any one of claims 1 to 4 wherein the triazine herbicide is ametryn.
- 25 30. A molecular complex according to claim 29 wherein the molar ratio of MCPA: ametryn is 1:1.
31. A molecular complex according to claim 29 or claim 30 wherein an X-ray powder diffractogram shows at least five of the following diffraction lines: 7.5, 7.6, 9.6, 10.2, 13.2, 13.6, 15.0, 15.4, 16.8, 18.1, 19.0, 20.0, 21.0, 21.4, 21.5, 22.2, 22.7, 23.1, 23.9, 24.3, 24.5, 25.0, 26.8, 29.3, 31.6 degrees two-theta $\pm$ 0.2 degrees 2-theta.
- 30

32. A molecular complex according to claim 29 or claim 30 with a melting point with an onset temperature of about 44 °C.
33. A method for preparing a molecular complex according to any one of the preceding claims, which comprises combining MCPA and a triazine herbicide in a
5 suitable solvent.
34. A method according to claim 33 comprising the steps of:
- (i) preparing an aqueous suspension of MCPA and a triazine herbicide;
 - (ii) milling the aqueous suspension.
35. A method for preparing a molecular complex according to any one of claims 1 to
10 32, the method comprising the step of applying dual asymmetric centrifugal forces to a mixture of MCPA and the triazine herbicide to form the molecular complex.
36. An herbicidal composition comprising a molecular complex according to any one of claims 1 to 32 and at least one agriculturally acceptable carrier.
37. A herbicidal composition according to claim 36 wherein the composition is a solid
15 formulation, such as a powder or granulated composition.
38. A herbicidal composition according to claim 36 wherein the composition is a liquid formulation, such as an aqueous suspension concentrate or a suspo-emulsion.
39. A herbicidal composition according to any one of claims 36 to 38 wherein the composition comprises between 10 and 90 wt% of the molecular complex based on the
20 total weight of the composition.
40. The use of an herbicidal composition according to any one of claims 36 to 39 for controlling undesired vegetation.
41. A method for controlling undesired vegetation comprising contacting the vegetation with a herbicidal composition according to any one of claims 36 to 39.



2-Theta - Scale

FIGURE 1

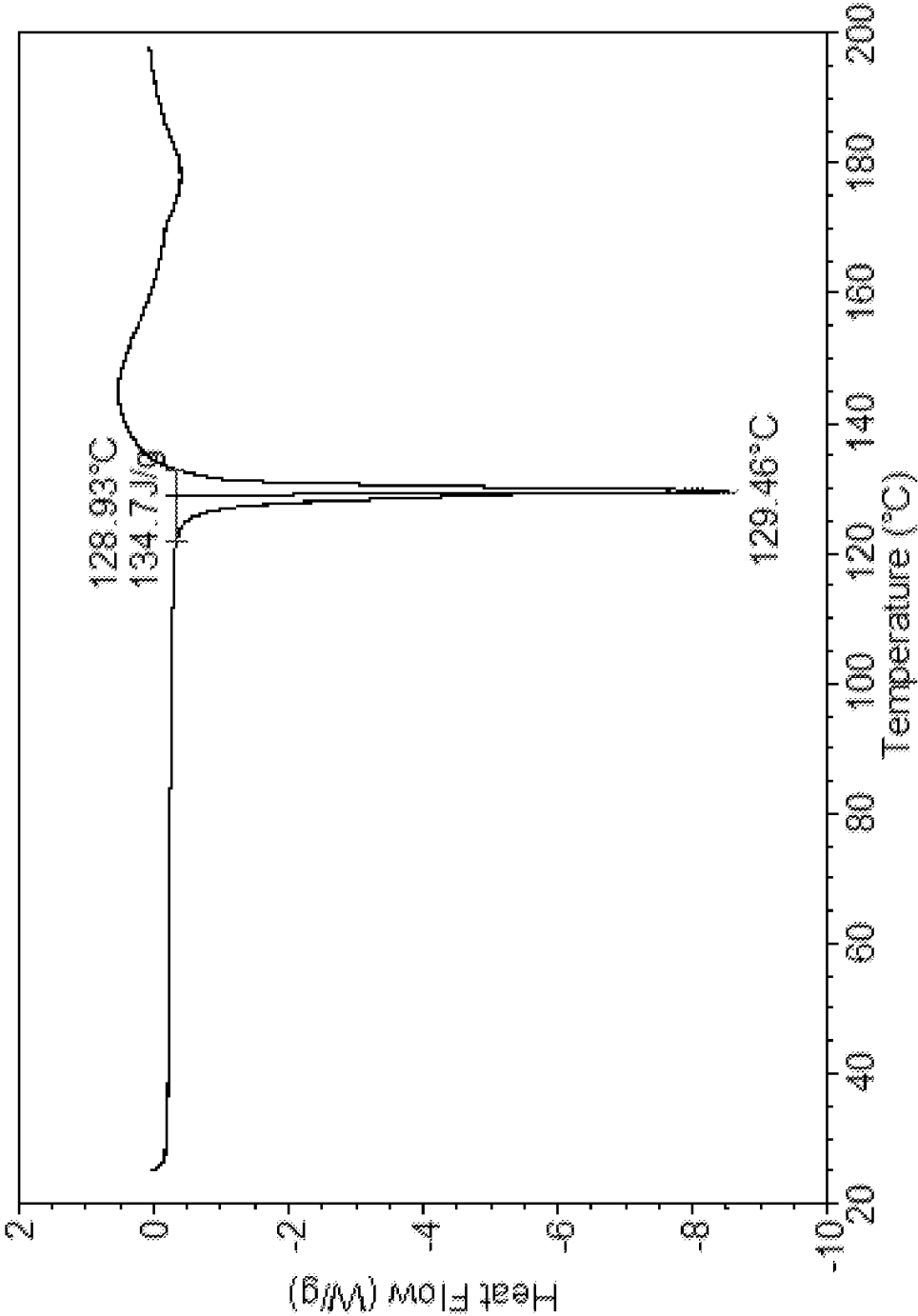
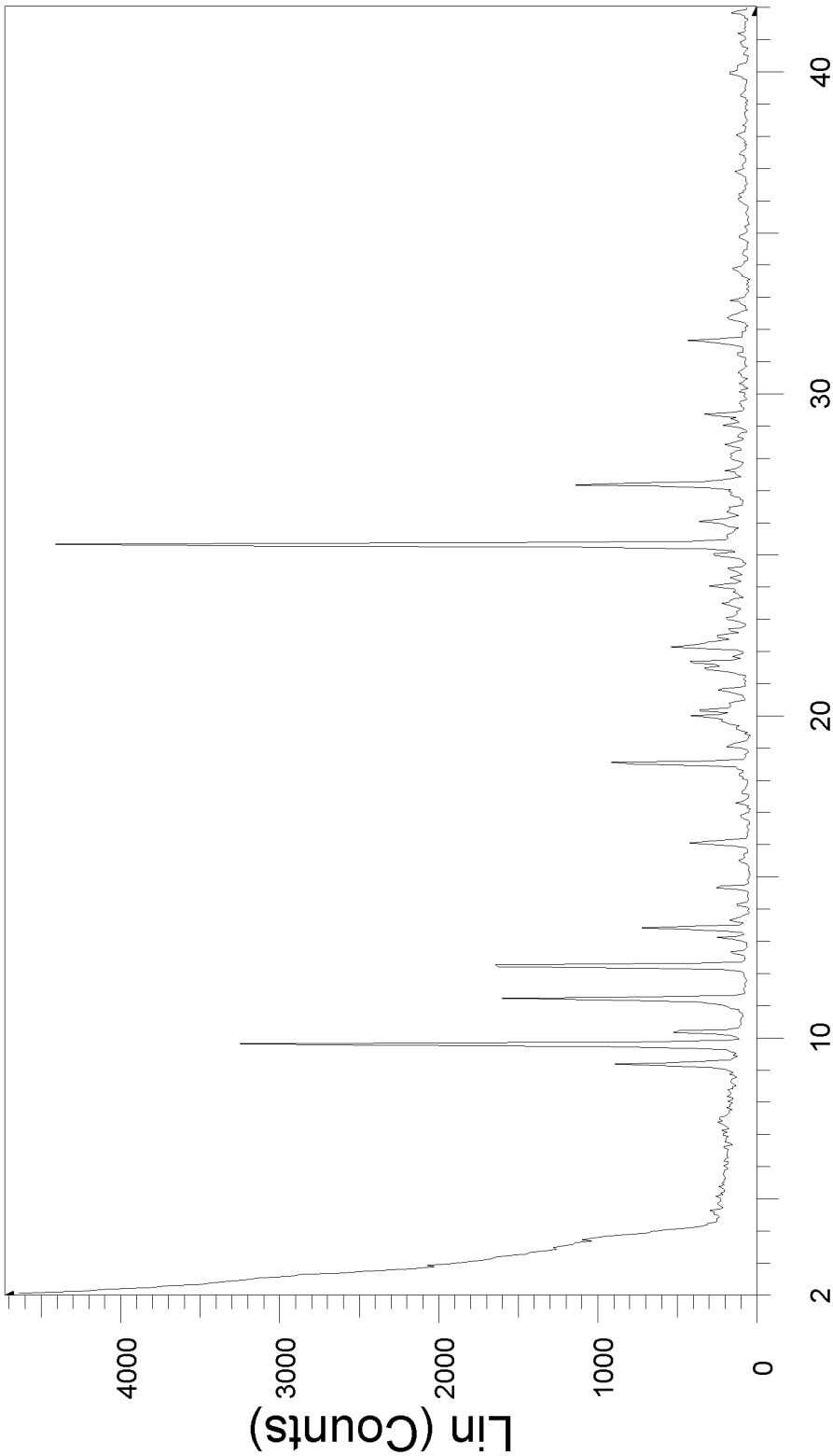


FIGURE 2



2-Theta - Scale

FIGURE 3

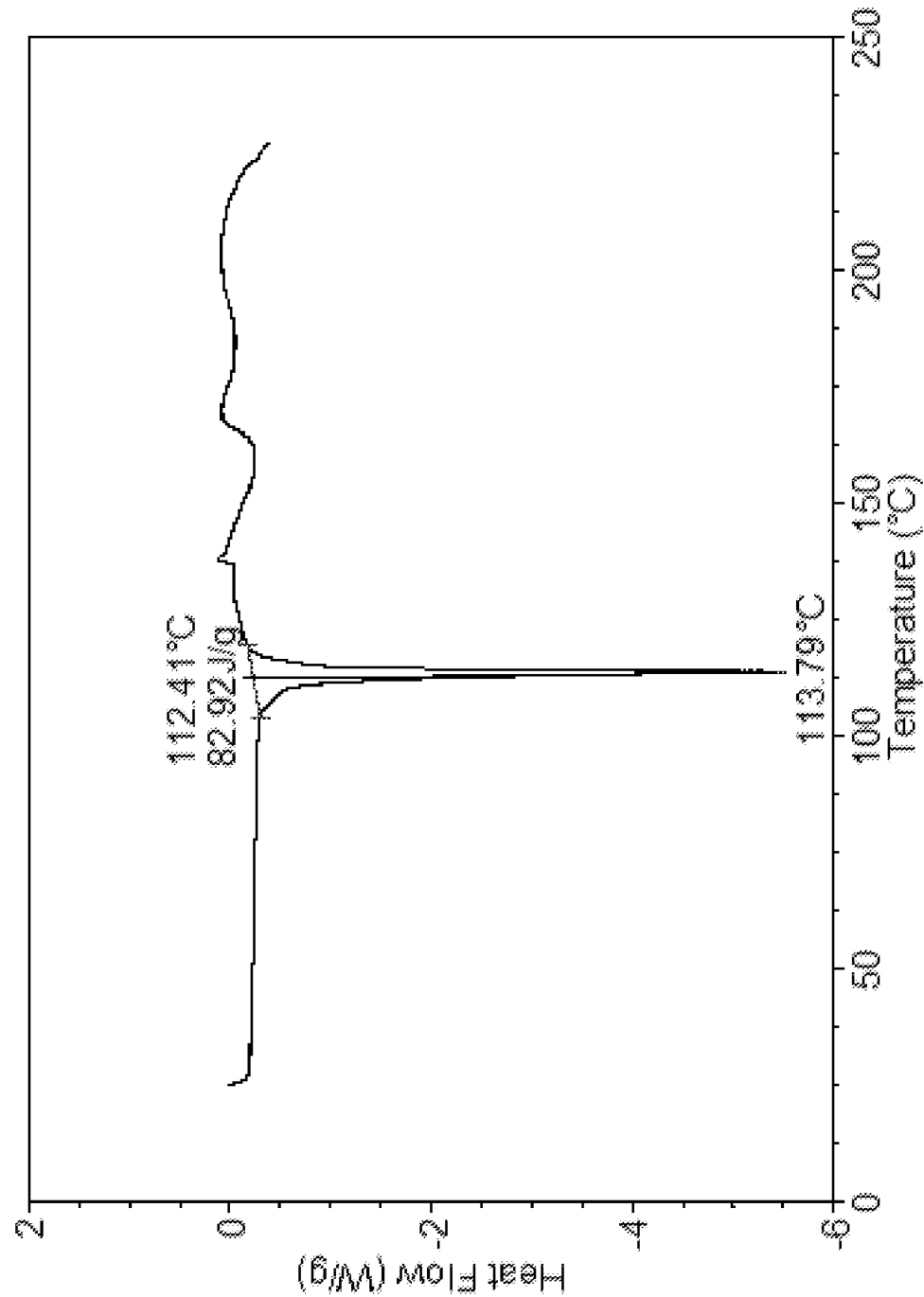
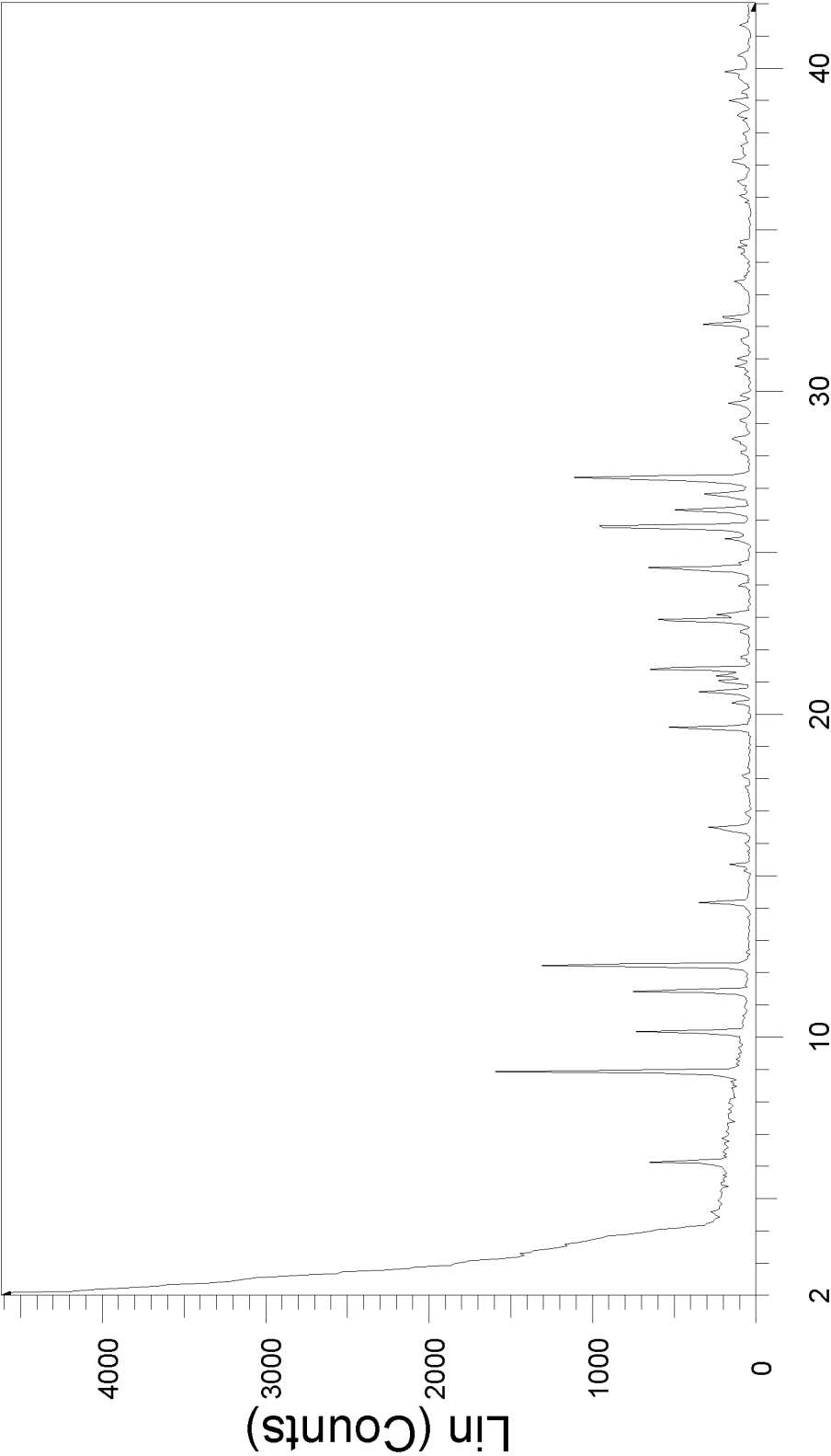


FIGURE 4



2-Theta - Scale

FIGURE 5

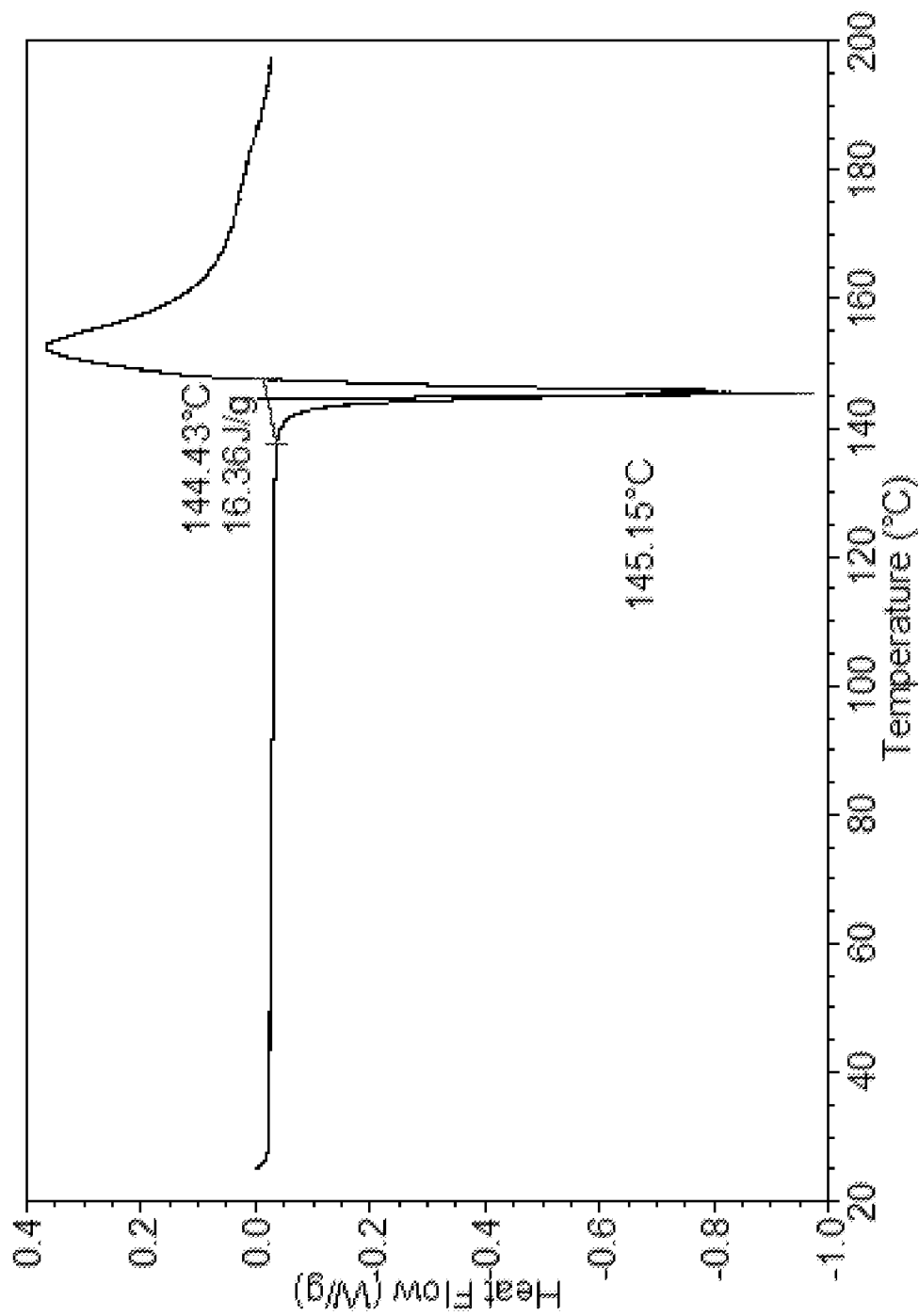
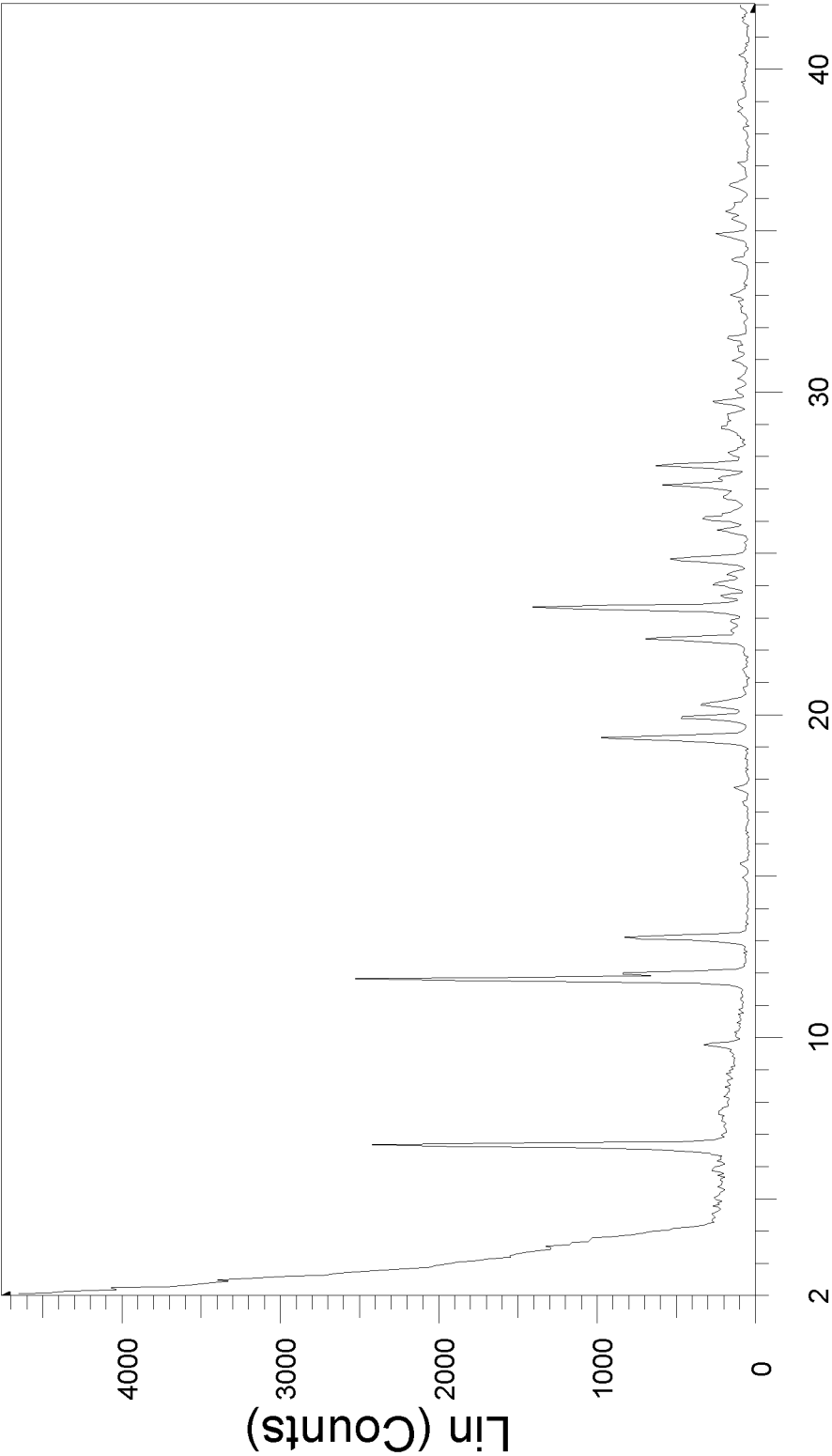


FIGURE 6



2-Theta - Scale

FIGURE 7

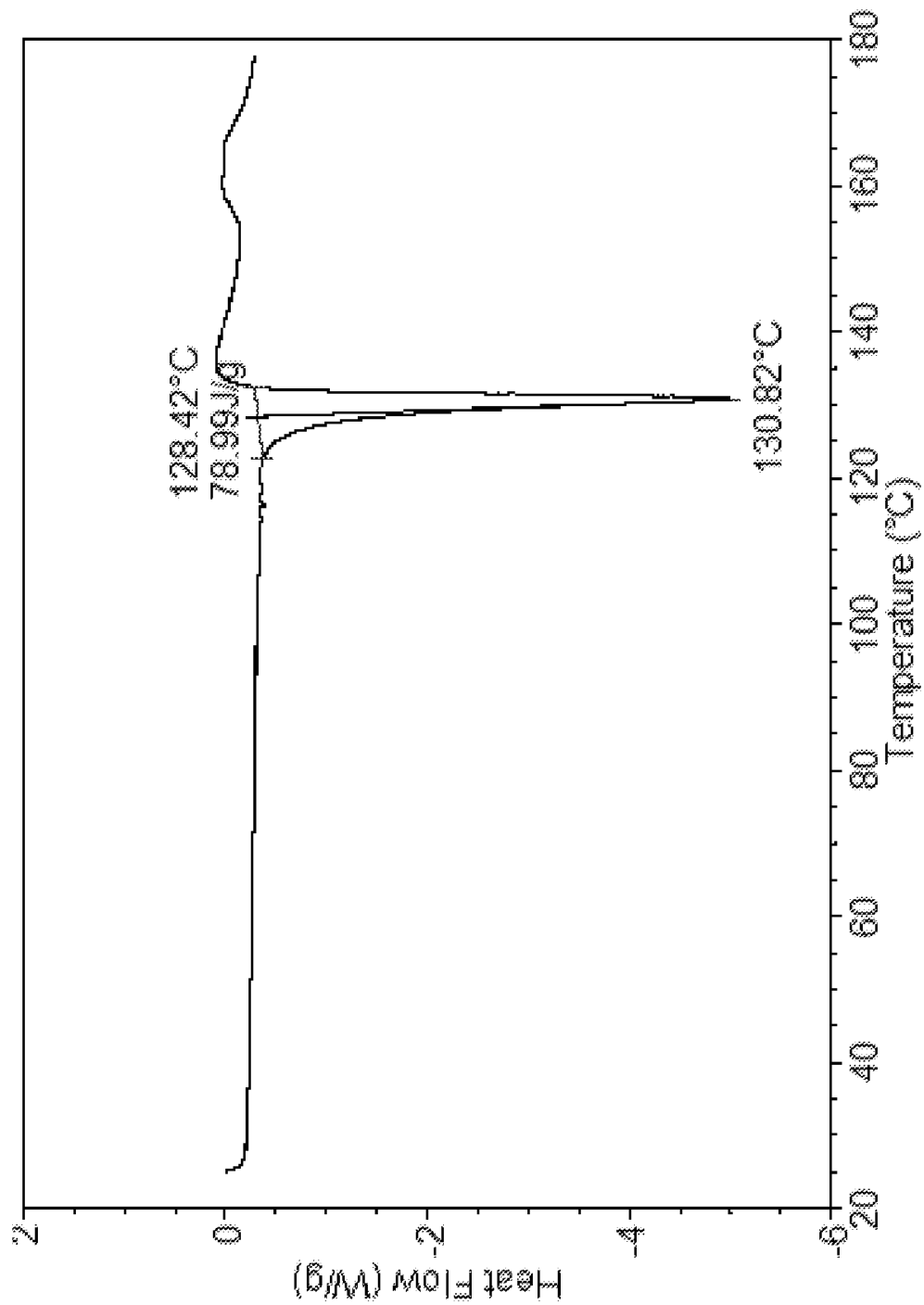
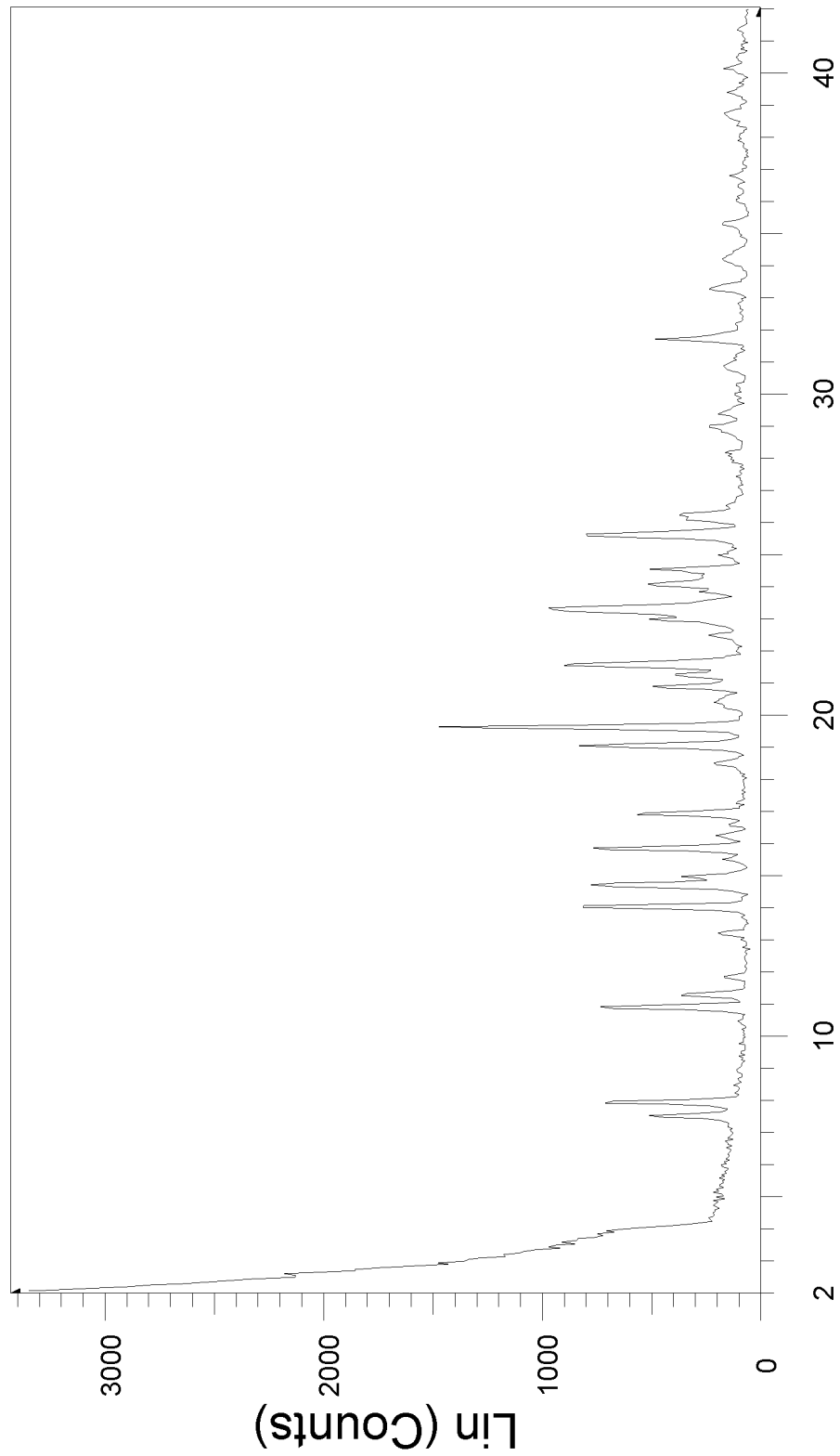


FIGURE 8



2-Theta - Scale

FIGURE 9

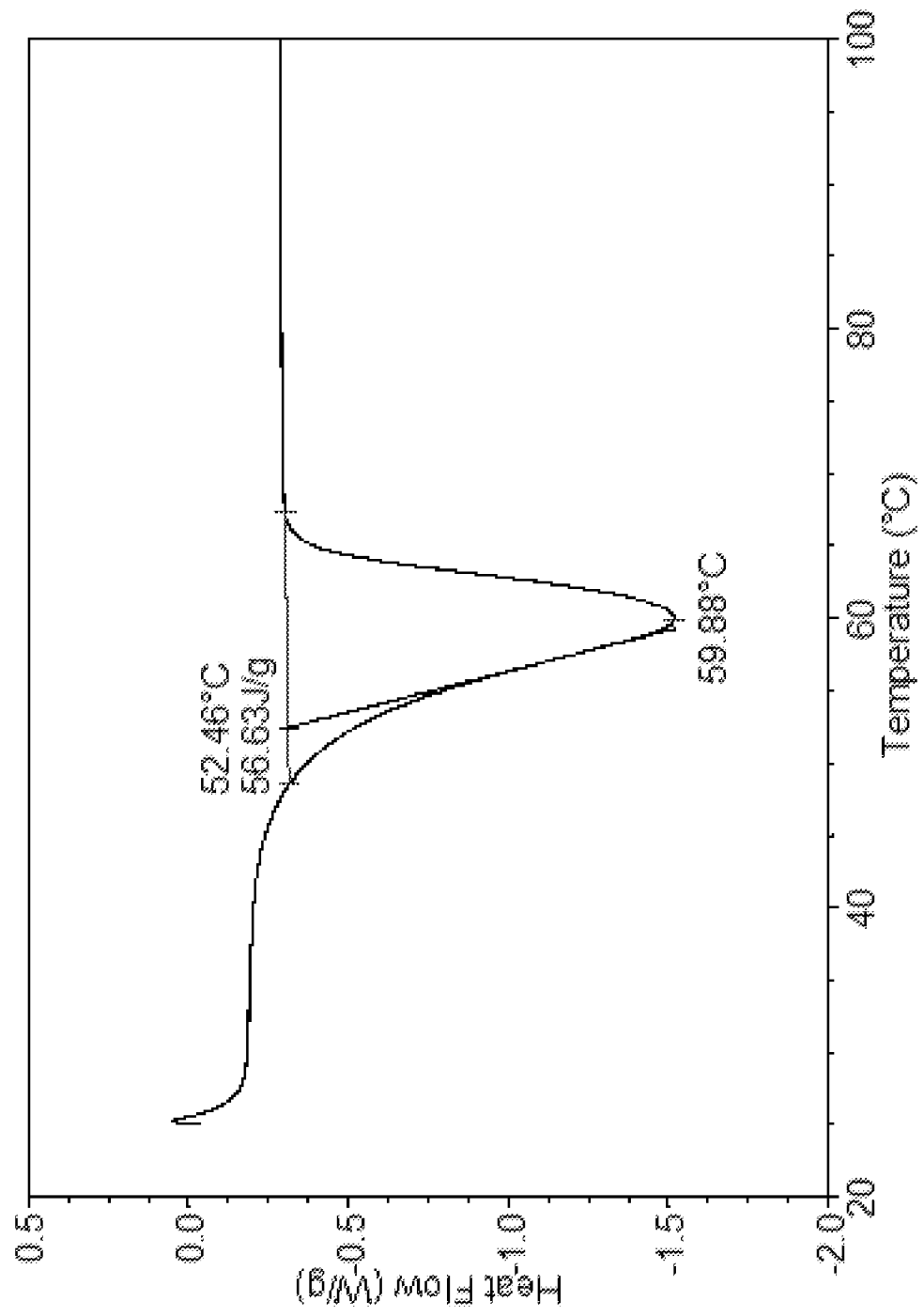
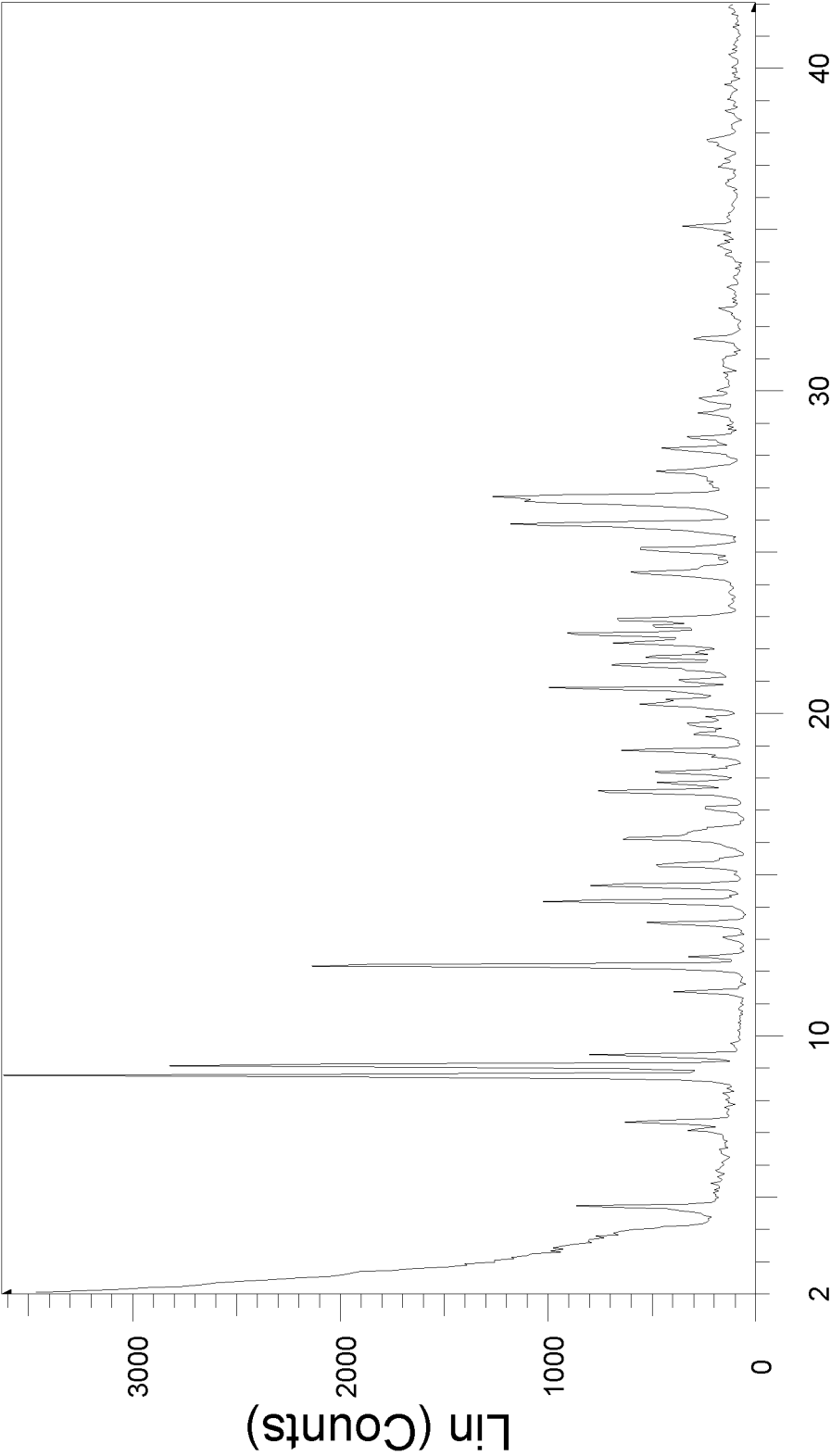


FIGURE 10



2-Theta - Scale

FIGURE 11

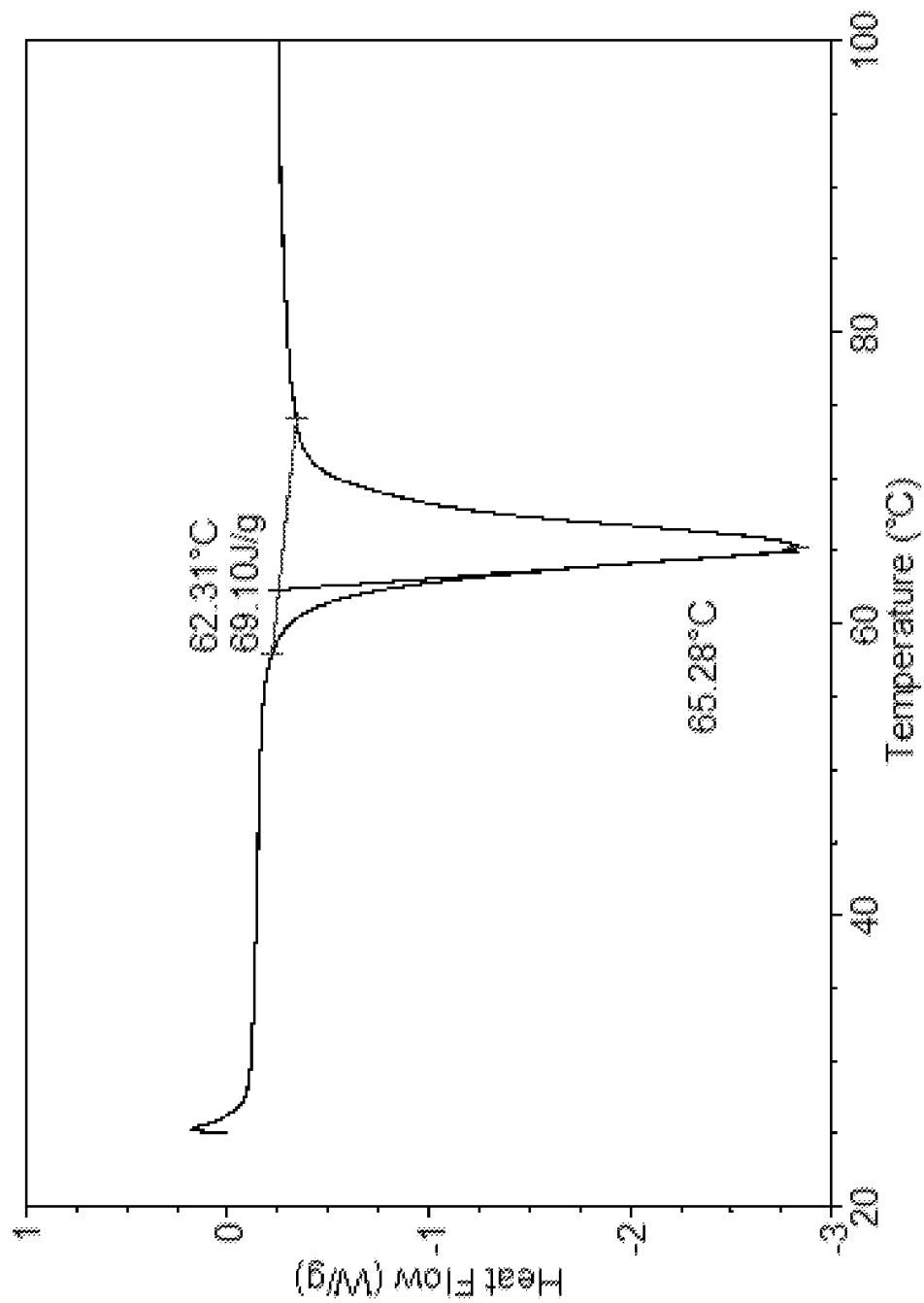
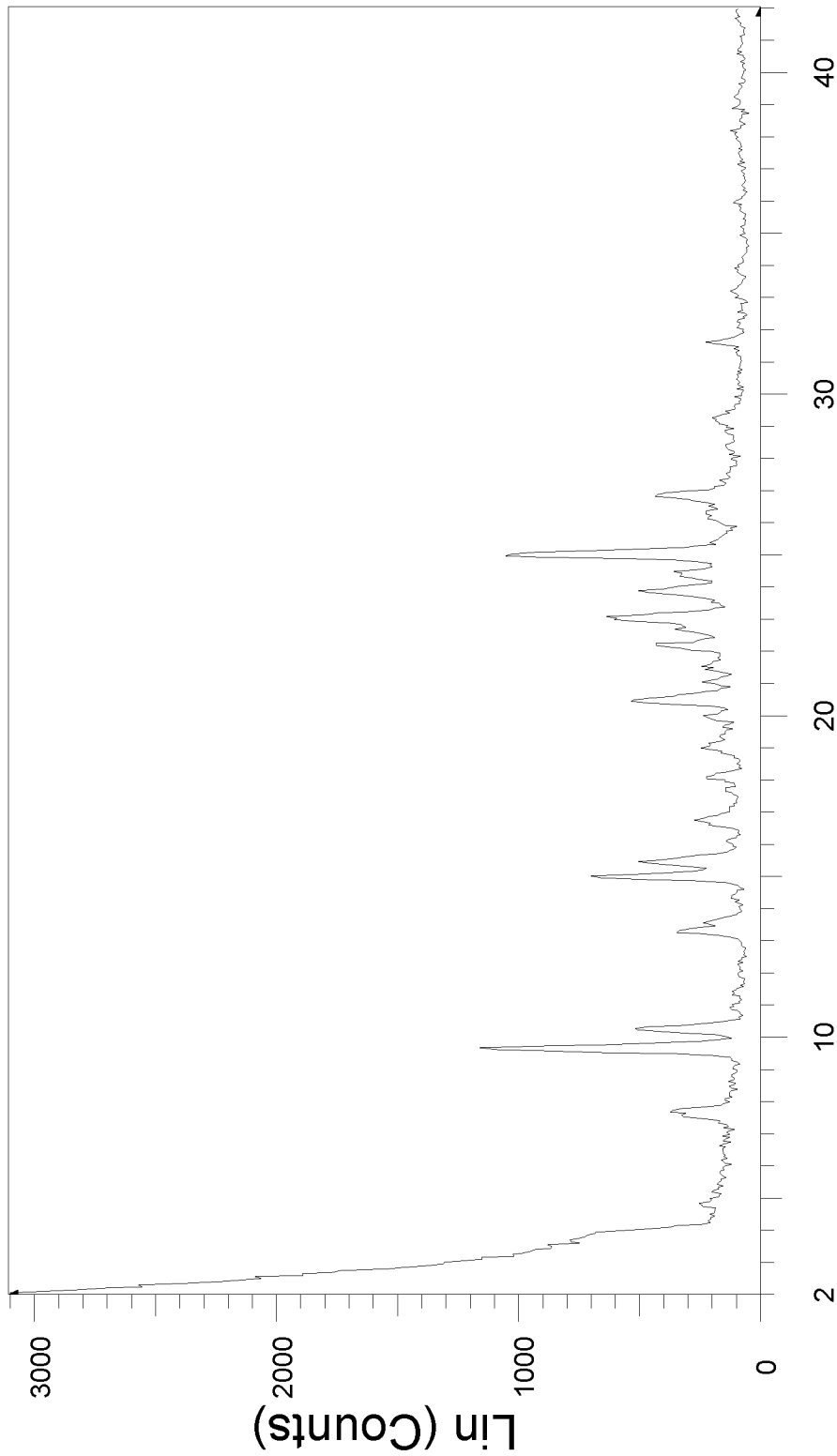


FIGURE 12



2-Theta - Scale

FIGURE 13

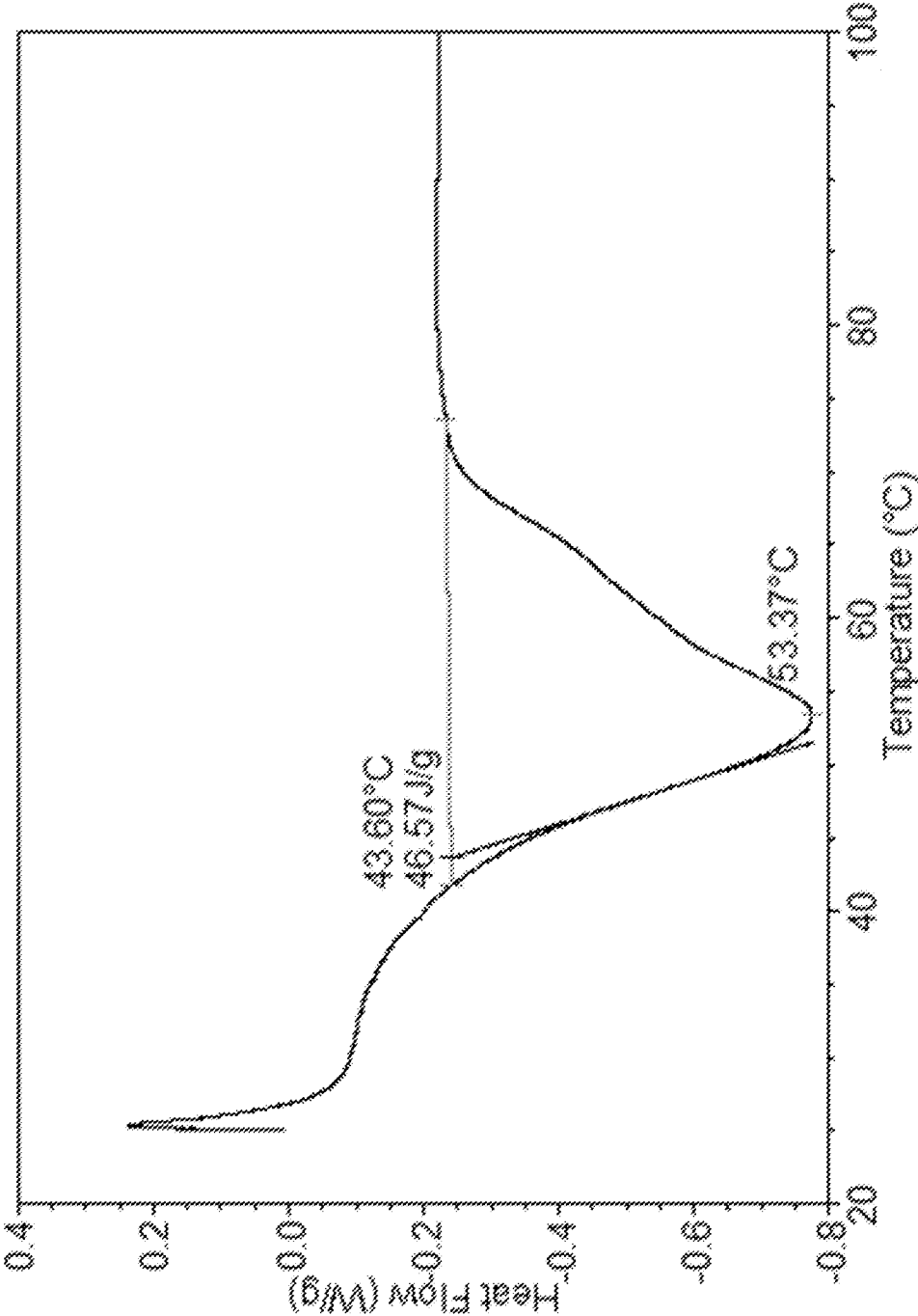


FIGURE 14

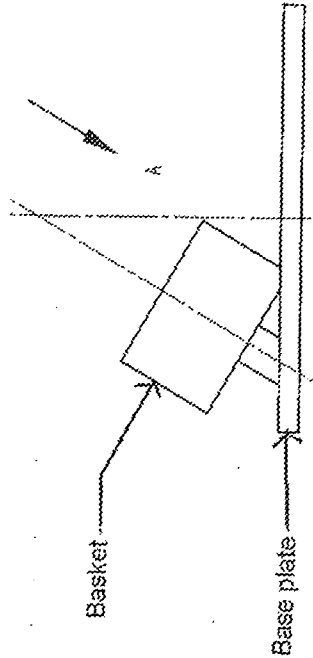
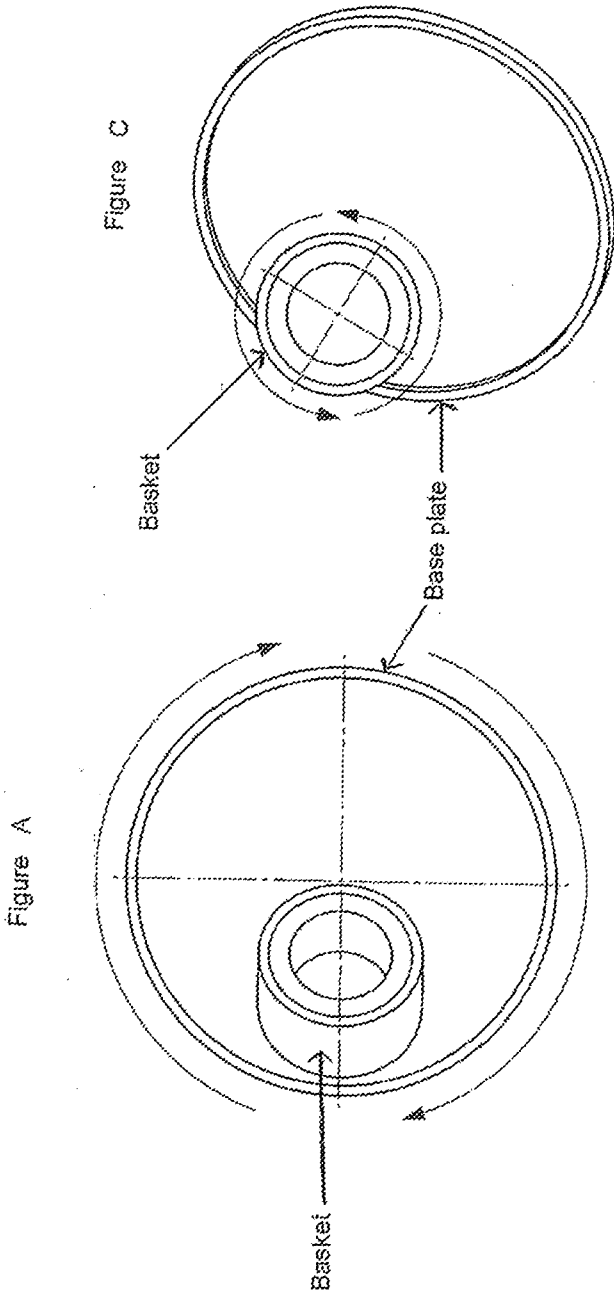


FIGURE 15

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2019/052217

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D251/52 C07D251/50 C07C59/70 A01N39/04 A01N43/70
ADD.

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)

C07D C07C 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)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 1 329 306 A (GEIGY AG J R) 7 June 1963 (1963-06-07)	1-6, 8-10, 12-14, 16-18, 20-22, 24-26, 28-30, 32-41
A	the whole document ----- GB 1 340 271 A (DEGUSSA) 12 December 1973 (1973-12-12) claims 1-8; example 6 -----	1-41



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"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

10 October 2019

Date of mailing of the international search report

23/10/2019

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Johnson, Claire

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2019/052217

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-6, 8-10, 12-14, 16-18, 20-22, 24-26, 28-30, 32-41(all partially)

According to p. 5, a molecular complex is a crystalline material. This feature is not present in claims 1-6, 8-10, 12-14, 16-18, 20-22, 24-26, 28-30, 32-41. However, as mixtures of MCPA with triazine herbicides are well-known in the prior art (see e.g. example 6 of GB 1340271), the present opinion is given for claims 1-41 only in so far as the molecular complex is a crystalline material.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2019/052217

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 1329306	A	07-06-1963	BE 620373 A	10-10-2019
			FR 1329306 A	07-06-1963
			NL 281108 A	10-10-2019

GB 1340271	A	12-12-1973	CA 980592 A	30-12-1975
			DE 2032176 A1	13-01-1972
			FR 2104767 A2	21-04-1972
			GB 1340271 A	12-12-1973
			ZA 7104077 B	26-07-1972
