(12) STANDARD PATENT (11) Application No. **AU 2022201342 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
A PROCESS FOR PREPARATION OF SULFENTRAZONE WITH TANK-MIX COMPATIBILITY

(51) International Patent Classification(s)
A01N 43/653 (2006.01) ***A01N 41/06*** (2006.01)
A01N 25/12 (2006.01)

(21) Application No: **2022201342** (22) Date of Filing: **2022.02.26**

(30) Priority Data

(31) Number	(32) Date	(33) Country
202121008116	**2021.02.26**	**IN**

(43) Publication Date: **2022.09.15**
(43) Publication Journal Date: **2022.09.15**
(44) Accepted Journal Date: **2024.09.26**

(71) Applicant(s)
UPL Limited

(72) Inventor(s)
PANCHAL, Digish Manubhai;PATEL, Rakesh Bhikubhai

(74) Agent / Attorney
Churchill Attorneys, PO BOX 3238, BURNLEY NORTH, VIC, 3121, AU

(56) Related Art
US 9440932 B2
US 2021/0032211 A1

202220134 26 Feb 2022

The present invention relates to an environment friendly process for preparing sulfentrazone having tank-mix compatibility comprising treating sulfentrazone with a base and isolating the pure sulfentrazone with an acid.

26 Feb 2022 2022201342

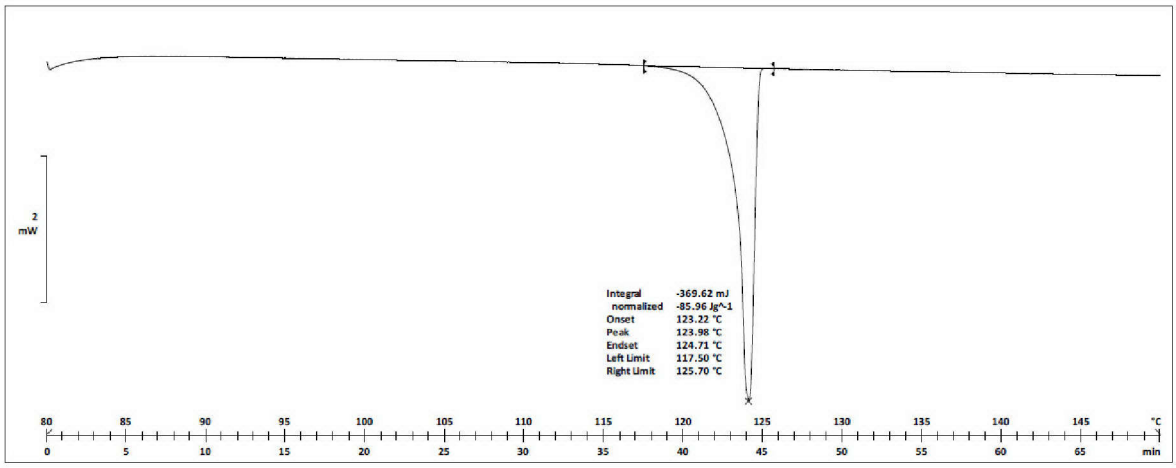


Figure 1

202220134 2 29 Aug 2024

TITLE: A PROCESS FOR PREPARATION OF SULFENTRAZONE WITH TANK-MIX COMPATIBILITY

FIELD OF THE INVENTION

The present invention relates to an environment friendly process for preparing sulfentrazone having tank-mix compatibility.

BACKGROUND OF THE INVENTION

Sulfentrazone is a herbicide belonging to the group of aryl triazolinone. It is chemically known as N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide. It has high efficiency, low toxicity and broad spectra.

Sulfentrazone works by disrupting membranes and inhibiting photosynthesis in plants by a process referred to as PPO inhibition. Sulfentrazone is received in the plants through the roots. As the plants come out of the soil, they die after exposure to light. It is suitable for soybeans, corn, sorghum, peanut, sunflower and so on. It can control annual broad leaf weeds, grasses and sedges.

Very few processes for preparation of sulfentrazone are known till date. Conventionally, sulfentrazone is prepared as per process provided in U.S. Patent 4,818,275. However, the sulfentrazone obtained by such conventional processes doesn't have the desired purity and requires further purification.

Standard methods for the purification of an organic molecules involve use of silica gel column chromatography, use of multiple organic solvents or multiple recrystallization steps. These standard processes are complicated, involves use of large volumes of organic solvents and are not suitable for large scale productions.

The processes reported in literature for obtaining sulfentrazone employ organic solvents like alcohols which have bad impact on environment when one is dealing with industrial scale. During the recovery of these solvents, there is particular loss of solvent which cannot be accounted, thus causing environment pollution and also considerable economical loss.

Furthermore, it was observed that even after employing such conventionally known methods for purification of sulfentrazone, the final product obtained had entrapped solvents, consists of residual solvents and is mixture of multiple polymorphic forms of sulfentrazone. The formulation prepared using sulfentrazone thus obtained, do not have desired quality or satisfactory performance.

Another challenge arises when an end-user of formulation of sulfentrazone, adds to the formulation, with dilution in water, a second agrochemical to form tank mixture. Such tank mixtures of sulfentrazone are widely used, but their use can be limited by tendency of creaming of the active ingredient that can settle and clog filters of nozzles of field spraying equipment. This tendency is another evidence of physical incompatibility of conventionally prepared sulfentrazone in tank-mixtures.

To overcome above discussed problems, the inventors of the present invention have consciously designed a highly desirable process for purification of sulfentrazone that

a) yields sulfentrazone having tank-mix compatibility;

b) doesn't require use of organic solvents;

c) is adaptable to high production volumes;

d) the product is a single component crystalline solid; and

e) reduces economic and environmental burden.

ASPECTS OF THE INVENTION

It is an aspect of the present invention to provide an environment friendly process for preparing sulfentrazone having tank-mix compatibility.

It is another aspect of the present invention to provide sulfentrazone having tank-mix compatibility.

It is another aspect of the present invention to provide sulfentrazone essentially free of organic solvents having purity of greater than 98% as determined by HPLC.

It is another aspect of the present invention to provide sulfentrazone in single component crystalline solid.

It is yet another aspect of the present invention to provide a simple, industrially viable, reproduceable, environment friendly and cost-effective process for preparing sulfentrazone having tank-mix compatibility.

SUMMARY OF THE INVENTION:

According to an aspect of the present invention, there is provided an environment friendly process for preparing a sulfentrazone..

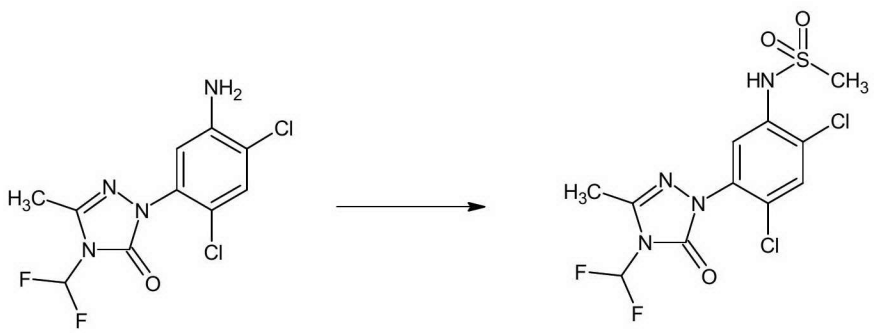
According to an aspect of the present invention, there is provided a process for preparing sulfentrazone which comprises treating a solid form of sulfentrazone with an aqueous base and isolating the pure sulfentrazone with an acid.

According to another aspect of the present invention, there provided a process for preparing sulfentrazone, comprising
a) treating a solid form of sulfentrazone with an aqueous base to obtain medium comprising sulfentrazone salt;
b) isolating the pure sulfentrazone by adjusting pH with an acid.

According to another aspect of the present invention, there is provided a process for preparing sulfentrazone,

comprising,

a) sulfonylating a compound of formula (II) to obtain a solid form of sulfentrazone of formula (I)



Formula (II) Formula (I)

b) treating the solid form of sulfentrazone of formula (I) with an aqueous base to obtain a medium comprising sulfentrazone salt;

c) isolating the pure sulfentrazone by adjusting pH with an acid.

According to another aspect of the present invention, there is provided sulfentrazone having tank-mix compatibility.

According to another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents having purity of greater than 98% as determined by HPLC.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, further characterized by having D_{90} particle size value of less than about 800µm, preferably less than about 700 µm.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, further characterized by having D_{50} particle size value of less than about 25µm, preferably less than about 20µm.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, is having bulk density of about 0.20 gm/ml to 0.70 gm/ml.

According to yet another aspect of the present invention, there is provided a salt of sulfentrazone and process for its preparation.

DESCRIPTION OF THE FIGURES

Figure 1 depicts differential scanning calorimetric (DSC) thermogram of Sulfentrazone having tank-mix compatibility obtained by the process provided in the present invention.

Figure 2 is a photograph showing results of tank mix compatibility test for sample 1.

Figure 3 is a photograph showing results of tank mix compatibility test for sample 2.

DESCRIPTION OF THE INVENTION

Those skilled in art will be aware that invention described herein is subject to variations and modifications other than those specifically described. It is to be understood that the invention described herein includes all such variations and modifications. The invention also includes all such steps, features, compositions and methods referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more said steps or features.

Definitions:

For convenience, before further description of the present invention, certain terms employed in the specification, examples are described here. These definitions should be read in light of the remainder of the disclosure and understood as by a person of skill in the art. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by a person of

ordinary skill in the art. The terms used throughout this specification are defined as follows, unless otherwise limited in specific instances.

The terms used herein are defined as follows.

The term “room temperature” unless stated otherwise, essentially means temperature in range of 20-35 °C

The term "purity" means purity as determined by HPLC ("High Pressure Liquid Chromatography").

The term “Salt" as used herein includes salts that can form with, for example, amines, ammonia, metals, alkali metals or alkaline earth metal bases or quaternary ammonium bases, including zwitter ions. Suitable metal and alkaline earth metal hydroxides as salt formers include the salts of barium, aluminium, nickel, copper, manganese, cobalt zinc, iron, silver, lithium, sodium, potassium, magnesium or calcium.

As used herein the term “medium comprising sulfentrazone salt” unless stated otherwise, means a mixture comprising a liquid medium within which finely divided solids are dispersed, suspended or dissolved completely, the liquid medium may be entirely water, partially water, or may not contain any water at all. The term can be used interchangeably with slurry, dispersion or solution.

The term “solid form of sulfentrazone” as used herein can generically refer to any form of sulfentrazone from solvates, polymorph forms, pseudo polymorph forms, amorphous form or mixture thereof.

Also, the term “solid form of sulfentrazone” is used for sulfentrazone obtained from the conventional process is herein referred to as “technical sulfentrazone” and is used interchangeably. The solid form of sulfentrazone may have 1 to 10% wt/wt organic solvent content.

202220134 2 29 Aug 2024

The term “pure sulfentrazone” as used herein can refer to sulfentrazone having compatibility obtained using process described in the present invention.

The term “sulfentrazone essentially free of organic solvent” as used herein means sulfentrazone containing less than 3% wt/wt of organic solvent content or less than 1% wt/wt of organic solvent content or less than 0.5% of organic solvent content.

The term “creaming” as used herein can refer to curding, coagulation, aggregation of solid particles, sedimentation or flocculation and is used interchangeably.

The term “tank-mix compatibility” as used herein means that no adverse effects or physical incompatibility occurs as a result of mixing sulfentrazone with active pesticide/s or adjuvant/s in a tank-mix.

In the context of this invention, it was found that the sulfentrazone prepared by conventional process deals with numerous problems like a mixture of crystalline modification forms is obtained or organic solvent used during the chemical procedures gets trapped into such crystals. When such conventionally prepared sulfentrazone is used in preparation of tank-mix along with other agrochemicals, the tank-mix obtained has exhibited instability and incompatibility issues.

The technique of tank mixing of various agrochemicals is well known and widely used, it saves time, labour and also reduce application costs. This technique with single supplication solves several purposes like controlling pests and diseases, application of foliar fertilizers etc. However, it was observed by the inventors of the present invention that the conventionally prepared sulfentrazone when used with other agrochemicals in tank-mix, it results in formation of large aggregates. These aggregates rapidly float to the surface, forming a layer, similar to cream. This is also known commonly as "cream formation" or "creaming". Thereby proving that the conventionally prepared sulfentrazone shows incompatibility in tank-mix. Due to the creaming in the tank-mix solution, the solid particles formed would settle and clog filters of nozzles of field spraying equipment. Hence, along with the purity and

other physio-chemical properties, it is very important to produce an agrochemical which has compatibility with wide range of other products and excipients. The compatibility of products not paid attention to may cause serious problems such as loss of efficacy of some of the active ingredients, physical incompatibility between different compounds, separation, blocking of spray systems, foaming, crystallisation and most importantly phytotoxicity.

Inventors of the present invention made several attempts to remove trapped/residual organic solvent from sulfentrazone and achieve a quality of sulfentrazone which has compatibility but the solution to this problem was either too expensive and resulted in decomposition of sulfentrazone or required use of large amount of organic solvent like alcohols which had adverse impact on environment.

After systematic studies, inventors of the present invention have now found that the instability and incompatibility of conventionally obtained sulfentrazone can be conquered by simple, environment friendly and cost-effective process. The inventors of the present invention hence designed a process which doesn't require use of any organic solvent or multiple recrystallizations.

According to an aspect of the present invention, there is provided an environment friendly process for preparing sulfentrazone.

According to an aspect of the present invention, there is provided a process for preparing sulfentrazone, which comprises treating the solid form of sulfentrazone with an aqueous base and isolating the pure sulfentrazone, with an acid.

According to an aspect of the present invention, there is provided a process for preparing sulfentrazone, which comprises treating the solid form of sulfentrazone with an aqueous base and isolating the pure sulfentrazone, with an acid wherein said process is carried out without requiring use of an organic solvent.

In an embodiment of the present invention, said solid form of sulfentrazone comprises any form of sulfentrazone, like amorphous sulfentrazone or a mixture of different crystalline modifications or solvates of sulfentrazone or a mixture of amorphous and/or crystalline sulfentrazone and/or solvates of sulfentrazone.

In an embodiment of the present invention, the solid form of sulfentrazone may contains organic solvents such as halogenated hydrocarbons like chlorobenzene, bromobenzene, dichlorobenzene, trifluoro methyl benzene and trichlorobenzene, ethers like diethyl ether, ethyl propyl ether, n-butyl ether, anisole, phenetole, cyclohexyl methyl ether, dimethyl ether, dimethyl glycol, diphenyl ether, dipropyl ether, diisopropyl ether, di-n-butyl ether, diisobutyl ether, diisoamyl ether, ethylene glycol dimethyl ether, isopropyl ethyl ether, methyl tert-butyl ether, tetrahydrofuran, methyltetrahydrofuran, dioxane, dichlorodiethyl ether, methyl-tetrahydrofuran, polyethers of ethylene oxide and/or propylene oxide, nitrated hydrocarbons like nitromethane, nitroethane, nitropropane, nitrobenzene, chloronitrobenzene and ethyl benzene), aliphatic, cycloaliphatic or aromatic hydrocarbons like pentane, n-hexane, n-heptane, n-octane, nonane, cymene, petroleum fractions having a boiling range of from 70 °C to 190 °C, cyclohexane, methylcyclohexane, petroleum ether, ligroin, octane, benzene toluene, xylene, dimethylbenzene, diethylbenzene, esters like malonates, n-butyl acetate, methyl acetate, ethyl acetate, isobutyl acetate, dimethyl carbonate, diethyl carbonate, dibutyl carbonate and ethylene carbonate, and aliphatic alcohols like methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-amyl alcohol), mesitylene, diethyl ketone, methyl ethyl ketone, acetonitrile and mixtures thereof.

In an embodiment of the present invention, the base used is selected from organic or inorganic base.

In an embodiment of the present invention, the base used is organic base such as methylamine, triethylamine, diethanolamine, piperidine, pyridine and the like.

In another embodiment of the present invention, the base used is inorganic base such as alkali or alkaline earth metal hydroxides, alkali metal or alkaline earth metal carbonates, alkaline earth metal oxides, p-block element carbonates, transition metal carbonates, ammonia and the likes.

Preferably the base is selected from alkali or alkaline earth metal hydroxides, alkali metal or alkaline earth metal carbonates, alkaline earth metal oxides, p-block element carbonates, transition metal carbonates, ammonia or amines.

Base such as sodium hydroxide, potassium hydroxide, silver hydroxide, ammonium hydroxide, barium hydroxide, magnesium hydroxide, calcium hydroxide, zinc hydroxide, iron(II) hydroxide, tin(II) hydroxide, lead(II) hydroxide, copper(II) hydroxide, Aluminium hydroxide, ferrous hydroxide, ammonia, lithium carbonate, lithium bicarbonate, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, magnesium carbonate, magnesium bicarbonate, calcium carbonate, calcium bicarbonate, barium carbonate, magnesium oxide, calcium oxide, barium oxide, thallium carbonate, lead carbonate, zinc carbonate, copper carbonate, silver carbonate, ferrous carbonate and the likes can be used.

In another preferred embodiment, the base used is selected from alkali metal carbonate such as lithium carbonate, lithium bicarbonate, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate or ammonia.

In an embodiment of the present invention, the amount of base used with respect to sulfentrazone is in the range of 0.5 to 5 moles.

According to another embodiment of the present invention, treating the solid form of sulfentrazone with an aqueous base to obtain medium comprising sulfentrazone salt; and isolating the pure sulfentrazone, by adjusting pH with an acid.

According to another embodiment of the present invention, treating the solid form of sulfentrazone with an aqueous base lead to formation of a medium comprising sulfentrazone salt.

According to another embodiment of the present invention, the step of treating the solid form of sulfentrazone with an aqueous base, may further comprise heating the medium to obtain a clear solution.

In an embodiment of the present invention, the medium is heated at temperature range of about 40°C to about 100°C.

According to another embodiment of the present invention, the traces of solvent entrapped in the solid form of sulfentrazone can be recovered during heating.

According to an embodiment of the present invention, the traces of solvent entrapped in the solid form of sulfentrazone can be recovered during heating, azeotropically.

According to another embodiment of the present invention, the clear solution obtained after heating the medium may be cooled before isolating said pure sulfentrazone. The clear solution is cooled below 40°C, preferably to room temperature or below.

According to an embodiment of the present invention, the pure sulfentrazone is precipitated from the clear solution obtained without cooling.

According to another aspect of the present invention, there is provided a process for preparing sulfentrazone, comprising
a) treating solid form of sulfentrazone with an aqueous base to obtain medium comprising sulfentrazone salt;
b) isolating the pure sulfentrazone by adjusting pH of the medium with an acid.

In an embodiment the process is carried out in the absence of an organic solvent.

In an embodiment of the present invention, said process is carried out in aqueous medium.

According to an embodiment of the present invention, the solid form of sulfentrazone on treatment with aqueous base results in formation of medium comprising sulfentrazone salt.

According to an embodiment, the sulfentrazone salt such as alkali metal salt, alkaline earth metal salt, salt of p-block elements, transition metal salt or ammonium salt is formed.

The sulfentrazone salt such as sodium, potassium, silver, ammonium, barium, magnesium, calcium, zinc, iron, tin, lead, copper, aluminium, ferrous, lithium, thallium can be formed, preferably salt like sodium, potassium, calcium or ammonium is formed.

According to an embodiment of the present invention, the sulfentrazone salt obtained in above mentioned process may be isolated by any method known in the art, for example by evaporating the solvent so as to obtain a solid, or by forming a precipitate of the salt (e.g., by addition of an anti-solvent), and separating the precipitate from the reaction mixtures, e.g., by filtration.

According to another embodiment of the present invention, the pure sulfentrazone is isolated by treatment with an acid.

According to yet another embodiment of the present invention, the pure sulfentrazone is precipitated by adjusting the pH of the medium to 3 to 6, preferably 4 to 5 with an acid.

Though the adjustment of pH to obtain product can be done by adding an acid to medium comprising sulfentrazone salt; or by said medium to an acid, it was preferred to add said medium to an acid.

It was observed that, when acid is added to medium comprising salt, there develops a problem of froth formation which makes the process cumbersome and tedious to handle. Hence, the preferred mode of addition is to add said medium to an acid.

The acid used for isolating the pure sulfentrazone is selected from an inorganic acid likes hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, boric acid, hydrofluoric acid, hydrobromic acid, perchloric acid, hydroiodic acid or an organic acid like acetic acid, formic acid, oxalic acid and the likes, preferably hydrochloric acid is used.

In an embodiment of the present invention, the amount of acid used with respect to sulfentrazone is in the range of 0.5 to 5 moles.

In an embodiment of the present invention, there is provided a composition comprising sulfentrazone prepared by the process of the present invention, and at least one agrochemically acceptable excipient.

According to another embodiment of the present invention, there is provided a sulfentrazone composition having tank-mix compatibility when mixed with one or more pesticide active compounds leading to a more uniform coverage of the pesticide active compounds on targeted plant surfaces.
According to an embodiment of the present invention, there is provided a sulfentrazone composition having tank-mix compatibility when mixed with a second active ingredient..
In an embodiment of the present invention, the second active ingredient is selected from, but not limited to, an herbicide.

In an embodiment of the present invention, the herbicide usedis selected from, but not limited to, an oxazole herbicide.

In an embodiment of the present invention, the oxazole herbicide usedis clomazone.

According to yet another embodiment of the present invention, the second pesticide active compound is in form of a formulation such as emulisifiable concentrate, soluble concentrate, suspension concentrate and the likes.

According to an embodiment of the present invention, there is provided a sulfentrazone composition having tank-mix compatibility with one or more adjuvants.

According to an embodiment of the present invention, the adjuvant used in tank mix is selected from, but not limited to, crop oil concentrates, vegetable oil, modified vegetable oil (usually esters like soya methyl ester or salts of fatty acids), paraffin oil, mineral (petroleum) oils, surfactants, and inorganic salts or fertilizer.

In an embodiment of the present invention, the tank -mix obtained using the composition comprising sulfentrazone prepared according to the present process is stable and demonstrates no sedimentation or creaming when mixed with another agrochemical active composition.

According to another aspect of the present invention, there is provided pure sulfentrazone essentially free of organic solvents.

According to yet another aspect of the present invention, there is provided pure sulfentrazone essentially free of organic solvents having purity of greater than 98% as determined by HPLC.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, is further characterized by having D_{90} particle size value of less than about 800µm, preferably less than about 700µm.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, further characterized by having D_{50} particle size value of less than about 25µm, preferably less than about 20µm.

According to yet another aspect of the present invention, there is provided sulfentrazone essentially free of organic solvents, is having bulk density of about 0.20 gm/ml to 0.70 gm/ml.

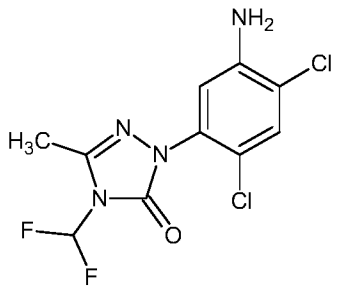
According to yet another aspect of the present invention, the pure sulfentrazone obtained is in single polymorphic form.

According to yet another aspect of the present invention, there is provided a salt of sulfentrazone and process for its preparation.

In an embodiment of the present invention, the salt of sulfentrazone obtained is sodium salt.

According to an embodiment of present invention, there is provided a process for preparing sulfentrazone having tank-mix compatibility, comprising
a) treating solid form of sulfentrazone with an aqueous alkali metal carbonate to obtain medium comprising sulfentrazone salt;
b) isolating the pure sulfentrazone having compatibility by adjusting pH of the medium to 3 to 6 with an acid, such as hydrochloric acid.

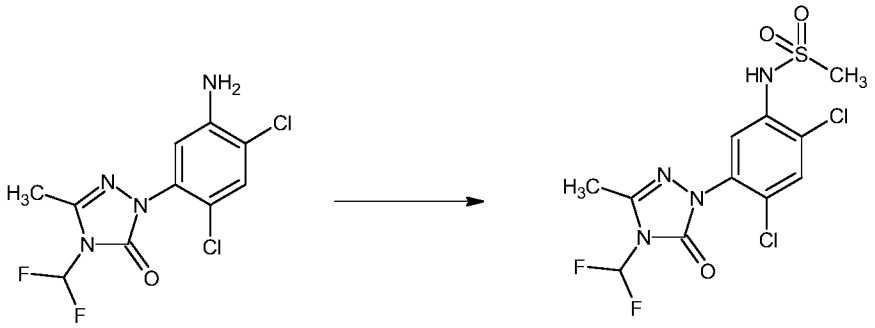
The solid form of sulfentrazone used as starting material in the present invention can be prepared conventionally by methods known in the art. For an instance, the solid form of sulfentrazone used as starting material in the present invention is prepared by sulfonylating a compound of formula (II).



Formula (II)

One of the methods for preparing the sulfentrazone formula (I) involves sulfonylation, which is done by reacting compound of formula (II) with methane

sulfonyl chloride in presence of a solvent such as toluene and a catalyst such as pyridine.

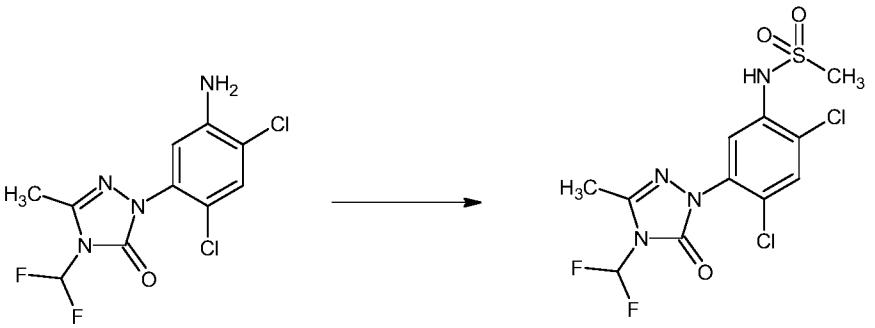


Formula (II) Formula (I)

According to another aspect of the present invention, there is provided a process for preparing sulfentrazone having tank-mix compatibility,

comprising,

a) sulfonylating a compound of formula (II) to obtain solid form of sulfentrazone of formula (I)



Formula (II) Formula (I)

b) treating the sulfentrazone with an aqueous base to obtain medium comprising sulfentrazone salt;

c) isolating the pure sulfentrazone having tank-mix compatibility by adjusting pH with an acid.

In an embodiment of the present invention, in step a), compound of formula (II) is sulfonylated to obtain sulfentrazone of formula (I).

The sulfonylating agent used in step a) is methane sulfonyl chloride.

The step a) may be carried out by reacting compound of formula (II) with methane sulfonyl chloride in presence of a catalyst and a solvent at temperature ranging from 50°C to 160°C.

The amount of methane sulfonyl chloride used with respect to compound of formula II is in the range of 0.5 to 2 moles.

The catalyst used is selected from an inorganic or organic base. The organic base such as alkylamine (as tertiary amine base etc.), pyridine, picoline, quinoline, quinuclidine, phosphazene, imidazole, benzimidazole and the likes, may be used.

The amount of catalyst used with respect to compound of formula II is in the range of 0.05 to 0.5.

The solvent such as halogenated hydrocarbons like chlorobenzene, bromobenzene, dichlorobenzene, trifluoro methyl benzene and trichlorobenzene, ethers like diethyl ether, ethyl propyl ether, n-butyl ether, anisole, phenetole, cyclohexyl methyl ether, dimethyl ether, dimethyl glycol, diphenyl ether, dipropyl ether, diisopropyl ether, di-n-butyl ether, diisobutyl ether, diisoamyl ether, ethylene glycol dimethyl ether, isopropyl ethyl ether, methyl tert-butyl ether, tetrahydrofuran, methyltetrahydrofuran, dioxane, dichlorodiethyl ether, methyl-tetrahydrofuran, polyethers of ethylene oxide and/or propylene oxide, nitrated hydrocarbons like nitromethane, nitroethane, nitropropane, nitrobenzene, chloronitrobenzene and ethyl benzene), aliphatic, cycloaliphatic or aromatic hydrocarbons like pentane, n-hexane, n-heptane, n-octane, nonane, cymene, petroleum fractions having a boiling range of from 70 °C to 190 °C, cyclohexane, methylcyclohexane, petroleum ether, ligroin, octane, benzene toluene, xylene, dimethylbenzene, diethylbenzene, esters like malonates, n-butyl acetate, methyl acetate, ethyl acetate, isobutyl acetate, dimethyl carbonate, diethyl carbonate, dibutyl carbonate and ethylene carbonate, and aliphatic alcohols like methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-amyl alcohol), mesitylene, diethyl ketone, methyl ethyl ketone, acetonitrile or mixtures thereof, can be used.

According to an embodiment of the present invention, the sulfentrazone is characterized by differential scanning calorimetric (DSC) thermogram having endotherm at about 123°C to 125°C.

The sulfentrazone having tank-mix compatibility obtained in accordance to the present invention is characterized by differential scanning calorimetric (DSC) thermogram represented by figure 1.

EXAMPLES

The following examples are presented to provide what is believed to be the most useful and readily understood description of procedures and conceptual aspects of this invention. The examples provided below are merely illustrative of the invention and are not intended to limit the same to disclosed embodiments. Variations and changes obvious to one skilled in the art are intended to be within the scope and nature of the invention.

Methods

Differential scanning calorimetry (DSC):

DSC thermogram was measured by a Differential scanning calorimeter (DSC 822, Mettler Toledo) with heating rates of 1, 2 or 5°/min in the range from 30° C. to 200° C.

HPLC Conditions:
Column: Cosmosil 5C1 8 (4.6 X 250 mm X 5 micron)
Mobile Phase: 0.1% H3PO4 in water: Acetonitrile (50:50)
Dilution System: Acetonitrile
Flow: 1.0 ml/min
UV-Wavelength: 210 nm
Injection volume: 3.0 µl

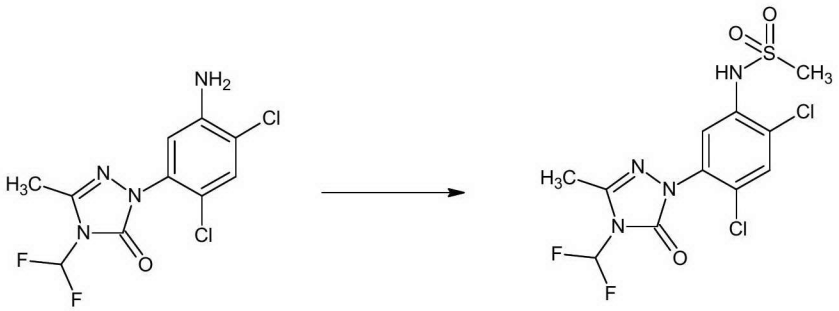
Column temperature: 40°C

Run time: 40 min

Example 1: Preparation of Sulfentrazone

Sulfentrazone (formula (I)) can be prepared by processes as described in U.S. Patent 4,818,275, U.S. Patent 5,990,315 or any of the method known in prior art, one of such known method is provided below.

Compound of formula (II) (466g) was taken in toluene (751g) and heated to 110°C ±2 to which pyridine (11g) and methanesulfonyl chloride (204g) was added and the reaction mixture was maintained at said temperature for 12 hours. After completion of reaction, toluene (2778g) was added at 110°C ±2. The mixture was cooled to room temperature and to it was added water (262g) and 20% sodium carbonate solution (41g). The mixture was then cooled to 5 to 10 °C, filtered and washed with chilled toluene to yield 728g of wet cake comprising sulfentrazone of formula (I).



Formula (II) Formula (I)

Example 2: Process for Preparing Sulfentrazone having Tank-mix Compatibility

Step a)

A solution of sodium carbonate (2040g, 5%) was heated to about 70°C followed by addition of wet cake (728g) obtained in Example 1. The mixture was then heated to 80-85°C and maintained for 1 hour to get clear solution. The clear solution obtained was cooled to room temperature to get slurry comprising sodium salt of sulfentrazone.

Step b)

The slurry comprising sodium salt of sulfentrazone of step a) was added to dilute hydrochloric acid (703 g, 10%) at room temperature and the pH of mixture was adjusted to 4-5. The mixture was maintained at 30-35°C for another hour and then filtered through Buckner funnel. The wet cake was washed with hot water and was dried in oven to remove moisture to get 485g (97.97% yield) of pure sulfentrazone having HPLC purity of 98.2% (wt/wt).

Particle Size Distribution: D_{10} = 1.84µm; D_{50} =17.1µm and D_{90} = 652µm

Bulk density: 0.3270 gm/ml

Toluene Content: less than 0.1%

The DSC thermogram exhibited an endothermic melting peak with onset at 123.22 °C and peak maximum at 123.98 °C.

Example 3: Process for Preparing Sulfentrazone having Tank-mix Compatibility

Step a)

A solution of potassium carbonate (428g, 5%) was heated to about 70°C followed by addition of wet cake (100g) obtained as in Example 1. The mixture was then heated to 80-85°C and maintained for 1 hour to get clear solution. The clear solution obtained was cooled to room temperature to get medium comprising potassium salt of sulfentrazone.

Step b)

The medium comprising potassium salt of sulfentrazone of step a) was added to dilute hydrochloric acid (113g, 10%) at room temperature and the pH of mixture was adjusted to 4-5. The mixture was maintained at 30-35°C for another hour and then filtered. The wet cake was washed with hot water and was dried in oven to remove moisture to get 80g (97.5% yield) of pure sulfentrazone having HPLC purity of 98% (wt/wt).

Example 4: Process for Preparing Sulfentrazone having Tank-mix Compatibility

Step a)

A solution of sodium hydroxide (248g, 5%) was heated to about 70°C followed by addition of wet cake (100g) obtained as in Example 1. The mixture was then heated to 80-85°C and maintained for 1 hour to get clear solution. The clear solution obtained was cooled to room temperature to get medium comprising sodium salt of sulfentrazone.

Step b)

The medium comprising sodium salt of sulfentrazone of step a) was added to dilute hydrochloric acid (113.8 g, 10%) at room temperature and the pH of mixture was adjusted to 4-5. The mixture was maintained at 30-35°C for another hour and then filtered. The wet cake was washed with hot water and was dried in oven to remove moisture to get 60g (75% yield) of pure sulfentrazone having HPLC purity of 94.6% (wt/wt).

Example 5: Process for Preparing Sulfentrazone having Tank-mix Compatibility

Step a)

A solution of ammonia (106g) was heated to about 80°C followed by addition of wet cake (100g) obtained as in Example 1. The mixture was then heated to 85-90°C and maintained for 1 hour to get clear solution. The clear solution obtained was cooled to room temperature to get medium comprising ammonium salt of sulfentrazone.

Step b)

The medium comprising ammonium salt of sulfentrazone of step a) was added to dilute hydrochloric acid (113.8 g, 10%) at room temperature and the pH of mixture was adjusted to 4-5. The mixture was maintained at 30-35°C for another hour and

then filtered. The wet cake was washed with hot water and was dried in oven to remove moisture to get 79g (96.6% yield) of pure sulfentrazone having HPLC purity of 98% (wt/wt).

Example 6

Using the standard method, a suspension concentrate formulation of sulfentrazone was prepared. Composition of formulation is as given below:

Sr. No.	**Ingredients**	**Quantity (% w/w)**
1	Sulfentrazone prepared according to example 2	42.25
2	Polyoxyethylene tristerylphenol phosphate, potassium salt	3.70
3	Sodium alkylnaphthalenesulfonate, formaldehyde condensate	1.00
4	Monoetylene Glycol	5.00
5	Magnesium aluminosilicate	0.60
6	Polydimethylsiloxane	0.50
7	Xanthan Gum	0.16
8	1,2-Benzoisothiazolin-3-one	0.10
9	Water	QS

Example 7-Comparative example

A suspension concentrate formulation of using sulfentrazone prepared according to Example 1 is prepared, remaining ingredients of the of formulation are same as that of example 6.

Performance evaluation:

Samples (Sample 1 and 2) prepared according to Example 6 & Example 7 were tested for performance. Physico-chemical properties of ambient (0 days) and AHS

(14 days) sample were checked as per CIPAC method. The observation was recorded as below

Sr. No.	Performance parameters	Specification	Sample 1		Sample 2	
			0 Days	14 Days AHS	0 Days	14 Days AHS
1	Appearance	White to off-white colour suspension	Complies	Complies	Complies	Complies
2	Active Content (gm/L)	475 to 525	516.88	511.24	501.06	498.61
3	Suspensibility on active bases (% w/w)	Min 80.0	99.0	97.62	97.3	96.61
4	Wet Sieve Test (Material retention)	0.20 % max on 45 µm 0.05 % max on 150 µm	Nil	Nil	Nil	Nil
5	Persistence foam (After 1 min)	15 ml	Nil	Nil	Nil	Nil

Tank mix compatibility test:

I) With other pesticide active compound

Samples prepared according to Example 6 & Example 7 were tested for compatibility with clomazone EC formulation (Up-Stage). The tank mix compatibility was checked as per the dosages mentioned below

Product to be used in tank mix	Active Ingredient	Concentration (gm/L)	Field dilution (Dosage in L/Ha)	Spraying Volume (L/Ha)

Sample 1 (prepared according to Example 6)	Sulfentrazone in accordance with example 2	500 SC	1.4	50
Sample 2 (prepared according to Example 7)	Sulfentrazone prepared in accordance with Example 1	500 SC	1.4	
Up-Stage	Clomazone	500 EC	2.0	

Method: Total 250ml of spray dilution solution was prepared using above mentioned composition wherein 7ml of each sample 1 and sample 2 were mixed with 10ml of Up-Stage and mixture was diluted with water.

Following observations were made

Sample No	**Observation**	**Result**
Sample 1 with Up-stage	No creaming observed after 3 hrs. There is very little, or no sediment observed when emulsion was passed through 60, 100 and 325 mesh size sieves (Refer Fig 2)	Compatible in tank mix test with Up-stage.
Sample 2 with Up-stage	Creaming observed after 3 hrs. There were lot of sediment found on the sieve when tank mix solution was passed through 60, 100 and 325 mesh size sieves. (Refer fig 3)	Not compatible in tank mix test with Up-Stage.

Conclusion: The conventionally prepared sulfentrazone showed occurrence of moderate to severe physical incompatibilities when mixed with clomazone EC formulation (Figure 3). The physical incompatibilities were in the form of moderate to severe creaming followed by settling and eventually the results in formation of large aggregates. The severity of the incompatibility would clog filters of nozzles of field spraying equipment and would likely affect the proper distribution of this herbicide during the application.

Whereas the sulfentrazone prepared in accordance with the present invention, when mixed with clomazone EC formulation did not result in any physical incompatibilities (Figure 2) and proved to be compatible.

Figure 2 is a photograph showing results of tank mix compatibility test for sample 1.

Figure 3 is a photograph showing results of tank mix compatibility test for sample 2.

II) With Adjuvants

Samples prepared according to Example 6 and was tested for compatibility with soya methyl ester (Strides). The tank mix compatibility was checked as per the dosages mentioned below

Product to be used in tank mix	**Active Ingredient**	**Concentration (gm/L)**	**Field dilution (Dosage in L/Ha)**	**Spraying Volume (L/Ha)**
Sample 3 (prepared according to Example 6)	Sulfentrazone in accordance with example 2	500 SC	1.4	50
Strides	Soya Methyl Ester	720	0.25	50

Method: Total 250ml of spray dilution solution was prepared using above mentioned dilution wherein 7ml of sample 3 were mixed with 1.25 ml Strides and mixture was diluted with water.

Following observations were made

Sample No	**Observation**	**Result**
Sample 3 with Strides	There is no flocculation/coagulation observed in dilution mixture after 3 hrs	Compatible in tank mix test with strides.

2022201342 29 Aug 2024

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for purifying sulfentrazone comprising

treating a solid form of sulfentrazone with an aqueous base to obtain a medium comprising a sulfentrazone salt, and

adding said medium comprising said sulfentrazone salt to an acid,

thereby isolating pure sulfentrazone with said acid, wherein said process is carried out without using an organic solvent.

2. The process as claimed in claim 1, wherein said process is carried out in an aqueous medium.

3. The process as claimed in claim 1 or claim 2, wherein said base is selected from organic and inorganic bases.

4. The process as claimed in any one of claims 1 to 3, wherein said base is selected from the group consisting of alkali and alkaline earth metal hydroxides, alkali metal and alkaline earth metal carbonates, alkaline earth metal oxides, p-block element carbonates, transition metal carbonates, ammonia, and amines.

5. The process as claimed in any one of claims 1 to 4, wherein said base is selected from the group consisting of lithium carbonate, lithium bicarbonate, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, and ammonia.

6. The process as claimed in any one of claims 1 to 5, wherein said acid is selected from organic and inorganic acids.

7. The process as claimed in any one of claims 1 to 6, wherein said acid is selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, boric acid, hydrofluoric acid, hydrobromic acid, perchloric acid, hydroiodic acid, acetic acid, formic acid and oxalic acid.

8. A process for purifying sulfentrazone comprising

a) treating a solid form of sulfentrazone with an aqueous base to obtain a medium comprising a sulfentrazone salt;

b) isolating pure sulfentrazone by adjusting pH of the medium of step (a) with an acid by adding said medium comprising said sulfentrazone salt to said acid.

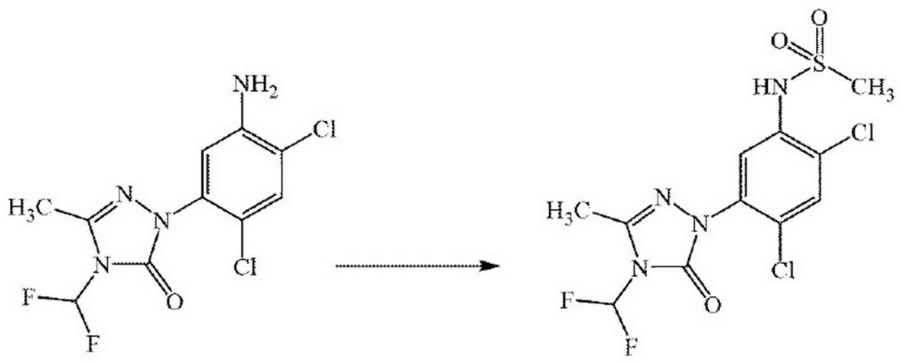
9. The process as claimed in claim 8, wherein said sulfentrazone salt is selected from the group consisting of an alkali metal salt, an alkaline earth metal salt, a salt of p-block elements, a transition metal salt, and an ammonium salt.

10. The process as claimed in claim 9, wherein said sulfentrazone salt is selected from group consisting of sodium, potassium, silver, ammonium, barium, magnesium, calcium, zinc, iron, tin, lead, copper, aluminium, ferrous, lithium, and thallium salts.

11. The process as claimed in any one of claims 8 to 10, wherein in step b) pure sulfentrazone is precipitated by adjusting the pH of the medium of step (a) to 3 to 6 with an acid.

12. A process for preparing sulfentrazone comprising

a) reacting a compound of formula (II) with a sulfonylating agent to obtain a solid form of sulfentrazone of formula (I)



Formula (II) Formula (I)

b) treating the solid form of sulfentrazone of formula (I) with an aqueous base to obtain a medium comprising sulfentrazone salt;

c) isolating pure sulfentrazone by adjusting pH with an acid by adding said medium comprising said sulfentrazone salt to said acid.

13. The process as claimed in claim 12, wherein said sulfonylating agent is methane sulfonyl chloride.

14. The process as claimed in any one of claims 1 to 13, wherein the pure sulfentrazone is essentially free of organic solvent.

15. The process as claimed in claim 14, wherein said sulfentrazone has a purity of greater than 98% by HPLC.

16. The process as claimed in any one of claims 1 to 15, wherein the pure sulfentrazone has a D_{50} particle size value of less than about 25 μm.

17. The process as claimed in any one of claims 1 to 16, wherein the pure sulfentrazone has a bulk density of about 0.20 gm/ml to 0.70 gm/ml.

20222013342 26 Feb 2022

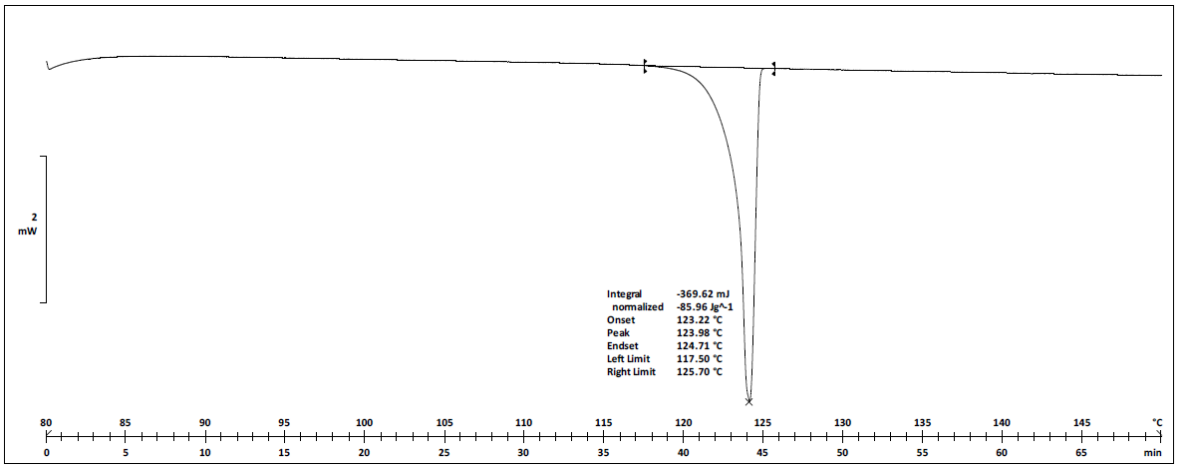


Figure 1

20222013426 Feb 2022

Figure 2

20222013426 Feb 2022

Figure 3