Abstract:

A controlled-release particle or granule comprises a solid carrier core and at least one crop protection active ingredient-containing coating thereon, with a hydrophobic overcoating. A controlled-release formulation containing the controlled-release particles is disclosed, as well as a method of preparing the controlled-release granular formulation, a method of reducing crop phytotoxicity, and a method of adjusting the release of a crop protection active ingredient from a granular formulation.
FIELD OF THE INVENTION

[0001] The present invention is related to the field of agricultural formulations, specifically to herbicidal formulations. The invention also is related to granular formulations from which the crop protection active ingredient is controllably released.

BACKGROUND OF THE INVENTION

[0002] Sulfentrazone is a herbicide for the control of broadleaf weeds and some grasses in crops such as soybeans, chickpeas, tobacco, sugarcane, rice and turf. Sulfentrazone is absorbed by both roots and foliage, and is translocated within the plant from the point of uptake. Certain crops evidence phytotoxicity upon foliar application of sulfentrazone.

[0003] US Patent Application Publication 2005/018952 discloses slow-release formulations useful for the preparation of seed- or particle-coated herbicidal compositions. The substrates to be coated can be plant seeds, or particles made of an ionic resin or other polymer, where the herbicide is covalently linked or ionically bound to the particle by strong interactions. The particles can be further micro-encapsulated, which can modulate the release of the herbicide.

[0004] Similarly, US Patent Application Publication 2007/0149409 discloses semi-stable complexes of pesticides with functionalized polymers with improved leaf retention, which can be in the form of granules or as coats for seeds and fertilizers. These again are based on ion exchangers and other mixed function substituted biopolymers that have the capacity to retain and or reversibly bind active ingredients.

[0005] There continues to be a need for methods for reducing crop phytotoxicity, as well as for extending the release of the herbicide to improve residual weed control.

SUMMARY OF THE INVENTION
Both improved residual weed control and reduced crop phytotoxicity are provided by the formulations and methods of the present invention.

One aspect of the present invention is directed to a controlled-release particle or granule comprising a solid carrier core and at least one crop protection active ingredient-containing coating thereon. The form of the particle can be spherical, substantially spherical, non-spherical, or irregularly shaped. In one embodiment, the carrier core of the controlled-release particle is a clay, a silica, peanut hull, a cellulosic, or other absorbent carrier material. In one embodiment the carrier core is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof, preferably montmorillonite clay. Preferably the particle is spherical or substantially spherical, and inert.

In one embodiment the crop protection active ingredient coating comprises a herbicide, preferably a protoporphyrinogen IX oxidase (PPO) inhibitor. The PPO inhibitor is preferably selected from the group consisting of a diphenyl ether, an oxadiazole, a cyclic imide, and a pyrazole. In one embodiment, the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlomitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen. In another embodiment the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazone. In another embodiment the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin. In another embodiment the pyrazole is selected from the group consisting of ET-751, JV 485 and nipyraclafen. Preferably the PPO inhibitor is sulfentrazone. In one embodiment the coating of active ingredient, preferably sulfentrazone, is about 0.1 wt% to about 5 wt% based on the weight of the finished granular particle.

Preferably the controlled-release particle further comprises a hydrophobic protectant coating, or overcoating, which is on the surface of the controlled-release particle, and on top of the active ingredient coating. The hydrophobic overcoating
preferably comprises hydrophobic oils and/or waxes, including vegetable oils, mineral oils, synthetic oils, natural waxes, synthetic waxes, and mixtures of two or more thereof. In a specific embodiment the coating is selected from the group consisting of linseed oil, refined mineral oil, carnauba wax, and mixtures of two or more thereof.

[0010] Another aspect of the present invention is directed to a controlled-release formulation comprising a population of controlled-release particles or granules comprising a solid carrier core, at least one crop protection active ingredient-containing coating thereon and a hydrophobic overcoating, where the crop protection active ingredient coating comprises a herbicide. The form of the particles can be spherical, substantially spherical or non-spherical, or irregularly shaped. Preferably the particles are spherical or substantially spherical. In one embodiment, the carrier core of the controlled-release particles is a clay, a silica, peanut hull, a cellulosic, or other absorbent carrier material. In one embodiment the carrier core is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof. Preferably the particles are inert. In one embodiment, the controlled-release particles comprise a material selected from the group consisting of peanut hull, silica, cellulosics and clay. In a preferred embodiment the particle material is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof, preferably montmorillonite clay.

[0011] In one embodiment of the controlled-release formulation, the herbicide of the active ingredient coating is a protoporphyrinogen IX oxidase (PPO) inhibitor. In one embodiment the PPO inhibitor is selected from the group consisting of a diphenyl ether, a oxadiazole, a cyclic imides, and a pyrazole. In one embodiment the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlomitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furylxylen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen. In another embodiment the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazon. In another embodiment the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidon-ethyl, flumiclora-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin. In another embodiment the pyrazole is selected from the group
consisting of ET-751, JV 485 and nipyraclafen. In a preferred embodiment the PPO inhibitor is sulfentrazone. In one embodiment the of the controlled-release formulation, the coating of sulfentrazone is about 0.1 wt% to about 5 wt% based on the finished formulation.

[0012] In one embodiment of the formulation, the protective coating comprises an oil selected from the group consisting of vegetable oils, mineral oils, synthetic oils, and mixtures of two or more thereof. In a preferred embodiment the hydrophobic coating comprises at least one of linseed oil, refined mineral oil, carnauba wax, beeswax or any combinations thereof.

[0013] Another aspect of the invention is directed to a method of reducing crop phytotoxicity to PPO inhibitors treatment, comprising: a) providing PPO inhibitor in a controlled-release formulation comprising particles comprising a carrier, a PPO inhibitor containing coating layer on the surface of said carrier, and a hydrophobic overcoating; b) applying said formulation to the area of interest; and c) reducing adherence of the particles to the crop plant. In at least one embodiment, the crop can be selected from the group consisting of soybeans, chickpeas, tobacco, sugarcane, rice and turf. In yet another embodiment, the invention is directed to a method of reducing crop phytotoxicity to sulfentrazone treatment, comprising: a) providing sulfentrazone in a controlled-release formulation comprising particles comprising a carrier, a sulfentrazone containing coating layer on the surface of said carrier, and a hydrophobic overcoating; b) applying said formulation to the area of interest; and c) reducing adherence of the particles to the crop plant.

[0014] Another aspect of the invention is directed to a method of adjusting the release of sulfentrazone from a granular formulation, comprising coating a sulfentrazone-containing granular formulation with a hydrophobic oil and/or a hydrophobic wax in an amount effective to provide the desired release rate. In one embodiment, the amount of the hydrophobic oil and/or wax is about 1 wt% to about 10 wt% based on the weight of the finished granular formulation.
Another aspect of the invention is directed to a method of preparing a controlled-release granular formulation of sulfentrazone, comprising: a) providing a granular carrier selected from the group consisting of peanut hull, cellulosics, silica including sands, and clay; b) applying a solution of sulfentrazone in an appropriate solvent to provide sulfentrazone-coated granules; and c) overcoating said sulfentrazone-coated granules with a hydrophobic oil or wax selected from the group consisting of linseed oil, refined mineral oil, natural and synthetic waxes including carnauba wax, and mixtures of two or more thereof. In one such embodiment, the solvent is preferably polypropylene glycol 200. In yet another embodiment, the granular carrier is preferably montmorillonite clay. In most preferred embodiment, the granules are spherical or substantially spherical, and inert.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a graph of sulfentrazone released in soil over time from various sulfentrazone formulations.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The herbicidal controlled-release granular formulations of the present invention eliminate or reduce phytotoxicity on desired crops while at the same time extending release of active herbicide from the granule to improve the residual control of weeds.

Without wishing to be bound by any particular theory, it is believed that the hydrophobically coated granular formulations disclosed herein, when appropriately applied to the foliage of a crop plant, do not significantly adhere to the foliage, but repel off the plant and fall to the soil surface. The slow release of the herbicidal active ingredient into the soil then provides desirable residual control of the target weeds without significant concomitant crop phytotoxicity. Further, the hydrophobic overcoating on the granule controls the release of the herbicide, and can be adjusted to fine tune the release rate of the herbicide, thereby extending the weed control capacity of the formulation. In order to control release of the active herbicide, the formulations and methods disclosed herein utilize simple hydrophobic oils and waxes as an overcoating or protective layer over the herbicide layer of the particle, in place of a
granular particle based on heavily charged polymers that bind the layer of herbicide molecules.

[0019] Thus, one aspect of the present invention is directed to a controlled-release particle or granule comprising a solid carrier core and at least one crop protection active ingredient-containing coating thereon. The form of the particle can be spherical, substantially spherical or non-spherical. The particle can also have an irregular shape or geometry. The particle can have a thickness or diameter ranging from about 500 microns to about 2500 microns.

[0020] Preferably the particle is a microparticle having a \( d_{50} \) of about 600 microns to about 1500 microns. In one embodiment, the carrier core of the controlled-release particle is a clay, a silica, peanut hull, a cellulosic, or other carrier material. In one aspect of the invention the carrier material is absorbent. In one embodiment the carrier core is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof. In one embodiment the particle has a diameter ranging from about 500 microns to about 1500 microns when the solid particle has a spherical shape, with the measurement referring to the delivered product, prior to disintegration. Preferably the particle is inert and does not react with the active ingredient to chemically bind, either covalently or ionically, the herbicide or other active ingredient molecules.

[0021] In one embodiment the crop protection active ingredient coating comprises a herbicide, preferably a protoporphyrinogen IX oxidase (PPO) inhibitor. The PPO inhibitor is preferably selected from the group consisting of a diphenyl ether, an oxadiazole, a cyclic imide, and a pyrazole. In one embodiment, the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlorotoluron (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furylxylen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen. In another embodiment the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazon. In another embodiment the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidin-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, fluropacil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin. In another embodiment the pyrazole is selected from the group
consisting of ET-751, JV 485 and nipyraclafen. Preferably the PPO inhibitor is sulfentrazone.

[0022] In one embodiment the coating of active ingredient, preferably sulfentrazone, is about 0.1 wt% to about 5 wt% based on the weight of the finished granular particle. In another embodiment the coating is about 0.15 wt% to about 3 wt% based on the finished granular particle. In a further embodiment the coating is about 0.2 wt% to about 1 wt% based on the finished granular particle. In one specific embodiment the sulfentrazone-containing coating is about 0.3 wt% based on the finished granular particle.

[0023] In another embodiment the controlled-release particle further comprises a hydrophobic protectant coating, or overcoating. Preferably the hydrophobic protectant coating is on the surface of the controlled-release particle, and on top of the active ingredient coating. Hydrophobic overcoatings preferably comprise hydrophobic oils and/or waxes, including vegetable oils, mineral oils, synthetic oils, natural waxes, synthetic waxes, and mixtures of two or more thereof. In one embodiment, the hydrophobic protectant coating comprises an oil selected from the group consisting of vegetable oils, mineral oils, synthetic oils, and mixtures of two or more thereof. Preferred oils include linseed oil, refined mineral oil and mixtures of two or more thereof. Suitable refined mineral oils include ORCHEX® agricultural spray oils such as ORCHEX® 796 and ORCHEX® 692, available from Calumet Specialty Products Partners, L.P. In at least one embodiment, the mineral oil may have a molecular weight ranging from 280-350 and a viscosity of 75 to 95 at 100°F, preferably 80 to 85, and more preferably at 82-83.

[0024] In one embodiment the hydrophobic protectant coating comprises a wax selected from the group consisting of natural waxes, synthetic waxes and mixtures of two or more thereof. In one embodiment the wax is selected from the group consisting of carnauba wax, beeswax, synthetic waxes which are solid at temperatures below 50°C, and mixtures of two or more thereof. A preferred wax is carnauba wax. In a specific embodiment the coating is selected from the group consisting of linseed oil, refined mineral oil, carnauba wax, beeswax and mixtures of two or more thereof.
In one embodiment the hydrophobic protectant coating of the controlled-release particle has a thickness ranging from about 1 micron to about 10 microns.

[0025] Another aspect of the present invention is directed to a controlled-release formulation comprising a population of controlled-release particles or granules comprising a solid carrier core, at least one crop protection active ingredient-containing coating thereon and a hydrophobic overcoating, where the crop protection active ingredient coating comprises a herbicide. The form of the particles can be spherical, substantially spherical or non-spherical. The particles can also have an irregular shape or geometry. The particles can have a thickness or diameter ranging from about 500 microns to about 2500 microns. Preferably the particles are microparticles having a D50 of about 600 microns to about 1500 microns. In one embodiment, the carrier core of the controlled-release particles is a clay, a silica, peanut hull, a cellulosic, or other carrier material. In one aspect of the invention the carrier material is absorbent. In another aspect of the invention the carrier material is adsorbent.

[0026] In one embodiment the carrier core is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof. In one embodiment the particles have diameters ranging from about 500 microns to about 1500 microns when the solid particles are spherical in shape. Preferably the particles are inert and do not react with the active ingredient to chemically bind, either covalently or ionically, the herbicide or other crop protection active ingredient molecule; however, the active ingredient can be either absorbed into or adsorbed onto the carrier. In one embodiment, the controlled-release particles comprise a material selected from the group consisting of peanut hull, silica, cellulosics and clay. In a preferred embodiment the particle material is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof. Preferably the clay is in the form of spherical or substantially spherical granules. In one specific embodiment the clay is montmorillonite clay.

[0027] In one embodiment of the controlled-release formulation, the herbicide of the active ingredient coating is a protoporphyrinogen IX oxidase (PPO) inhibitor. In one
embodiment the PPO inhibitor is selected from the group consisting of a diphenyl ether, a oxadiazole, a cyclic imides, and a pyrazole. In one embodiment the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlomitrofen (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen. In another embodiment the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazon. In another embodiment the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidion-ethyl, flumiclora-pentyl, flumioxazin, flumipropyn, flupracil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin. In another embodiment the pyrazole is selected from the group consisting of ET-751, JV 485 and nipyraclofen. In a preferred embodiment the PPO inhibitor is sulfentrazone.

[0028] In one embodiment the of the controlled-release formulation, the coating of sulfentrazone is about 0.1 wt% to about 5 wt% based on the finished formulation, preferably about 0.15 wt% to about 3 wt% based on the finished formulation. In a further embodiment the coating is about 0.2 wt% to about 1 wt% based on the finished granular formulation. In a specific embodiment sulfentrazone is present in an amount of about 0.3 wt% based on the finished formulation.

[0029] In one embodiment of the formulation, the protective coating comprises an oil selected from the group consisting of vegetable oils, mineral oils, synthetic oils, and mixtures of two or more thereof. In one embodiment the oil is selected from the group consisting of linseed oil, refined mineral oil, other natural harvested oils, other synthetic oils, and mixtures of two or more thereof. In another embodiment the coating comprises a wax selected from the group consisting of natural waxes, synthetic waxes and mixtures of two or more thereof. Preferably the wax is selected from the group consisting of carnauba wax, beeswax and mixtures thereof. In a preferred embodiment the hydrophobic coating comprises at least one of linseed oil, refined mineral oil, carnauba wax, beeswax or any combinations thereof.

[0030] Another aspect of the invention is directed to a method of reducing crop phytotoxicity to sulfentrazone treatment, comprising: a) providing sulfentrazone in a controlled-release formulation comprising particles comprising a carrier, a
sulfentrazone containing coating layer on the surface of said carrier, and a
hydrophobic overcoating; b) applying said formulation to the area of interest; and c)
reducing adherence of the particles to the crop plant. In one embodiment the crop is
selected from the group consisting of soybeans, chickpeas, tobacco, sugarcane, rice
and turf.

[0031] Another aspect of the invention is directed to a method of adjusting the release
of sulfentrazone from a granular formulation, comprising coating a sulfentrazone-
containing granular formulation with a hydrophobic oil and/or a hydrophobic wax in
an amount effective to provide the desired release rate. In one embodiment the
amount of the hydrophobic oil and/or wax is about 1 wt% to about 10 wt% based on
the weight of the finished granular formulation, preferably about 1.5 wt% to about 5
wt% based on the finished granular formulation. In a further embodiment the amount
of the hydrophobic oil and/or wax is about 2 wt% to about 4 wt% based on the
finished granular formulation. In a specific embodiment the amount of the
hydrophobic oil and/or wax is about 3 wt% based on the weight of the finished
granular formulation.

[0032] Another aspect of the invention is directed to a method of preparing a
controlled-release granular formulation of sulfentrazone, comprising: a) providing a
granular carrier selected from the group consisting of peanut hull, cellulosics, silica
and clay; b) applying a solution of sulfentrazone in an appropriate solvent to provide
sulfentrazone-coated granules; and c) overcoating said sulfentrazone-coated granules
with a hydrophobic oil or wax selected from the group consisting of linseed oil,
refined mineral oil, carnauba wax, beeswax and mixtures of two or more thereof.

[0033] In one embodiment the solvent is polypropylene glycol 200. In another
embodiment the granular carrier is montmorillonite clay. In a specific embodiment
the clay is in the form of spherical granules. Preferably the granular carrier is inert.
Preferably the granular carrier is spherical or substantially spherical in form.

[0034] A variety of absorbent granular carriers are suitable for the presently disclosed
granular formulations. Such granular carriers include materials selected from peanut
hulls, clays, cellulosics such as paper, and other such carriers known in the
formulation arts. Clays include montmorillonite, attapulgite, kaolin, and continental clays, as well as other clays known in the formulation arts. A preferred clay is montmorillonite. Preferably the granules are spherical or substantially spherical. Preferred granules include Verge™ granules and BIODAC® granules, available from Verge Granules, 410 N. Michigan Ave., Suite 400, Chicago, IL 60611, and Kadant GranTek Inc., 607 Liberty Street, Green Bay, WI 54304, respectively. Verge™ granules are inert dustless carrier granules made from clay. BIODAC® granules are inert dustless carrier granules made from cellulose/paper.

EXAMPLES

Example 1: Sulfentrazone 0.3% Granule

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfentrazone</td>
<td>0.3</td>
</tr>
<tr>
<td>Polyethylene Glycol 200</td>
<td>4.18</td>
</tr>
<tr>
<td>Verge™ Granules</td>
<td>95.52</td>
</tr>
</tbody>
</table>

[0035] Preparation: Sulfentrazone was dissolved in polyethylene glycol 200 (PEG 200) under mild heating. Into a weighed sample of Verge™ granules under continuous mixing in a granular mixer (Hobart blender) at room temperature, the PEG 200 solution of sulfentrazone was sprayed onto the granules using a DeVilbiss compressed air driven sprayer. Mixing was continued until the solution was completely absorbed by the granules.

Example 2: Sulfentrazone 0.3% Granule coated with carnauba wax

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfentrazone</td>
<td>0.3</td>
</tr>
<tr>
<td>Polyethylene Glycol 200</td>
<td>4.18</td>
</tr>
<tr>
<td>Carnauba wax</td>
<td>3.0</td>
</tr>
<tr>
<td>Verge™ Granules</td>
<td>92.52</td>
</tr>
</tbody>
</table>

[0036] Preparation: As per Example 1, sulfentrazone was dissolved in PEG 200 under mild heating. Into a weighed sample of Verge™ granules under continuous mixing in a Hobart blender at room temperature, the PEG 200 solution of sulfentrazone was sprayed onto the granules using a DeVilbiss compressed air driven
sprayer. Immediately thereafter warmed, liquefied carnauba wax was sprayed onto the granules under continuous mixing, using a DeVilbiss or similar compressed air driven sprayer, which is heated if necessary. After the wax was sprayed onto the granules, mixing was continued until the materials were completely absorbed.

Example 3: Sulfentrazone 0.3% Granule coated with Linseed Oil

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfentrazone</td>
<td>0.3</td>
</tr>
<tr>
<td>Polyethylene Glycol 200</td>
<td>4.18</td>
</tr>
<tr>
<td>Linseed Oil</td>
<td>3.0</td>
</tr>
<tr>
<td>Verge™ Granules</td>
<td>92.52</td>
</tr>
</tbody>
</table>

[0037] Preparation: The method of Example 2 was used with the following modification. After the PEG 200 solution of sulfentrazone was sprayed onto the granules, warmed linseed oil (liquid at room temperature) was applied by DeVilbiss sprayer under continuous mixing. After all of the linseed oil was applied the granules were mixed until the materials were completely absorbed.

Example 4: Sulfentrazone 0.3% Granule coated with ORCHEX® Crop Oil

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfentrazone</td>
<td>0.3</td>
</tr>
<tr>
<td>Polyethylene Glycol 200</td>
<td>4.18</td>
</tr>
<tr>
<td>ORCHEX® Crop Oil</td>
<td>3.0</td>
</tr>
<tr>
<td>Verge™ Granules</td>
<td>92.52</td>
</tr>
</tbody>
</table>

[0038] Preparation: Sulfentrazone was dissolved in PEG 200 under mild heating. Into a weighed sample of Verge™ granules under continuous mixing in a granular mixer (Hobart blender) at room temperature, the PEG 200 solution of sulfentrazone was sprayed onto the granules using a DeVilbiss compressed air driven sprayer. After the solution was applied, warmed ORCHEX® Crop Oil (liquid at room temperature) was sprayed onto the granules under continuous mixing. After all of the ORCHEX® Crop Oil was sprayed onto the granules, mixing was continued until the materials were completely absorbed.

Example 5: Release Rate Studies
5.1 Visible Dispersion studies

[0039] Procedure: 1 gram of each of the above Examples 1 through 4 was placed into a petri dish containing 17 mL of deionized water. The granules were visualized for time to dispersal, with data summarized in the following table.

<table>
<thead>
<tr>
<th>Time from distillation of granules in petri dish</th>
<th>Visuals: Example 1</th>
<th>Visuals: Example 2</th>
<th>Visuals: Example 3</th>
<th>Visuals: Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>Quick dispersion of 50% of granules which became submerged</td>
<td>Granules floating, no dispersion</td>
<td>Granules submerged, no dispersion</td>
<td>Granules floating, no dispersion</td>
</tr>
<tr>
<td>4 minutes</td>
<td>90% granules dispersed</td>
<td>50% of granules still floating, minor number have dispersed</td>
<td>Granules submerged, no dispersion</td>
<td>Granules sank into water, no dispersion</td>
</tr>
<tr>
<td>20 minutes</td>
<td>Virtually 100% granules dispersed</td>
<td>50% of granules still floating, more granules dispersed</td>
<td>Granules submerged, virtually none have dispersed</td>
<td>100% now dispersed</td>
</tr>
</tbody>
</table>

5.2 In-Vitro release of sulfentrazone

[0040] Procedure: An in-vitro method of measuring the release of sulfentrazone in aqueous media was developed. In brief, a 1-Liter container was filled to the mark with deionized water (water of any pH, salinity, mineral composition or temperature can be used). The water was at room temperature (approx. 20°C). A sample of treated granules encased in a container with one face being of 100 mesh (US) screen (equivalent to 150 micron mesh) was placed in the water. The water was agitated with a magnetic stirrer placed to the side of the container of granules. At various time points an aliquot of the solution was withdrawn from the beaker. A UV spectrum was run on the aliquot to measure the concentration of sulfentrazone. The UV assay was performed at a wavelength of 250 nm using a 1-cm cuvette. The aliquot was then
added back to the test beaker, and the beaker was tightly covered to avoid evaporation of the solution. The change in sulfentrazone concentration over time was recorded.

5.3 Results of selected solubilization experiments:

<table>
<thead>
<tr>
<th>Time, Hours</th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.021</td>
<td>0.052</td>
</tr>
<tr>
<td>4</td>
<td>0.035</td>
<td>--</td>
</tr>
<tr>
<td>24</td>
<td>0.264</td>
<td>--</td>
</tr>
<tr>
<td>48</td>
<td>0.353</td>
<td>--</td>
</tr>
<tr>
<td>72</td>
<td>0.357</td>
<td>0.248</td>
</tr>
<tr>
<td>96</td>
<td>0.354</td>
<td>0.307</td>
</tr>
<tr>
<td>120</td>
<td>--</td>
<td>0.341</td>
</tr>
<tr>
<td>144</td>
<td>--</td>
<td>0.349</td>
</tr>
</tbody>
</table>

1 Trial 1: 0.3% sulfentrazone on Verge™ LpH D140
2 Trial 2: 0.3% sulfentrazone on Verge™ LpH D140 + 3% carnauba wax coating

5.4 Sulfentrazone Release from Soil

[0041] Objective: To determine how much granular soil-applied sulfentrazone is bioavailable as free sulfentrazone at various time intervals post treatment.

[0042] Methods and Materials:
Whatman Unifilter® 24-well plates 10 mL volume (minicolumn), equipped with a UniVac 3 Vacuum to collection manifold for plates
Whatman Multi-Chem™ Microplates 24 wells 10 mL volume
Agilent Series 1100 HPLC with UV Detection

[0043] Procedure:
In duplicate for each sample tested, 2.5 grams of dry soil was weighed into a Whatman Unifilter® 24-well plates (minicolumn plates). The soil was pre-wet by adding 2.0 mL of distilled water, and the water was removed by vacuum filtration. Each soil sample was then treated at rate of ~ 20 µg of sulfentrazone/column with the formulations of Examples 1-4, plus SPARTAN®4F and technical sulfentrazone as controls. SPARTAN®4F is a flowable formulation containing four pounds of sulfentrazone per gallon, available from FMC Corporation. The formulations were applied to the top of the soil column. The
columns were incubated for 1 hour and then eluted at Time 0 and seven days after treatment.

[0044] Sampling:
The collection plate Whatman Unifilter® 24-well plates 10 mL volume was placed underneath the test plates and each minicolumn was eluted with a 5.0 ml aliquot of water, allowed to drain for 15 minutes and then vacuum filtered. The eluate from the collection plates was transferred into HPLC vials and analyzed for sulfentrazone.

[0045] As shown in Figure 1, technical sulfentrazone and SPARTAN® 4F responded in a manner consistent with the historical norms for those materials, with most of the sulfentrazone eluting at Time 0. The granular formulations protected the sulfentrazone from immediate release. Only slightly less sulfentrazone was eluted at the 1 week sampling period from the granular formulations of Examples 1-4.

[0046] Under the moist soil conditions used in the minicolumn study, the granules of Examples 1-4 start to release sulfentrazone immediately, but do not release their entire load when compared to the control formulations technical sulfentrazone and SPARTAN® 4F. Since the granules start to release AI (Active Ingredient) on contact with moisture, under dry agronomic conditions the dry granules would be expected to lie on the soil and not release AI until rain or irrigation occurred.

[0047] Without further elaboration, it is believed that one skilled in the art, using the preceding description, can utilize the present invention to its fullest extent. Furthermore, while the present invention has been described with respect to aforementioned specific embodiments and examples, it should be appreciated that other embodiments utilizing the concept of the present invention are possible, and within the skill of one in the art, without departing from the scope of the invention. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.
CLAIMS

What is claimed is:

1. A controlled-release particle comprising a solid carrier core and at least one crop protection active ingredient-containing coating, wherein said active ingredient coating comprises a protoporphyrinogen IX oxidase (PPO) inhibitor.

2. The controlled-release particle of claim 1, further comprising a hydrophobic protectant coating.

3. The controlled-release particle of claim 2, wherein the hydrophobic protectant coating is on the surface of said controlled-release particle and on top of the active ingredient coating.

4. The formulation of claim 1, wherein the PPO inhibitor is selected from the group consisting of a diphenyl ether, an oxadiazole, a cyclic imide, and a pyrazole.

5. The formulation of claim 4, wherein the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlorimuron (CNP), ethoxyfen, fluorodifen, fluoroglycofen-ethyl, fomesafen, furylxylen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen; wherein the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazon; wherein the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin; and wherein the pyrazole is selected from the group consisting of ET-751, JV 485 and nipyraclofen.

6. The controlled-release particle of claim 4, wherein the PPO inhibitor is sulfentrazone.

7. The controlled-release particle of claim 1, wherein said carrier core is a clay, a silica, peanut hull, or a cellulosic.

8. The controlled-release particle of claim 7, wherein the carrier core is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof.

9. The controlled-release particle of claim 2, wherein said hydrophobic protectant coating comprises an oil selected from the group consisting of vegetable oils, mineral oils, synthetic oils, and mixtures of two or more thereof.

10. The controlled-release particle of claim 9, wherein said oil is selected from the group consisting of linseed oil, refined mineral oil, and mixtures thereof.
11. The controlled-release particle of claim 2, wherein said hydrophobic protectant coating comprises a wax selected from the group consisting of natural waxes, synthetic waxes and mixtures of two or more thereof.

12. The controlled-release particle of claim 11, wherein said wax is selected from the group consisting of carnauba wax, beeswax, synthetic waxes which are solid at temperatures below 50°C, and mixtures of two or more thereof.

13. The controlled-release particle of claim 2, wherein said coating is selected from the group consisting of linseed oil, refined mineral oil, carnauba wax, beeswax and mixtures of two or more thereof.

14. The controlled-release particle of claim 13, wherein said hydrophobic protectant coating has a thickness ranging from about 1 micron to about 10 microns.

15. The controlled-release particle of claim 2, wherein said particle has a diameter ranging from about 500 microns to about 1500 microns when the solid particle has a spherical shape.

16. The controlled-release particle of claim 6, wherein said coating of sulfentrazone is about 0.1 wt% to about 5 wt% based on the weight of the finished granular particle.

17. A controlled-release formulation comprising a population of controlled-release particles comprising a solid carrier core and at least one crop protection active ingredient-containing coating and a hydrophobic coating, wherein said active ingredient coating comprises a protoporphyrinogen IX oxidase (PPO) inhibitor.

18. The formulation of claim 17, wherein said carrier is inert and comprises a material selected from the group consisting of peanut hull, cellulosics, silica and clay.

19. The formulation of claim 18, wherein said material is a clay selected from the group consisting of montmorillonite clay, continental clay, kaolin clay, attapulgite clay and mixtures of two or more thereof.

20. The formulation of claim 19, wherein said clay is montmorillonite clay.

21. The formulation of claim 20, wherein said clay is in the form of spherical or substantially spherical granules.

22. The formulation of claim 17, wherein the PPO inhibitor is selected from the group consisting of a diphenyl ether, a oxadiazole, a cyclic imides, and a pyrazole.
23. The formulation of claim 22, wherein the diphenyl ether is selected from the group consisting of acifluorfen, acifluorfen-sodium, aclonifen, bifenox, chlomitrofen (CNP), ethoxyfen, fluorodifen, floroglycofen-ethyl, fomesafen, furyloxyfen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen; wherein the oxadiazole is selected from the group consisting of oxadiargyl and oxadiazon; wherein the cyclic imide is selected from the group consisting of azafenidin, butafenacil, cinidon-ethyl, flumiclorac-pentyl, flumioxazin, flumipropyn, flupropacil, fluthiacet-methyl, sulfentrazone, carfentrazone-ethyl and thidiazimin; and wherein the pyrazole is selected from the group consisting of ET-751, JV 485 and nipyraclofen.

24. The formulation of claim 17, wherein the PPO inhibitor is sulfentrazone.

25. The formulation of claim 17, wherein said coating of sulfentrazone is about 0.1 wt% to about 5 wt% based on the finished formulation.

26. The formulation of claim 17, wherein sulfentrazone is present in an amount of about 0.3 wt% based on the finished formulation.

27. The formulation of claim 17, wherein said coating comprises an oil selected from the group consisting of vegetable oils, mineral oils, synthetic oils, and mixtures of two or more thereof.

28. The formulation of claim 27, wherein said oil is selected from the group consisting of linseed oil, refined mineral oil, and mixtures thereof.

29. The formulation of claim 17, wherein said coating comprises a wax selected from the group consisting of natural waxes, synthetic waxes and mixtures of two or more thereof.

30. The formulation of claim 29, wherein said wax is selected from the group consisting of carnauba wax, beeswax, synthetic waxes which are solid at temperatures below 50°C, and mixtures of two or more thereof.

31. The formulation of claim 17, wherein said hydrophobic coating comprise at least one of linseed oil, refined mineral oil, carnauba wax, beeswax or any combinations thereof.

32. A method of reducing crop phytotoxicity to sulfentrazone treatment, comprising:
a) providing sulfentrazone in a controlled-release formulation comprising particles comprising a carrier, a sulfentrazone containing coating layer on the surface of said carrier, and a hydrophobic overcoating; b) applying said formulation to the area of interest; and c) reducing adherence of the particles to the crop plant.

33. A method of adjusting the release of sulfentrazone from a granular formulation, comprising coating a sulfentrazone-containing granular formulation with a hydrophobic oil and/or a hydrophobic wax in an amount effective to provide the desired release rate.

34. The method of claim 33, wherein the amount of said hydrophobic oil and/or wax is about 1 wt% to about 10 wt% based on the weight of the finished granular formulation.

35. The method of claim 34, wherein the amount of said hydrophobic oil and/or wax is about 3 wt% based on the weight of the finished granular formulation.

36. A method of preparing a controlled-release granular formulation of sulfentrazone, comprising:

   a) providing a granular carrier selected from the group consisting of peanut hull, cellulosics, silica and clay;

   b) applying a solution of sulfentrazone in an appropriate solvent to provide sulfentrazone-coated granules; and

   c) overcoating said sulfentrazone-coated granules with a hydrophobic oil or wax selected from the group consisting of linseed oil, refined mineral oil, carnauba wax, beeswax and mixtures of two or more thereof.

37. The method of claim 36, wherein said solvent is polypropylene glycol 200.

38. The method of claim 36, wherein said granular carrier is montmorillonite clay.

39. The method of claim 38, wherein said clay is in the form of spherical granules.

40. The method of claim 32, wherein said crop is selected from the group consisting of soybeans, chickpeas, tobacco, sugarcane, rice and turf.
Sulfentrazone Released (ng) vs. Time (Days after Treatment)

- Technical sulfentrazone
- Example 1
- Example 2
- Example 3
- Example 4
- SPARTAN® 4F
### A. CLASSIFICATION OF SUBJECT MATTER

**IPC(8) Classification:**
- A01N 43/08, 43/40, 37/38 (2015.01)

**CPC:**
- A01N 43/08, 43/40, 37/38

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)

**IPC(8) Classification(s):** A01N 59/00, 43/08, 43/40, 37/38; A01 P 13/00 (2015.01)

**CPC Classification(s):** A01N 59/00, 43/08, 43/40, 37/38; A01 P 13/00

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)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; ProQuest; EBSCO Discovery; herbicide, core, particle, granule, coating, clay silica, PPO inhibitor, hydrophobic oil, protectant, oil, wax, linseed, beeswax, sulfentrazone, phytotoxicity

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>US 20110028324 A1 (CORDINGLEY, MR et al.) 03 February 2011; paragraphs [0014], [0036]-[0048]; claims 2, 21-22</td>
<td>1, 4-8, 16-26, 32, 40</td>
</tr>
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<td>Y</td>
<td>WO 2001052650 A2 (ISHIHARA SANGYO KAISHA LTD) 26 July 2001; page 11, lines 19-23; page 12, table 1; claim 6</td>
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* Further documents are listed in the continuation of Box C.

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<td>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</td>
<td>document containing new or additional matter which is not considered to be of particular relevance</td>
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<tr>
<td>document referring to an oral disclosure, use, exhibition of other means</td>
<td>document published prior to the international filing date but later than the priority date claimed</td>
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### Date of the actual completion of the international search

01 September 2015 (01.09.2015)

### Date of mailing of the international search report

01 OCT 2015

### Name and mailing address of the ISA/Authorized officer

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