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(54) Title: NITRIFICATION INHIBITOR COMPOSITIONS AND METHODS FOR PREPARING THE SAME

(57) Abstract: Enhanced nitrification inhibitor dry fertilizer compositions, methods for making the same, and their use in agricultural applications are disclosed.

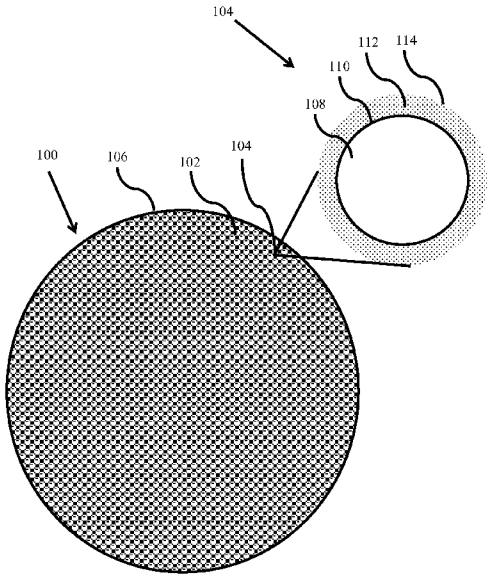


FIG. 1

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NITRIFICATION INHIBITOR COMPOSITIONS AND METHODS FOR PREPARING THE SAME

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to International Application No. PCT/CN2014/095828, filed December 31, 2014, the disclosure of which is hereby expressly incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The present disclosure relates to compositions that inhibit nitrificationand methods of making the same. In some aspects, these compositions are formulated to include other agricultural materials, such as nitrogen-rich fertilizers.

BACKGROUND AND SUMMARY

[0003] Nitrogen fertilizer added to the soil is readily transformed through a number of undesirable biological and chemical processes, including nitrification, leaching, and evaporation. Many transformation processes reduce the level of nitrogen available for uptake by the targeted plant. The decrease in available nitrogen has undesirable consequences and requires the addition of more nitrogen rich fertilizer to compensate for the loss of agriculturally active nitrogen available to the plants. These concerns intensify the demand for improved management of nitrogen for economic efficiency and protection of the environment. Nitrification is the process by which certain widely occurring soil bacteria metabolize the ammonium (NH_4^+) form of nitrogen in the soil transforming the nitrogen into nitrite and nitrate forms, which are more susceptible to nitrogen loss through leaching or volatilization via denitrification.

[0004] Methods for reducing nitrification include treating soil with agriculturally active compounds that inhibit or at least reduce the metabolic activity of at least some microbes in the soil that contribute to nitrification.These compounds include (trichloromethyl)pyridines, such as

nitrapyrin, which have been used as nitrification inhibitors in combination with fertilizers as described in U.S. Pat. No. 3,135,594, the disclosure of which is incorporated herein by reference in its entirety.These compounds help to maintain agriculturally-applied ammonium nitrogen in the ammonium form (stabilized nitrogen), thereby enhancing plant growth and crop yield.These compounds have been used efficaciously with a number of plant crops, includingcorn, sorghum, and wheat.

[0005] Compounds such as nitrapyrin are unstable in soil in part because they are very volatile. For example, nitrapyrin has a relatively high vapor pressure (2.8×10^{-3} mm Hg at 23° Celsius), and because of this it has a tendency to volatilize and must be applied immediately or somehow protected from rapid loss after the fertilizer is treated with nitrapyrin. One approach is to add nitrapyrin to a volatile fertilizer, namely anhydrous ammonia which itself must be added to the soil in manner that reduces the amount of the volatile fertilizer lost to the atmosphere. This method is problematic in that it requires the use of anhydrous ammonia, which is corrosive and must be injected into the soil. This application method, while stabilizing nitrapyrin below the soil surface, is not preferred or completely suitable for many other fertilizer types and their application practices such as dry fertilizer granules, which most often are broadcasted onto the soil surface.

[0006] Additionally, the melting point of nitrapyrin is about 62°C-63°C, and the boiling point is about 136°C-138°C at 1.5kPa (11 mm Hg). Therefore, it is difficult to process nitrapyrin in certain high-temperature fertilizer manufacturing processes. For example, urea manufacturing processes are carried out at about between 130°C and 140°C.

[0007] Still other approaches to stabilize nitrapyrin include applying it to the surface of the soil and then mechanically incorporating it into the soil, or wateringit into the soil generally within 8 hours after its application to reduce its loss to the atmosphere. Encapsulated nitrapyrin

for rapid or dump release have been formulated with lignin sulfonates as disclosed in U.S. Pat. No. 4,746,513, the disclosure of which is incorporated herein by reference in its entirety.Unfortunately, these formulations are difficult and costly to produce, and while these formulations are less volatile than simple nitrapyrin,these formulations are water solubleandcannot be used effectively with liquid urea ammonium nitrate ("UAN") fertilizers.

[0008] Another approach to stabilizing nitrapyrin includes polycondensation encapsulation. Additional information regarding this approach can be found in U.S. Pat. No. 5,925,464, the disclosure of which is incorporated herein by reference in its entirety. Some of these formulations enhance handling safety and storage stability of the nitrapyrin using polyurethane rather than polyurea to form at least a portion of the capsule shell.

[0009] In some instances,polyurea encapsulation has been used to produce enhanced nitrification inhibitor compositions for delayed, steady release of nitrification inhibitors for application with fertilizers. Such encapsulated forms of nitrapyrin are disclosed in U.S. Pat. No. 8,377,849 and U.S. Pat. No. 8,741,805, the disclosures of which are incorporated herein by reference in their entirety.

[0010] Independent application of nitrification inhibitors such as nitrapyrin has some drawbacks. Many farmers are reluctant to separately apply a nitrogen fertilizer and a nitrification inhibitor composition because: (1) such separate application consumes considerable time and human resources; (2) there is a large potential for non-uniform distribution of nitrapyrin, which may lead to performance loss and ineffective use of nitrapyrin; and (3) sequential application may skew the fertilizer to inhibitor ratio in soil, which may lead to performance loss.

[0011] Accordingly, nitrapyrin and nitrogen based fertilizes may be applied at the same time by mixing the compounds and applying them from a common reservoir. Premixing many formulations of nitrapyrin with fertilizers also has certain disadvantages including: (1) extra time,

human resources, and cost in the premixing process; (2) difficulty in combining dry fertilizer granules, such as, for example, urea granules, with nitrapyrin products most commonly sold in emulsifiable concentrate ("EC") liquid form; (3) large differences in application rates, which may make preparation of homogeneous blends difficult. For example, the application rate of nitrogen fertilizers such as urea, (in some embodiments is on the order of about 20-50 kg/Mu). This is hundreds of times greater than the application rates of nitrification inhibitors such as nitrapyrin (for example Entrench™, is often times applied at a rate of about 170 ml/Mu); and (4) the mismatch in particle size between nitrogen fertilizer granules and encapsulated nitrapyrin which may causeparticle classification issues during and after mixing the fertilizer and the inhibitor. For example, the particle size of certain available nitrapyrin products, such as Entrench™ or INSTINCT™, is about 1-10 μm, while a typical nitrogen fertilizer granule, such as urea, is often about 1-3 mm.

[0012] Furthermore, water,which is present in many preparations of nitrapyrin, may cause problems such as theagglomeration and/or crystallization of urea particles. Therefore, there is an advantage to being able to avoid having to use emulsifiable concentrates or aqueous capsule suspensions ("CS") of nitrapyrin with dry nitrogen fertilizer granules.At least in part because water ispresent in somenitrapyrin products or coating processes, this has the potential to negatively influence dry fertilizers, and it is desirable to avoid the addition of extra water in the formula of nitrapyrin mixed with dry actives such as granulated urea.

[0013] While considerable progress has been made in the delivery and stability of nitrification inhibitors such as nitrapyrin, there remains a need for still more efficacious formulations of compounds such as (trichloromethyl)pyridines. There remains a special need for compositions that effectively include at least one nitrogen fertilizerand the nitrification inhibitor. In these compositions, the nitrification inhibitor can be applied along with the fertilizerwithout

the need for additional mixing and/or application steps and under process conditions that can carefully control the relative amount of the inhibitor and the fertilizer in the composition.

[0014] Some aspects of the invention include compositions that include one or more nitrogen fertilizers with one or more nitrification inhibitors. In some embodimentsof the present disclosure, encapsulated nitrification inhibitors, such as, for example, nitrapyrin, are physically incorporated into a fertilizer matrix, such as, for example, a dry fertilizer such as urea. Such dry fertilizer/nitrification inhibitor compositionsincrease ease-of-use, exhibit controlled nitrogen release, increase fertilizer efficiency, and decrease pollution of the soil and air through reduced nitrification. Some of the inventive compositions disclosed herein also exhibit good nitrapyrin stability even at elevated temperatures.

[0015] Some embodiments of the invention include granules of urea. Still other embodiments may include other fertilizers such as other formulations of nitrogen, and/or phosphorous, and/or potassium and/or combinations of two or more or all three ("NPK") fertilizers, and/or bulk blends of fertilizers. In some embodiments, compounding fertilizers, potassium salts, potash, micronutrients, and physical blends of any of the preceding fertilizers can be used. Fertilizer application can be surface broadcasted or sub-surface incorporated, and can be applied before, during, or after planting of one or more crops.

[0016] Therefore, in a first embodiment, disclosed herein is an agricultural composition, comprising: a substantially solid fertilizermatrix, the matrix comprising at least one fertilizer and an outer surface; a plurality of encapsulated particles disposed within the fertilizer matrix, the particles including at least one inhibitor of nitrification and a polymeric shell; and a protective coating disposed between the plurality of encapsulated particles and the fertilizer matrix.

[0017] In a second embodiment, the protective coating of the first embodiment substantially encompasses the polymeric shell of the plurality of encapsulated particles.

[0018] In a third embodiment, the protective coating of any of the prior embodiments comprises one or more materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof.

[0019] In a fourth embodiment, the protective coating of any of the prior embodiments comprises methyl cellulose.

[0020] In a fifth embodiment, the protective coating of any of the prior embodiments comprises sugar.

[0021] In a sixth embodiment, the fertilizer matrix of any of the prior embodiments comprises a solid form of urea.

[0022] In a seventh embodiment, the encapsulated particles of any of the prior embodiments comprise nitrapyrin.

[0023] In an eighth embodiment, the encapsulated particles of any of the prior embodiments include a polyurea shell and have a volume median particle size of from about 1 to about 10 microns.

[0024] In a ninth embodiment, the weight ratio of the one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 1:20 to about 1:1, such as about 1:10.

[0025] In a tenth embodiment, the weight percentage of the one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 0.1 wt% to about 5 wt%.

[0026] In an eleventh embodiment, the weight percentage of the one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 0.3 wt% to about 1.5 wt%.

[0027] In a twelfth embodiment, the agricultural composition of any of the prior embodiments comprises particles between about 0.1 mm to about 5 mm.

[0028] In a thirteenth embodiment, the agricultural composition of any of the prior embodiments comprises particles between about 1 mm to about 3.5 mm.

[0029] In a fourteenth embodiment, the agricultural composition of any of the prior embodiments comprises from about 0.5 wt% to about 10 wt% of the at least one inhibitor of nitrification.

[0030] In a fifteenth embodiment, the agricultural composition of any of the prior embodiments comprises from about 2 wt% to about 8 wt% of the at least one inhibitor of nitrification.

[0031] In a sixteenth embodiment, the agricultural composition of any of the prior embodiments comprises from about 4 wt% to about 8 wt% of the at least one inhibitor of nitrification.

[0032] In a seventeenth embodiment, the agricultural composition of any of the prior embodiments comprises about 8 wt% of the at least one inhibitor of nitrification.

[0033] In an eighteenth embodiment, the agricultural composition of any of the prior embodiments comprises from about 0.5 wt% to about 10 wt% of nitrapyrin.

[0034] In a nineteenth embodiment, the composition of any of the prior embodiments comprises from about 2 wt% to about 8 wt% of nitrapyrin.

[0035] In a twentieth embodiment, the composition of any of the prior embodiments comprises from about4 wt% to about 8 wt% of nitrapyrin.

[0036] In a twenty-first embodiment, the composition of any of the prior embodiments comprises about8 wt% of nitrapyrin.

[0037] Additionally disclosed in a twenty-second embodiment is a method for preparing a fertilizer composition comprising the steps of: preparing a plurality of encapsulated particles, the particles including at least one inhibitor of nitrification; dispersing the plurality of encapsulated particles in a fertilizer melt, wherein the melt comprises at least one melted fertilizer; cooling the melt to form a solid; and forming combined nitrification inhibiting fertilizer particles from the solid.

[0038] In a twenty-third embodiment, the plurality of encapsulated particles of any of the prior embodiments is in an aqueous capsule suspension concentrate, and the step of preparing further comprises drying the plurality of encapsulated particles.

[0039] In a twenty-fourth embodiment, drying of any of the prior embodiments is accomplished by the step of spray drying.

[0040] In a twenty-fifth embodiment, the step of spray drying of any of the prior embodiments further comprises diluting the aqueous capsule suspension concentrate by aqueous diluent by about 3 to about 150 times.

[0041] In a twenty-sixth embodiment, the step of preparing of any of the prior embodiments further comprises providing a protective coating disposed on the plurality of encapsulated particles.

[0042] In a twenty-seventh embodiment, the protective coating of any of the prior embodiments comprises one or more materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof.

[0043] In a twenty-eighth embodiment, the protective coating of any of the prior embodiments comprises methyl cellulose.

[0044] In a twenty-ninth embodiment, the protective coating of any of the prior embodiments comprises sugar.

[0045] In a thirtieth embodiment, the step of cooling of any of the prior embodiments the melt to form a solid further comprises forming a fertilizer matrix disposed around the plurality of encapsulated particles.

[0046] In a thirty-first embodiment, the fertilizer matrix of any of the prior embodiments comprises a solid form of urea.

[0047] In a thirty-second embodiment, the fertilizer melt of any of the prior embodiments is heated at about between 130° C and 148° C.

[0048] In a thirty-third embodiment, the encapsulated particles of any of the prior embodiments comprise nitrapyrin.

[0049] In a thirty-fourth embodiment, the encapsulated particles of any of the prior embodiments include polyurea and have a volume median particle size of from about 1 to about 10 microns.

[0050] In a thirty-fifth embodiment, the weight ratio of one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 1:20 to about 1:1.

[0051] In a thirty-sixth embodiment, the weight percentage of the one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 0.1 wt% to about 5 wt%.

[0052] In a thirty-seventh embodiment, the weight percentage of the one or more materials in the protective coating to the encapsulated particles of any of the prior embodiments is between about 0.3 wt% to about 1.5 wt%.

[0053] In a thirty-eighth embodiment, the step of forming of any of the prior embodiments further comprises forming particles between about 0.1 mm to about 5 mm.

[0054] In a thirty-ninth embodiment, the step of forming of any of the prior embodiments further comprises forming particles between about 1 mm to about 3.5 mm.

[0055] In a fortieth embodiment, the composition of any of the prior embodiments comprises from about 0.5 wt% to about 10 wt% of the at least one inhibitor of nitrification.

[0056] In a forty-first embodiment, the composition of any of the prior embodiments comprises from about 2 wt% to about 8 wt% of the at least one inhibitor of nitrification.

[0057] In a forty-second embodiment, the composition of any of the prior embodiments comprises from about 4 wt% to about 8 wt% of the at least one inhibitor of nitrification.

[0058] In a forty-third embodiment, the composition of any of the prior embodiments comprises about 8 wt% of the at least one inhibitor of nitrification.

[0059] In a forty-fourth embodiment, the composition of any of the prior embodiments comprises from about 0.5 wt% to about 8 wt% of nitrapyrin.

[0060] In a forty-fifth embodiment, the composition of any of the prior embodiments comprises from about 2 wt% to about 8 wt% ofnitrapyrin.

[0061] In a forty-sixth embodiment, the composition of any of the prior embodiments comprises from about 4 wt% to about 8 wt% of nitrapyrin.

[0062] In a forty-seventh embodiment, the composition of any of the prior embodiments comprises about 8 wt% of nitrapyrin.

[0063] In a forty-eighth embodiment, the fertilizer melt of any of the prior embodiments is selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, and mixtures thereof.

BRIEF DESCRIPTION OF THE FIGURES

[0064] The features of this disclosure, and the manner of attaining them, will become more apparent and the disclosure itself will be better understood by reference to the following description of embodiments of the disclosure taken in conjunction with the accompanying drawings.

[0065] **FIG. 1** provides a perspective view of one exemplary embodiment of a nitrification-inhibiting fertilizer combined particle that includes an encapsulatednitrification inhibitor.

[0066] **FIG. 2** provides a process diagram for one exemplary method for manufacturinga nitrification-inhibiting fertilizer combined particle that includes an encapsulated nitrification inhibitor.

[0067] Corresponding reference characters indicate corresponding parts throughout the several views. Although the drawings represent embodiments of the present disclosure, the drawings are not necessarily to scale and certain features may be exaggerated in order to better illustrate and explain the present disclosure. The exemplifications set out herein illustrate an exemplary embodiment of the disclosure, in one form, and such exemplifications are not to be construed as limiting the scope of the disclosure in any manner.

DETAILED DESCRIPTION

[0068] (Trichloromethyl)pyridine compounds useful in the composition of the presentdisclosure include compounds having a pyridine ring which is substituted with at least onetrichloromethyl group, and mineral acid salts thereof. Suitable compounds include thosecontaining chlorine or methyl substituents on the pyridine ring in addition to atrichloromethyl group, and are inclusive of chlorination products of methyl pyridines such as lutidine, collidine and picoline.Suitable salts include hydrochlorides, nitrates, sulfates and phosphates.The (trichloromethyl)pyridine compounds useful in the practice of the present disclosure are typically oily liquids or crystalline solids dissolved in a solvent. Other suitable compounds are described in U.S. Pat. No. 3,135,594.A preferred(trichloromethyl)pyridine is 2-chloro-6-(trichloromethyl)pyridine, also known as nitrapyrin, and the active ingredient of the product N-SERVE™. (Trademark of DowAgroSciences LLC).

[0069] Referring now to **FIG. 1,** a perspective view of one exemplary embodiment of a nitrification-inhibiting fertilizer ("NI-F") combined particle **100** is shown. NI-F combined particle **100** includes a fertilizer matrix **102** with encapsulated nitrification-inhibitingparticles **104**, embedded in the fertilizer matrix **102**as shown. One such encapsulated NI particle **104** is shown enlarged in **FIG. 1**.

[0070] **FIG. 1** shows encapsulated NI particles **104** distributed evenly throughout fertilizer matrix **102**, but in other embodiments, encapsulated NI particles **104** need not be distributed throughout the entirety of combined particle **100**. For example, encapsulated NI particles **104**, in some embodiments are distributed discontinuously and/or unevenly on and throughout combined particle **100**.

[0071] In some embodiments, fertilizer matrix **102** is a dry particle/granule fertilizer, such as, for example, urea. The fertilizer matrix **102** allows for encapsulated NI particles **104** to be disposed throughout combined particle **100**.In some embodiments, fertilizer matrix **102** is any suitable dry fertilizer for application to fields and/or crops, such as, for example, a nitrogen-containing fertilizer such as urea. Fertilizer matrix **102** can also include any other agricultural active ingredient including, but not limited to, pesticides, fungicides, herbicides, miticides, insecticides, safeners, and arthropocides. In some embodiments, fertilizer matrix **102** comprises at least one of the following fertilizers: a nitrogen-based fertilize,a potassium-based fertilizer, a phosphorus-based fertilizer, and/or any blend or mixture of the foregoing. In some embodiments, fertilizer matrix **102** comprises urea.

[0072] The desired particle size and cell wall thickness for encapsulated NI particles **104** will depend upon the actual application. Some currently commercially available encapsulated NI particles **104** have a volume median particle size of from about 1 to about 10 microns and a capsule wall thickness of from about 10 to about 125nanometers. In one embodiment, the desired particle size may be from about 2 microns to about 10 microns, with a wall thickness of from about 10 to about 25 nanometers. In other embodiments, the desired particle size may be from about 1-10microns, with cell wall thicknesses of from about 75 to about 125 nanometers.

[0073] NI-F combined particle **100**also has outer surface **106**, which is depicted in **FIG. 1**to be substantially spherically shaped (substantially circular in the cross-section), however, any

other suitable shape is envisioned, such as a cylinder, a square, a rectangle or an irregular shape, so long as NI-F combined particle **100** can be applied to fields and/or crops and release the composition into the soil. The volume median particle size of NI-F combined particle **100**may be similar to the size of commercially available dry fertilizer products, such as between about 0.1mm to about 5mm, and for nitrogen-based fertilizers, such as, for example, solid urea often between about 0.3mm and about 3mm.

[0074] Still referring to **FIG. 1**, one encapsulated NI particle **104** is shown to be enlarged. Encapsulated NI particle **104** includes nitrification-inhibiting core **108**, polymeric shell **110**, protective coating **112**, and outer surface **114**. NI core **108**may include at least one inhibitor of nitrification, such as, for example, (trichloromethyl)pyridine compounds like nitrapyrin. NI core **108** can be in any suitable physical form within a polymeric shell **110**, including, but not limited to a solid, liquid, and/or a gel. Polymeric shell **110** can comprise any suitable polymer, including, but not limited to, polyurea. NI core **108** and polymeric shell **110**, in some embodiments, are one or more embodiments of those microcapsules disclosed and claimed in U.S. Pat. No. 8,377,849 and U.S. Pat. No. 8,741,805. In some embodiments, the microcapsules include polyurea and are between about 1 μm and about 10 μm in size.

[0075] Disposed around polymeric shell **110** is protective coating **112**. In some embodiments, protective coating **112** prevents active loss of nitrapyrin from NI core **108** through polymeric shell **110** at high temperatures, such as high temperatures as may be experienced during processing, storage, and/or transportation. In some embodiments, protective coating **112** includes biodegradable and/or environmentally friendly components that are readily degradable in soil and do not negatively influence the release profile of NI core **108**to the soil from NI-F combined particle **100**.

[0076] Protective coating **112** can include materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof.

[0077] Any suitable material to form protective coating **112** is envisioned. Such suitable materials include, but are not limited to, materials that are capable of coating encapsulated NI particles **104**, such that they prevent excessive NI loss due to high temperatures, pressure, abrasion, and/or other environmental factors during processing, storage, transport, and preparation. In some embodiments, the coating material(s) is also capable of dissolving and/or releasing NI core **108**, which in some embodiments is microencapsulated nitrapyrin. In some embodiments, the fertilizer matrix **102** is a fertilizer, which is released once the composition is applied to the field and comes into contact with high levels of moisture (possibly rain or irrigation).

[0078] Encapsulated NI particle **104** includes outer surface **114**, which in the embodiment shown is shown to be substantially spherically shaped (substantially circular in the cross-section), however, any other suitable shape is envisioned, such as a cylinder, rectangle, square and/or irregular shape, so long as encapsulated NI particle **104** can be applied to fields and/or crops with NI-F combined particle **100**and release nitrification inhibitor from NI core **108**.

[0079] Protective coating**112**, in the embodiment shown, wholly covers polymeric shell**110**, however, in other embodiments, protective coating**112** need not wholly cover

polymeric shell **110**. For example, in some embodiments, portions of polymeric shell **110** may be in direct contact with fertilizer matrix **102** where protective coating**112** is discontinuous. Therefore, protective coating **112** may substantially or wholly encompass polymeric shells **110** encapsulating NI particles **104**, or protective coating **112** may be discontinuous around some or all of encapsulated NI particles **104**.

[0080] Now referring to **FIG. 2**, a process diagram is shown for one exemplary method for manufacturing a nitrification-inhibiting agricultural active ingredient combined particle that includes an encapsulated nitrification inhibitor.

[0081] In a first step, an encapsulated nitrification inhibitor, for example one or more embodiments of the microcapsules disclosed and claimed in U.S. Pat. No. 8,377,849 and U.S. Pat. No. 8,741,805, is coated to form a protective coating **112**. In some embodiments, the encapsulated nitrification inhibitor is in a water dispersion of microcapsules, such as INSTINCT™ or ENTRENCH™ (commercially available forms of microencapsulated nitrapyrin, produced by Dow AgroSciences LLC). The material used to form the protective coating layer is dissolved and/or suspended in the water dispersion of microcapsules.

[0082] As noted above, protective coating **112** can include materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof. In some

embodiments, the weight ratio of the materials used to form protective coating **112** to the encapsulated nitrification inhibitor particles is between about 1:20 to about 1:1.

[0083] After the one or more materials used to form protective coating **112** are dissolved and/or suspended in the water dispersion of encapsulated nitrification inhibitor, the mixture is diluted with water and/or another water miscible diluent. The mixture may be optionally dried, in some embodiments by spray drying, and a coated, encapsulated nitrification inhibitor is produced, as shown by **FIG. 2**. In some embodiments, for example, if spray drying is used, the water dispersion containing the encapsulated nitrification inhibiting particles and the materials for protective coating **112** will be diluted from about 3 to about 150 times. After drying the coated, encapsulated nitrification-inhibitor including particles, they are re-dispersible and stable at high temperatures, in some embodiments at temperatures up to about 148°C.

[0084] Other coating devices and methods known in the art could also be used. Equipment that can be used to prepare coated encapsulated NI particles **104** includes, but is not limited to a pan coater, a rotating drum, a spray coater, a fluid bed, and/or screens.

[0085] After the coated, encapsulated nitrification inhibitor particles are obtained and optionally dried, the particles can be dispersed in a fertilizer melt. In the embodiments depicted in **FIG. 2**, a urea melt is shown. Urea is a suitable material because the melting point of urea is about 133°C. Accordingly, the coated, encapsulated nitrification inhibitor particles (stable up to about 148°C) can be dispersed in the urea melt. In other embodiments, other fertilizer melts can be used as long as the melting temperature of the fertilizer is low enough that it allows the coated, encapsulated nitrification inhibitor particles to remain stable within the melt. One of skill in the art could modify protective coating **112** to adjust the conditions including the temperature up to which the particles would be stable and therefore could select other fertilizers to melt, based on

the melting temperature of the fertilizer and the stability of the nitrification inhibitors present in the encapsulated particles.

[0086] In some embodiments, protective coating **112** around polymeric shell **110** is not explicit or neat once embedded in fertilizer matrix **102**, i.e. portions of protective coating **112** may be partially or substantially fully embedded and blended within fertilizer matrix **102**. In some embodiments, portions of polymeric shell **110** may be in contact with fertilizer matrix **102**. In other embodiments, fertilizer matrix **102** may not be in contact with polymeric shell **110**.

[0087] In some embodiments, to embed coated, encapsulated nitrapyrin microparticles in a fertilizer melt, such as urea, the temperature of the melt should be from about 60°C to about 148°C. If urea is chosen, the temperature for processing should be from about 130°C to about 148°C.

[0088] After the coated, encapsulated nitrification inhibitor particles are dispersed within the fertilizer, optionally urea melt, the melt is cooled to solidify the melt and granulated according to granulation processes known in the art. In some preferred embodiments, the final water content of NI-F combined particle **100** is less than about 3 wt% based on the total weight of NI-F combined particle **100**. In some embodiments, the size of NI-F combined particle **100** is between about 0.1mm to about 5mm. In some preferred embodiments in which urea is used as the fertilizer matrix, the final size of NI-F combined particle **100** is between about 1mm to about 3.5mm.

[0089] In some embodiments, the nitrification inhibitor, optionally nitrapyrin, content ranges from about 0.5 wt% to about 10 wt% based on the total weight of NI-F combined particles **100**.

[0090] In some embodiments, NI-F combined particle **100** is a dry formulation. In some embodiments, NI-F combined particle **100**,along with fertilizer matrix **102** and embedded

encapsulated nitrification-inhibiting particles **104** will dissolve in water (in soil conditions) and then release encapsulated nitrapyrin. Nitrapyrin will then diffuse into the soil to function as an inhibitor for nitrification of fertilizers, optionally nitrogen-based fertilizers.

[0091] Examples of typical solvents which can be used to dissolve crystalline(trichloromethyl)pyridine compounds, such as nitrapyrin, include aromatic solvents, particularly alkylsubstituted benzenes, such as xylene or propylbenzene fractions, and mixed naphthaleneand alkyl naphthalene fractions; mineral oils; kerosene; dialkyl amides of fatty acids,particularly the dimethylamides of fatty acids such as the dimethyl amide of caprylic acid;chlorinated aliphatic and aromatic hydrocarbons such as 1,1,1-trichloroethane andchlorobenzene; esters of glycol derivatives, such as the acetate of the *n*-butyl, ethyl, ormethyl ether of diethyleneglycol and the acetate of the methyl ether of dipropylene glycol; ketones such as isophorone and trimethylcyclohexanone (dihydroisophorone); and the acetate products such as hexyl or heptyl acetate. The preferred organic liquids include xylene, alkyl substituted benzenes, such as propyl benzene fractions, and alkyl naphthalene fractions.

[0092] In general, the amount of solvent employed, if desired, in the preparation of microencapsulated nitrapyrin is typically from about 40,preferably from about 50 to about 70, preferably to about 60 weight percent, based on thetotal weight of the (trichloromethyl)pyridine/solvent solution. The amount ofa (trichloromethyl)pyridine within a (trichloromethyl)pyridine/solvent solution is typically from about 30, preferably from about 40 to about 60, preferably to about 50 weight percent, based on the weight of a (trichloromethyl)pyridine/solvent solution.

[0093] Microcapsules useful in the present disclosure can be prepared by the polycondensation reaction of a polymeric isocyanate and a polyamine to form a polyureashell. Methods of microencapsulation are well known in the art and any such method can be utilized in

the present disclosure to provide a suitable capsule suspension formulation. In general, the capsule suspension formulation can be prepared by first mixing a polymeric isocyanate with a (trichloromethyl)pyridine /solvent solution. This mixture is thencombined with an aqueous phase which may include an emulsifier to form a two phasesystem. The organic phase is emulsified into the aqueous phase by shearing until the desired particle size is achieved. An aqueous crosslinking polyamine solution is then added dropwise while stirring to form the encapsulated particles of(trichloromethyl)pyridine as an aqueous suspension.

[0094] The desired particle size and cell wall thickness will depend upon the actual application. The microcapsules typically have a volume median particle size of from about 1 to about 10 microns and a capsule wall thickness of from about 10 to about 125nanometers.In one embodiment, the desired particle size may be from about 2 to about 10 microns, with a cell wall of from about 10 to about 25 nanometers. In another embodiment, requiring soil surface stability, the desired particle size may be from about 1-10microns, with cell wall thicknesses of from about 75 to about 125 nanometers.

[0095] Other additives may also be incorporated into the formulation such as emulsifiers, dispersants, thickeners, biocides, pesticides, salts and film-forming polymers.

[0096] Dispersing and emulsifying agents include condensation products of alkyleneoxides with phenols and organic acids, alkyl aryl sulfonates, polyoxyalkylene derivatives of sorbitan esters, complex ether alcohols, mahogany soaps, lignin sulfonates, polyvinylalcohols, and the like. The surface-active agents are generally employed in the amount offrom about 1 to about 20 percent by weight of the microcapsule suspension formulation.

[0097] The ratio of the suspended phase to the aqueous phase within exemplary microcapsule suspension formulations of the present disclosure is dependent upon the desired concentration of (trichloromethyl)pyridine compound in the final formulation.Typicallythe ratio

will be from about 1:0.75 to about 1:20.Generally the desired ratio is about 1:1to about 1:7, and is preferably from about 1:1 to about 1:4.

[0098] The presence of a (trichloromethyl)pyridine compound suppresses the nitrification of ammonium nitrogen in the soil or growth medium, thereby preventing the rapid loss of ammonium nitrogen originating from nitrogen fertilizers, organic nitrogen constituents, or organic fertilizers and the like.

[0099] The enhanced nitrification inhibitor dry fertilizer compositions of the present disclosure can be applied in any manner which will benefit the crop of interest.In one embodiment the enhanced nitrification inhibitor dry fertilizer compositions are applied to growth mediums in a band or row application. In another embodiment, the compositions are applied to or throughout the growth medium prior to seeding or transplanting the desired crop plant. In yet another embodiment, the compositions can be applied to the root zone of growing plants.

[00100] Additionally, the compositions can be applied with the application of nitrogen fertilizers. The composition can be applied prior to, subsequent to, or simultaneously with the application of fertilizers.

[00101] The compositions of the present disclosure have the added benefit that they can be applied to the soil surface, without additional water or mechanical incorporation into the soil for days to weeks. Alternatively, if desired, the compositions of the present disclosure can be incorporated into the soil directly upon application.

[00102] Soil treatment compositions may be prepared by dispersing the nitrification inhibitor dry fertilizer compositions in fertilizers such as ammonium or organic nitrogen fertilizer. The resulting fertilizer composition may be employed as such or may be modified, as by dilution with additional nitrogen fertilizer or with inert solid carrier to obtain a composition containing the desired amount of active agent for treatment of soil.

[00103] The soil may be prepared in any convenient fashion with the nitrification inhibitor dry fertilizer compositions of the present disclosure, including mechanically mixed with thesoil; applied to the surface of the soil and thereafter dragged or diced into the soil to adesired depth; or transported into the soil such as by injection, spraying, dusting orirrigation.In irrigation applications, the nitrification inhibitor dry fertilizer composition may be introduced to irrigation water in an appropriate amount in order to obtain a distribution of the (trichloromethyl)pyridine compound to the desired depth of up to 6 inches (15.24 cm).

[00104] Due to the controlled release of nitrapyrin in the nitrification inhibitor dry fertilizer compositions of the present disclosure, several advantages can be attained. First, the amount of nitrapyrin can be reduced since it is more efficiently released into the soil over an extended period of time. Additionally, the nitrification inhibitor dry fertilizer composition of the present disclosure can be applied and left on the surface to be naturally incorporated into the soil, without the need for mechanical incorporation if desired.

[00105] Additionally, the nitrification inhibitor dry fertilizer compositions of the present disclosure can be combined or used in conjunction with pesticides, including arthropodicides, bactericides, fungicides, herbicides, insecticides, miticides, nematicides, nitrification inhibitors such as dicyandiamide, urease inhibitors such as N-(n-butyl) thiophosphoric triamide, and the like or pesticidal mixtures and synergistic mixtures thereof. In such applications, the nitrification inhibitor dry fertilizer compositions of the present disclosure can be tank mixed with the desired pesticide(s) or they can be applied sequentially.

[00106] Exemplary herbicides include, but are not limited to acetochlor, alachlor,aminopyralid, atrazine, benoxacor, bromoxynil, carfentrazone, chlorsulfuron, clodinafop,clopyralid, dicamba, diclofop-methyl, dimethenamid, fenoxaprop, flucarbazone,flufenacet, flumetsulam, flumiclorac, fluroxypyr, glufosinate-ammonium,

glyphosate,halosulfuron-methyl, imazamethabenz, imazamox, imazapyr, imazaquin, imazethapyr,isoxaflutole, quinclorac, MCPA, MCP amine, MCP ester, mefenoxam, mesotrione,metolachlor, s-metolachlor, metribuzin, metsulfuron methyl, nicosulfuron, paraquat,pendimethalin, picloram, primisulfuron, propoxycarbazone, prosulfuron, pyraflufen ethyl,rimsulfuron, simazine, sulfosulfuron, thifensulfuron, topramezone, tralkoxydim, triallate,triasulfuron, tribenuron, triclopyr, trifluralin, 2,4-D, 2,4-D amine, 2,4-D ester and the like.

[00107] Exemplary insecticides include, but are not limited to1,2 dichloropropane, 1,3 dichloropropene,abamectin, acephate, acequinocyl, acetamiprid, acethion, acetoprole, acrinathrin,acrylonitrile, alanycarb, aldicarb, aldoxycarb, aldrin, allethrin, allosamidin, allyxycarb,alpha cypermethrin, alpha ecdysone, amidithion, amidoflumet, aminocarb, amiton,amitraz, anabasine, arsenous oxide, athidathion, azadirachtin, azamethiphos, azinphosethyl, azinphos methyl, azobenzene, azocyclotin, azothoate,barium hexafluorosilicate, barthrin, benclothiaz, bendiocarb,benfuracarb, benoxafos, bensultap, benzoximate, benzyl benzoate, beta cyfluthrin, betacypermethrin, bifenazate, bifenthrin, binapacryl, bioallethrin, bioethanomethrin,biopermethrin, bistrifluron, borax, boric acid, bromfenvinfos, bromo DDT, bromocyclen,bromophos, bromophos ethyl, bromopropylate, bufencarb, buprofezin, butacarb,butathiofos, butocarboxim, butonate, butoxycarboxim,cadusafos, calcium arsenate, calcium polysulfide, camphechlor, carbanolate,carbaryl, carbofuran, carbon disulfide, carbon tetrachloride, carbophenothion, carbosulfan,cartap, chinomethionat, chlorantraniliprole, chlorbenside, chlorbicyclen, chlordane,chlordecone, chlordimeform, chlorethoxyfos, chlorfenapyr, chlorfenethol, chlorfenson,chlorfensulphide, chlorfenvinphos, chlorfluazuron, chlormephos, chlorobenzilate,chloroform, chloromebuform, chloromethiuron, chloropicrin, chloropropylate,chlorphoxim, chlorprazophos, chlorpyrifos, chlorpyrifos methyl,

chlorthiophos,chromafenozide, cinerin I, cinerin II, cismethrin, cloethocarb, clofentezine, closantel,clothianidin, copper acetoarsenite, copper arsenate, copper naphthenate, copper oleate,coumaphos, coumithoate, crotamiton, crotoxyphos, cruentaren A &B, crufomate, cryolite,cyanofenphos, cyanophos, cyanthoate, cyclethrin, cycloprothrin, cyenopyrafen,cyflumetofen, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyphenothrin, cyromazine,cythioate,d-limonene, dazomet, DBCP, DCIP, DDT, decarbofuran, deltamethrin,demephion, demephion O, demephion S, demeton, demeton methyl, demeton O, demeton O methyl, demeton S, demeton S methyl, demeton S methylsulphon, diafenthiuron,dialifos, diamidafos, diazinon, dicapthon, dichlofenthion, dichlofluanid, dichlorvos,dicofol, dicresyl, dicrotophos, dicyclanil, dieldrin, dienochlor, diflovidazin, diflubenzuron,dilor, dimefluthrin, dimefox, dimetan, dimethoate, dimethrin, dimethylvinphos, dimetilan,dinex, dinobuton, dinocap, dinocap 4, dinocap 6, dinocton, dinopenton, dinoprop,dinosam, dinosulfon, dinotefuran, dinoterbon, diofenolan, dioxabenzofos, dioxacarb,dioxathion, diphenyl sulfone, disulfiram, disulfoton, dithicrofos, DNOC, dofenapyn,doramectin,ecdysterone, emamectin, EMPC, empenthrin, endosulfan, endothion, endrin, EPN,epofenonane, eprinomectin, esfenvalerate, etaphos, ethiofencarb, ethion, ethiprole,ethoate methyl, ethoprophos, ethyl DDD, ethyl formate, ethylene dibromide, ethylenedichloride, ethylene oxide, etofenprox, etoxazole, etrimfos, EXD,famphur, fenamiphos, fenazaflor, fenazaquin, fenbutatin oxide, fenchlorphos,fenethacarb, fenfluthrin, fenitrothion, fenobucarb, fenothiocarb, fenoxacrim, fenoxycarb,fenpirithrin, fenpropathrin, fenpyroximate, fenson, fensulfothion, fenthion, fenthion ethyl,fentrifanil, fenvalerate, fipronil, flonicamid, fluacrypyrim, fluazuron, flubendiamide,flubenzimine, flucofuron, flucycloxuron, flucythrinate, fluenetil, flufenerim, flufenoxuron,flufenprox, flumethrin, fluorbenside, fluvalinate, fonofos, formetanate, formothion,formparanate, fosmethilan, fospirate, fosthiazate, fosthietan, fosthietan,

furathiocarb,furethrin, furfural,gamma cyhalothrin, gamma HCH, halfenprox, halofenozide, HCH, HEOD, heptachlor, heptenophos, heterophos, hexaflumuron, hexythiazox, HHDN, hydramethylnon, hydrogen cyanide, hydroprene, hyquincarb, imicyafos, imidacloprid, imiprothrin, indoxacarb, iodomethane, IPSP, isamidofos, isazofos, isobenzan, isocarbophos, isodrin, isofenphos, isoprocarb, isoprothiolane, isothioate, isoxathion, ivermectin jasmolin I, jasmolin II, jodfenphos, juvenile hormone I, juvenile hormone II,juvenile hormone III,kelevan, kinoprene,lambda cyhalothrin, lead arsenate, lepimectin, leptophos, lindane, lirimfos,lufenuron, lythidathion,malathion, malonoben, mazidox, mecarbam, mecarphon, menazon, mephosfolan,mercurous chloride, mesulfen, mesulfenfos, metaflumizone, metam, methacrifos,methamidophos, methidathion, methiocarb, methocrotophos, methomyl, methoprene,methoxychlor, methoxyfenozide, methyl bromide, methyl isothiocyanate,methylchloroform, methylene chloride, metofluthrin, metolcarb, metoxadiazone,mevinphos, mexacarbate, milbemectin, milbemycin oxime, mipafox, mirex, MNAF,monocrotophos, morphothion, moxidectin,naftalofos, naled, naphthalene, nicotine, nifluridide, nikkomycins, nitenpyram,nithiazine, nitrilacarb, novaluron, noviflumuron,omethoate, oxamyl, oxydemeton methyl, oxydeprofos, oxydisulfoton,paradichlorobenzene, parathion, parathion methyl, penfluron, pentachlorophenol,permethrin, phenkapton, phenothrin, phenthoate, phorate, phosalone, phosfolan, phosmet,phosnichlor, phosphamidon, phosphine, phosphocarb, phoxim, phoxim methyl,pirimetaphos, pirimicarb, pirimiphos ethyl, pirimiphos methyl, potassium arsenite,potassium thiocyanate, pp' DDT, prallethrin, precocene I, precocene II, precocene III,primidophos, proclonol, profenofos, profluthrin, promacyl, promecarb, propaphos,propargite, propetamphos, propoxur, prothidathion, prothiofos, prothoate, protrifenbute,pyraclofos, pyrafluprole, pyrazophos, pyresmethrin, pyrethrin I, pyrethrin II, pyridaben,pyridalyl, pyridaphenthion, pyrifluquinazon, pyrimidifen, pyrimitate,

pyriprole,pyriproxyfen,quassia, quinalphos, quinalphos, quinalphos methyl, quinothion, quantifies,rafoxanide, resmethrin, rotenone, ryania,sabadilla, schradan, selamectin, silafluofen, sodium arsenite, sodium fluoride,sodium hexafluorosilicate, sodium thiocyanate, sophamide, spinetoram, spinosad,spirodiclofen, spiromesifen, spirotetramat, sulcofuron, sulfiram, sulfluramid, sulfotep,sulfur, sulfuryl fluoride, sulprofos,tau fluvalinate, tazimcarb, TDE, tebufenozide, tebufenpyrad, tebupirimfos,teflubenzuron, tefluthrin, temephos, TEPP, terallethrin, terbufos, tetrachloroethane,tetrachlorvinphos, tetradifon, tetramethrin, tetranactin, tetrasul, theta cypermethrin,thiacloprid, thiamethoxam, thicrofos, thiocarboxime, thiocyclam, thiodicarb, thiofanox,thiometon, thionazin, thioquinox, thiosultap, thuringiensin, tolfenpyrad, tralomethrin,transfluthrin, transpermethrin, triarathene, triazamate, triazophos, trichlorfon,trichlormetaphos 3, trichloronat, trifenofos, triflumuron, trimethacarb, triprene,vamidothion, vamidothion, vaniliprole, vaniliprole,XMC, xylylcarb,zeta cypermethrin and zolaprofos.

[00108] Additionally, any combination of the above pesticides can be used.Additionally, Rynaxypyr™, a new anthranilic diamide (Chlorantraniliprole)crop protection chemistry from DuPontwith efficacy in controlling target pests can be used.

[00109] The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

EXAMPLES

[00110] Unless indicated otherwise, where shown the nitrapyrin weight content in NI-F combined particles was determined by gas chromatography ("GC"). The instrument condition was aligned with DN 0025728 "Analytical method and validation for the determination of

nitrapyrin in GF-2017 formulation." The extraction process was carried out according to the noted documentation, and based on solvent mix hexane/acetone (volume ratio from about 3:1 to about 1:3). The nitrapyrin content can be analyzed before and after processing in order to determine the loss, if any, of nitrapyrin from NI-F combined particlesdue to volatilization and/or chemical instability.

[00111] To test the dry storage stability of commercially available encapsulated nitrapyrin (such as INSTINCT™ or ENTRENCH™) polyurea encapsulated nitrapyrin particles were incubated in a Jar Mill Oven (Lindberg/Blue M, Thermal Electron Corporation) at 130-148°Celsius for about 5 minutes to about 30 minutes. After thermal treatment, nitrapyrin content loss was measured to determine the thermal stability of encapsulated nitrapyrin particles.

[00112] For nitrapyrin content detection in the NI-F combined particles, the NI-F combined particles were dissolved in a saturated NaCl solution, and then extracted using acetone/hexane in a 4:1 mixture. The extract was analyzed by the above-mentioned GC method. This analytical method was validated by comparing the measured values to values measured using a recovery test method (spike encapsulated nitrapyrin dry powder into urea).

[00113] **Table 1**provides a list of some of the materials used to make the exemplary compositions which were formed and tested as described herein.

Table 1. Raw Materials.

Category	Ingredient	Supplier
Nitrapyrin source	Nitrapyrin (chemical purity)	Sinopham Chemical Reagent Co., Ltd. Shanghai, China
	Entrench (Polyurea encapsulated water dispersion)	The Dow Chamical Company, Midland, U.S.A.
Protective Coating Materials	Alginate (Manucol DM)	FMC Company, Shanghai, China
	METHOCEL A 15 (methyl cellulose)	The Dow Chemical Company, Midland, U.S.A.

Category	Ingredient	Supplier
	Laponite RD (inorganic layered silicate, aqueous rheology modifier)	Rockwood Additives Ltd. USA
	PVA-1788 ("Polyvinyl alcohol")	Dongfang Chemical Company, Beijing, China
	Attapulgite Agriculture Grade	Anhui DiYuan Fertilizer Company, Hefei, China
	CMC Walocel CRT 100	The Dow Chemical Company, Midland, U.S.A.
	Sugar (food grade)	Taikoo Custer Sugar, Hongkong, China
Urea	Urea fertilizer particles	Sinochem Company, Beijing, China
	Urea standard	Sinopharm Chemical Reagent Co., Ltd. Shanghai, China

[00114] In some examples of a spray-drying method for producing coated, encapsulated nitrification inhibiting microcapsules, water dispersions of encapsulated nitrapyrin (including, for example, ENTRENCH™ and INSTINCT™, commercial concentrates produced by Dow AgroSciences LLC) were diluted between about 5 to about 200 times with deionized water according to the experimental design. Materials used to form the protective coating around the nitrification inhibiting microcapsules included powders, which were dispersed into the diluted water dispersions of the encapsulated nitrapyrin by stirring at about 200-1500 rpm for about 5 minutes. The combined dispersions were incubated at room temperature for about 10 to about 30 minutes with stirring at about 500-2000 rpm. After the materials used to form the protective coating were dissolved or homogeneously dispersed in the dilutions, spray drying was conducted according to the following process.

[00115] The diluted dispersions were spray dried according to the following conditions: the inlet temperature of the spray drier was about 25°C to about 80°C and the air temperature was approximately 100°C to about 140°C. In some embodiments, the air temperature was less than about 120 ^{0}C. The atomizer spin rate was about 20,000 RPM, using a V24 wheel. The

liquid feed rate was between about 20 to about 50 ml/min and the drying gas flow rate was around 98kg/hr.

[00116] A separate fertilizer melt was prepared. Urea particles were melted and incubated at between about 130°C to about 148°C with stirring at about 100-500 rpm. The coated, encapsulated particles prepared by the process described above were dispersed into the melted urea with stirring at about 200-1000 rpm for about 5 minutes. Then, the urea melt with dispersed particles was cooled to form a solid. Cooling processes can include, but are not limited to, direct cooling by heat dispersion, molding, and/or pelleting.

[00117] **Table 2** provides a list of coated or uncoated microcapsules and NI-F particle formulations prepared as described herein.

Table 2.Nitrapyrin samples prepared for evaluation of thermal stability.

Examples	Diluted times (in spray drying)	Encapsulation materials	Protective Coating materials/wt%[1]	The wt% of Nitrapyrin in Urea
1[2]	-	None	None	Not combined with urea melt
2	0X	PAPI27+ Ethylene Diamine	None	
3	50X	PAPI27+ Ethylene Diamine	None	
4	50X	PAPI27+ Ethylene Diamine	Methocel A 15 0.36%	
5	50X	PAPI27+ Ethylene Diamine	Walocel CRT 100 0.36%	
6	50X	None	Laponite RD 0.36%	
7	50X	PAPI27+ Ethylene Diamine	PVA 0.36%	
8	50X	PAPI27+ Ethylene Diamine	ATP 1%	
9[2]	-	None	None	0.2% (in urea fertilizer)
10[2]	-	None	None	50% (in urea fertilizer)

Examples	Diluted times (in spray drying)	Encapsulation materials	Protective Coating materials/wt%[1]	The wt% of Nitrapyrin in Urea
11	50	PAPI27+ Ethylene Diamine	MethocelA 15 .036%	0.2% (in urea fertilizer)
12	50	PAPI27+ Ethylene Diamine	MethocelA 15 0.36%	8% (in urea fertilizer)
13	50	PAPI27+ Ethylene Diamine	Sugar 0.36%	0.2% (in urea fertilizer)
14	50	PAPI27+ Ethylene Diamine	Sugar 0.36%	4% (in urea fertilizer)
15	50	PAPI27+ Ethylene Diamine	Sugar 0.36%	8% (in urea fertilizer)
16	50	PAPI27+ Ethylene Diamine	Sugar 1.5%	8% (in urea fertilizer)
17[3]	50	PAPI27+ Ethylene Diamine	Sugar 0.36%	8% (in urea standard)

[1]wt% is based on the total weight of diluted Entrench/INSTINCT products; [2]control sample containing technical nitrapyrin; [3]utilized urea standard material for preparation of Example 17, whereas urea fertilizer particles were used for the other Examples.

[00118] An investigation was conducted to determine the active loss of nitrapyrin during the spray drying process. The sample described in Example 2 (Table 2)was spray-dried according to the process described above. The nitrapyrin content in the dried particle was measured. The comparison between theoretical nitrapyrin content and the measured nitrapyrin content is summarized below in **Table 3**. This investigation was repeated four times. The difference in content between the theoretical content and the analytically detected content was just 0.07%. The results show that encapsulated nitrapyrin is stable during the spray drying process.

Table 3.Active loss of nitrapyrin for the formulation of Example 2 after the spray drying process.

Example 2	Detected Nitrapyrin wt%	Average Nitrapyrin wt%	Theoretical Nitrapyrin wt%	Delta active wt%
Repeat 1	28.60	29.67	29.61	0.07%
Repeat 2	27.55			
Repeat 3	31.32			
Repeat 4	31.21			

[00119] **Table 4**lists the thermal stability of certain exemplary formulations (noted in **Table 2**) as determined by exposing the exemplary formulation to heat.

Table 4.Thermal stability of certain exemplary formulations from Table 2 determined by heat treating the indicated exemplary formulation.

Example	Heat treatment conditions	Nitrapyrin loss wt%
1	148°C, 30 min	99%
2	148°C, 30 min	75%
3	148°C, 30 min	34%
4	148°C, 30 min	14%
5	148°C, 30 min	20%
6	148°C, 60 min	84%
7	148°C, 30 min	26%
8	148°C, 30 min	60%

[a]wt% is based on the theoretical Nitrapyrin wt% in dried particles before thermal treatment.

[00120] Referring now to **Table 4**, the thermal stability of the nitrification inhibitor (NI)can be significantly improved by the use of the compositions and methods of the present disclosure. Example 1 (**Table 2**) is a formulation comprising unencapsulated nitrapyrin active.

As shown by the data summarized in **Table 4**, after thermal treatment at 148° C, less than 0.5% nitrapyrin remained in the formulation. The significant loss of nitrapyrin observed with Example 1 is likely due to the relatively high volatility of unencapsulated nitrapyrin. This result demonstrates that raw nitrapyrin (unencapsulatednitrapyrin) is a poor material for use in a manufacturing process which is carried out at elevated temperatures.

[00121] Still referring to **Table 4**, dilution of the starting materials in the formulation appears to be closely related to the thermal stability of nitrapyrin in the encapsulated particles. The aqueous concentrate of encapsulated nitrapyrin microparticles (ENTRENCH™ and/or INSTINCT™) in Example 2 (**Table 2**) was spray dried without dilution. After thermal treatment at 148°C, Example 2 exhibited significant loss of nitrapyrin, about 75%. In Example 3 (**Table 2**), ENTRENCH/INSTINCT was diluted about 50 fold in water before spray drying the formulation. The nitrapyrin loss observed with Example 3 was only about 34%.

[00122] Still referring to **Table 4**, the introduction of a protective coating also improved the thermal stability of the encapsulated nitrapyrin particles, as shown in Example 4 (**Table 2**). A cellulose ether based coating was applied to the formulation of Example 4 to protect the nitrapyrin rich, polyurea shell microencapsulated particles in the formulation. A sample of the formulation of Example 4 was tested to measure its thermal stability. The formulation of Example 4 lost 14% of the nitrapyrin after it was exposed to 148°C, for 30 minutes; indicating the cellulose ether coating increased the thermal stability of the formulation.

[00123] In order to prepare the NI-F particles, as described above and depicted in**FIG. 2**, urea particles were placed in a glass bottle. Next the glass bottle was incubated in a heated oil bath at about 130°C to about 148°C until all of the urea particles in the bottle melted. Previouslyspray-dried coated, encapsulated nitrapyrin particles were poured into the urea melt with stirring at about 100-1000 rpm. After 5 minutes, the oil bath was removed. The urea and

particle mixture was allowed to cool, forming pellets. The nitrapyrin content of the NI-Fpellets was measured by extraction using NaCl andacetone/hexane solvent. The level of nitrapyrin in the extract was measured using the gas chromatography methodology described earlier.

[00124] **Table 5**provides thermal stability data measured using certain exemplary formulations of NI-F (urea) composite particles.

Table 5. Thermal stability of certain exemplary formulations of NI-F combined particles.

Example	Temperature of urea melt	Dispensing conditions	Nitrapyrin loss wt%[a]
9	138° C	300 rpm, 5min, N_2protection	>99%
	138°C	300 rpm, 5min, air conditions	>99%
10	138° C	300 rpm, 5min, N_2protection	>99%
	138° C	300 rpm, 5min, air conditions	>99%
11	140° C	1000rpm, 10min, air conditions	90%
	136° C	300 rpm, 5min, N_2 Protection	76%
	138° C	300 rpm, 5min, air conditions	
12	136° C	300 rpm, 5min, air conditions	19%
13	136° C	300 rpm, 5min, air conditions	92%
14	138° C	300 rpm, 5 min, air conditions	18%
15	136° C	300 rpm, 5min, air conditions	10%
16	136° C	300 rpm, 5min, air conditions	14%
17	136° C	300 rpm, 5min, air conditions	5%

[a]wt% is versus total weight of build-in urea system.

[00125] Referring now to **Table 5**, in some embodiments, the loss of nitrification inhibitor from the NI-F particle is under 20%. Formulations made with unencapsulated nitrapyrin Examples 9 and 10 (**TABLE 2**), lost more than 99 percent of the starting nitrapyrin. Still referring to **Table 5**, the high loss of nitrapyrin observed with Exemplary formulations 9 and 10 is not improved by limiting the contact of materials with air during the formation of the particle, N_2 in place of air. The retention of nitrapyrin is not improved by merely increasing the amount of the active in the formulation when no protective coating is used. These results indicate that the

claimed shell reduces nitrapyrin loss during the process of forming an effective NI-F combined particle.

[00126] Still referring to **Table 5**, in Examples 11 and 12 (**Table 2**), both a polyurea and a cellulose ether shell (A15) were supplied to thenitrapyrin. The data with these two exemplary formulations indicate that when the nitrapyrin content in the formulation is lower than 0.5%, (such as 0.2% in Example 11), the loss of nitrapyrin during the manufacturing process is greater than 20%. The effect of changing the processing conditions on the stability of nitrapyrin in Example 11 was tested. Changing processing parameters such as the operating temperature (from 136-138° C), dispensing time (from 5-10 mm), or air contact (in N_2), did not significantly reduce the loss of nitrapyrin observed in the exemplary in NI-Fformulation. Referring now to Example 12 (**Tables 2 and 5**), increasing the nitrification inhibitor content to 8% of the total NI-F did significantly reduced the loss of nitrapyrin activity to 19%.

[00127] Still referring to **Table 5**, other Examples with different protective coating materials also showed similar results as shown in Examples 13-17 (**Table 2**). In some Examples, sugar was utilized as a protective coating material along with the polyurea shell encapsulating the nitrapyrin including component of the composition. When tested for thermal stability at 136°C, Example 13, which had a nitrapyrin content of 0.2%, exhibited a substantial loss of nitrapyrin activity (92 %). When tested for thermal stability at 138° C, Example 14 which had a nitrapyrin content of 4 %, lost only about 18% of its nitrapyrin activity. When tested for thermal stability at 136°C, Example 15 which had a nitrapyrin content of 8 %, lost only about 10% of its nitrapyrin of its nitrapyrin activity. Increasing the sugar concentration in the formulation (Example 16, **Table 2**) and the type of urea in the formulation (Example 17) did not negatively influence the retention of nitrapyrin protection in the inventive formulations.

[00128] While the novel technology has been illustrated and described in detail in the figures and foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiments have been shown and described and that all changes and modifications that come within the spirit of the novel technology are desired to be protected. As well, while the novel technology was illustrated using specific examples, theoretical arguments, accounts, and illustrations, these illustrations and the accompanying discussion should by no means be interpreted as limiting the technology. All patents, patent applications, and references to texts, scientific treatises, publications, and the like referenced in this application are incorporated herein by reference in their entirety.

CLAIMS

1. An agricultural composition, comprising:

a substantially solid fertilizer matrix, the fertilizer matrix comprising at least one fertilizer and an outer surface;

a plurality of encapsulated particles disposed within the fertilizer matrix, the plurality of encapsulated particles including at least one inhibitor of nitrification and a polymeric shell; and

a protective coating disposed between the plurality of encapsulated particles and the fertilizer matrix.

2. The composition according to claim 1, wherein the protective coating substantially encompasses the polymeric shell of the plurality of encapsulated particles.

3. The composition according to claim 1, wherein the protective coating comprises one or more materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof.

4. The composition according to claim 3, wherein the protective coating comprises methyl cellulose.

5. The composition according to claim 3, wherein the protective coating comprises sugar.

6. The composition according to claim 1, wherein the fertilizer matrix comprises a solid form of urea.

7. The composition according to claim 6, wherein the encapsulated particles comprise nitrapyrin.

8. The composition according to claim 7, wherein the encapsulated particles include polyurea and have a volume median particle size of from about 1 to about 10 microns.

9. The composition according to claim 3, wherein the weight ratio of the one or more materials in the protective coating to the encapsulated particles is between about 1:20 to about 1:1.

10. The composition according to claim 3, wherein the weight percentage of the one or more materials in the protective coating to the encapsulated particles is between about 0.1 wt% to about 5 wt%.

11. The composition according to claim 3, wherein the weight percentage of the one or more materials in the protective coating to the encapsulated particles is between about 0.3 wt% to about 1.5 wt%.

12. The composition according to claim 1, wherein the composition comprises particles between about 0.1 mm to about 5 mm.

13. The composition according to claim 1, wherein the composition comprises particles between about 1 mm to about 3.5 mm.

14. The composition according to claim 1, wherein the composition comprises from about 0.5 wt% to about 10 wt% of the at least one inhibitor of nitrification.

15. The composition according to claim 1, wherein the composition comprises from about 2 wt% to about 8 wt% of the at least one inhibitor of nitrification.

16. The composition according to claim 1, wherein the composition comprises from about 4 wt% to about 8 wt% of the at least one inhibitor of nitrification.

17. The composition according to claim 1, wherein the composition comprises about 8 wt% of the at least one inhibitor of nitrification.

18. The composition according to claim 7, wherein the composition comprises from about 0.5 wt% to about 10 wt% of nitrapyrin.

19. The composition according to claim 7, wherein the composition comprises from about 2 wt% to about 8 wt% of nitrapyrin.

20. The composition according to claim 7, wherein the composition comprises from about 4 wt% to about 8 wt% of nitrapyrin.

21. The composition according to claim 7, wherein the composition comprises about 8 wt% of nitrapyrin.

22. A method for preparing an agricultural composition comprising the steps of:

preparing a plurality of encapsulated particles including at least one inhibitor of nitrification;

dispersing the plurality of encapsulated particles in a fertilizer melt, wherein the melt comprises at least one melted fertilizer;

cooling the melt to form a solid; and

forming combined nitrification inhibiting-fertilizer particles from the solid.

23. The method according to claim 22, wherein the plurality of encapsulated particles is in an aqueous suspension, and the step of preparing further comprises drying the plurality of encapsulated particles.

24. The method according to claim 23, wherein drying is accomplished by the step of spray drying.

25. The method according to claim 24, wherein the step of spray drying further comprises diluting the aqueous suspension with an aqueous diluent by about 3 to about 150 times.

26. The method according to claim 22, wherein the step of preparing further comprises providing a protective coating disposed on the plurality of encapsulated particles.

27. The method according to claim 26, wherein the protective coating comprises one or more materials selected from the group consisting of: hydroxypropyl methylcellulose ("HPMC"), ethyl cellulose ("EC"), methyl cellulose ("MC"), carboxymethyl cellulose ("CMC"), polyvinyl alcohol ("PVA"), polyvinylpyrrolidone ("PVP"), polyoxyethylene and its copolymers, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel materials, alginate, xantham, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, water-soluble agricultural active ingredients in aqueous solvent, oil-soluble agricultural active ingredients in oil solvent, and mixtures thereof.

28. The method according to claim 27, wherein the protective coating comprises methyl cellulose.

29. The method according to claim 27, wherein the protective coating comprises sugar.

30. The method according to claim 22, wherein the step of cooling the melt to form a solid further comprises forming a fertilizer matrix disposed around the plurality of encapsulated particles.

31. The method according to claim 30, wherein the fertilizer matrix comprises a solid form of urea.

32. The method according to claim 30, wherein the fertilizer melt is heated at about between 130° C and 148° C.

33. The method according to claim 22, wherein the encapsulated particles comprise nitrapyrin.

34. The method according to claim 22, wherein the encapsulated particles include polyurea and have a volume median particle size of from about 1 to about 10 microns.

35. The method according to claim 27, wherein the weight ratio of one or more materials in the protective coating to the encapsulated particles is between about 1:20 to about 1:1.

36. The method according to claim 27, wherein the weight percentage of the one or more materials in the protective coating to the encapsulated particles is between about 0.1 wt% to about 5 wt%.

37. The method according to claim 27, wherein the weight percentage of the one or more materials in the protective coating to the encapsulated particles is between about 0.3 wt% to about 1.5 wt%.

38. The method according to claim 22, wherein the step of forming further comprises forming particles between about 0.1 mm to about 5 mm.

39. The method according to claim 22, wherein the step of forming further comprises forming particles between about 1 mm to about 3.5 mm.

40. The method according to claim 22, wherein the composition comprises from about 0.5 wt% to about 10 wt% of the at least one inhibitor of nitrification.

41. The method according to claim 22, wherein the composition comprises from about 2 wt% to about 8 wt% of the at least one inhibitor of nitrification.

42. The method according to claim 22, wherein the composition comprises from about 4 wt% to about 8 wt% of the at least one inhibitor of nitrification.

43. The method according to claim 22, wherein the composition comprises about 8 wt% of the at least one inhibitor of nitrification.

44. The method according to claim 33, wherein the composition comprises from about 0.5 wt% to about 10 wt% of nitrapyrin.

45. The method according to claim 33, wherein the composition comprises from about 2 wt% to about 8 wt% of nitrapyrin.

46. The method according to claim 33, wherein the composition comprises from about 4 wt% to about 8 wt% of nitrapyrin.

47. The method according to claim 33, wherein the composition comprises about 8 wt% of nitrapyrin.

48. The method according to claim 22, wherein the fertilizer melt is selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, and a mixture thereof.

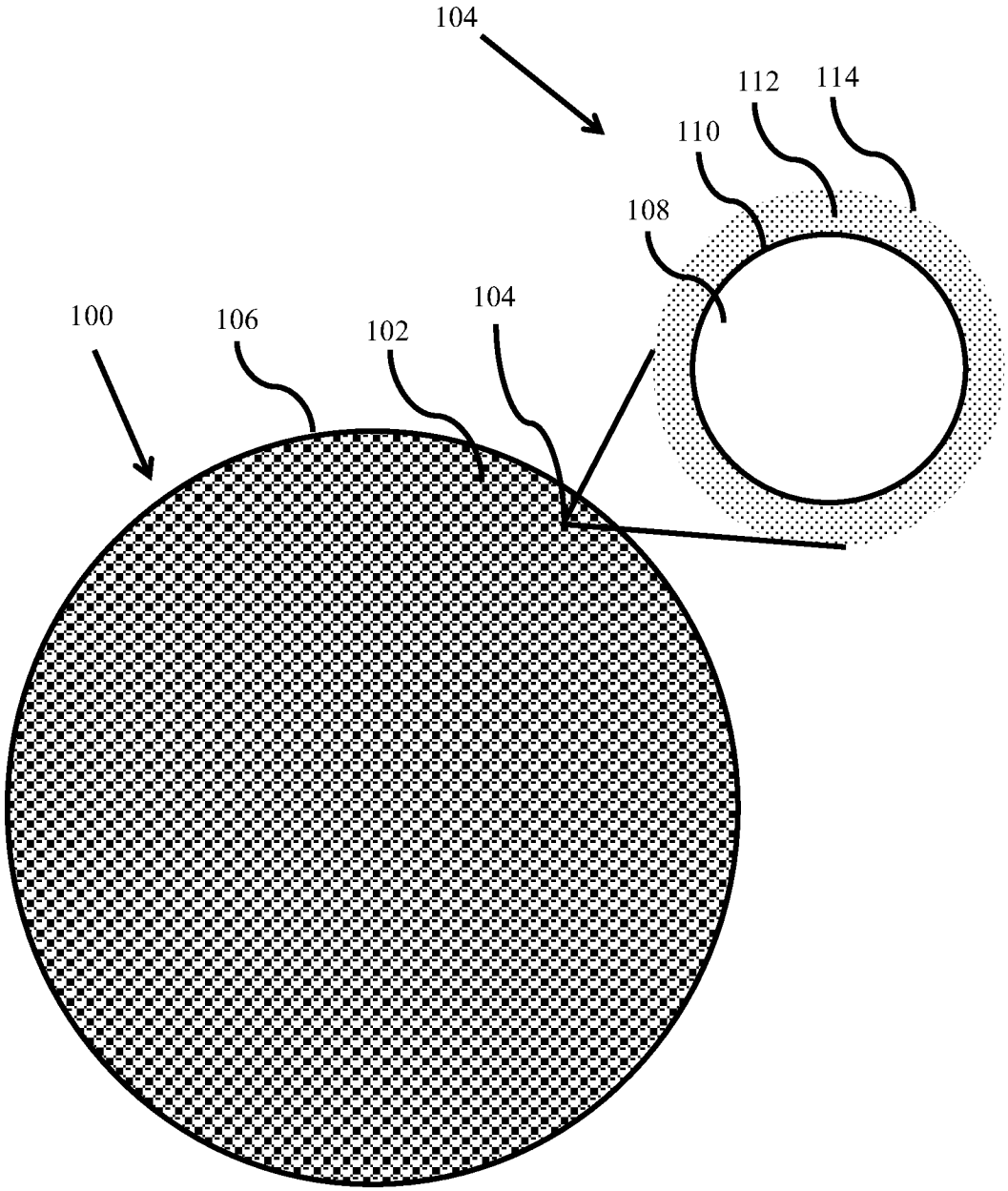


FIG. 1

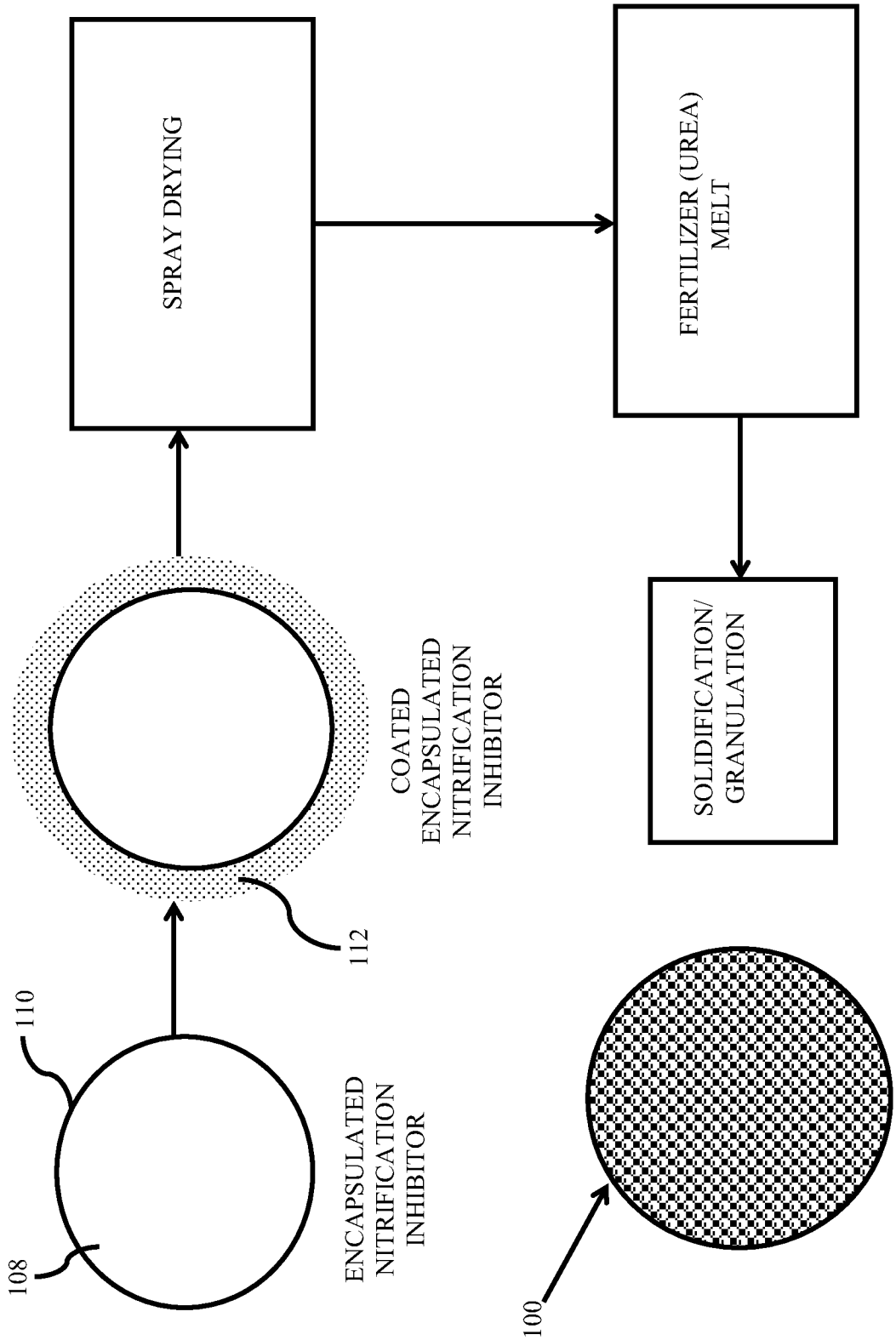

SPRAY DRYING
FERTILIZER (UREA) MELT
SOLIDIFICATION/ GRANULATION
COATED ENCAPSULATED NITRIFICATION INHIBITOR
ENCAPSULATED NITRIFICATION INHIBITOR
112
110
108
100

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/099427

A. CLASSIFICATION OF SUBJECT MATTER

C05G 3/02(2006.01)i; C05G 3/00(2006.01)i; A01N 59/00(2006.01)i; A01N 43/40(2006.01)i

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)

C05G/-; A01N59/-; A01N43/-

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)

WPI,EPODOC,CNKI,CNPAT,dow, core, shell, fertilizer, NITRIFICATION, nitrapyrin, +capsul+, surface, around, fertilizer, cellulose, polyoxyethylene, polyamides, sugar, glucose, maltose, starch, guar, urea, hydrogel, alginate, xantham, polysaccharides, polyethers, isocyanates, polyacrylate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 102276356 A (GUANGXI IDYLLIC BIOCHEMISTRY CO. LTD.) 14 December 2011 (2011-12-14) Claims 1-13	1-48
Y	US 2008/0176745 A1 (DOW AGROSCIENCES LLC.) 24 July 2008 (2008-07-24) paragraphs 7-12	1-48
Y	US 2009227458 A1 (DOW AGROSCIENCES LLC.) 10 September 2009 (2009-09-10) paragraphs 7-12	1-48
A	CN 102351608 A (GUANGXI IDYLLIC BIOCHEMISTRY CO. LTD.) 15 February 2012 (2012-02-15) claims 1-16	1-48
A	CN 202201840 U (GUANGXI IDYLLIC BIOCHEMISTRY CO. LTD.) 25 April 2012 (2012-04-25) the whole document	1-48
A	CN 101500410 A (OMS INVESTMENTS INC.) 05 August 2009 (2009-08-05) Claims 1-46	1-48

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 February 2016	**23 March 2016**
Name and mailing address of the ISA/CN **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **ZHOU,Wei** Telephone No. **(86-10)82246712**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 200981854 Y (ANHUI NINGGUO SITE FERTILIZER CO. LTD.) 28 November 2007 (2007-11-28) the whole document	1-48

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/099427

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	102276356	A	14 December 2011	CN	102276356	B	18 June 2014
US	2008/0176745	A1	24 July 2008	US	2013157850	A1	20 June 2013
				US	8377849	B2	19 February 2013
				WO	2008091538	A1	31 July 2008
US	2009227458	A1	10 September 2009	US	8741805	B2	03 June 2014
				US	2014329678	A1	06 November 2014
CN	102351608	A	15 February 2012	CN	102351608	B	18 June 2014
CN	202201840	U	25 April 2012		None		
CN	101500410	A	05 August 2009	CA	2623740	A1	12 April 2007
				AU	2006297275	B2	20 December 2012
				ES	2462542	T3	23 May 2014
				EP	1928231	A4	28 April 2010
				EP	2545775	A2	16 January 2013
				EP	2545775	A3	29 May 2013
				EP	1928231	A2	11 June 2008
				AU	2006297275	A1	12 April 2007
				WO	2007041234	A2	12 April 2007
				WO	2007041234	A3	16 April 2009
				US	2011111956	A1	12 May 2011
				US	9012363	B2	21 April 2015
				CA	2623740	C	26 August 2014
				BR	PI0616469	A2	25 December 2012
				US	8497229	B2	30 July 2013
				WO	2007041234	A8	15 May 2008
				EP	1928231	B1	12 March 2014
				US	2013310255	A1	21 November 2013
				CN	104387157	A	04 March 2015
				US	2007072775	A1	29 March 2007
CN	200981854	Y	28 November 2007		None		