NITRIFICATION INHIBITOR COMPOSITIONS AND METHODS FOR PREPARING THE SAME

Abstract: Enhanced nitrification inhibitor dry fertilizer compositions, methods for making the same, and their use in agricultural applications are disclosed.
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NITRIFICATION INHIBITOR COMPOSITIONS AND METHODS FOR PREPARING THE SAME

PRIORITY CLAIM

[0001] This application claims priority to PCT/CN2014/093583 filed on December 11, 2014, the entire disclosure of which is hereby expressly incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present disclosure relates to compositions that inhibit nitrification and methods of making the same. In some aspects, these compositions are formulated to include other agriculturally active compounds, 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. One such process is nitrification, a process by which certain widely occurring soil bacteria metabolize the ammonium 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] The decrease in available nitrogen due to nitrification necessitates 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, in order to reduce costs associated with the use of additional nitrogen fertilizer.
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 including corn, sorghum, and wheat.

Compounds such as nitrapyrin are unstable in soil in part because they are very volatile. For example, nitrapyrin has a relatively high vapor pressure ($2.8 \times 10^{-3} \text{ mm Hg at } 23^0 \text{ Celsius}$), 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 active 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 method of applying nitrapyrin, while stabilizing nitrapyrin below the soil surface, is not preferred. This method is unsuitable for many other fertilizer types and their standard application practices such as dry fertilizer granules, which most often are broadcasted onto the soil surface.

Still other approaches to stabilize nitrapyrin and reduce its loss to the atmosphere include applying it to the surface of the soil and then mechanically incorporating it into the soil, or watering it into the soil generally within 8 hours after its application to reduce its loss to the
atmosphere. Still another approach is to encapsulated nitrapyrin for rapid or dump release. Such encapsulated forms of nitrapyrin 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. While these formulations are less volatile than simple nitrapyrin, these formulations are better suited for use with liquid urea ammonium nitrate (“UAN”) or liquid manure fertilizers than with dry 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 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) there is an uncontrolled fertilizer to inhibitor ratio in soil, which may lead to performance loss.
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") or capsule suspension ("CS") liquid form; (3) large differences in application rates, which make preparation of homogeneous blends difficult, for example, the application rate of nitrogen fertilizers (in some embodiments about 20-50 kg/Mu, such as, for example, urea) is hundreds of times that of nitrification inhibitors such as nitrapyrin (for example Entrench®, which is about 170 ml/Mu); and (4) only temporary stability against volatilization loss for nitrapyrin products, commercially available such as Instinct® or Entrench®, when impregnated onto fertilizer granules, such as, for example, urea. Such fertilizer product must be applied shortly after impregnation to minimize the loss of performance.

Furthermore, water in many preparations of nitrapyrin may cause problems such as the attachment and crystallization of urea particles, and therefore there is an advantage to avoiding use of liquid concentrates (EC or CS) of nitrapyrin with nitrogen fertilizer granules, such as urea.

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 agricultural compositions that effectively include at least one agriculturally active ingredient ("AI"), such as a nitrification inhibitor, that that can be applied along with nitrogen fertilizers without the need for additional mixing and/or application steps.
Some aspects of the invention include agricultural compositions that include one or more nitrogen fertilizers with one or more nitrification inhibitors. In some embodiments, encapsulated nitrapyrin is coated on nitrogen fertilizer particles or granules, with one or more particulates, optionally hygroscopic particulate [volatilization barrier]s, and optionally inorganic hygroscopic particulate [volatilization barrier]s. Such dry nitrogen fertilizer/nitrification inhibitor compositions increase ease-of-use, exhibit controlled release of the nitrification inhibitor and the nitrogen fertilizer, increase nitrogen fertilizer efficiency, and decrease pollution of the soil, water, and air through reduced nitrification. Some of the inventive compositions disclosed herein also exhibit good nitrapyrin stability even at elevated temperatures.

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.

Therefore disclosed herein are agricultural compositions, comprising: a substantially solid core, the core optionally having at least one agricultural material and an outer surface; a plurality of encapsulated particles disposed around the outer surface, the particles including at least one inhibitor of nitrification; and hygroscopic particulate [volatilization barrier] referred to herein as HP, disposed around the plurality of encapsulated particles. In some embodiments, the hygroscopic particulate [volatilization barrier] is not in contact with the core. In other embodiments, the core includes at least one agricultural material that is a fertilizer selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a
phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, an iron-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer, a sulfur-containing micronutrient fertilizer, and mixtures thereof.

[0017] Still in other embodiments, the core comprises a solid form of urea. In yet other embodiments, the encapsulated particles comprise nitrapyrin. In some exemplary embodiments, the encapsulated particles that comprise nitrapyrin also include polyurea as the encapsulating material and have a volume median particle size of from about 1 to about 10 microns. In other embodiments, the hygroscopic particulate [volatilization barrier] is an inorganic hygroscopic particulate [volatilization barrier]. In some embodiments, the hygroscopic particulate [volatilization barrier] is comprised of at least one material selected from the group consisting of: attapulgite, talc, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof.

[0018] Still in other embodiments, the agricultural composition comprises a binder, said binder being disposed predominately on the outer surface of the core and said binder immobilizing the plurality of the encapsulated particles comprising nitrapyrin. In some embodiments, the binder is at least one material selected from the group consisting of: hydroxypropyl methylcellulose, ethyl cellulose, methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, lignosulfonates, guar, urea, alginate, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, and mixtures thereof. In some embodiments, the binder comprises hydroxypropyl methylcellulose. In some embodiments, the binder comprises
any combination of one or more of hydroxypropyl methylcellulose, polyvinyl alcohol, and urea. In some embodiments, the binder comprises any combination of one or more latexes that may include, but are not limited to, polyacrylate latexes and their copolymer latexes.

[0019] Still in other embodiments, the agricultural composition comprises between about 80% and about 99% by weight of fertilizer granules. In some preferred embodiments, the agricultural composition comprises between about 90% and about 99% by weight of fertilizer granules.

[0020] In other embodiments, the agricultural composition comprises nitrapyrin in a range between any lower concentration selected from about: 0.01% wt., 0.05% wt., 0.10% wt., 0.20% wt., 0.30% wt., 0.40% wt., and 0.50% wt. and any upper concentration selected from about: 10.00% wt., 5.00% wt., 4.00% wt., 3.00% wt., 2.50% wt., 2.00% wt., and 1.00% wt. In some embodiments, the agricultural composition comprises nitrapyrin in a range selected from the group of ranges consisting of: about 0.01% wt. to about 10.00% wt.; about 0.05% wt. to about 5.00% wt.; about 0.10% wt. to about 4.00% wt.; about 0.20% wt. to about 3.00% wt.; about 0.30% wt. to about 2.50% wt.; about 0.40% wt. to about 2.00% wt.; and about 0.50% wt. to about 1.00% wt.

[0021] Still in yet other embodiments, the agricultural composition comprises between about 0.01% and about 10% by weight of the binder.

[0022] In some embodiments, the agricultural composition comprises between about 0.01% and about 5% of the binder. In other embodiments, the agricultural composition comprises between about 1.00% and about 10.00% of the hygroscopic particulate [volatilization barrier]. In some exemplary embodiments, the agricultural composition comprises between about 2.00% and about 7.00% of the hygroscopic particulate [volatilization barrier]. Still in other embodiments, the agricultural composition comprises particles of a volume median particle size of from about
0.5 to about 5 millimeters. In other embodiments, the ratio of the binder to the agriculturally active ingredient is from about 0:100 to about 1:100.

[0023] Still in other embodiments, the ratio of the binder to the agriculturally active ingredient that is an inhibitor of nitrification is from about 0:100 to about 0.3:100. In yet other embodiments, the ratio of the inhibitor of nitrification to the fertilizer is from about 0.01:100 to about 3:100. Still in other embodiments, the ratio of the inhibitor of nitrification to the fertilizer is from about 0.2:100 to about 2.0:100. In some exemplary embodiments of the composition, the ratio of the hygroscopic particulate [volatilization barrier] to the fertilizer is from about 1:500 to about 20:100. Still in yet other embodiments, the ratio of the hygroscopic particulate [volatilization barrier] to the fertilizer is from about 1:100 to about 10:100.

[0024] Additionally disclosed herein are methods for preparing the agricultural compositions comprising the steps of: preparing a solution comprising a plurality of encapsulated particles, the particles including at least one inhibitor of nitrification and coating a plurality of substantially solid core particles, the core particles comprising one or more fertilizers and having an outer surface, with the solution to create coated combined particles.

[0025] In some embodiments, the method further comprises the step of adding a binder to the solution. In other embodiments, the preparing step further comprises dissolving fertilizer granules within the solution. Still in other embodiments, the method comprises the step of drying the combined particles. Still in other embodiments, the core particles comprise at least one fertilizer selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, a sulfur-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer, a sulfur-containing
micronutrient fertilizer, and mixtures thereof. In some embodiments, the core particles comprise urea. In some embodiments, the core particles comprise an NPK fertilizer.

[0026] In still yet other embodiments, the encapsulated particles comprise nitrapyrin. In some embodiments, the encapsulated particles comprise polyurea as the encapsulating material and have a volume median particle size of from about 1 to about 10 microns. In other embodiments, the binder is at least one compound selected from the group consisting of: hydroxypropyl methylcellulose, ethyl cellulose, methyl cellulose, carboxymethylcellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, lignosulfonates, guar, urea, alginate, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, and mixtures thereof. Still in other embodiments, the solution comprises hydroxypropyl methylcellulose, polyvinyl alcohol, and water. In some embodiments, the binder comprises any combination of one or more latexes that may include, but are not limited to, polyacrylate latexes and their copolymer latexes.

[0027] In other exemplary embodiments, the method further comprises the step of adding hygroscopic particulate [volatilization barrier] to be disposed on the coated combined particles. In some embodiments, the hygroscopic particulate [volatilization barrier] is inorganic hygroscopic particulate [volatilization barrier]. In other embodiments, the hygroscopic particulate [volatilization barrier] is at least one material selected from the group consisting of: attapulgite, talc, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof.

[0028] Still yet in other embodiments, the agricultural composition comprises between about 80% and about 99% by weight of core particles. In still other embodiments, the
agricultural composition comprises between about 90% and about 99% by weight of core particles. In other embodiments, the composition comprises between about 0.10% and about 2.00% of nitrapyrin.

[0029] In still other embodiments of the method, the agricultural composition comprises nitrapyrin in a range between any lower concentration selected from about: 0.01% wt., 0.05% wt., 0.10% wt., 0.20% wt., 0.30% wt., 0.40% wt., and 0.50% wt. and any upper concentration selected from about: 10.00% wt., 5.00% wt., 4.00% wt., 3.00% wt., 2.50% wt., 2.00% wt., and 1.00% wt. In some embodiments, the agricultural composition comprises between about 0.01% and about 10.00% of the binder. In other embodiments, the agricultural composition comprises between about 0.01% and about 5.00% of the binder. Still in other embodiments, the agricultural composition comprises between about 1.00% and about 10.00% of the hygroscopic particulate [volatilization barrier]. Still in other embodiments, the agricultural composition comprises between about 2.00% and about 7.00% of the hygroscopic particulate [volatilization barrier]. In yet other embodiments, the agricultural composition comprises coated fertilizer particles of a volume median particle size of from about 0.5 to about 5 millimeters.

[0030] In still other embodiments, the ratio of the binder to the core particles is from about 0:100 to about 1:100. In some embodiments, the ratio of the binder to the core particles is from about 0:100 to about 0.3:100. In some exemplary embodiments, the ratio of the inhibitor of nitrification to the core particles is from about 0.01:100 to about 5:100. In other embodiments, the ratio of the inhibitor of nitrification to the core particles is from about 0.2:100 to about 2.0:100. In yet other embodiments, the ratio of the hygroscopic particulate [volatilization barrier] to the core particles is from about 1:500 to about 20:100.

[0031] In still other embodiments, the ratio of the hygroscopic particulate [volatilization barrier] to the core particles is from about 1:100 to about 10:100. In yet other embodiments, the
The step of coating incorporates one or more devices selected from the group consisting of: a pan coater, a rotating drum, a spray coater, a fluid bed, screens, and mixtures thereof.

**BRIEF DESCRIPTION OF THE FIGURES**

[0032] 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.

[0033] FIG. 1 provides a side cut-away view of one exemplary embodiment of a particle that includes a nitrification inhibitor and a core which optionally includes at least one fertilizer.

[0034] FIG. 2 provides a process diagram for one exemplary method of preparing a particle that includes a nitrification inhibitor and a core which optionally includes at least one fertilizer.

[0035] FIGS. 3A-C provide a photographic comparison of urea granules to one exemplary embodiment of particles, the particles being comprised of a core which includes granulated urea coated with a composition that includes the nitrification inhibitor nitrapyrin.

[0036] FIGS. 4A-D provide enlarged images of the morphology of the coated urea granule of the composition recited in Example 2 of this disclosure.

[0037] FIG. 5 provides a chart showing percent change in weight as a function of time of a dried nitrapyrin capsule suspension (polyurea-encapsulated nitrapyrin by Dow AgroSciences LLC) stored at 54° C.

[0038] 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**

[0039] (Trichloromethyl)pyridine compounds useful in the composition of the present disclosure include compounds having a pyridine ring which is substituted with at least one trichloromethyl group and mineral acid salts thereof. Suitable compounds include those containing chlorine or methyl substituents on the pyridine ring in addition to a trichloromethyl 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).

[0040] Referring now to FIG. 1, a side cut-away view of one exemplary embodiment of an enhanced nitrification inhibitor dry fertilizer combined particle is shown. Combined particle 100 includes core 102, which in some embodiments may be a fertilizer, and in some embodiments is a fertilizer granule. Combined particle 100 also includes Nitrification Inhibiting (“NI”) interface 104, NI layer 106, NI-hygroscopic particulate [volatilization barrier] (“HP”) interface 108, and HP layer 110. Particle 100 is shown to be substantially spherically shaped (substantially circular in the cross-section), however, any other suitable shape is envisioned, such
as, for example, a cylinder, cube, square in the cross-section, and/or ellipse in the cross-section, so long as particle 100 can be applied to fields and/or crops and release the composition into the soil.

[0041] Core 102 forms the core or inner-most substituent of particle 100, and in some embodiments is any suitable agricultural material, such as, for example, dry fertilizer for application to fields and/or crops, such as, for example, a nitrogen-containing fertilizer such as urea. Core 102 can also include any other agricultural active ingredients including, but not limited to, fungicides, herbicides, miticides, nitrification inhibitors, insecticides, safeners, arthropocides, and mixtures thereof.

[0042] In some embodiments, core 102 comprises at least one of a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, an iron-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer, a sulfur-containing micronutrient fertilizer, and a mixture thereof and/or any blend or mixture of the foregoing. Such exemplary embodiments may be in dry granular form.

[0043] In some embodiments, core 102 comprises urea. The volume median particle size of core 102 can be similar to the size of commercially available dry fertilizer products, such as between about 0.1mm to about 10mm, preferably from about 0.1mm to about 7mm, and more preferably from about 0.1mm to about 5mm, and for nitrogen-based fertilizers, such as, for example, urea between about 0.3mm and about 3mm.

[0044] NI layer 106, in the embodiment shown, wholly covers core 102 creating NI interface 104 around the outer surface of core 102. In other embodiments, NI layer 106 need not wholly cover core 102. For example, in some embodiments, portions of core 102 may be open to
the atmosphere where NI layer 106 is discontinuous. NI layer 106 includes at least one nitrification inhibiting active ingredient, such as, for example, nitrapyrin. In some embodiments, NI layer 106 includes microcapsules comprising nitrapyrin. Such microcapsules can be 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 as the encapsulating material and are between about 1 μm and about 10 μm in size.

[0045] NI layer 106 optionally includes a binder which can be any aqueous, oil-based, and/or polymeric substance, which allows at least one nitrification inhibiting compound, such as nitrapyrin, to be disposed around core 102. Exemplary optional binders suitable for use with NI layer 106 include, but are not limited to hydroxypropyl methylcellulose (“HPMC”), ethyl cellulose (“EC”), methyl cellulose (“MC”), carboxymethyl cellulose (“CMC”), polyvinyl alcohol (“PVA”), polyvinylpyrrolidone (“PVP”), polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, lignosulfonates, guar, urea, alginate, 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 binder comprises any combination of one or more latexes that may include, but are not limited to, polyacrylate latexes and their copolymer latexes.

[0046] Any optional binder is envisioned that is capable of holding the nitrapyrin around the outer surface of core 102 and is capable of dissolving and/or releasing the nitrapyrin, which in some embodiments is microencapsulated, and the core 102, which in some embodiments is a fertilizer, once particle 100 is applied to a field or crop. The optional binder can be used to help immobilize nitrification inhibitors, optionally encapsulated nitrapyrin, around a core particle, such as core 102. The binder can also help adhere particulate, such as hygroscopic particulate...
[volatilization barrier], around NI layer 106. Furthermore, binder may be used to adjust the formulation’s viscosity and/or flowability.

[0047] HP layer 110 is shown, which forms NI-HP interface 108 around NI layer 106. In some embodiments, no HP layer is used with combined particle 100. In other embodiments, HP layer 110 is discontinuous around NI layer 106. Hygroscopic particulate [volatilization barrier]s can include, but are not limited to, one or more of attapulgite, talc powder, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof. Any material is envisioned as being used for a HP, so long as the material can coat the outer layer of NI layer 106, and is capable of dissolving and/or releasing the NI layer, and the core 102, such as, for example, a fertilizer, once particle 100 is applied to a field or crop.

[0048] Hygroscopic particulate [volatilization barrier], in some embodiments, serves as a drying agent to avoid core particle agglomeration, which may be caused by sticking between the nitrification inhibitor layers of different core particles. The hygroscopic particulate can also serve as a protectant for the nitrification inhibiting layer, optionally containing encapsulated nitrapyrin, by preventing the nitrification inhibitor from peeling away from the core particle by mechanical abrasion. The hygroscopic particulate [volatilization barrier] layer, in some embodiments, serves as a layer of protection to reduce the sensitivity of the combined particles to the environment, such as the environment during processing, storage, shipping, and use. In some embodiments, the hygroscopic particulate [volatilization barrier] layer aids in reducing the volatility of the core particle and/or the nitrification inhibiting layer.

[0049] Any portion of combined particle 100, including core 102, NI layer 106, and/or HP layer 110 may contain any other physically compatible agricultural active ingredient including, but not limited to, fungicides, herbicides, miticides, insecticides, safeners,
arthropocides, and mixtures or blends of any of the foregoing. Physically compatible agricultural active ingredients include any AI that can be formulated with combined particle 100 for stable storage, transport, and distribution to a field and for suitable, consistent release of combined particle 100 to the soil, field, and/or crop.

[0050] In some embodiments, microencapsulated nitrapyrin particles, encapsulated with polyurea, are coated onto the surface of urea or other dry fertilizer granules/particles, for use in fields and/or crops. In some embodiments, combined particle 100 is a dry formulation. In some embodiments, core102, NI layer 106, and HP layer 110 will dissolve in water (in soil conditions) and then release encapsulated nitrapyrin. Nitrapyrin will then diffuse into the soil to function as an inhibitor of the nitrification of nitrogen-containing fertilizers.

[0051] In some embodiments of combined particle 100, the ratio of the hygroscopic particulate [volatilization barrier] to the urea and/or fertilizer is from about 1:500 to about 20:100, preferably from about 1:100 to about 10:100. In some embodiments, the ratio of the binder to the urea and/or fertilizer is from about 0:100 to about 10:100, preferably from about 0.1:100 to about 5:100. In some embodiments, the ratio of the nitrification inhibitor, optionally nitrapyrin, to the urea and/or fertilizer is from about 0.01:100 to about 3:100, preferably from about 0.2:100 to about 2.0:100.

[0052] Referring now to FIG. 2, a process diagram for one exemplary method of preparing an enhanced nitrification inhibitor dry fertilizer combined particle is shown. In the embodiment shown, core102 is provided, which in some embodiments is a dry fertilizer granule, such as urea. In the next step, a binder solution or coating liquid is prepared to partially or wholly coat core102. In some embodiments, the binder solution or coating liquid is an aqueous suspension of microencapsulated nitrapyrin, such as Entrench® and/or Instinct®.
In one exemplary embodiment, HPMC powder is dispersed into water by stirring at 200-1500 rpm for 5 minutes, and the mixture is then incubated at 60-90 degrees Celsius for about 10 minutes with stirring at 500-2000 rpm. The mixture is then cooled down and further dispersed under shearing until the powder is completely dissolved.

In another exemplary embodiment, PVA powder is dispersed into water by stirring at 200-1500 rpm for 5 minutes, and the mixture is then incubated at 60-90 degrees Celsius for about 10 minutes with stirring at 500-2000 rpm. The mixture is then cooled down and further dispersed under shearing until the powder is completely dissolved.

The binder solution or coating liquid may comprise both solutions above including HPMC and PVA, but in other embodiments the binder solution or coating liquid may comprise only one polymeric binder, multiple polymeric binders, or no polymeric binders. In some embodiments, following the preparation of a binder solution or coating liquid with polymeric binders, a water suspension of encapsulated nitrapyrin (such as, for example, Entrench® and/or Instinct® by Dow AgroSciences LLC) is mixed with the binder solution or coating liquid at room temperature. Optionally, one or more fertilizers, such as urea, can also be added to the binder solution, optionally with water or other solvents, such as oil.

In some embodiments, a water suspension of encapsulated nitrapyrin (such as, for example, Entrench® and/or Instinct® by Dow AgroSciences LLC) is mixed with one or more water-soluble fertilizers dissolved in aqueous solution and/or one or more oil-soluble fertilizers dissolved in oil solvent to form a coating liquid, without any polymeric binder. In some embodiments, the dissolved fertilizer is the same as the fertilizer to be coated in a granule form. In other embodiments, the dissolved fertilizer is different than the fertilizer to be coated in a granule form.
In some embodiments, the final suspension including the binder solution, one or more fertilizers, one or more solvents, and the water suspension of encapsulated nitrapyrin is mixed for an additional period of time, preferably about 2 hours, prior to coating core\textsuperscript{102} in order to arrive at a homogenous final suspension to coat core\textsuperscript{102}.

Core\textsuperscript{102} can be coated by the final binder solutions or coating liquids above optionally inside a pan coater with a rotating drum. Other coating devices known in the art could also be used. A prescribed amount of bare cores, such as core\textsuperscript{102}, optionally fertilizer granules, are first charged into a coater. Then, the final suspension including the binder solution are added to the pan coater and/or sprayed onto the granules. In one embodiment, the pan speed is kept at 60 rpm during the coating process. After addition of one or more of the final suspensions above, the pan coater is kept rotating, preferably for between about 5 and about 30 minutes. After these steps, core \textsuperscript{102} with NI layer \textsuperscript{106}, optionally containing encapsulated nitrification inhibitor (and optionally a fertilizer),is obtained.

After NI layer \textsuperscript{106} is added to core\textsuperscript{102}, a hygroscopic particulate [volatilization barrier] layer (HP layer) can be applied to NI layer \textsuperscript{106}. For example, after the coating liquid is evenly coated on core\textsuperscript{102}, an HP powder, such as for example talc or diatomaceous earth, can be added to the pan coater under rotation. After addition of the HP, the pan can be kept rotating, preferably for about 10 minutes, to allow the HP to evenly coat on NI layer\textsuperscript{106}. One or more of such powders create HP layer \textsuperscript{110}. As shown, HP layer \textsuperscript{110} is continuous around NI layer \textsuperscript{106}, however, in other embodiments HP layer \textsuperscript{110} can be discontinuous around NI layer \textsuperscript{106}. Hygroscopic particulate may also be embedded in NI layer \textsuperscript{106}. Equipment that can be used to prepare combined particle \textsuperscript{100} includes, but is not limited to a pan coater, a rotating drum, a spray coater, a fluid bed, and/or screens.
[0060] In some embodiments, NI-HP interface 108 around NI layer 106 is not explicit or neat, i.e. portions of HP layer 110 including hygroscopic particulate [volatilization barrier] may be partially or substantially fully embedded within NI layer 106. In some embodiments, portions of HP layer 110 may be in contact with core102. In other embodiments, HP layer 110 may not be in contact with core102.

[0061] Combined particle 100 can be dried, preferably at about 20 to about 80 degrees Celsius for about 10 to about 60 minutes to remove water and obtain the final dry combined particles. Alternatively, drying may be omitted. The coated fertilizer comprising combined particles can be applied without additional drying.

[0062] Referring now to FIGS. 3A-C, a photographic comparison of bare urea granules to exemplary combined particles of the present disclosure is provided. FIG. 3A shows bare urea, FIG. 3B shows the composition of Example 2 (Table 3) provided below, and FIG. 3C shows the composition of Example 4 (Table 3) provided below. The particle size and shape of the nitrapyrin-urea combined dry granules, FIGS. 3B-C, is similar to the bare urea particle size and shape. The particle size is about 2-4 mm in diameter. However, the urea granules of FIG. 3C for Example 4 (prepared without a particulate layer) were sticky and agglomerated to form big pieces of granule aggregates, which are difficult to process and apply.

[0063] FIGS. 4A-D provide enlarged images of the morphology of the coated urea granule of Example 2 (Table 3) below. These images show the microstructure of the nitrapyrin-fertilizer dry granules produced in Example 2 below. The element mapping images for Si, Al, and Mg in the inorganic hygroscopic particulate [volatilization barrier] layer, nitrogen from urea, and Cl from the active nitrapyrin are shown in FIGS. 4A, B, and D, respectively. The images indicate that the particulate was evenly coated on the surface of the fertilizer granules, and the polyurea-encapsulated nitrapyrin microcapsules were intact and imbedded in the coating layer;
also, transfer of nitrapyrin from the microcapsules into the coating layer appeared to occur. **FIG. 4C** shows an SEM image of the coating layer of the coated urea, and the image insert is an image of the polyurea-encapsulated nitrapyrin particles.

**[0064]** FIG. 5 provides a chart showing percent change in weight as a function of time of a dried nitrapyrin capsule suspension (polyurea-encapsulated nitrapyrin by Dow AgroSciences LLC) stored at 54°C. As shown, after about 2 weeks (14 days) at 54°C, the loss of nitrapyrin in weight percent is about 30%.

**[0065]** Examples of typical solvents which can be used to dissolve crystalline (trichloromethyl)pyridine compounds include aromatic solvents, particularly alkyl substituted benzenes such as xylene or propylbenzene fractions, and mixed naphthalene and 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 and chlorobenzene; esters of glycol derivatives, such as the acetate of the n-butyl, ethyl, or methyl ether of diethylene glycol 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 are xylene, alkyl substituted benzenes, such as propyl benzene fractions, and alkyl naphthalene fractions.

**[0066]** In general, the amount of solvent employed, if desired, is typically from about 40, preferably from about 50 to about 70, preferably to about 60 weight percent, based on the total weight of a (trichloromethyl)pyridine/solvent solution. The amount of (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. In some embodiments of the present
disclosure, nitrapyrin technical can be used in the formulation of combined particle 100, in any portion of combined particle 100. Nitrapyrin technical comprises about 90% to about 100% pure nitrapyrin depending on the impurity level. Therefore, in some embodiments the amount of solvent employed might be about 0% to about 10%, while the amount of nitrapyrin technical might be about 90% to about 100% pure.

[0067] The microcapsules useful in the present disclosure can be prepared by the polycondensation reaction of a polymeric isocyanate and a polyamine to form a polyurea shell. Methods of microencapsulation are well known in the art and any such method can be utilized in the present disclosure to provide a 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 then combined with an aqueous phase which includes an emulsifier to form a two phase system. 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 drop-wise while stirring to form the encapsulated particles of (trichloromethyl)pyridine in an aqueous suspension.

[0068] 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 125 nanometers. In some embodiments, the microcapsules 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 150 nanometers. In one embodiment, the desired particle size may be from about 2 to about 10 microns, with a cell wall thickness of from about 10 to about 50 nanometers. In some embodiments, the desired particle size may be from about 2 to about 10 microns, with a cell wall thickness of from about 10 to about 25 nanometers.
In one embodiment, particularly requiring soil surface stability, the desired particle size may be from about 1-5 microns, with cell wall thicknesses of from about 50 to about 150 nanometers. In another embodiment, particularly requiring soil surface stability, the desired particle size may be from about 1-5 microns, with cell wall thicknesses of from about 75 to about 125 nanometers.

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

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 of from about 1 to about 20 percent by weight of the microcapsule suspension formulation.

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. Typically the ratio will be from about 1:0.60 to about 1:20. Generally the desired ratio is about 1:0.8 to about 1:9, and is preferably from about 1:0.8 to about 1:4.

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.

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.

[0075] 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.

[0076] 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.

[0077] The enhanced nitrification inhibitor dry fertilizer compositions of the present disclosure typically have a concentration of (trichloromethyl)pyridine compound in amounts of from about 0.01 to about 10, preferably from about 0.10 to about 5.00, and more preferably from about 0.10 to about 2.50, percent by weight, based on the total weight of the nitrification inhibitor dry fertilizer composition.

[0078] 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.

[0079] The soil may be prepared in any convenient fashion with the nitrification inhibitor dry fertilizer compositions of the present disclosure, including mechanically mixed with the soil; applied to the surface of the soil and thereafter dragged or diced into the soil to a desired depth; or transported into the soil such as by injection, spraying, dusting or irrigation. 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).

[0080] 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.

[0081] 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 mixed or blended with the desired pesticide(s) or they can be applied sequentially.

[0082] 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.

Exemplary insecticides include, but are not limited to 1,2 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, bifenthirin, 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, carbonolate, carbaryl, carbofuran, carbon disulfide, carbon tetrachloride, carbophenothion, carbosulfan, cartap, chinomethionat, chlorantraniliprole, chlorbenside, chlorbicyclen, clordane, chlordecone, chloridimeform, chlorethoxyfos, chlorfenapyr, chlorfenethol, chlorfenson, chlorfensulphide, chlorfenvinphos, chlorfluazuron, chlorinephos, chlorobenzilate, chloroform, chloromebuform, chloromethiuron, chloropicrin, chloropropylate, chlorphoxim, chlorprazophos, chlorpyrifos, chlorpyrifos methyl, chlorothiophos, chromafenozide, cinerin I, cinerin II, cismethrin, cloethocarb, clofentezine, closantel, clothianidin, copper acetoarsenite, copper arsenate, copper naphthenate, copper oleate, coumaphos, coumiflurate, crotamiton, crotovinphos, cruuentaren A & B, crufomate, cryolite, cyanofenphos, cyanophos, cyanothoate, cyflufenos, cyhexatin, cyclothrin, cycloprothrin,
cyenopyrafen, cyflumetofen, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyphenothrin, cyromazine, cythioate, d-limonene, daizomet, 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, dichlofuanid, dichlorvos, dicofol, dicresyl, dicrotophos, dicyclanil, dielcdn, dienochlor, diflovidazin, diflubenzuron, dilor, dimefluthrin, dimetan, dimethoate, dimethrin, dimethylvinphos, dimetilan, dinex, dinobuton, dinocap, dinocap 4, dinocap 6, dinocoton, dinopenton, dinoprop, dinosam, dinsulfon, dinotefuran, dinoterbon, diofenolan, dioxabenzofos, dioxacarb, dioxathion, diphenyl sulfone, disulfiram, disulfoton, dithicrofos, DNOC, dofenapyn, doramectin, ecdysterone, emamectin, EMPC, empenthrin, endosulfan, endothion, endrin, EPN, epofenonane, epinomectin, 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, fenpropatrin, fenpyroximate, fenson, fensulfothion, fenthion, fenthion ethyl, fentrifanil, fenvalerate, fipronil, flonicamid, fluacrypyrim, fluazuron, flubendiamide, flubenzimine, flucofuron, flucycloxuron, flucytrinate, flueneril, flufenerim, flufenoxuron, flufenprox, flumethrin, fluorbenside, fluvalinate, fonofos, formetanate, formothion, formparanate, fosmethilan, fospirate, fosthiazate, fosthietan, fosthietan, furathicarb, furathiocarb, furfural, gamma cyhalothrin, gamma HCH, halifenprox, 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, isopropcarb, isoprothiolane, isothioate, isoxathion, ivermectin jasmolin I, 
jasminol II, jodfenphos, juvenile hormone I, juvenile hormone II, juvenile hormone III, kelevan, 
kinoprene,lambda cyhalothrin, lead arsenate, lepimectin, lepsothos, lindane, lirimagos, lufenuron, 
lythidathion, malathion, malonoben, mazidox, mecarbam, mecarphon, menazon, 
mephosfolan, mercurous chloride, mesulfen, mesulfenos, metaflumizone, metam, 
methacrifos, methamidophos, methidathion, methiocarb, methocrotrophos, methomyl, 
methoprene, methoxychlor, methoxyfenozone, methyl bromide, methyl 
isothiocyanate, methylchloroform, methylene chloride, metofluthrin, metolcarb, 
metoxadiazone, mevinphos, mexacarbate, milbemectin, milbemycin oxime, mipafox, mirex, 
MNAF, monocrotrophos, 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, phenhoatge, 
phorate, phosalone, phosfolan, phosmet, phosniclor, 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, pyrimtate, 
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, thiocyanate, thiometon, thionazin, thioquinox, thiosultap, thuringiensin, tolfenpyrad, tralomethrin, transfluthrin, transpermethrin, triarathene, triazamate, triazophos, trichlorfon, trichlorometaphos 3, trichloronat, trifenofos, triflumuron, trimethacarb, tripene, vamidothion, vaniliprole, vaniliprole, XMC, xylylcarb, zeta cypermethrin and zolaprofos.

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

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**

In the following examples, nitrapyrin weight content in coated urea 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 according to the noted documentation, and based on solvent mix hexane/acetone (volume ratio from about 1:4 to about 4:1). The nitrapyrin content was analyzed before and after processing to calculate losses of nitrapyrin due to volatilization or chemical instability from the coated fertilizer particles.
To test the storage stability of the nitrapyrin coated fertilizer compositions, the retention of nitrapyrin during storage was evaluated by storing the samples for a certain period of time in double zip-lock bags or closed glass bottles at 54 degrees Celsius. After thermal treatment, nitrapyrin content loss was measured to demonstrate the storage stability of the nitrapyrin coated fertilizer granules.

Nitrapyrin weight content determination method. The nitrapyrin coated fertilizer granules were dissolved in saturated NaCl solution, and then extracted by acetone/hexane in a 4:1 mixture. The extract was analyzed by the above-mentioned GC method. The method was validated by a recovery test method. For each sample, the nitrapyrin content (referred to as Nitrification Inhibitor “NI” content in the Tables below) was tested for 3 times; then the average of 3 data points was calculated.

Table 1 provides the raw materials used to make the exemplary compositions provided in the Tables that follow.

<table>
<thead>
<tr>
<th>Category</th>
<th>Ingredient</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active source</td>
<td>Entrench®</td>
<td>The Dow Chemical Company, Midland, U.S.A. (contains 200 g/L; 17.76 wt% nitrapyrin)</td>
</tr>
<tr>
<td></td>
<td>(Polyurea encapsulated aqueous suspension)</td>
<td></td>
</tr>
<tr>
<td>Fertilizer</td>
<td>Urea</td>
<td>Sinopharm Chemical Reagent Co., Ltd. Shanghai, China.</td>
</tr>
<tr>
<td></td>
<td>NPK</td>
<td>SinoFert Co., Ltd. Beijing, China</td>
</tr>
<tr>
<td>Binder</td>
<td>PVA (polyvinyl alcohol)</td>
<td>Dongfang Chemical Company, Beijing, China</td>
</tr>
<tr>
<td></td>
<td>HPMC (hydroxypropyl methylcellulose) K99</td>
<td>The Dow Chemical Company, Midland, U.S.A.</td>
</tr>
<tr>
<td></td>
<td>Polyacrylate latex AC261P</td>
<td>The Dow Chemical Company, Midland, U.S.A.</td>
</tr>
<tr>
<td></td>
<td>Potassium pyrophosphate trihydrate</td>
<td>Sinopharm Chemical Reagent Co.</td>
</tr>
<tr>
<td></td>
<td>Mineral oil</td>
<td>Sinopharm Chemical Reagent Co.</td>
</tr>
<tr>
<td>Particulate</td>
<td>ATP (attapulgite)</td>
<td>Jiu Chuan company, Jiang Su China</td>
</tr>
<tr>
<td></td>
<td>Kaolin</td>
<td>Sinopharm Chemical Reagent Co.</td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>Sinopharm Chemical Reagent Co.</td>
</tr>
<tr>
<td></td>
<td>Diatomite</td>
<td>Sinopharm Chemical Reagent Co.</td>
</tr>
</tbody>
</table>
Table 2 provides a variety of formulations as exemplary coating liquids to create binder layers.

### Table 2. Formulations of Coating Liquids.

<table>
<thead>
<tr>
<th>Coating liquid No.</th>
<th>Entrench (g)</th>
<th>Binder&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Urea (g)</th>
<th>Total Weight Coating Liquid (g)</th>
<th>Composition of the coating liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Binder Type</td>
<td>Binder wt (g)</td>
<td>Coating liquid wt (%)</td>
<td>Urea NI&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>40.01</td>
<td>HPMC K99</td>
<td>0.50</td>
<td>37.76</td>
<td>100.04</td>
</tr>
<tr>
<td>2</td>
<td>24.00</td>
<td>HPMC K99</td>
<td>0.20</td>
<td>12.69</td>
<td>40.01</td>
</tr>
<tr>
<td>3</td>
<td>16.00</td>
<td>/</td>
<td>0.00</td>
<td>15.21</td>
<td>40.04</td>
</tr>
<tr>
<td>4</td>
<td>16.00</td>
<td>PVA 1788</td>
<td>0.20</td>
<td>15.10</td>
<td>40.00</td>
</tr>
<tr>
<td>5</td>
<td>16.04</td>
<td>HPMC K99</td>
<td>0.20</td>
<td>15.11</td>
<td>40.08</td>
</tr>
<tr>
<td>6</td>
<td>35.08</td>
<td>AC261P</td>
<td>0</td>
<td>284.37&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>260.80</td>
<td>AC261P</td>
<td>0</td>
<td>649.9&lt;sup&gt;4&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>2057.00</td>
<td>AC261P</td>
<td>0</td>
<td>5126.0&lt;sup&gt;5&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>33.63</td>
<td>AC261P</td>
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<td>88.98&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
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<td>56.847</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
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<td>50.046&lt;sup&gt;7&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>19.61</td>
<td>AC261P</td>
<td>0</td>
<td>47.813&lt;sup&gt;8&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>28.29</td>
<td>Salt&lt;sup&gt;9&lt;/sup&gt;</td>
<td>18.99g salt&lt;sup&gt;10&lt;/sup&gt; + 9.35g water</td>
<td>0</td>
<td>56.628</td>
</tr>
<tr>
<td>14</td>
<td>31.17</td>
<td>AC261P</td>
<td>0</td>
<td>31.173</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>1869.85</td>
<td>/</td>
<td>1096.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>24.00</td>
<td>HPMC K99</td>
<td>0.2</td>
<td>12.69</td>
<td>40.01</td>
</tr>
<tr>
<td>17</td>
<td>40.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>40.0</td>
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</tbody>
</table>

<sup>1</sup>Polyacrylate latex AC261P contains 50 wt% solids; <sup>2</sup>NI is nitrification inhibiting ingredient, the nitrification inhibiting ingredient is nitrapyrin; <sup>3</sup>Contains 12.0 g mineral oil and 37.14 g diatomite; <sup>4</sup>Contains 30.7 g mineral oil and 97.6 g diatomite; <sup>5</sup>Contains 242.0 g mineral oil and 770.0 g diatomite; <sup>6</sup>Contains 4.88 g mineral oil and 16.87 g diatomite; <sup>7</sup>Contains 1869.85 g mineral oil and 1096.7 g diatomite; <sup>8</sup>Contains 5.078 g diatomite; <sup>9</sup>Contains 4.151 g mineral oil and 4.447 g diatomite; <sup>9</sup>Salt is potassium pyrophosphate trihydrate.
General procedure for preparation of coating liquids in Table 2: First the binder dispersion was prepared, in the case of using an inorganic salt as binding agent, the salt powder was first added into water, and kept stirring until the powder was dissolved completely at room temperature, then other additives, such as filler, oil, coalescence, etc., were added under stirring. Second, the binder dispersion was mixed with Entrench dispersion and finally, some water was added to adjust solid content of the coating liquid under stirring. In the case of using waterborne polymer dispersions as binding agent (HPMC, PVA, polyacrylate latex), the dispersion was mixed with other additives directly, and then with the suspension of Entrench, and other additives were added followed the same procedure described above. Coating liquid was freshly prepared prior to each coating operation.

General procedure for preparation of coated fertilizer granules in Table 3: (1) Liquid coating: The coated fertilizer could be prepared inside a pan coater. A prescribed amount of bare fertilizer granules was first charged into the rotating drum of the coater. Then coating liquid (containing the binder) prepared above was added/sprayed onto the granules. The pan speed was kept at 60 rpm during the coating process. After addition of coating liquid, the coater was kept rotating for about 5-30 min prior to addition of the filler coating; (2) Filler coating: After the coating liquid was evenly coated onto the granule surface, filler powder (i.e., the hygroscopic particulate [volatilization barrier]) was added to the coated granules while the pan was rotating. After addition of the filler, the pan was kept rotating for another 10 min to allow the filler to evenly coat the core fertilizer granules; (3) Drying: The coated fertilizer granules were dried @ 20-80 degree Celsius for about 10-60 min to remove water and obtain the final dry fertilizer system. Alternatively, drying may be omitted and the coated fertilizer may be applied to the soil without additional drying.
Modified procedure for preparation of Examples 17 and 20 in Table 3: Entrench® (nitrapyrin capsule suspension) was first coated onto the fertilizer granules, followed by the filler coating (i.e., the hygroscopic particulate [volatilization barrier]), and then the granules were further coated with binder dispersion, followed by another round of filler coating (i.e., the hygroscopic particulate [volatilization barrier]).

1) Entrench® coating and filler coating: A prescribed amount of bare fertilizer granules was first charged into the rotating drum of the coater. Then Entrench® dispersion was added/sprayed onto the granules. The pan speed was kept at 60 rpm during the coating process. After addition of Entrench® dispersion, the coater was kept rotating for about 5-30 min prior to filler coating. After the Entrench® dispersion was evenly coated onto the granule surface, filler powder (i.e., the hygroscopic particulate [volatilization barrier]) was added to the pan while rotating. After addition of the filler, the pan was kept rotating for another 10 min to allow the filler to evenly coat the core fertilizer granules.

2) Binder coating and then filler coating: The Entrench® and filler coated fertilizer granules were further coated with the binder dispersion. The binder dispersion was added/sprayed onto the granules. The pan speed was kept at 60 rpm during the coating process. After addition of the binder dispersion, the coater was kept rotating for about 5-30 min. After the binder dispersion was evenly coated onto the granule surface, the filler coating, using the filler powder (i.e., the hygroscopic particulate [volatilization barrier]), was created following the same procedure as described above.

The equipment that could be used to prepare the coated fertilizer granules are a pan coater or a fluid bed, or other coating/mixing equipment.

Table 3 provides exemplary formulations of particulate coatings, core granules and compositions of the final dry Entrench®/fertilizer samples.
Table 3. Formulations of particulate coating, core granule and compositions of final polyurea encapsulated nitrapyrin/fertilizer samples.

<table>
<thead>
<tr>
<th>Example</th>
<th>Coating Liquid</th>
<th>Core granule</th>
<th>Composition of final Entrench/urea dry fertilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coating type</td>
<td>Fertilizer</td>
<td>Weight (g) Particulate type</td>
</tr>
<tr>
<td>1</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.3</td>
</tr>
<tr>
<td>2</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.4</td>
</tr>
<tr>
<td>3</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.2</td>
</tr>
<tr>
<td>4</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.4</td>
</tr>
<tr>
<td>5</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.3</td>
</tr>
<tr>
<td>6</td>
<td>PVA 1788</td>
<td>urea</td>
<td>300.8</td>
</tr>
<tr>
<td>7</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.7</td>
</tr>
<tr>
<td>8</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.4</td>
</tr>
<tr>
<td>9</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.3</td>
</tr>
<tr>
<td>10</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.1</td>
</tr>
<tr>
<td>11</td>
<td>HPMC K99</td>
<td>urea</td>
<td>300.0</td>
</tr>
<tr>
<td>12</td>
<td>HPMC K99</td>
<td>NPK</td>
<td>300.3</td>
</tr>
<tr>
<td>13</td>
<td>HPMC K99</td>
<td>KCl</td>
<td>300.3</td>
</tr>
<tr>
<td>14</td>
<td>HPMC K99</td>
<td>CaPhos 2</td>
<td>300.3</td>
</tr>
<tr>
<td>15</td>
<td>AC261P</td>
<td>NPK</td>
<td>4000</td>
</tr>
<tr>
<td>16</td>
<td>AC261P</td>
<td>NPK</td>
<td>4000</td>
</tr>
<tr>
<td>17</td>
<td>AC261P</td>
<td>NPK</td>
<td>30000</td>
</tr>
<tr>
<td>18</td>
<td>AC261P</td>
<td>NPK</td>
<td>30000</td>
</tr>
<tr>
<td>19</td>
<td>AC261P</td>
<td>NPK</td>
<td>411.2</td>
</tr>
<tr>
<td>20</td>
<td>AC261P</td>
<td>NPK</td>
<td>501.5</td>
</tr>
<tr>
<td>21</td>
<td>AC261P</td>
<td>NPK</td>
<td>501.2</td>
</tr>
<tr>
<td>22</td>
<td>AC261P</td>
<td>NPK</td>
<td>404.3</td>
</tr>
<tr>
<td>23</td>
<td>AC261P</td>
<td>NPK</td>
<td>352.3</td>
</tr>
<tr>
<td>24</td>
<td>Salt 3</td>
<td>NPK</td>
<td>504.4</td>
</tr>
<tr>
<td>25</td>
<td>HPMC K99+Urea</td>
<td>NPK</td>
<td>300.2</td>
</tr>
</tbody>
</table>

1 Time taken to conduct the Entrench coating was ca. 30 min; 2 Calcium phosphate fertilizer; 3 Samples 17 and 20 were prepared following a modified procedure as described herein; 4 Salt is potassium pyrophosphate trihydrate.

Table 4 provides the density of the exemplified polyurea encapsulated nitrapyrin/urea dry fertilizers. The density of bare urea is about 1.30 g/cm³, and that of the exemplified
combined-particle fertilizer granules was about 1.32-1.371 \text{g/cm}^3. As the density of bare urea and coated urea were similar, dry blending of uncoated and coated urea, or other agricultural actives, appears favorable and without the risk of granule classification.

Table 4. Density of the polyurea encapsulated nitrapyrin-urea dry fertilizer.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare urea</td>
<td>1.30</td>
</tr>
<tr>
<td>Example 1</td>
<td>1.34</td>
</tr>
<tr>
<td>Example 2</td>
<td>1.36</td>
</tr>
<tr>
<td>Example 7</td>
<td>1.35</td>
</tr>
<tr>
<td>Example 8</td>
<td>1.37</td>
</tr>
<tr>
<td>Example 9</td>
<td>1.32</td>
</tr>
</tbody>
</table>

[0097] Table 5 provides the nitrification inhibitor “NI” (nitrapyrin) content after processing and storage. Considering the high relative volatility of nitrapyrin ($2.8 \times 10^{-3}$ mm Hg at 23$^\circ$ Celsius), the loss of nitrapyrin is a key to evaluating the ability of the exemplified combined particles to retain nitrapyrin during processing and storage. To compare the nitrapyrin stability and retention between various formulations, the calculated nitrapyrin content applied in each formulation was normalized to 100% and the nitrapyrin content measured after processing was normalized based on the theoretical content. The retention of NI during storage was also evaluated by storing the samples in an oven at 54 degree Celsius for 2 weeks.

[0098] The effect of nitrapyrin loading level in the dry formulation is shown in Table 5. In examples 1-3, the nitrapyrin content after processing increased from 87.2 wt% to 92.5 wt% as nitrapyrin loading level in the dry formulation increases from 0.2 wt% to 0.56 wt%. Example 26 was carried out by mixing urea granules with encapsulated nitrapyrin liquid emulsion at theoretical NI of 0.09%. This was roughly equivalent to a nitrapyrin concentration with field
application rates of 500 lbs/acre urea with 35 oz/acre Entrench®. The NI retention was about 49% after 2 weeks at 54°C.

Table 5. NI content of combined particles after processing and storage

<table>
<thead>
<tr>
<th>Examples</th>
<th>Theoretical NI wt%</th>
<th>Binder</th>
<th>Particulate</th>
<th>Theoretical NI wt% (normalized)</th>
<th>NI wt% after processing (normalized)</th>
<th>Storage Container</th>
<th>NI wt% after stored @ 54°C for 2 week (normalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>HPMC K99</td>
<td>ATP</td>
<td>100%</td>
<td>87.2</td>
<td>Glass bottle</td>
<td>75.7</td>
</tr>
<tr>
<td>2</td>
<td>0.37</td>
<td>HPMC K99</td>
<td>ATP</td>
<td>100%</td>
<td>90.5</td>
<td>Glass bottle</td>
<td>79.0</td>
</tr>
<tr>
<td>3</td>
<td>0.56</td>
<td>HPMC K99</td>
<td>ATP</td>
<td>100%</td>
<td>92.5</td>
<td>Glass bottle</td>
<td>90.6</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>HPMC K99</td>
<td>/</td>
<td>100%</td>
<td>78.1</td>
<td>Glass bottle</td>
<td>57.3</td>
</tr>
<tr>
<td>5</td>
<td>0.36</td>
<td>/</td>
<td>ATP</td>
<td>100%</td>
<td>93.7</td>
<td>Glass bottle</td>
<td>85.4</td>
</tr>
<tr>
<td>6</td>
<td>0.37</td>
<td>PVA 1788</td>
<td>ATP</td>
<td>100%</td>
<td>98.3</td>
<td>Glass bottle</td>
<td>77.5</td>
</tr>
<tr>
<td>7</td>
<td>0.36</td>
<td>HPMC K99</td>
<td>Kaolin</td>
<td>100%</td>
<td>88.6</td>
<td>Glass bottle</td>
<td>87.1</td>
</tr>
<tr>
<td>8</td>
<td>0.36</td>
<td>HPMC K99</td>
<td>Tale</td>
<td>100%</td>
<td>94.0</td>
<td>Glass bottle</td>
<td>78.4</td>
</tr>
<tr>
<td>9</td>
<td>0.37</td>
<td>HPMC K99</td>
<td>Diatomite</td>
<td>100%</td>
<td>99.5</td>
<td>Glass bottle</td>
<td>84.9</td>
</tr>
<tr>
<td>10</td>
<td>0.96</td>
<td>/</td>
<td>Diatomite</td>
<td>100%</td>
<td>/</td>
<td>Glass bottle</td>
<td>95.8</td>
</tr>
<tr>
<td>11</td>
<td>1.34</td>
<td>/</td>
<td>Diatomite</td>
<td>100%</td>
<td>/</td>
<td>Glass bottle</td>
<td>–100</td>
</tr>
<tr>
<td>12</td>
<td>0.55</td>
<td>HPMC K99</td>
<td>Diatomite</td>
<td>100%</td>
<td>102.2</td>
<td>Glass bottle</td>
<td>88.5</td>
</tr>
<tr>
<td>13</td>
<td>0.56</td>
<td>HPMC K99</td>
<td>Diatomite</td>
<td>100%</td>
<td>94.6</td>
<td>Glass bottle</td>
<td>87.5</td>
</tr>
<tr>
<td>14</td>
<td>0.56</td>
<td>HPMC K99</td>
<td>Diatomite</td>
<td>100%</td>
<td>101.8</td>
<td>Glass bottle</td>
<td>89.9</td>
</tr>
<tr>
<td>15</td>
<td>0.13</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>93.6</td>
<td>Ziplock bag</td>
<td>89.8</td>
</tr>
<tr>
<td>16</td>
<td>0.80</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>97.1</td>
<td>Ziplock bag</td>
<td>98.3</td>
</tr>
<tr>
<td>17</td>
<td>1.01</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>95.8</td>
<td>Ziplock bag</td>
<td>83.9</td>
</tr>
<tr>
<td>18</td>
<td>0.98</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>94.4</td>
<td>Ziplock bag</td>
<td>83.4</td>
</tr>
<tr>
<td>19</td>
<td>0.94</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>88.1</td>
<td>Ziplock bag</td>
<td>84.0</td>
</tr>
<tr>
<td>20</td>
<td>1.01</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>106.4</td>
<td>Ziplock bag</td>
<td>75.2</td>
</tr>
<tr>
<td>21</td>
<td>0.90</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>88.0</td>
<td>Ziplock bag</td>
<td>86.8</td>
</tr>
<tr>
<td>22</td>
<td>0.85</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>89.3</td>
<td>Ziplock bag</td>
<td>75.2</td>
</tr>
<tr>
<td>23</td>
<td>0.87</td>
<td>AC261P</td>
<td>Diatomite</td>
<td>100%</td>
<td>85.8</td>
<td>Ziplock bag</td>
<td>82.6</td>
</tr>
<tr>
<td>24</td>
<td>0.82</td>
<td>Salt¹</td>
<td>Diatomite</td>
<td>100%</td>
<td>83.6</td>
<td>Ziplock bag</td>
<td>62.4</td>
</tr>
<tr>
<td>25</td>
<td>0.56</td>
<td>HPMC + Diatomite</td>
<td>100%</td>
<td>92.5</td>
<td>Ziplock bag</td>
<td>49.0</td>
<td></td>
</tr>
<tr>
<td>26²</td>
<td>0.09</td>
<td>/</td>
<td>/</td>
<td>100%</td>
<td>97.8</td>
<td>Glass bottle</td>
<td>49.5</td>
</tr>
<tr>
<td>27³</td>
<td>17.79</td>
<td>/</td>
<td>/</td>
<td>100%</td>
<td>/</td>
<td>Ziplock bag</td>
<td>30.0</td>
</tr>
</tbody>
</table>

¹Samples were only stored for 1 week at 54°C; ²Salt is potassium pyrophosphate trihydrate; ³Sample was prepared by coating fertilizer granules with Entrench; ⁴Sample was dried Entrench capsule suspension.

Still referring to Table 5, the hygroscopic particulate [volatilization barrier] appears to affect nitrapyrin retention during processing. In Example 4, no particulate was used,
and in other Examples (1-3 and 5-9) hygroscopic particulate [volatilization barrier] was used in the dry formulation, including ATP, talc, Kaolin and diatomite. In the Examples with hygroscopic particulate [volatilization barrier], the nitrapyrin content after processing was 87-94%, while in the Example without hygroscopic particulate [volatilization barrier], nitrapyrin content was 78%. So, the hygroscopic particulate [volatilization barrier] has a significant contribution in improving nitrapyrin retention during processing.

[0100] As shown in FIG. 5, after about 2 weeks (14 days) at 54°C, the loss of nitrapyrin in weight percent is about 30% for dried nitrapyrin capsules (microencapsulated nitrapyrin in polyurea, typically in an aqueous suspension).

[0101] Still referring to Table 5, in Examples 2, 5 and 6 where the NI loading level ranges from 0.36-0.37% and the particulate used is ATP, a different binder was employed for each sample with the retention of the NI ranging from 77.5 to 85.4% after storage. Still referring to Table 5, the hygroscopic particulate [volatilization barrier] appears to boost nitrapyrin retention during processing. In Example 4, where no particulate was used, the nitrapyrin content measured after storage at 54 degree Celsius for 2 weeks was only 57%. When hygroscopic particulate [volatilization barrier] such as attapulgite, talc, kaolin and diatomite were used the nitrapyrin content after storage was more than 76%. The type of particulate appears to have little effect on the levels of nitrapyrin retained.

[0102] 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 core, the core having an outer surface;
   a plurality of encapsulated particles disposed around the outer surface, the
   particles including at least one inhibitor of nitrification; and
   hygroscopic particulate disposed around the plurality of encapsulated particles.

2. The composition according to claim 1, wherein the hygroscopic particulate is not
   in contact with the core.

3. The composition according to claim 1, wherein the core is at least one fertilizer
   selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based
   fertilizer, a phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a
   copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, an
   iron-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer,
   a sulfur-containing micronutrient fertilizer, and mixtures thereof.

4. The composition according to claim 3, wherein the core comprises a solid form of
   urea.

5. The composition according to claim 1, wherein the encapsulated particles
   comprise nitrapyrin.

6. The composition according to claim 5, wherein the encapsulated particles include
   polyurea and have a volume median particle size of from about 1 to about 10 microns.

7. The composition according to claim 1, wherein the hygroscopic particulate is an
   inorganic hygroscopic particulate.
8. The composition according to claim 1, wherein the hygroscopic particulate is at least one material selected from the group consisting of: attapulgite, talc, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof.

9. The composition according to claim 1, further comprising a binder, said binder being disposed predominately on the outer surface of the core and said binder immobilizing the plurality of the encapsulated particles.

10. The composition according to claim 9, wherein the binder is at least one material selected from the group consisting of: hydroxypropyl methylcellulose, ethyl cellulose, methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, lignosulfonates, guar, urea, alginate, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, polyacrylate latexes and their copolymer latexes, and mixtures thereof.

11. The composition according to claim 10, wherein the binder comprises hydroxypropyl methylcellulose, a polyacrylate latex or a copolymer of a polyacrylate latex.

12. The composition according to claim 1, wherein the composition comprises between about 80% and about 99% by weight of fertilizer granules.

13. The composition according to claim 1, wherein the composition comprises between about 90% and about 99% by weight of fertilizer granules.

14. The composition according to claim 1, wherein the composition comprises nitrapyrin in a range selected from the group of ranges consisting of: about 0.01 % wt. to
about 10.00% wt.; about 0.05% wt. to about 5.00% wt.; about 0.10% wt. to about 4.00% wt.; about 0.20% wt. to about 3.00% wt.; about 0.30% wt. to about 2.50% wt.; about 0.40% wt. to about 2.00% wt.; and about 0.50% wt. to about 1.00% wt.

15. The composition according to claim 1, wherein the composition comprises between about 0.20% and about 2.00% of nitrpyrin.

16. The composition according to claim 9, wherein the composition comprises between about 0.01% and about 10% of the binder.

17. The composition according to claim 9, wherein the composition comprises between about 0.01% and about 5% of the binder.

18. The composition according to claim 1, wherein the composition comprises between about 1.00% and about 10.00% of the hygroscopic particulate.

19. The composition according to claim 1, wherein the composition comprises between about 2.00% and about 7.00% of the hygroscopic particulate.

20. The composition according to claim 1, wherein the composition comprises particles of a volume median particle size of from about 0.5 to about 5 millimeters.

21. The composition according to claim 9, wherein the ratio of the binder to the at least one inhibitor of nitrification is from about 0:100 to about 1:100.

22. The composition according to claim 9, wherein the ratio of the binder to the at least one inhibitor of nitrification is from about 0:100 to about 0.3:100.

23. The composition according to claim 3, wherein the ratio of the inhibitor of nitrification to the fertilizer is from about 0.01:100 to about 3:100.

24. The composition according to claim 3, wherein the ratio of the inhibitor of nitrification to the fertilizer is from about 0.2:100 to about 2.0:100.
25. The composition according to claim 3, wherein the ratio of the hygroscopic particulate to the fertilizer is from about 1:500 to about 20:100.

26. The composition according to claim 3, wherein the ratio of the hygroscopic particulate to the fertilizer is from about 1:100 to about 10:100.

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

preparing a solution comprising a plurality of encapsulated particles, the particles including at least one inhibitor of nitrification; and

coating a plurality of substantially solid core particles, the core particles having an outer surface, with the solution to create coated combined particles.

28. The method according to claim 27, further comprising the step of adding a binder to the solution.

29. The method according to claim 27, wherein the preparing step further comprises dissolving fertilizer granules within the solution.

30. The method according to claim 27, further comprising the step of drying the combined particles.

31. The method according to claim 27, wherein the core particle is at least one fertilizer selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, an iron-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer, a sulfur-containing micronutrient fertilizer, and mixtures thereof.

32. The method according to claim 27, wherein the core particles comprise urea.

33. The method according to claim 27, wherein the encapsulated particles comprise nitrpyrin.
34. The method according to claim 27, wherein the encapsulated particles comprise polyurea and have a volume median particle size of from about 1 to about 10 microns.

35. The method according to claim 28, wherein the binder is at least one compound selected from the group consisting of: hydroxypropyl methylcellulose, ethyl cellulose, methyl cellulose, carboxymethylcellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, guar, urea, alginate, polysaccharides, aqueous polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, polyacrylate latexes and their copolymer latexes, and mixtures thereof.

36. The method according to claim 35, wherein the binder is hydroxypropyl methylcellulose, polyvinyl alcohol, a polyacrylate latex or a copolymer of a polyacrylate latex.

37. The method according to claim 27, further comprising the step of adding hygroscopic particulate to be disposed on the coated combined particles.

38. The method according to claim 37, wherein the hygroscopic particulate is an inorganic hygroscopic particulate.

39. The method according to claim 37, wherein the hygroscopic particulate is at least one material selected from the group consisting of: attapulgite, talc, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof.

40. The method according to claim 27, wherein the composition comprises between about 80% and about 99% by weight of core particles.
41. The method according to claim 27, wherein the composition comprises between about 90% and about 99% by weight of core particles.

42. The method according to claim 27, wherein the composition comprises nitrapyrin in a range selected from the group consisting of: about 0.01% wt. to about 10.00% wt.; about 0.05% wt. to about 5.00% wt.; about 0.10% wt. to about 4.00% wt.; about 0.20% wt. to about 3.00% wt.; about 0.30% wt. to about 2.50% wt.; about 0.40% wt. to about 2.00% wt.; and about 0.50% wt. to about 1.00% wt.

43. The method according to claim 27, wherein the composition comprises between about 0.20% and about 2.00% of nitrapyrin.

44. The method according to claim 28, wherein the composition comprises between about 0.01% and about 10.00% of the binder.

45. The method according to claim 25, wherein the composition comprises between about 0.01% and about 5.00% of the binder.

46. The method according to claim 37, wherein the composition comprises between about 1.00% and about 10.00% of the hygroscopic particulate.

47. The method according to claim 37, wherein the composition comprises between about 2.00% and about 7.00% of the hygroscopic particulate.

48. The method according to claim 27, wherein the composition comprises coated combined particles of a volume median particle size of from about 0.5 to about 5 millimeters.

49. The method according to claim 28, wherein the ratio of the binder to the core particles is from about 0:100 to about 1:100.

50. The method according to claim 28, wherein the ratio of the binder to the core particles is from about 0:100 to about 0.3:100.
51. The method according to claim 27, wherein the ratio of the inhibitor of nitrification to the core particles is from about 0.01:100 to about 3:100.

52. The method according to claim 27, wherein the ratio of the inhibitor of nitrification to the core particles is from about 0.2:100 to about 2.0:100.

53. The method according to claim 37, wherein the ratio of the hygroscopic particulate to the core particles is from about 1:500 to about 20:100.

54. The method according to claim 36, wherein the ratio of the hygroscopic particulate to the core particles is from about 1:100 to about 10:100.

55. The method according to claim 26, wherein the step of coating incorporates one or more devices selected from the group consisting of: a pan coater, a rotating drum, a spray coater, a fluid bed, screens, and mixtures thereof.

56. An agricultural composition, comprising:
   a substantially solid core, the core having an outer surface;
   at least one inhibitor of nitrification disposed around the outer surface; and
   hygroscopic particulate disposed around the at least one inhibitor of nitrification.

57. The composition according to claim 56, wherein the at least one inhibitor of nitrification comprises a plurality of encapsulated particles.

58. The composition according to claim 56, wherein the hygroscopic particulate is not in contact with the core.

59. The composition according to claim 56, wherein the core is at least one fertilizer selected from the group consisting of: a nitrogen-based fertilizer, a potassium-based fertilizer, a phosphorus-based fertilizer, a zinc-containing micronutrient fertilizer, a copper-containing micronutrient fertilizer, a boron-containing micronutrient fertilizer, an
iron-containing micronutrient fertilizer, a manganese-containing micronutrient fertilizer, a sulfur-containing micronutrient fertilizer, and mixtures thereof.

60. The composition according to claim 59, wherein the core comprises a solid form of urea.

61. The composition according to claim 57, wherein the encapsulated particles comprise nitrapyrin.

62. The composition according to claim 57, wherein the encapsulated particles include polyurea and have a volume median particle size of from about 1 to about 10 microns.

63. The composition according to claim 56, wherein the hygroscopic particulate is an inorganic hygroscopic particulate.

64. The composition according to claim 56, wherein the hygroscopic particulate is at least one material selected from the group consisting of: attapulgite, talc, diatomite, kaolin, silica, clay, mica, bentonite, montmorillonite, white carbon black, carbon black, coal ash, plant ash, wollastonite, zeolite, sepiolite, vermiculite perlite, starch, wax, and mixtures thereof.

65. The composition according to claim 56, further comprising a binder, said binder being disposed predominately on the outer surface of the core and said binder immobilizing the plurality of the encapsulated particles.

66. The composition according to claim 65, wherein the binder is at least one compound selected from the group consisting of: hydroxypropyl methylcellulose, ethyl cellulose, methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyoxyethylene and its copolymers, latexes, polyamides, sugar, glucose, maltose, starch, lignosulfonates, guar, urea, alginate, polysaccharides, aqueous
polyester, polyethers, epoxy resin, isocyanates, ethylene vinyl acetate copolymer, polyacrylate and its copolymer emulsions, polyacrylate latexes and their copolymer latexes, and mixtures thereof.

67. The composition according to claim 66, wherein the binder comprises hydroxypropyl methylcellulose, a polyacrylate latex or a copolymer of a polyacrylate latex.

68. The composition according to claim 56, wherein the composition comprises between about 80% and about 99% by weight of fertilizer granules.

69. The composition according to claim 56, wherein the composition comprises between about 90% and about 99% by weight of fertilizer granules.

70. The composition according to claim 56, wherein the composition comprises nitrapyrin in a range selected from the group of ranges consisting of: about 0.01% wt. to about 10.00% wt.; about 0.05% wt. to about 5.00% wt.; about 0.10% wt. to about 4.00% wt.; about 0.20% wt. to about 3.00% wt.; about 0.30% wt. to about 2.50% wt.; about 0.40% wt. to about 2.00% wt.; and about 0.50% wt. to about 1.00% wt.

71. The composition according to claim 56, wherein the composition comprises between about 0.20% and about 2.00% of nitrapyrin.

72. The composition according to claim 65, wherein the composition comprises between about 0.01% and about 10% of the binder.

73. The composition according to claim 65, wherein the composition comprises between about 0.01% and about 5% of the binder.

74. The composition according to claim 56, wherein the composition comprises between about 1.00% and about 10.00% of the hygroscopic particulate.
75. The composition according to claim 56, wherein the composition comprises between about 2.00% and about 7.00% of the hygroscopic particulate.

76. The composition according to claim 56, wherein the composition comprises particles of a volume median particle size of from about 0.5 to about 5 millimeters.

77. The composition according to claim 65, wherein the ratio of the binder to the at least one inhibitor of nitrification is from about 0:100 to about 1:100.

78. The composition according to claim 65, wherein the ratio of the binder to the at least one inhibitor of nitrification is from about 0:100 to about 0.3:100.

79. The composition according to claim 59, wherein the ratio of the inhibitor of nitrification to the fertilizer is from about 0.01:100 to about 3:100.

80. The composition according to claim 59, wherein the ratio of the inhibitor of nitrification to the fertilizer is from about 0.2:100 to about 2.0:100.

81. The composition according to claim 59, wherein the ratio of the hygroscopic particulate to the fertilizer is from about 1:500 to about 20:100.

82. The composition according to claim 59, wherein the ratio of the hygroscopic particulate to the fertilizer is from about 1:100 to about 10:100.
Dried Nitrapyrin Capsules

\[ y = -1.536x - 8.239 \]

\[ R^2 = 0.8696 \]