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(54) Titre : SYSTEMES DE SOLVANTS AMELIORES POUR LE DICYANDIAMIDE ET/OU LE TRIAMIDE ALKYLTHIOPHOSPHORIQUE ET LEUR UTILISATION DANS DES APPLICATIONS AGRICOLES

(54) Title: IMPROVED SOLVENT SYSTEMS FOR DICYANDIAMIDE AND/OR ALKYL THIOPHOSPHORIC TRIAMIDE AND USE IN AGRICULTURAL APPLICATIONS

(57) Abrégé/Abstract:
An inhibitor composition contains dicyandiamide as a nitrification inhibitor, alkyl thiophosphoric triamide as a urease inhibitor, or a combination thereof, dissolved in a liquid medium comprising an organic solvent selected from, among others, one or more polar aprotic solvents, including one or more organophosphates, amine solvents, heterocyclic alcohol solvents, and mixtures thereof, is useful in making fertilizer compositions and in a method of fertilizing target plants.

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(54) **Title**: IMPROVED SOLVENT SYSTEMS FOR DICYANDIAMIDE AND/OR ALKYL THIOPHOSPHORIC TRIAMIDE AND USE IN AGRICULTURAL APPLICATIONS

(57) **Abstract**: An inhibitor composition contains dicyandiamide as a nitrification inhibitor, alkyl thiophosphoric triamide as a urease inhibitor, or a combination thereof, dissolved in a liquid medium comprising an organic solvent selected from, among others, one or more polar aprotic solvents, including one or more organophosphates, amine solvents, heterocyclic alcohol solvents, and mixtures thereof, is useful in making fertilizer compositions and in a method of fertilizing target plants.

IMPROVED SOLVENT SYSTEMS FOR DICYANDIAMIDE AND/OR ALKYL THIOPHOSPHORIC TRIAMIDE AND USE IN AGRICULTURAL APPLICATIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of US Provisional Patent Application No. 62/066,513 filed October 21, 2014, incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to liquid compositions comprising dicyandiamide and/or an alkyl thiophosphoric triamide, methods for incorporating such compositions with agricultural fertilizer compositions, agricultural fertilizer compositions comprising dicyandiamide and/or an alkyl thiophosphoric triamide, and the use of such compositions.

BACKGROUND OF THE INVENTION

[0003] In the agrochemical industry, farmers use various fertilizers to impart macronutrients to plants either by application to the soil or application to plant leaves. Nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur are macronutrients that must be supplied to the plants and soil manually by farmers. In many crops, the amount of nitrogen supplied is critical to the overall quality and growth of the crop. Nitrogen is typically supplied in the form of nitrogenous, i.e., nitrogen precursor-containing, fertilizer compounds, such as urea, ammonium nitrate, or ammonium phosphate fertilizer compounds. Due to the high water solubility of these salts, however, applied nitrogen values may be lost due to run-off and leaching of the nitrogenous fertilizer compounds. Once applied, the nitrogenous fertilizer compounds are typically degraded, for example, by microorganisms present in the soil, to nitrogenous species such as NH_4^+, NO_2^-, NO_3^-, and ammonia gas, that may be even

more readily lost through evaporation, run-off, and leaching than the fertilizer compounds themselves. If degradation of the fertilizer compounds occurs at a rate that is faster than the nitrogenous degradation products can be used by the plants, then the nitrogen values in the degradation products are at increased risk of being lost.

[0004] Nitrification and/or urease inhibitors are of potential use in delaying degradation of fertilizer compounds and thereby reducing losses of nitrogenous degradation products that would otherwise occurred in the absence of the inhibitors. The use of nitrification and/or urease inhibitors in combination with nitrogenous fertilizer compounds tends to increase the amount of time the nitrogen source remains in the soil and available for absorption by the plants, which tends to increase the effectiveness of the fertilizer and positively impact crop yield and quality.

[0005] Aqueous end use fertilizer solutions are typically prepared in the field by diluting commercially available concentrated fertilizer compositions with water. Commonly used concentrated fertilizer compositions include concentrated ammonium nitrate compositions, such as, for example, UAN 18, UAN 28, UAN 30 and UAN 32.

[0006] Dicyandiamide is potentially useful as a nitrification inhibitor in such aqueous end use fertilizer compositions, but has very low solubility (about 41 grams per liter ("g/l")) in water and so is difficult to incorporate into the aqueous end use fertilizer compositions, particularly under field conditions

SUMMARY OF THE INVENTION

[0007] Urease inhibitors can be used with a fertilizer (i.e., incorporated into a urea-containing fertilizer, e.g., urea and urea ammonium nitrate (UAN)) to slow the conversion of ammonium to ammonia gas and thus slow the loss of ammonia to volatilization, thus making ammonium available to plants in the soil for longer periods of time. In many crops, the amount of nitrogen supplied is critical to the overall quality and

growth of the crop. Nitrogen is supplied in either urea or ammonium phosphate forms. Due to the high water solubility of these salts, however, much of the nitrogen applied is lost to run-off and leaching. In ammonium-based products, if the nitrogen is not lost to leaching or run-off, it is being converted to ammonia gas by an enzyme called urease. Although ammonia can bind to soil particles, conversion occurring near the surface of the soil does not allow for binding and, thus, ammonia is lost to the atmosphere. Urease inhibitors are used to protect a farmer's investment in fertilizers by preventing the breakdown of urea by urease, the soil microbe responsible for converting urea to usable ammonia in the soil. This increases the amount of time the nitrogen remains in the soil and is available to the plant for absorption.

[0008] Similarly, nitrification inhibitors can be used with a fertilizer (i.e., incorporated into a urea-containing fertilizer, e.g., urea and urea ammonium nitrate (UAN)) to slow the process of ammonium conversion to nitrate, and subsequently the loss of nitrate to leeching, thus making ammonium available to plants in the soil for longer periods of time. Ammonium is one of the main forms of nitrogen that can be utilized by plants. Increasing the amount of time that the nitrogen is available to the plant increases the effectiveness of the fertilizer which positively impacts crop yield and quality.

[0009] Fertilizers, in one embodiment, are common water soluble inorganic fertilizers that provide nutrients such as phosphorus-based, nitrogen-based, potassium-based or sulphur-based fertilizers. Examples of such fertilizers include: for nitrogen as the nutrient: nitrates and or ammonium salts such as ammonium nitrate, including in combination with urea e.g. as Uram type materials, calcium ammonium nitrate, ammonium suphate nitrate, ammonium phosphates, particularly mono-ammonium phosphate, di-ammonium phosphate and ammonium polyphosphate, ammonium sulphate, and the less commonly used calcium nitrate, sodium nitrate, potassium nitrate and ammonium chloride. It is understood that a fertilizer composition can comprise one or a combination of the fertilizers described herein.

[0010] A typical urease inhibitor, alkyl thiophosphoric triamide, and, more particularly,

NBPT (N-(n-butyl)-thiophosphoric triamide), however, faces drawbacks in its use as NBPT is extremely difficult to handle. NBPT is a sticky, waxy, heat and water sensitive material, which cannot be used in its solid form, as it is used at low concentrations making it difficult to evenly distribute on urea prills (i.e., large granules) and in soil. In order to evenly distribute the NBPT onto the urea, the NBPT should be dispersed into a carrier prior to being sprayed onto the urea. Thus, the use of a solvent system containing the NBPT is desirable as, in its liquid form, the solvent system is capable of distributing the NBPT into granular urea (e.g., urea prills) and into liquid fertilizers containing urea. By introducing the NBPT to liquid fertilizers containing urea (for example, urea-ammonium nitrate solutions or UAN) in a solvent system, the NBPT is capable of being better dispersed in the liquid fertilizer.

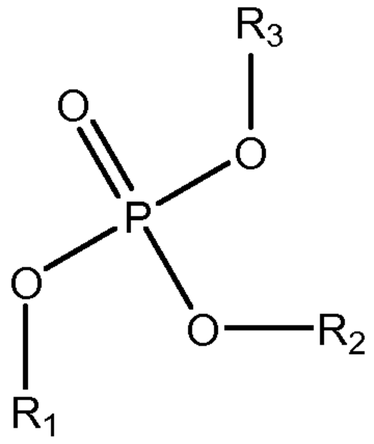
[0011] Dicyandiamide is useful as a nitrification inhibitor in aqueous agricultural applications, e.g., end use fertilizer compositions, but similar to urease inhibitors face similar drawbacks. Nitrification inhibitors, such as dicyandiamide, generally have very low solubility (about 41 grams per liter ("g/l")) in water and so it is difficult to incorporate into the aqueous end use fertilizer compositions, particularly under field conditions. As nitrification inhibitors, such as dicyandiamide, have a generally low solubility, they are used at low concentrations in water making it difficult to evenly distribute on urea-containing prills (i.e., large granules) and in soil. In order to evenly distribute the dicyandiamide onto the urea-containing prills or granules, dicyandiamide should be dispersed into a solvent carrier prior to being sprayed onto the urea. Thus, the use of a solvent system containing dicyandiamide (herein, also termed "DCD") is desirable as, in its liquid form, the solvent system is capable of distributing the dicyandiamide onto urea granules or prills, urea ammonium nitrate granules or prills or, otherwise, urea-containing granules or prills, and into liquid fertilizers containing urea or urea ammonium nitrate. By introducing the dicyandiamide to liquid fertilizers containing urea (for example, urea-ammonium nitrate solutions or UAN) in a solvent system, the dicyandiamide is capable of being better dispersed in the liquid fertilizer.

[0012] In one embodiment, concentrated fertilizer compositions include concentrated

ammonium nitrate compositions, such as, for example, UAN 18, UAN 28, UAN 30 and UAN 32.

[0013] Thus, it is desirable to have a solvent system containing alkyl thiophosphoric triamide, and in particular, (N-(n-butyl)-thiophosphoric triamide), that has a favorable toxicological and/or ecological profile and desirable characteristics in terms of low volatility, biodegradability or ready biodegradability (i.e., readily biodegradable), low toxicity or low hazard level. It is desirable to have a solvent system containing dicyandiamide, that has a favorable toxicological and/or ecological profile and desirable characteristics in terms of low volatility, biodegradability or ready biodegradability (i.e., readily biodegradable), low toxicity or low hazard level. It is also desirable to have a solvent system containing a combination of dicyandiamide and an alkyl thiophosphoric triamide, in particular, (N-(n-butyl)-thiophosphoric triamide), that has a favorable toxicological and/or ecological profile and desirable characteristics in terms of low volatility, biodegradability or ready biodegradability (i.e., readily biodegradable), low toxicity or low hazard level.

[0014] The present invention described herein will become apparent from the following detailed description and examples, which comprises in one aspect, a liquid composition for use in agricultural applications comprising: at least one of a nitrification inhibitor or a urease inhibitor (and, in some embodiments, both a nitrification inhibitor and a urease inhibitor); and at least one organophosphate compound (or, hereinafter, synonymously referred to as an “organophosphate solvent”) of formula (VIII):



(VIII),

[0015] wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R3 is not H. Optionally, the liquid composition can further comprise at least one co-solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, and mixtures thereof. The liquid composition can further comprise one or more stabilizers.

[0016] In another aspect, described herein are methods of making a solid or concentrated liquid fertilizer compositions comprising treating (e.g., contacting or spray applying) one or more nitrogenous fertilizer compounds with a liquid inhibitor composition. The liquid inhibitor composition comprises at least one of a nitrification inhibitor or a urease inhibitor (or, in some embodiment, a combination of at least one nitrification inhibitor and at least one urease inhibitor), homogenously dissolved or dispersed in a solvent comprising at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. The liquid inhibitor composition, in one embodiment, further comprises at least one co-solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, and mixtures thereof.

[0017] The term treating, in one embodiment, includes spray applying the liquid inhibitor composition with the one or more nitrogenous fertilizer compounds. The term treating, in one embodiment, includes but is not limited to contacting the inhibitor composition with the one or more nitrogenous fertilizer compounds. In one embodiment, the nitrification inhibitor is dicyandiamide. In another embodiment, the urease inhibitor is an alkyl thiophosphoric triamide.

[0018] In yet another aspect, described herein are concentrated liquid fertilizer compositions comprising, based on weight of the composition: (a) up to about 99 wt%, by weight of composition, of one or more nitrogenous fertilizer compounds, (b) at least one of a dicyandiamide or an alkyl thiophosphoric triamide (or a combination of both), (c) a solvent comprising at least one organophosphate solvent according to formula

(VIII), wherein R_1, R_2 and R_3 are as described above.

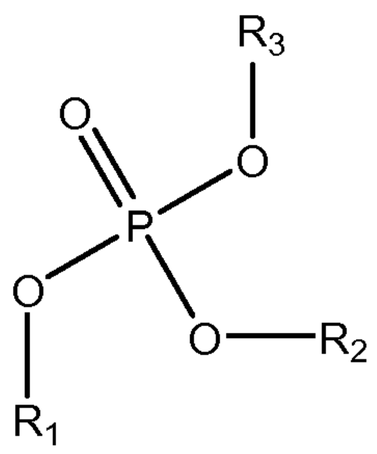
[0019] In a further aspect, described herein are concentrated liquid fertilizer compositions comprising, based on weight of the composition: (a) up to about 99 wt%, by weight of composition, of one or more nitrogenous fertilizer compounds, (b) at least one of a dicyandiamide or an alkyl thiophosphoric triamide (or, in some embodiments, both), (c) a solvent comprising at least one organophosphate solvent according to formula (VIII), (d) optionally, at least one co-solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, and mixtures thereof, and (e) optionally, water. The concentrated liquid fertilizer compositions can further comprise one or more stabilizers.

[0020] In yet another aspect, described herein are solid or substantially solid fertilizer compositions comprising: (a) solid particles of one or more nitrogenous fertilizer compounds, and (b) an inhibitor composition comprising at least one of a dicyandiamide or an alkyl thiophosphoric triamide supported on at least a portion of the solid particles.

[0021] In another aspect, described herein are methods of making a liquid or aqueous fertilizer composition comprising contacting one or more nitrogenous fertilizer compounds, with a liquid inhibitor composition that comprises at least one of a nitrification inhibitor or a urease inhibitor, homogenously dissolved or dispersed in a solvent comprising at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above.

[0022] The solvent can, optionally, further comprise an co-solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, and mixtures thereof.

[0023] In another aspect, the organic solvent is an organophosphate compound having the formula (VIII)



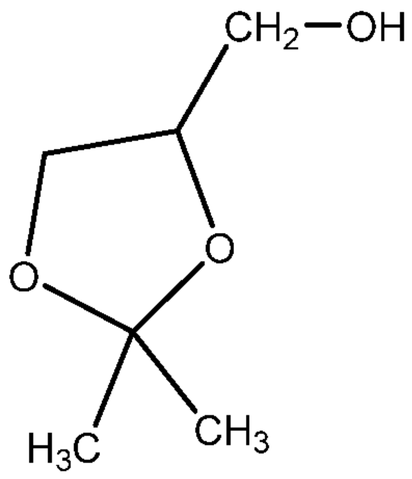
(VIII),

[0024] wherein wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H. In another embodiment, R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{12} alkyl group, a C_1-C_{12} alkenyl, group, a C_1-C_{12} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H. In one embodiment, R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_4 alkyl group, a C_4-C_8 alkyl group, a C_1-C_{12} alkenyl, group, a C_1-C_4 alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H.

[0025] In yet another embodiment, R_1, R_2 and R_3, are each independently chosen from a C_1-C_{12} alkyl group, a C_1-C_{12} alkenyl, group, a C_1-C_{12} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group. In one embodiment, R_1, R_2 and R_3, are each independently chosen from a C_1-C_{12} alkyl group, more typically, a C_2-C_8 alkyl group.

[0026] In another aspect, described herein are methods for fertilizing target plants, comprising applying an aqueous end use fertilizer composition that comprises: (a) one or more nitrogenous fertilizer compounds, (b) at least one of a dicyandiamide or an alkyl thiophosphoric triamide, (c) an organic solvent having formula (VIII), wherein R_1, R_2 and R_3 are as described above, and, (d) optionally, a co-solvent selected from dimethyl sulfoxide, dimethyl formamide, the dimethyl ester of succinic acid, dimethyl ester of

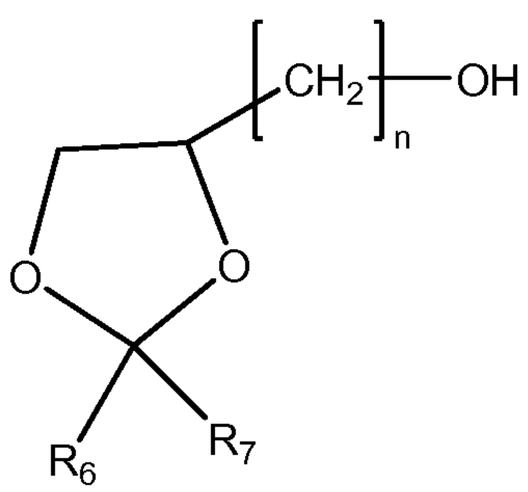
ethyl succinic acid, the dimethyl ester of glutaric acid, the dimethyl ester of methyl glutaric acid, and the dimethyl ester of adipic acid, diethylene triamine, or monoethanolamine, methyl-5-(dimethylamino)-2-methyl-oxopentanoate, dimethylaminoethanol, triethanol amine, a heterocyclic alcohol according to structure (IIIb):



(IIIb),

or mixtures thereof, and, optionally, (d) water, to the target plants or to an environment for the target plants. It is understood that the term heterocyclic alcohol includes dioxolane compounds. The end use fertilizer composition can also comprise, in some embodiments, at least one stabilizer. In one embodiment, the stabilizer is monoethanolamine.

[0027] In one embodiment, the alkyl thiophosphoric triamide is N-(n-butyl)-thiophosphoric triamide. In another embodiment, the liquid composition further comprises a co-solvent selected from the group consisting of: (a) at least one dioxolane compound of formula (III):



(III),

[0028] wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10; b) at least one dibasic ester; c) at least one compound of formula (IIa):

$R_3OOC\text{-}A\text{-}CONR_4R_5$

(IIa),

[0029] wherein R_3 comprises a C_1-C_{36} alkyl group; wherein R_4 and R_5 individually comprise a C_1-C_{36} alkyl group, wherein R_4 and R_5 can optionally together form a ring; and wherein A is a linear or a branched divalent C_2-C_6 alkyl group; d) at least one alkyldimethylamide; e) at least one alkyl lactate; f) ethyl levulinate; g) at least one alkyoxyalcohol, ether alcohol, amine alcohol, amino alcohol or alcohol; h) at least one glycerine or glycerine derivative; i) at least one alkylene carbonate; j) dimethylsulfoxide; and k) any combination thereof. In one embodiment, the co-solvent is dimethylsulfoxide.

[0030] In another aspect, the present invention is directed to a nitrification inhibitor composition comprising dicyandiamide dissolved in a liquid medium that comprises an organic solvent selected from polar aprotic solvents, dibasic esters, amines, amino alcohols, heterocyclic alcohols, and mixtures thereof.

[0031] In yet another aspect, the present invention is directed to a method of making a solid or concentrated liquid fertilizer composition comprising treating (e.g., contacting, spray applying, brushing, etc.) one or more nitrogenous fertilizer compounds with a nitrification inhibitor composition that comprises dicyandiamide dissolved in a liquid medium that comprises an organic solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, and mixtures thereof.

[0032] In a further aspect, the present invention is directed to a concentrated liquid fertilizer composition comprising, by weight of the composition:

(a) up to about 99 wt% of one or more nitrogenous fertilizer compounds,

(b) dicyandiamide or an alkyl thiophosphoric triamide (or both dicyandiamide and an alkyl thiophosphoric triamide);

(c) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2

and R_3 are as described above;

(d) optionally, at least one co-solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, or mixtures thereof, and

(d) optionally, water.

[0033] In another aspect, the present invention is directed to a concentrated solid fertilizer composition comprising:

(a) solid particles of one or more nitrogenous fertilizer compounds, and

(b) dicyandiamide or an alkyl thiophosphoric triamide supported on at least a portion of the solid particles.

[0034] In yet another aspect, the present invention is directed to a method of making an aqueous end use fertilizer composition comprising contacting one or more nitrogenous fertilizer compounds with a urease inhibitor composition that comprises an alkyl thiophosphoric triamide dissolved in a liquid medium that comprises an organic solvent selected from polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, or mixtures thereof.

[0035] In a further aspect, the present invention is directed to a method for fertilizing target plants, comprising applying an aqueous end use fertilizer composition that comprises:

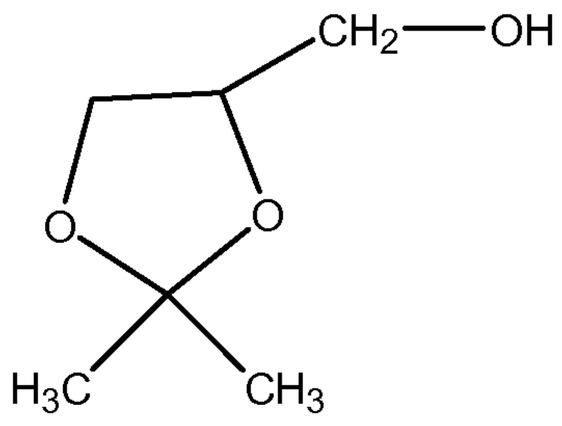
(a) one or more nitrogenous fertilizer compounds;

(b) dicyandiamide, an alkyl thiophosphoric triamide, or a mixture thereof;

(c) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above,

(d) optionally, at least one organic solvent selected from dimethyl sulfoxide, dimethyl formamide, the dimethyl ester of succinic acid, dimethyl ester of ethyl succinic acid, the dimethyl ester of glutaric acid, the dimethyl ester of methyl glutaric acid, and the dimethyl ester of adipic acid, diethylene triamine, or monoethanolamine, methyl-5-(dimethylamino)-2-methyl-oxopentanoate, dimethylaminoethanol,

triethanol amine, a heterocyclic alcohol according to structure (IIIb):



(IIIb),

Or mixtures thereof; and

(e) optionally, water,

to the target plants or to an environment for the target plants.

BRIEF DESCRIPTION OF DRAWINGS

[0036] FIG. 1 is a chart illustrating the Residual Pressure of a Comparative Sample (without the organophosphate compound) labeled as “Unstabilized” and of Formulation 1 (with the organophosphate compound) labeled as “Stabilized”, both as a function of Temperature.

DETAILED DESCRIPTION

[0037] As used herein, the term "alkyl" means a saturated straight chain, branched chain, or cyclic hydrocarbon radical, including but not limited to, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, pentyl, n-hexyl, and cyclohexyl.

[0038] As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon radical containing one or more six-membered carbon rings in which the unsaturation may be represented by three conjugated double bonds, which may be substituted one or more of carbons of the ring with hydroxy, alkyl, alkenyl, halo, haloalkyl, or amino, including but not limited to, phenoxy, phenyl, methylphenyl, dimethylphenyl, trimethylphenyl, chlorophenyl, trichloromethylphenyl, aminophenyl, and tristyrylphenyl.

[0039] As used herein, the term "alkylene" means a divalent saturated straight or

branched chain hydrocarbon radical, such as for example, methylene, dimethylene, trimethylene.

[0040] As used herein, the term "alkoxyl" means an oxy radical that is substituted with an alkyl group, such as for example, methoxyl, ethoxyl, propoxyl, isopropoxyl, or butoxyl, which may optionally be further substituted on one or more of the carbon atoms of the radical.

[0041] As used herein, the term "alkoxyalkyl" means an alkyl radical that is substituted with one or more alkoxy substituents, more typically a (C_1-C_{22})alkyloxy-(C_1-C_6)alkyl radical, such as methoxymethyl, and ethoxybutyl.

[0042] As used herein, the term "alkenyl" means an unsaturated straight or branched hydrocarbon radical, more typically an unsaturated straight, branched, (which, in one particular embodiment, is C_1-C_{75}) hydrocarbon radical, that contains one or more carbon-carbon double bonds, such as, for example, ethenyl, n-propenyl, iso-propenyl.

[0043] As used herein, the term "arylalkyl" means an alkyl group substituted with one or more aryl groups, more typically a (C_1-C_{18})alkyl substituted with one or more (C_6-C_{14})aryl substituents, such as, for example, phenylmethyl, phenylethyl, and triphenylmethyl.

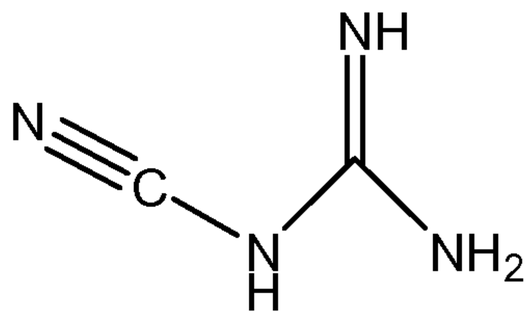
[0044] As used herein, the term "aryloxy" means an oxy radical substituted with an aryl group, such as for example, phenyloxy, methylphenyl oxy, isopropylmethylphenyloxy.

[0045] As used herein, the terminology "(C_r-C_s)" in reference to an organic group, wherein r and s are each integers, indicates that the group may contain from r carbon atoms to s carbon atoms per group.

[0046] In one embodiment, non-limiting examples of nitrification inhibitors comprise any one or more of N-2,5-dichlorophenyl succinamic acid, dicyandiamide (DCD), zinc ethylene-bis-dithiocarbamate, 2,4,6-triehloroaniline, pentachlorophenol, thio-urea, ammonium thiosulphate (ATS) or 3,4-dimethypyrazole phosphate (DMPP).

[0047] In one embodiment, non-limiting examples of urease inhibitors comprise any one or more of N-butyl thiophosphoric triamide (NBPT), N-(w-butyl)phosphoric triamide, miophosphoryl triamide, cyclohexyl phosphoric triamide, cyclohexyl thiophosphoric triamide, phosphoric triamide, hydroquinone, p-benzoquinone, hexamidocyclotriphosphazene, thiopyridines, thiopyrimidines, thiopyridine-N-oxides, N,A'-dihalo-2-imidazolidinone, N-halo-2- oxazolidinone, ammonium thiosulphate (ATS), N-cyclohexyl phosphoric triamide (CHPT), phenyl phosphorodiamidate (PPT) and 2-nitrophenyl phosphoric triamide (2- NPT).

[0048] Dicyandiamide is a known compound according to formula (I):



(I).

[0049] Dicyandiamide, also known as “2-cyanoguanidine”, is typically made by treating cyanamide with base and is commercially available.

[0050] In one embodiment, the compositions according to the present invention comprise a urease inhibitor, such as an alkyl thiophosphoric triamide or ammonium thiosulfate, a nitrification inhibitor, or a combination of both a urease inhibitor and a nitrification inhibitor.

[0051] In one embodiment, alkyl thiophosphoric triamide is N-(n-butyl)-thiophosphoric triamide (“NBPT”). The at least one of alkyl thiophosphoric triamide or dicyandiamide (or combination thereof) can be present in the liquid agricultural composition at a lower range of 2% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at a lower range of 3% by weight of the composition. The at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at a lower range of 5% by

weight of the composition.

[0052] In another embodiment, at least one of alkyl thiophosphoric triamide or dicyandiamide (or a combination of both) can be present in the liquid agricultural composition at a lower range of 0.5%, or 1%, or 2%, or 3%, or 4%, or 5%, 6%, or 8%, or 10% or 12 % or 14%, by weight of the composition. The at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 75%, or 65%, or 60% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 60% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 55% by weight of the composition. In another embodiment, at least one of alkyl thiophosphoric triamide and/or dicyandiamide can be present in the liquid agricultural composition at an upper range of 59%, or 57%, or 55% or 53 % or 50%, by weight of the composition. In another embodiment, at least one of alkyl thiophosphoric triamide and/or dicyandiamide can be present in the liquid agricultural composition at an upper range of 48%, or 46%, or 45% or 42 % or 40%, by weight of the composition.

[0053] In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 70% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 65% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 60% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 55% by weight of the composition. In another

embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 40% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 35% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 30% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide or combination thereof can be present in the liquid agricultural composition at an upper range of 25% by weight of the composition.

[0054] In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the liquid agricultural composition in an amount between about 7% by weight of the composition to about 55% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the composition in an amount between about 8% by weight of the composition to about 50% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the liquid agricultural composition in an amount between about 7% by weight of the composition to about 45% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the liquid agricultural composition in an amount between about 7% by weight of the composition to about 40% by weight of the composition. In another embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the liquid agricultural composition in an amount between about 7% by weight of the composition to about 35% by weight of the composition.

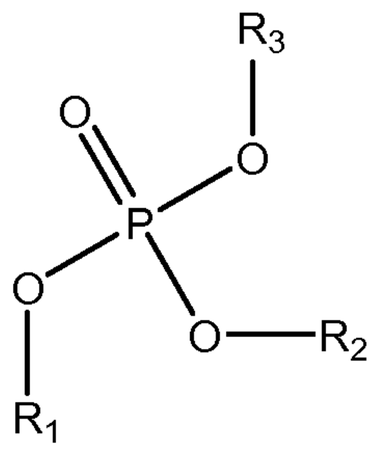
[0055] The at least one of alkyl thiophosphoric triamide or dicyandiamide can be present in the composition in an amount between about 0.5 % by weight of the composition and about 60 % by weight of the composition or, in another embodiment, can be present in

the composition in an amount between about 1 % by weight of the composition and about 40 % by weight of the composition, and, in another embodiment, can be present in the composition in an amount between about 0.5 % by weight of the composition and about 20 % by weight of the composition. In one particular embodiment, the at least one of alkyl thiophosphoric triamide or dicyandiamide is present in the composition in an amount between about 1 % by weight of the composition and about 30 % by weight of the composition. The at least one of alkyl thiophosphoric triamide or dicyandiamide means that alkyl thiophosphoric triamide can be solely present, dicyandiamide can be solely present, or a combination of both alkyl thiophosphoric triamide and dicyandiamide are present.

[0056] Compounds suitable as the organic solvent component of the composition and methods of the present invention are organophosphate solvents according to formula (VIII) (wherein R_1, R_2 and R_3 are as described above), polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, or mixtures thereof, that form liquid, or otherwise stable, compositions with the nitrification and/or urease inhibitor, at temperatures of from -16 ºC to 54 ºC, in other embodiments, -10 ºC to 40 ºC, in other embodiments, -5 ºC to 40 ºC, in other embodiments, -2ºC to 40 ºC, or in other embodiments, 0 ºC to 40 ºC.

[0057] In another embodiment, compounds suitable as the organic solvent component of the composition and methods of the present invention are organophosphate solvents according to formula (VIII) (wherein R_1, R_2 and R_3 are as described above), polar aprotic solvents, amine solvents, heterocyclic alcohol solvents, or mixtures thereof, that form liquid, or otherwise stable, compositions with the nitrification and/or urease inhibitor at temperatures at or greater than -16 ºC, in alternative embodiments, greater than -14 ºC, in other embodiments, greater than -12 ºC, in other embodiments, greater than -10 ºC, in further embodiments, greater than -8 ºC, in other embodiments, greater than -5 ºC, in other embodiments, greater than -3 ºC, in other embodiments, greater than -2 ºC, in other embodiments, greater than 0 ºC, in other embodiments, greater than 2 ºC, in other embodiments, greater than 4 ºC, in other embodiments, greater than 5 ºC.

[0058] In some embodiments, at the specified temperature ranges or at greater than a specified temperature (as described herein), the liquid agricultural composition or liquid fertilizer composition is stable, meaning the urease and/or nitrification inhibitor(s) do not react with the solvent or solvent component under anticipated manufacturing, storage, and use conditions. In one embodiment, at the specified temperature ranges or at greater than a specified temperature (as described herein), the liquid agricultural composition or liquid fertilizer composition is stable, meaning the liquid agricultural composition or liquid fertilizer composition is or substantially is in one phase, i.e., no visible crystals, no visible precipitation, and/or no visible multiple liquid phases. In one embodiment, at the specified temperature ranges or at greater than a specified temperature (as described herein), the described liquid fertilizer composition is stable, meaning the degradation of the inhibitor component (which in one embodiment is NBPT) is slowed or delayed as compared with a fertilizer composition without the stabilizer or stabilizing component as described herein. In one embodiment, the stabilizer or stabilizing component is an organophosphate solvent of formula (VIII):



(VIII)

[0059] wherein R1, R2 and R3, are each independently chosen from H, a C1-C16 alkyl group, a C1-C16 alkenyl, group, a C1-C16 alkoxyalkyl group, a C7-C30 alkylarylalkyl group, a C7-C30 arylalkyl group, or an aryl group; provided that at least one of R1, R2 or R3 is not H. In one embodiment, R1, R2 and R3, are each independently a C1-C16 alkyl group. In one embodiment, R1, R2 and R3, are each independently a C1-C8 alkyl group. In one embodiment, R1, R2 and R3, are each independently a C1-C4 alkyl group. In one embodiment, R1, R2 and R3, are each independently a C1-C2 alkyl group.

[0060] In some embodiments, at high temperature ranges or at greater than a specified temperature (as described herein), the liquid agricultural composition or liquid fertilizer composition is stable, meaning the urease and/or nitrification inhibitor(s) do not react with the solvent or solvent component under anticipated manufacturing, storage, and use conditions. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 25°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 27°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 29°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 30°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 32°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 34°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 35°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 37°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 40°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 42°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 44°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 45°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 47°C. In one embodiment, the liquid agricultural compositions or liquid fertilizer compositions are stable at a temperature greater than 50°C.

[0061] In one embodiment, at the specified temperature ranges or at greater than a

specified temperature (as described herein), the liquid agricultural composition or liquid fertilizer composition is stable, meaning the liquid agricultural composition or liquid fertilizer composition is or substantially is in one phase, i.e., no visible crystals, no visible precipitation, and/or no visible multiple liquid phases. In another embodiment, the liquid agricultural composition or liquid fertilizer composition is stable, meaning the liquid agricultural composition or liquid fertilizer composition is or substantially is in one phase and shows little or slight discoloration.

[0062] In one embodiment, the solvent comprises at least one of an organophosphate solvent according to formula (VIII) (wherein R_1, R_2 and R_3 are as described above), a polar aprotic solvent, amine solvent, heterocyclic alcohol solvent, or mixtures thereof in which dicyandiamide has a solubility at 25 ºC of greater than or equal to 50 grams per liter (g/l), more typically greater than or equal to 200 g/l. In one embodiment, the solvent comprises at least one of an organophosphate solvent according to formula (VIII) (wherein R_1, R_2 and R_3 are as described above), optionally, with one or more co-solvents, in which in inhibitor component has a solubility at 25 ºC of greater than or equal to 240 grams per liter (g/l), or in other embodiments, greater than or equal to 220 g/l, or in other embodiments, greater than or equal to 280 g/l, or in other embodiments, greater than or equal to 300 g/l, or in other embodiments, greater than or equal to 340 g/l, or in other embodiments, greater than or equal to 360 g/l, or in other embodiments, greater than or equal to 380 g/l. Reference to “inhibitor component” includes at least one nitrification inhibitor, or in some embodiments, at least one urease inhibitor, or in alternative embodiments, a combination of at least one urease inhibitor and at least one nitrification inhibitor. In one particular embodiment, the inhibitor component comprises a combination of NBPT and DCD.

[0063] Suitable polar aprotic organic solvents include, for example, dichloromethane, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, ethyl acetate, hexamethylphosphoramide, dimethyl sulfone, sulfolane, 1,3-dimethyl-2-imidazoidinone, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone, methyl acetate, ethyl lactate, methylpyrrolidone, tetrahydrofuran, propylene carbonate, and dibasic ester solvents.

[0064] In one embodiment, the formulations as described herein further comprise one or more stabilizers. In one embodiment, the organophosphate compound of formula (VIII) is a stabilizer.

In one embodiment, the organophosphate compound of formula (VIII), when added to the formulations/compositions as described herein, provides stability to the formulation over a period of at least 24 hours. In one embodiment, the organophosphate compound of formula (VIII), when added to the formulations/compositions as described herein, provides stability to the formulation over a period of at least 48 hours. In a further embodiment, the organophosphate compound of formula (VIII), when added to the formulations/compositions as described herein, provides stability to the formulation over a period of at least 72 hours. In another embodiment, the organophosphate compound of formula (VIII), when added to the formulations/compositions as described herein, provides stability to the formulation over a period of at least 4 days, or at least 5 days, or at least 6 days, or at least 7 days, or at least 8 days, or at least 9 days, or at least 10 days, or at least 11 days, or at least 12 days. In a further embodiment, the organophosphate compound of formula (VIII), when added to the formulations/compositions as described herein, provides stability to the formulation over a period of at least 14 days.

[0065] Suitable dibasic ester solvents include, for example, dialkyl esters of dicarboxylic acids, more typically, the di(C_1-C_{12})alkyl esters of saturated linear or branched (C_2-C_8)aliphatic carboxylic acids or a mixture thereof. In one embodiment, the dibasic ester component comprises one or more compounds according to structure (II):

$R^1OOC\text{-}A\text{-}CONR^2R^3$ (II)

wherein:

A is a divalent linear or branched (C_2-C_8)aliphatic group, and

R^1, R^2, and R^3 are each independently $(C_1\text{-}C_{12})$alkyl, $(C_1\text{-}C_{12})$aryl, $(C_1\text{-}C_{12})$alkaryl or $(C_1\text{-}C_{12})$arylalkyl, and R^2 and R^3 may each optionally be substituted with one or more hydroxyl groups.

[0066] In one embodiment, the dibasic ester solvent component of the compositions and methods of the present invention comprises one or more dimethyl esters of saturated linear or branched $(C_4\text{-}C_6)$aliphatic carboxylic acids, such the dimethyl ester of succinic acid, dimethyl ester of ethyl succinic acid, the dimethyl ester of glutaric acid, the dimethyl ester of methyl glutaric acid, and the dimethyl ester of adipic acid, and mixtures thereof. In one embodiment, the dibasic ester component comprises the dimethyl ester of succinic acid, the dimethyl ester of glutaric acid, and optionally, the dimethyl ester of adipic acid, In another embodiment, the dibasic ester component comprises the dimethyl ester of ethyl succinic acid, the dimethyl ester of methyl glutaric acid, and optionally, the dimethyl ester of adipic acid.

[0067] In one embodiment, the dibasic ester solvent component of the compositions and methods of the present invention comprises one or more dialkyl esters of saturated linear or branched $(C_4\text{-}C_6)$aliphatic carboxylic acids, such the dialkyl ester of succinic acid, dialkyl ester of ethylsuccinic acid, the dialkyl ester of glutaric acid, the dialkyl ester of methylglutaric acid, and the dialkyl ester of adipic acid, and mixtures thereof. In one embodiment, the dibasic ester component comprises the dialkyl ester of succinic acid, the dialkyl ester of glutaric acid, and optionally, the dimethyl ester of adipic acid, In another embodiment, the dibasic ester component comprises the dialkyl dimethyl ester of ethylsuccinic acid, the dialkyl ester of methylglutaric acid, and optionally, the dialkyl ester of adipic acid. Each alkyl group in the dialkyl group, one embodiment, individually comprise a $C_1\text{-}C_8$ alkyl. In another embodiment, each alkyl group in the dialkyl group, one embodiment, individually comprise a $C_1\text{-}C_4$ alkyl. In another embodiment, each alkyl group in the dialkyl group, one embodiment, individually comprise a $C_1\text{-}C_6$ alkyl.

[0068] Suitable amine solvents include primary amines, including monoalkylamines,

such as propylamine, secondary amines, including dialkyl amines and diaryl amines, such as dimethylamine and diphenylamine, and tertiary amines, such as diethylene triamine and methyl-5-(dimethylamino)-2-methyl-oxopentanoate.

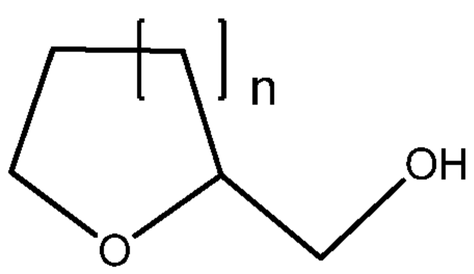
[0069] In one embodiment, the amine solvent component of the compositions and methods of the present invention is selected from aliphatic or aromatic primary, secondary, or tertiary amines that do not comprise any functional group other than one or more amino groups.

[0070] In one embodiment, the amine solvent component of the compositions and methods of the present invention is selected from aliphatic or aromatic primary, secondary, or tertiary amines may optionally further comprise one or more additional functional groups, such as hydroxyalkyl groups, hydroxyl groups, carbonyl groups, or alkyl ester groups, other than one or more amino groups.

[0071] In one embodiment, the organic solvent component of the compositions and methods of the present invention comprises an amino alcohol. Compounds suitable as the amino alcohol solvent component of the compositions and methods of the present invention are those compounds that comprise at least one primary, secondary, or tertiary amino moiety per molecule and at least one hydroxyalkyl moiety per molecule, more typically In one embodiment, the amino alcohol is a linear, branched, or cyclic, saturated or unsaturated hydrocarbon that is substituted on at least one carbon atom with an amino group and on at least one other carbon atom with hydroxyalkyl or hydroxyl group, such as monoethanolamine, ethylaminoethanol, dimethylaminoethanol, isopropylaminoethanol, diethanolamine, triethanolamine, methylaminoethanol, aminopropanol, methylaminopropanol, dimethylaminopropanol, aminobutanol, dimethylaminobutanol, aminobutanediol, trihydroxymethylaminoethane, diethylaminopropanediol, 1-amino-cyclopentane methanol, and aminobenzyl alcohol, or a heterocyclic ring that comprises at least one nitrogen atom as a ring member and/or is substituted on at least one carbon atom with an amino group and that is substituted on at least one other carbon atom with a hydroxyalkyl or hydroxyl group, such as

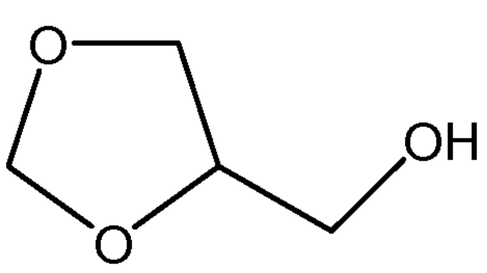
methylaminomethyl-1,3-dioxolane.

[0072] Suitable heterocyclic alcohol solvents include, for example, 5- or 6-membered heterocyclic rings that include 1 or 2 oxygen atoms as ring member, that are substituted on at least one carbon atom of the ring with a (C_1-C_6)hydroxyalkyl group, and that may optionally be substituted on one or more carbon atoms of the ring with one or more (C_1-C_4)alkyl groups. It is understood that the term heterocyclic alcohol includes dioxolane compounds. In one embodiment, the heterocyclic alcohol component of the present invention comprises a one or more compounds selected from heterocyclic alcohols according to structures (IV), (IVa), (V), (VI), and (VII):

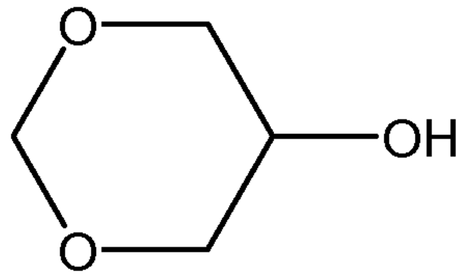


(IV)

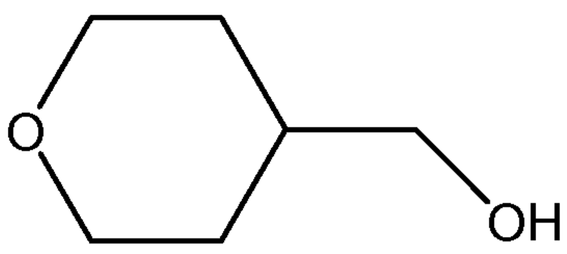
wherein n = 1 or 2,



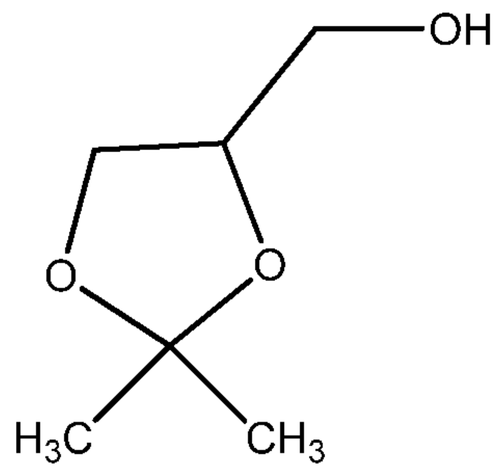
(IVa)



(V)



(VI)

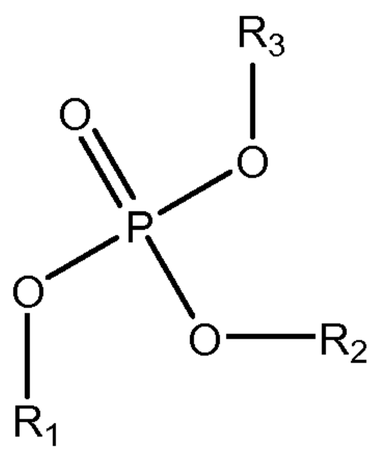


(VI).

[0073] In one embodiment, the organic solvent component of the composition and methods of the present invention comprises one or more organophosphate solvents as described herein, polar aprotic solvents, one or more dibasic ester compounds according to structure (II), one or more amino alcohols, one or more tertiary amines, one or more heterocyclic alcohols according to structure (III), or mixtures thereof.

[0074] In one embodiment, the organic solvent component of the composition and methods of the present invention comprises dimethyl sulfoxide, dimethyl formamide, the dimethyl ester of succinic acid, dimethyl ester of ethyl succinic acid, the dimethyl ester of glutaric acid, the dimethyl ester of methyl glutaric acid, and the dimethyl ester of adipic acid, diethylene triamine, or monoethanolamine, methyl-5-(dimethylamino)-2-methyl-oxopentanoate, dimethylaminoethanol, triethanol amine, a heterocyclic alcohol according to structure (III), or a mixture thereof.

[0075] In one embodiment, the organic solvent component of the liquid agricultural composition comprises at least one organophosphate compound having the formula (VIII)



(VIII),

[0076] wherein wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H. In another embodiment, R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{12} alkyl group, a C_1-C_{12} alkenyl, group, a C_1-C_{12} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H. In one embodiment, R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_4 alkyl group, a C_4-C_8 alkyl group, a C_1-C_{12} alkenyl, group, a C_1-C_4 alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H. In one embodiment, the organophosphate compound of formula (VIII) is the stabilizer.

[0077] In yet another embodiment, R_1, R_2 and R_3, are each independently chosen from a linear or branched C_1-C_{12} alkyl group, a linear or branched C_1-C_{12} alkenyl, group, a linear or branched C_1-C_{12} alkoxyalkyl group, a linear or branched C_7-C_{30} alkylarylalkyl group, a linear or branched C_7-C_{30} arylalkyl group, or an aryl group. In one embodiment, R_1, R_2 and R_3, are each independently chosen from a C_1-C_{12} alkyl group, more typically, a C_2-C_8 alkyl group.

[0078] In one embodiment, R_1, R_2 and R_3, are each independently a C_1-C_3 alkyl group, typically an ethyl group. In another embodiment, R_1, R_2 and R_3, are each independently a branched C_1-C_{12} alkyl group, typically, a 2-ethylhexyl group. In one embodiment, R_1, R_2 and R_3, are each independently a C_1-C_{12} alkoxyalkyl group, typically a butoxyethyl group.

[0079] In one embodiment, the organic solvent component of the composition and methods of the present invention comprises dimethyl sulfoxide, dimethyl formamide, diethylene triamine, monoethanolamine, or a mixture thereof.

[0080] In one embodiment, the organic solvent component of the composition and methods of the present invention comprises a mixture of at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above, and dimethyl sulfoxide.

[0081] In one embodiment, a compound utilized as the solvent or as a component in the solvent blend is a compound of general formula (II):

$R_3OOC\text{-}A\text{-}CONR_4R_5$

(II),

[0082] According to one embodiment, the expression "compound" denotes any compound corresponding to the general formula (II). In other embodiments, the term "compound" also refers to mixtures of several molecules corresponding to general

formula (II). It may therefore be a molecule of formula (II) or a mixture of several molecules of formula (II), wherein both fall under the definition of the term “compound” when referring to formula (II).

[0083] The R_3, R_4 and R_5 groups can be, in some embodiments, identical or, in other embodiment, different. In one embodiment, may be groups chosen from C_1-C_{20} alkyl, aryl, alkaryl or arylalkyl groups or the phenyl group. In another embodiment, may be groups chosen from C_1-C_{12} alkyl, aryl, alkaryl or arylalkyl groups or the phenyl group. Mention is made especially of Rhodiasolv® PolarClean (Manufactured by Rhodia Inc. of Cranbury, NJ). The R_4 and R_5 groups may optionally be substituted. In one particular embodiment, the groups are substituted with hydroxyl groups.

[0084] In one embodiment, R_3 group is chosen from methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, isoamyl, n-hexyl, cyclohexyl, 2-ethylbutyl, n-octyl, isooctyl, 2-ethylhexyl, tridecyl groups.

[0085] R_4 and R_5 groups, which are identical or different, in one embodiment, may especially be chosen from methyl, ethyl, propyl (n-propyl), isopropyl, n-butyl, isobutyl, n-pentyl, amyl, isoamyl, hexyl, cyclohexyl or hydroxyethyl groups. The R_4 and R_5 groups may also be such that they form, together with the nitrogen atom, a morpholine, piperazine or piperidine group. According to some embodiments, R_4 and R_5 are each methyl, or R_4 and R_5 are each ethyl, or R_4 and R_5 are each hydroxyethyl.

[0086] According to one embodiment, if A comprises a linear group of formula -- CH_2-- CH_2-- and/or of formula -- CH_2-- CH_2-- CH_2-- CH_2-- and/or of formula --(CH_2)$_8$-- then it is a mixture of A groups. According to one particular embodiment, if A is linear, then it is a mixture of A groups, for example a mixture of two or three -- CH_2-- CH_2-- (ethylene); -- CH_2-- CH_2-- CH_2-- (n-propylene); and -- CH_2-- CH_2-- CH_2-- CH_2-- (n-butylene) groups (or isomers thereof).

[0087] According to a first particular embodiment of the invention, the A group is a

divalent linear alkyl group chosen from the groups of the following formulae: -- CH_2-- CH_2-- (ethylene); -- CH_2-- CH_2-- CH_2-- (n-propylene); -- CH_2-- CH_2-- CH_2-- CH_2-- (n-butylene), and mixtures thereof.

[0088] In one embodiment, the inhibitor composition of the present invention comprises, based on 100 parts by weight ("pbw") of the composition:
[0089] from about 4 to about 60 pbw, more typically from about 10 to about 55 pbw, and even more typically from about 20 to about 40 pbw dicyandiamide, and
[0090] from about 55 to about 96 pbw, more typically from about 58 to about 90 pbw, and even more typically from about 60 to about 80 pbw of the organic solvent.

[0091] In one embodiment, the inhibitor composition of the present invention comprises one or more urease inhibitors, such as, for example, NBPT or ammonium thiosulfate.

[0092] The nitrogenous fertilizer compound is treated with the inhibitor composition by contacting the nitrogenous fertilizer composition with the inhibitor composition described herein (e.g., nitrification inhibitor or urease inhibitor or a combination of both). The nitrogenous fertilizer composition may be in solid or liquid form.

[0093] Suitable nitrogenous fertilizers are those containing a nitrogenous compound such as urea, nitrate salts, ammonium salt, or a mixture thereof, such as ammonium nitrate, ammonium sulfate, ammonium thiosulfate, ammonium polysulfide, ammonium phosphates, ammonium chloride, ammonium bicarbonate, anhydrous ammonia, calcium nitrate, nitrate soda, calcium cyanamide. In one embodiment, the nitrogenous fertilizer comprises ammonium nitrate. Suitable ammonium nitrate-containing fertilizers include, for example, UAN 18, UAN 28, and UAN 30.

[0094] In one embodiment, the nitrogenous fertilizer composition is in solid particulate form, and the contacting of the nitrogenous fertilizer composition with the inhibitor composition is conducted by, for example, spraying the composition of the present invention on the particles of solid fertilizer composition.

[0095] In one embodiment, the concentrated fertilizer composition of the present invention is a solid nitrification-inhibited fertilizer composition that comprises, based on 100 pbw of the composition:

from about 60 pbw to about 99.999, more typically from about 70 pbw to about 99.999, and even more typically from about 80 pbw to about 99.999 solid particles of one or more nitrogenous fertilizer compounds, and

from about 0.001 to about 40 pbw, more typically from about 0.001 to about 30 pbw, and even more typically from about 0.001 to about 20 pbw, dicyandiamide.

[0096] In one embodiment, the solid nitrification-inhibited fertilizer composition of the present invention further comprises one or more urease inhibitors, more typically NBPT.

[0097] In one embodiment, the end use fertilizer composition of the present invention is made by combining the inhibitor composition of the present invention with a solid nitrogenous fertilizer to form a solid nitrification–inhibited fertilizer composition and subsequently dissolving the solid nitrification-inhibited fertilizer composition in an aqueous medium, typically water, in a ratio of up to about 500 pbw, more typically from 100 to 500 pbw and even more typically from about 100 to about 300 pbw, of the aqueous medium per 1 pbw of the solid nitrification-inhibited fertilizer composition.

[0098] In one embodiment, the fertilizer compound is in liquid form and the contacting of the fertilizer composition with the inhibitor composition is conducted by mixing the inhibitor composition with the liquid fertilizer composition .

[0099] In one embodiment, the concentrated fertilizer composition of the present invention is a concentrated liquid nitrification-inhibited fertilizer composition that comprises, based on 100 pbw of the composition:

from about 20 to about 99.989 pbw, more typically from about 30 to about 99.985 pbw, and even more typically from about 40 to about 99.98 pbw of one or more nitrogenous fertilizer compounds,

from about 0.001 to 40 pbw, more typically from about 0.005 to 30 pbw, and even more typically from about 0.01 to 20 pbw dicyandiamide, and

from about 0.01 to 60 pbw, more typically from about 0.01 to about 40 pbw, and even more typically from about 0.01 to about 30 pbw of the organic solvent or solvent mixture, as described herein.

[00100] In one embodiment, the concentrated liquid nitrification-inhibited fertilizer composition of the present invention further comprises one or more urease inhibitors, more typically NBPT.

[00101] In one embodiment, the end use fertilizer composition of the present invention is made by combining the inhibitor composition of the present invention with a concentrated nitrogenous fertilizer to form a concentrated liquid nitrification-inhibited fertilizer composition and subsequently diluting the concentrated liquid nitrification-inhibited fertilizer composition with an aqueous medium, typically water in a ratio of up to about 500 pbw, more typically from about 10 to about 500 pbw and even more typically from about 100 to about 300 pbw, of the aqueous medium per 1 pbw concentrated liquid nitrogenous fertilizer composition.

[00102] In one embodiment, the end use fertilizer composition of the present invention is made by combining the inhibitor composition of the present invention, a solid or concentrated liquid nitrogenous fertilizer, and an aqueous medium.

[00103] In one embodiment, the end use fertilizer composition of the present invention is an aqueous liquid composition that comprises water, one or more nitrogenous fertilizer compounds, and dicyandiamide, typically in an amount of from 2 x 10^{-6} pbw to about4 pbw dicyandiamide per 100 pbw of the end use fertilizer composition.

[00104] In one embodiment, the end use fertilizer composition of the present invention comprises water and based on 100 parts by weight of the composition:

from about 0.04 to about 10 pbw, more typically from about 0.06 to about 10 pbw, and even more typically from about 0.08 pbw to about 10 pbw to of one or more nitrogenous fertilizer compounds,

from about 2×10^{-6} to about 4 pbw, more typically from about 1×10^{-5} to about 3 pbw, and even more typically from about 2×10^{-4} to about 2 pbw dicyandiamide, and

from about 2×10^{-4} to about 6 pbw, more typically from about 2×10^{-4} to about 4 pbw, and even more typically from about 2×10^{-4} to about 3 pbw of the organic solvent.

[00105] In one embodiment, the end use fertilizer composition of the present invention comprises one or more urease inhibitors, more typically NBPT, alone or in combination with the nitrification inhibitor.

[00106] In one embodiment, the end use fertilizer composition of the present invention comprises from about 0.001 to about 5 pbw, more typically from about 0.01 to about 2 pbw dicyandiamide per 100 pbw of the one or more nitrogenous fertilizer compounds.

[00107] In one embodiment, the end use fertilizer composition is applied to target plants or to an environment for the target plants, i.e., to ground on or within which the target plants are growing or to be grown, at a rate of from about 0.01 pounds to about 5 pounds of the fertilizer composition, more typically from about 0.05 pounds to about 2 pounds of the fertilizer composition, per 100 square feet of ground.

[00108] In one embodiment, the end use fertilizer composition is applied to target plants or to an environment for the target plants at a rate effective to provide a dosage of nitrogenous fertilizer compound of from about 0.01 pounds to about 5 pounds of fertilizer compound, more typically from about 0.05 pounds to 2 pounds of fertilizer compound, per 100 square feet of ground.

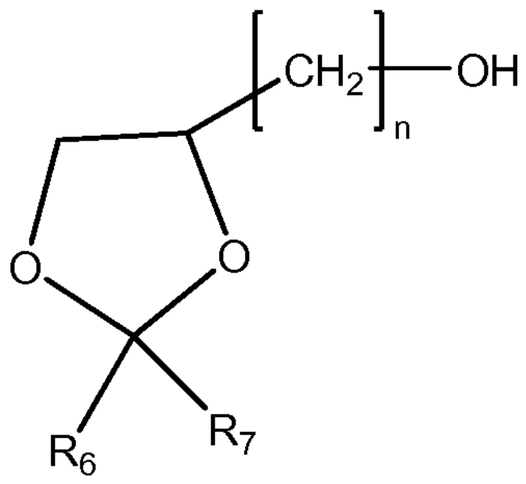
[00109] In one embodiment, the end use fertilizer composition is applied to target

plants or to an environment for the target plants at a rate effective to provide a dosage of dicyandiamide of from about 0.01 pounds to 5 pounds of dicyandiamide, more typically from about 0.05 pounds to 2 pounds of dicyandiamide, per 1000 square feet of ground.

[00110] The composition of the present invention provides improved ease of handling of dicyandiamide, improved solubility characteristics, low toxicity of the organic solvents; good storage characteristics, and excellent miscibility with aqueous compositions, such as aqueous nitrogenous fertilizer formulations.

[00111] In one embodiment the composition comprises, by weight of composition, at least 50 wt% of DCD and/or NBPT, the remainder being solvent or a mixture of solvents. By way of example, in one embodiment, the fertilizer composition comprises, by weight of composition, at least 50 wt% of NBPT and less than or equal to 50 wt% of a solvent blend of DMSO and at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. By way of another example, in one embodiment, the fertilizer composition comprises, by weight of composition, at least 50 wt% of DCD and 50 wt% of a solvent blend of DMSO and at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. By way of another example, in one embodiment, the fertilizer composition comprises, by weight of composition, at least 50 wt% of DCD and less than or equal to 50 wt% of at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. Optionally, other components such as dyes and the like can be added.

[00112] In one embodiment the composition comprises, by weight of composition, at least 25 wt% or 30 wt% of DCD and/or NBPT, the remainder being solvent or a mixture of solvents. By way of example, in one embodiment, the fertilizer composition comprises, by weight of composition, at least 25 wt% of a combination of DCD and NBPT and less than or equal to 70 wt% of a solvent blend of: (i) at least one dioxolane compound of formula (III):



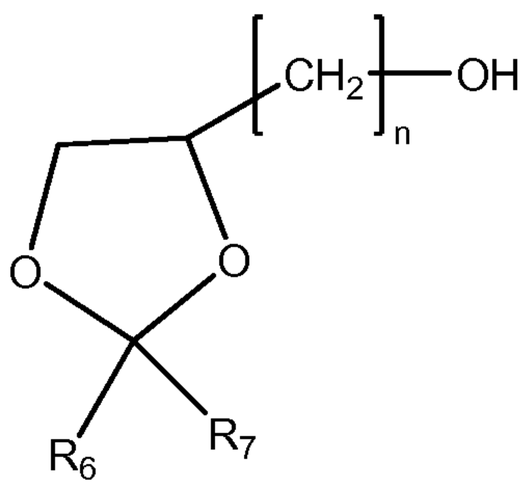
(III),

[00113] wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10; and

[00114] (ii) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. Optionally, other components such as dyes and the like can be added.

[00115] By way of example, in another embodiment, the fertilizer composition comprises, by weight of composition, at least 25 wt%, typically as least 30 wt%, of a combination of DCD and NBPT, and less than or equal to 70 wt% of a solvent blend of:

(i) at least one dioxolane compound of formula (III):



(III),

[00116] wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10; and

[00117] (ii) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above. Optionally, other components such as dyes and the like can be added.

[00118] In one embodiment the composition comprises, by weight of composition, greater than 40 pbw of DCD and/or NBPT, the remainder being solvent or a mixture of solvents.

[00119] In one embodiment the composition comprises, by weight of composition, greater than 35 pbw of DCD and/or NBPT, the remainder being solvent or a mixture of solvents.

[00120] In one embodiment the composition comprises, by weight of composition, greater than 45 pbw of DCD and/or NBPT, the remainder being solvent or a mixture of solvents. By way of example, in one embodiment, the fertilizer composition comprises, by weight of composition, 45 wt% of DCD and 55 wt% of a solvent blend of: (i) at least one dioxolane compound of formula (III), wherein R_6 and R_7 are as described above; and
(ii) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above.

[00121] In one embodiment the composition comprises, by weight of composition, greater than 55 pbw of DCD and/or NBPT, the remainder being solvent or a mixture of solvents. By way of example, in one embodiment, the fertilizer composition comprises, by weight of composition, at least 55 wt% of DCD and/or NBPT and less than or equal to 45 wt% of a solvent blend of: (i) at least one dioxolane compound of formula (III), wherein R_6 and R_7 are as described above; and
(ii) at least one organophosphate solvent according to formula (VIII), wherein R_1, R_2 and R_3 are as described above.

[00122] Experiments:

[00123] Formulation 1

DV-10607

Components	wt% (by weight of total formulation)
NBPT	50.0
DMSO	39.7
TEP	9.9
Blue Dye	0.24
Yellow Dye	0.16
Total	100

[00124] Formulation 2

DV-10662	
Components	wt% (by weight of total formulation)
DCD	24.0
NBPT	6.0
DMSO	68.2
TEP	1.5
Blue Dye	0.18
Yellow Dye	0.12
Total	100

[00125] A Comparative Sample was prepared with the same NBPT and solvent source as Formulation 1, except the Comparative Sample did not contain TEP as a stabilizer. Both Formulation 1 and the Comparative Sample were set aside at 45 °C for 2 weeks. It was observed that both Formulation 1 and the Comparative Sample showed color evolution, as both started colorless. After 2 weeks it was observed that the Comparative Sample turned a dark amber color. However, Formulation 1 turned a slight yellow, transparent color, which indicated a lower NBPT degradation curve versus the Comparative Example, which did not containing the stabilizer.

[00126] Referring to FIG. 1, both Formulation 1 and the Comparative Sample were analyzed by ARC (Accelerated Rate Calorimetry) up to 100 °C in a stainless steel test

cell using standard HWS (Heat-wait-search mode) methodology. Test were performed under an air atmosphere. An onset of ~76 °C was determined for the unstabilized sample (i.e., the Comparative Sample), while no onset was determined for the stabilized one (i.e., Formulation 1). It is believed that this onset is an exotherm reaction giving an indication of instability. Referring back to FIG. 1, a chart illustrates the residual pressure of a Comparative Sample (without the organophosphate compound, i.e., unstabilized) and of Formulation 1 (with the organophosphate compound, i.e., stabilized), both as a function of Temperature.

[00127] Lower residual pressure is an indication of lower volatile components, an indirect measure of degradation. In other words, there were less volatile components measured for the Stabilized formulation (Formulation 1) over the temperature range as compared to the Comparative Sample. The measurement of less volatile components over the temperature range indicates that less NBPT is degraded in Formulation 1 as compared to the Comparative Sample (i.e., more NBPT was degraded in the Comparative Sample). This supports the visual observation of the two samples after 2 weeks at 45 °C, in which the Comparative Sample turned a much darker color, indicating more degradation of NBPT related to Formulation 1.

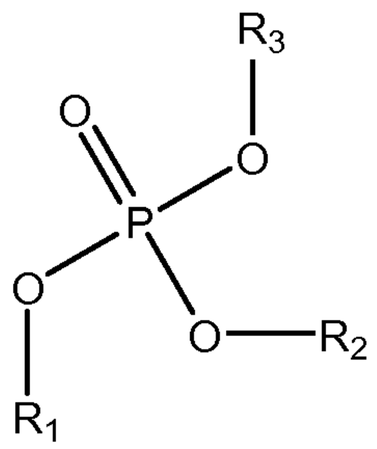
CLAIMS

What is claimed is:

1. A liquid agricultural composition comprising

-at least one of a nitrification inhibitor, a urease inhibitor or a mixture thereof;

-an organophosphate solvent of formula (VIII):

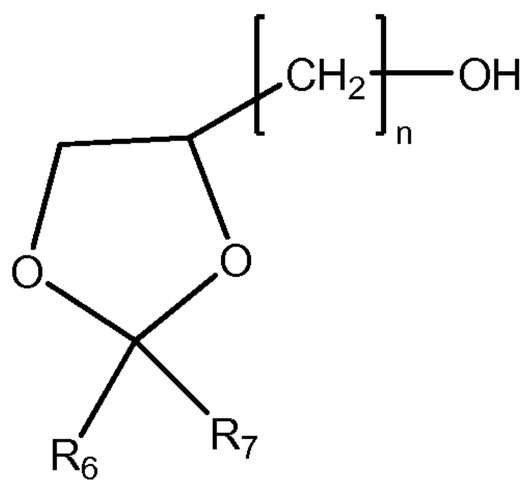


(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H; and

-optionally, at least one co-solvent selected from:

(a) at least one dioxolane compound of formula (III):



(III),

wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10;

b) at least one dibasic ester;

c) at least one compound of formula (IIa):

$R_3OOC\text{-}A\text{-}CONR_4R_5$

(IIa),

wherein R_3 comprises a C_1-C_{36} alkyl group; wherein R_4 and R_5 individually comprise a C_1-C_{36} alkyl group, wherein R_4 and R_5 can optionally together form a ring; and wherein A is a linear or a branched divalent C_2-C_6 alkyl group;

d) at least one alkyldimethylamide;

e) at least one alkyl lactate;

f) ethyl levulinate;

g) at least one alkyoxyalcohol, ether alcohol, amine alcohol, amino alcohol or alcohol;

h) at least one glycerine or glycerine derivative;

i) at least one alkylene carbonate; or

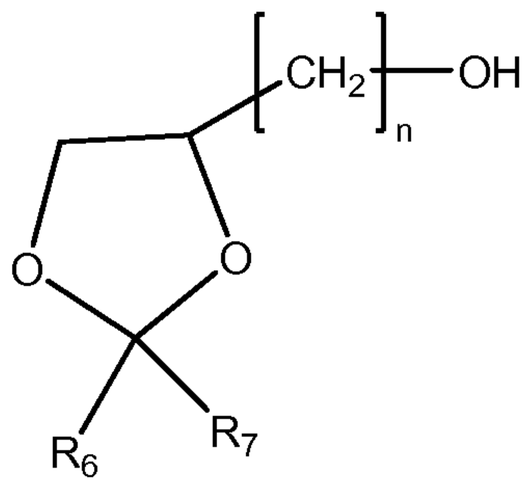
j) dimethylsulfoxide.

2. The liquid agricultural composition of claim 1 wherein the nitrification inhibitor is dicyandiamide.

3. The liquid agricultural composition of claim 1 wherein the urease inhibitor is N-(n-

butyl)-thiophosphoric triamide.

4. The liquid agricultural composition of claim 1 wherein the at least one co-solvent is present and comprises at least one dioxolane compound of formula (III):



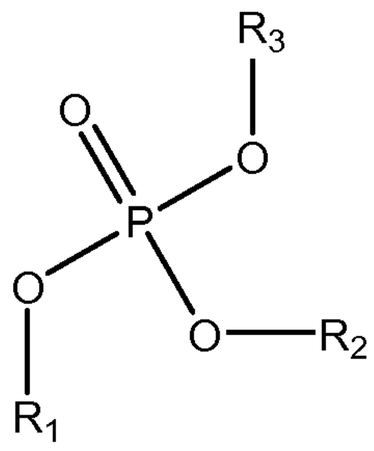
(III),

wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10.

5. The liquid agricultural composition of claim 1 wherein the composition comprises:

-at least one nitrification inhibitor;

-an organophosphate solvent of formula (VIII):



(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H; and

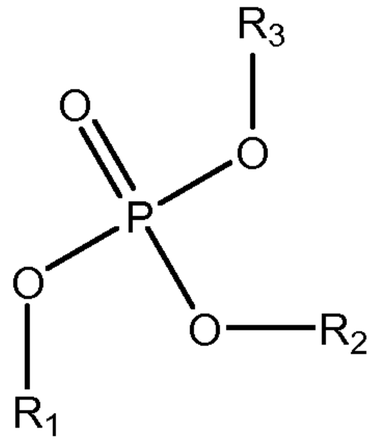
-dimethylsulfoxide.

6. The liquid agricultural composition of claim 1 wherein the at least one of a nitrification inhibitor, a urease inhibitor or a mixture thereof is present up to 65 wt%, by total weight of composition.

7. The liquid agricultural composition of claim 1 wherein the at least one of a nitrification inhibitor, a urease inhibitor or a mixture thereof is present up to 55 wt%, by total weight of composition.

8. The liquid agricultural composition of claim 1 wherein the at least one of a nitrification inhibitor, a urease inhibitor or a mixture thereof is present up to 50 wt%, by total weight of composition.

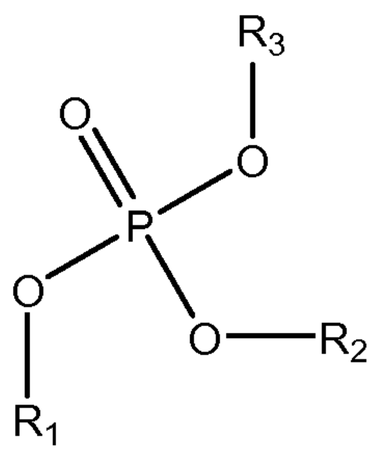
9. The liquid agricultural composition of claim 1 wherein the organophosphate solvent is of formula (VIII):



(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group.

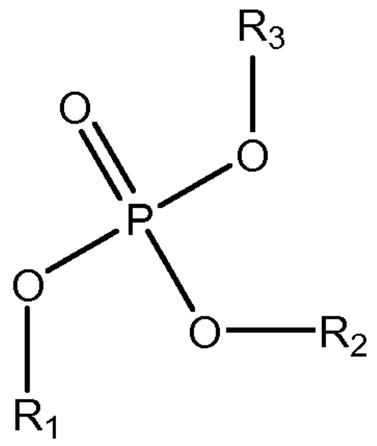
10. A method of making a solid or concentrated liquid fertilizer composition comprising treating one or more nitrogenous fertilizer compounds with a liquid inhibitor composition that comprises at least one of a dicyandiamide or an alkyl thiophosphoric triamide, the inhibitor composition dispersed in a liquid medium comprising at least one solvent of formula (VIII):



(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H.

11. The method of claim 10 wherein the organophosphate solvent is of formula (VIII):



(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group.

12. The method of claim 10 wherein the liquid medium further comprises dimethylsulfoxide.

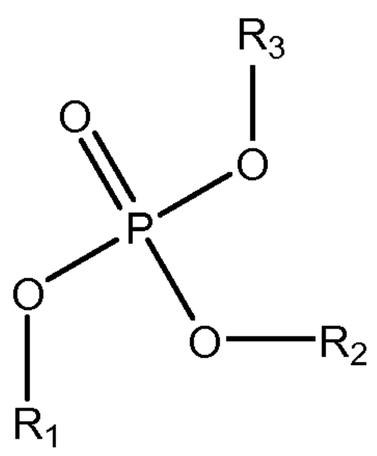
13. The method of claim 10 wherein the liquid inhibitor composition further comprises at least one stabilizer.

14. A concentrated liquid fertilizer composition comprising, based on 100 parts by weight of the composition:

(a) up to about 99 parts by weight of one or more nitrogenous fertilizer compounds,

(b) at least one of a dicyandiamide or an alkyl thiophosphoric triamide,

(c) at least one organophosphate solvent of formula (VIII):

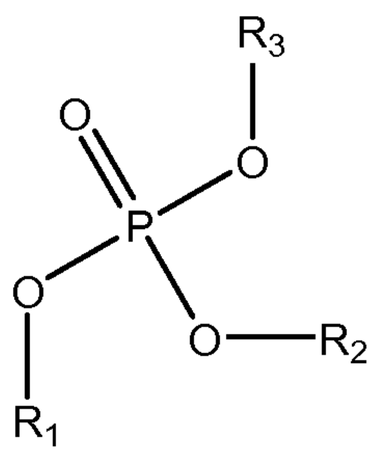


(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H, and

(d) optionally, at least one co-solvent.

15. The concentrated liquid fertilizer composition of claim 14 wherein the organophosphate solvent is of formula (VIII):

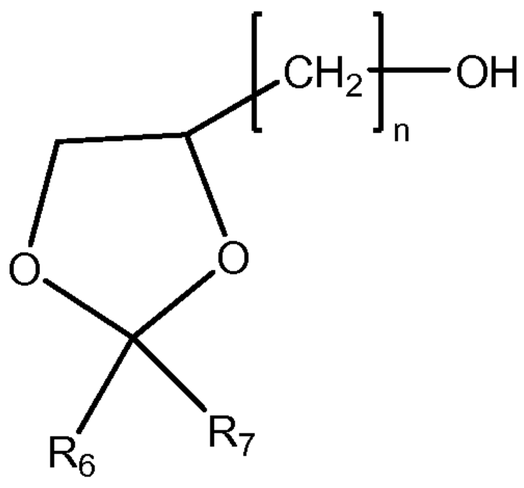


(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group.

16. The concentrated liquid fertilizer composition of claim 14 wherein the at least one co-solvent of (d) is present and comprises:

(a) at least one dioxolane compound of formula (III):



(III),

wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10;

b) at least one dibasic ester;

c) at least one compound of formula (IIa):

$R_3OOC\text{-}A\text{-}CONR_4R_5$

(IIa),

wherein R_3 comprises a C_1-C_{36} alkyl group; wherein R_4 and R_5 individually comprise a C_1-C_{36} alkyl group, wherein R_4 and R_5 can optionally together form a ring; and wherein A is a linear or a branched divalent C_2-C_6 alkyl group;

d) at least one alkyldimethylamide;

e) at least one alkyl lactate;

f) ethyl levulinate;

g) at least one alkyoxyalcohol, ether alcohol, amine alcohol, amino alcohol or alcohol;

h) at least one glycerine or glycerine derivative;

i) at least one alkylene carbonate;

j) dimethylsulfoxide; or

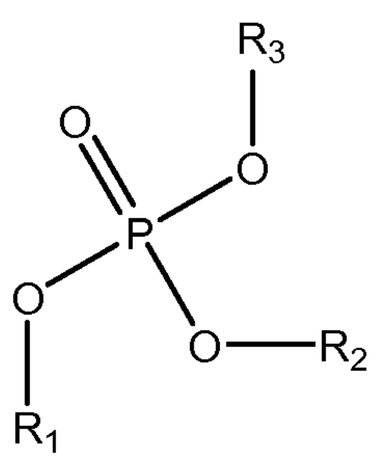
k) any combination thereof.

17. The concentrated liquid fertilizer composition of claim 14, comprising:

(a) up to about 99 parts by weight of one or more nitrogenous fertilizer compounds,

(b) an alkyl thiophosphoric triamide,

(c) at least one organophosphate solvent of formula (VIII):

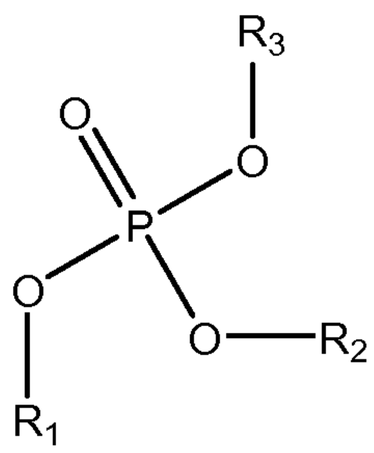


(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H, and

(d) dimethylsulfoxide.

18. A method of making an aqueous end use fertilizer composition comprising contacting one or more nitrogenous fertilizer compounds with an inhibitor composition, the inhibitor compositing comprising at least one of a dicyandiamide or an alkyl thiophosphoric triamide, dispersed in a liquid medium comprising at least one solvent of formula (VIII):

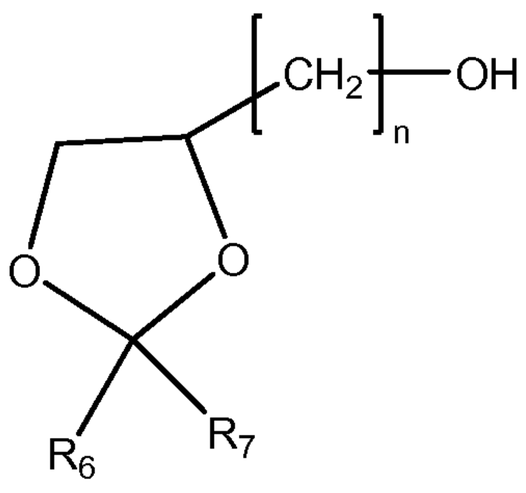


(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from H, a C_1-C_{16} alkyl group, a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; provided that at least one of R_1, R_2 or R_3 is not H.

19. The method of claim 18 wherein the liquid medium further comprises at least one co-solvent selected from:

(a) at least one dioxolane compound of formula (III):



(III),

wherein R_6 and R_7 individually comprises a hydrogen, an alkyl group, an alkenyl group, or a phenyl group, wherein n is an integer of from 1 to 10;

b) at least one dibasic ester;

c) at least one compound of formula (IIa):

R_3OOC-A-$CONR_4R_5$

(IIa),

wherein R_3 comprises a C_1-C_{36} alkyl group; wherein R_4 and R_5 individually comprise a C_1-C_{36} alkyl group, wherein R_4 and R_5 can optionally together form a ring; and wherein A is a linear or a branched divalent C_2-C_6 alkyl group;

d) at least one alkyldimethylamide;

e) at least one alkyl lactate;

f) ethyl levulinate;

g) at least one alkyoxyalcohol, ether alcohol, amine alcohol, amino alcohol or alcohol;

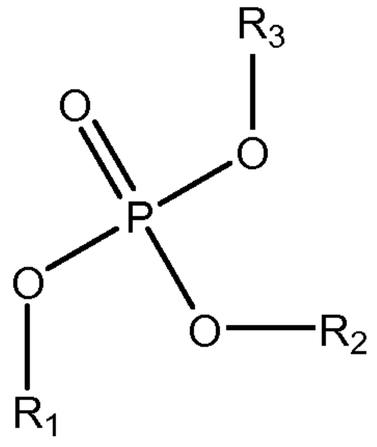
h) at least one glycerine or glycerine derivative;

i) at least one alkylene carbonate; or

j) dimethylsulfoxide.

20. The method of claim 18 wherein the liquid medium comprises:

-at least one solvent of formula (VIII):



(VIII)

wherein R_1, R_2 and R_3, are each independently chosen from a C_1-C_{16} alkyl group,

a C_1-C_{16} alkenyl, group, a C_1-C_{16} alkoxyalkyl group, a C_7-C_{30} alkylarylalkyl group, a C_7-C_{30} arylalkyl group, or an aryl group; and

-dimethylsulfoxide.

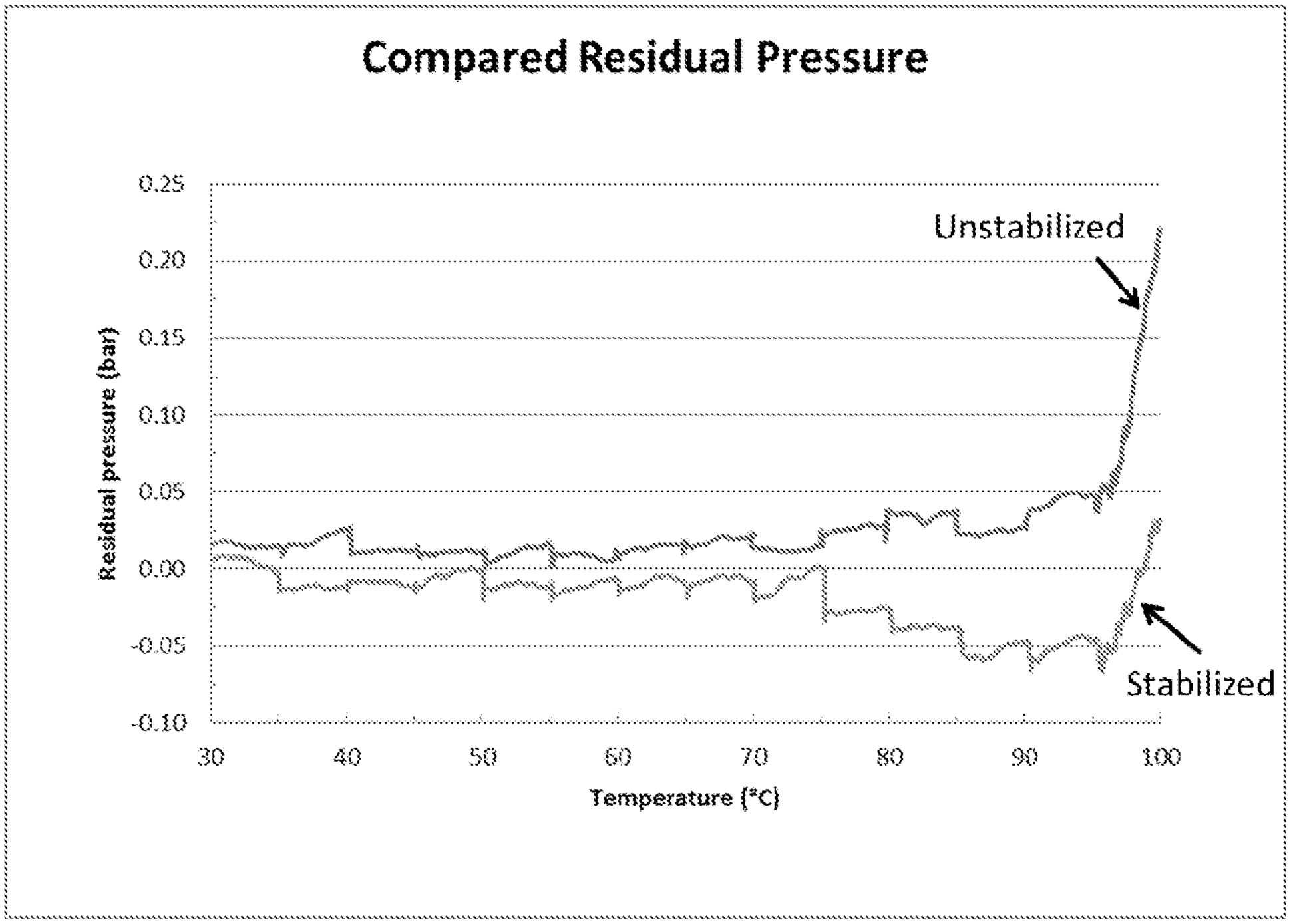

Compared Residual Pressure
Residual pressure (bar)
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
Unstabilized
Stabilized
30
40
50
60
70
80
90
100
Temperature (°C)

FIG. 1