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(54) Title: COMPOSITIONS AND METHODS FOR IMPROVING THE COMPATIBILITY OF WATER SOLUBLE HERBICIDE SALTS

(57) Abstract: Methods and compositions for improving the compatibility of aqueous herbicide solutions containing at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, and a water soluble salt of glyphosate by adding a surface active compatibilizer are provided.

COMPOSITIONS AND METHODS FOR IMPROVING THE COMPATIBILITY OF WATER SOLUBLE HERBICIDE SALTS

BACKGROUND

Aqueous concentrate formulations of pesticidal and plant growth modifying chemicals are widely used in agricultural, industrial, recreational, and residential areas worldwide. The active ingredients of such concentrates frequently contain acid functional groups such as carboxylic or phosphonic acids, more commonly in the form of their water soluble salts. An aqueous concentrate is essentially a solution of the active ingredient in water at relatively high concentration, intended for dilution in water prior to application by spraying or other means. Typically the aqueous concentrate is diluted in about 10 to about 500 times its own volume of water prior to application.

In today's agrochemical market with the continued demand for improved productivity it is increasingly common to combine more than one formulated product in a spray tank in order to achieve the optimal spectrum of control, efficacy, and delivery efficiency of the products. In doing this, however, spray tank incompatibilities between products can occur when components of a spray tank mixture or solution chemically or physically interact to cause an adverse effect on the stability, homogeneity, or other properties of the spray tank mixture that would reduce the effectiveness of the spray applied product. The incompatibility of a spray tank mixture or solution may physically manifest itself through the formation of crystalline precipitates, surface scum, oily droplets, gels, excessive foam or clumps of solid matter, and may result in clogged spray nozzles or screens.

Compatible aqueous pesticide mixtures or solutions are defined as those mixtures or solutions that, when formed by the combination or mixing of one or more pesticide products and/or other commonly used ingredients, result in a homogeneous liquid with little or no solids precipitation or phase separation and the retention of their full biological efficacy.

SUMMARY

Methods are described for improving the compatibility of aqueous herbicide solutions including at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, or a water soluble salt of glyphosate by adding to the aqueous herbicide solution one or more surface active compatibilizers.

Further, aqueous herbicide solutions of improved compatibility that include at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, or a water soluble salt of glyphosate, and one or more surface active compatibilizers also are provided.

Additionally, dry herbicide compositions including a water soluble salt of 2,4-D and/or a water soluble salt of glyphosate, and one or more surface active compatibilizers also are provided.

DETAILED DESCRIPTION

Aqueous herbicide solutions containing at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, and a water soluble salt of glyphosate, and one or more surface active compatibilizers and methods of creating such solutions are provided. The aqueous herbicide solutions described herein have improved compatibility over previously known aqueous herbicide solutions containing water soluble salts of aryloxyalkanoic acids, water soluble salts of pyridyloxyalkanoic acids, and/or water soluble salts of glyphosate that do not contain the surface active compatibilizers described herein. The surface active compatibilizers described herein maintain the homogeneity of the described solutions by suppressing the formation of solids or phase separations. These surface active compatibilizers are especially useful when inorganic or organo ammonium cations are present and provide compatibilization without the need to raise the pH of the solution.

Aqueous solutions containing a water soluble salt of an aryloxyalkanoic acid, such as salts of 2,4-D, can have compatibility issues leading to the formation of precipitated solids under conditions where the acid equivalent (ae) concentration is about 0.3 weight percent or higher, the pH is about 6.5 or lower, and there is a sufficient concentration of inorganic cations such as, for example, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Fe^{2+}, Fe^{3+}, and the like. The exact conditions necessary for the formation of precipitated solids from these solutions of 2,4-D salts will also depend on the temperature and hardness of the water used and the actual composition and concentrations of the components in the solution. For example, a spray tank mixture made from concentrates of DMA®-6 herbicide (Dow AgroSciences LLC, Indianapolis, IN; 2,4-D dimethyl ammonium salt solution with a pH value of about 7) at a rate of 800 g ae/hectare and Roundup WeatherMax® herbicide (Monsanto, St. Louis, MO; glyphosate potassium salt solution with a pH value of about 4.7) at 840 g ae/hectare and a spray volume of about 47 liters/hectare would have a pH value of about 5 and will be incompatible and result in the significant formation of solids.

The common practice of adding ammonium sulfate to aqueous herbicide spray mixtures containing glyphosate to improve herbicide performance may also lead to compatibility problems. For example, if a herbicide such as 2,4-D dimethyl ammonium (DMA) is present in a spray mixture containing glyphosate to which ammonium sulfate has been added, crystallization of solids can occur if the pH and the 2,4-D concentration are in the ranges just described.

Methods and compositions for improving the compatibility of aqueous herbicide solutions containing at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, and a water soluble salt of glyphosate, and further including one or more surface active compatibilizers are provided. Surface active compatibilizers useful in the aqueous herbicide solutions described herein include, for example, 1) polyvinylpyrrolidones and copolymers or grafted polymers thereof; 2) polyvinyl alcohols and copolymers or grafted polymers thereof; 3) polymethacrylates grafted with polyethylene oxide side chains; 4) polyacrylates grafted with polyethylene oxide side chains; 5) polymeric amphoteric dispersants; 6) ethylene oxide-propylene oxide block copolymers; 7) synthetic latexes; 8) sulfonated lignins (also known as lignosulfonates); and mixtures of any of the surface active compatibilizers described herein. The surface active compatibilizer can be in the form of a salt such as, for example, an organic amine salt or salts containing inorganic cations. Examples of organic amine salts include organo ammonium salts. Examples of organo ammonium cations present in such salts include monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof. Examples of useful inorganic cations include, for example, ammonium, sodium, potassium, magnesium, and calcium. It is possible for the surface active compatibilizer in the form of a salt to partially be in its acid form, e.g., partially with a hydrogen cation rather than an organo amine or other cation. The surface active compatibilizer may include one or more carboxylic, sulfonic, or phosphonic acid groups attached to the polymer and these acid groups may exist in a salt form.

As used herein, the term copolymer refers to a chain-like macromolecule formed by the polymerization of two or more different monomer units in a random or block arrangement. The term grafted polymer as used herein refers to a chain-like macromolecule formed by the polymerization of a single monomer which is further reacted (grafted) with one or more chain-like molecules of different chemistry to form side chains or branches at a random or regular arrangement on the chain-like polymer backbone structure. Such grafted polymers may include ethylenically unsaturated carboxylic acid monomer units in the chain-like polymer backbone.

Suitable surface active compatibilizers for use in the methods and compositions described herein include, polvinylpyrrolidones (such as Agrimer® 15, 30, 60, 90), polvinylpyrrolidones grafted with alkyl chains (such as Agrimer®AL-10, AL-25, AL-22, AL30), vinylpyrrolidone-vinylacetate copolymers (such as, Agrimer® VA 3, VA 6, VA5, VA7), and vinylpyrrolidone-styrene block copolymers such as Agrimer® ST, the Agrimer® products being available from International Specialty Products, a division of Ashland (Wayne, NJ); polyvinyl alcohols, copolymers, and derivatives thereof such as Erkol®M05/290 and M05/190 which are available from Celanese (Dallas, TX); polymethacrylate polymers grafted with polyethylene oxide side chains such as Atlox®4913 and polymeric amphoteric dispersants such as Atlox® 4915 which are both available from Croda (Edison, NJ); and ethylene oxide-propylene oxide block copolymers such as Pluronic®F-68 and Tetronic®304 which are available from BASF (Florham Park, NJ).

Suitable synthetic latexes for use in the methods and compositions described herein include acrylic, styrene-butadiene, acrylonitrile-butadiene-styrene, polyvinyl acetate, and vinyl-acrylic latexes of which UCAR™ Latex 162 and ENCOR™ 162 latex are examples and are available from Arkema, Inc. (King of Prussia, PA).

Surface active compatibilizers for use in the methods and compositions described herein also include sulfonated lignins, also known as lignosulfonates, which are byproducts produced in the kraft or sulfite processes used to prepare delignified wood pulp used in making paper. Suitable lignosulfonates include, but are not limited to, Borresperse NA, Borresperse CA, Ultrazine NA, Ultrazine CA, Norlig A, Norlig TSD, Ufoxane 3A, Ufoxane 2 and Marasperse AG, all of which are available from Borregaard Lignotech USA

(Rothschild, WI). Especially suitable examples of these lignosulfonates include Polyfon® F, H, O, and T, also Reax® 83A, 85A, 907, and 910, all of which are available from MeadWestvaco (Charleston, SC), and combinations of one or more of a lignosulfonate with a sodium naphthalene sulfonate such as Kraftsperse® DD-6, also available from MeadWestvaco. The sulfonated lignins described herein may also include one or more inorganic alkaline cations selected from, but not limited to, hydrogen, ammonium, sodium, and calcium, and one or more organo ammonium cations selected from, but not limited to, monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline).

Water soluble salts of aryloxyalkanoic acids as described herein include, for example, 2,4-D ((2,4-dichlorophenoxy)acetic acid), 2,4-DB, dichloroprop, mecoprop, MCPA, and MCPB. Pyridyloxyalkanoic acids as described herein include, for example, triclopyr and fluroxypyr. The water soluble salts of the aryloxyalkanoic acids and the pyridyloxyalkanoic acids include those containing an organo ammonium cation such as, for example, monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof. Aqueous solutions containing the water soluble salts of an aryloxyalkanoic acids or a pyridyloxyalkanoic acid may include herbicidal spray solutions or herbicide concentrates.

The methods and compositions described herein for improving the compatibility of aqueous herbicide solutions may also be used with aqueous solutions containing water soluble salts of arylcarboxylic acid and/or heteroarylcarboxylic acid herbicides such as aminopyralid, clopyralid, dicamba, picloram, and the like.

Water soluble salts of glyphosate as described herein include those salts where the cation is selected from potassium, sodium, and ammonium, also organo ammonium such as, for example, isopropyl ammonium, dimethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, triethanol ammonium, choline, and the like, and trimethylsulfonium cation, and mixtures thereof.

The inorganic cations as described herein are those that when present in appreciable amounts or concentrations may cause aqueous solutions of the water soluble salts of an aryloxyalkanoic acid, a pyridyloxyalkanoic acid, an arylcarboxylic acid, and/or a heteroarylcarboxylic acid (optionally containing glyphosate) to become incompatible and form solids. These inorganic cations include, for example, alkali metal cations, such as sodium and potassium; alkaline earth metal cations, such as calcium and magnesium; transition metal cations, such as manganese, copper, zinc and iron; and ammonium. Aqueous solutions containing water soluble salts of 2,4-D and glyphosate at pH levels below about pH 6.5 tend to be more incompatible in the presence of appreciable concentrations of inorganic cations than are such solutions at higher pH levels.

The term appreciable concentration of inorganic cations as used herein refers to the concentration of inorganic cations present in an aqueous herbicide solution containing at least one of a soluble salt of an aryloxyalkanoic acid, a soluble salt of a pyridyloxyalkanoic acid, a soluble salt of an arylcarboxylic acid, a soluble salt of a heteroarylcarboxylic acid, and glyphosate that will lead to the precipitation of solids from that solution if all of the other conditions necessary for incompatibility of the solution exist, such as the composition and concentration of the herbicidal carboxylic acid salt present in the solution, and the temperature, hardness, and pH of the water. For example, a concentration of glyphosate potassium of about 0.8 weight percent (wt%) on an acid equivalent (ae) basis or higher in an aqueous solution at room temperature containing greater than about 0.8 wt% of 2,4-D DMA on an ae basis and made with water with a hardness of 342 parts per million (ppm) and with a final pH of about 5 will be incompatible. The compatibility of such a herbicide solution will depend, in addition to the other factors discussed herein, on the total concentration and actual composition of the inorganic cations present in the solution.

Ingredients that may contribute inorganic cations to the aqueous herbicide solutions described herein may include, but are not limited to, products or aqueous solutions containing fertilizers, micronutrients, hard water, co-formulation ingredients, and the like, as well as, water soluble salts of glyphosate containing inorganic cations such as, for example, potassium, sodium, and ammonium.

Fertilizers are optionally included in the methods and compositions described herein and may be dispersed or dissolved in water and may contain inorganic cations such as, for example, ammonium, and potassium, in sufficient amounts so as to cause incompatibility problems when mixed with an aqueous solution containing the water soluble salt of at least one of an aryloxyalkanoic acid, a pyridyloxyalkanoic acid, an arylcarboxylic acid, a heteroarylcarboxylic acid, and glyphosate. The amount of fertilizer that may be optionally included in the methods and compositions described herein is less than or equal to 30 percent, less than or equal to 28 percent, less than or equal to 26 percent, less than or equal to 24 percent, less than or equal to 22 percent, less than or equal to 20 percent, less than or equal to 18 percent, less than or equal to 16 percent, less than or equal to 14 percent, less than or equal to 13 percent, less than or equal to 12 percent, less than or equal to 11 percent, less than or equal to 10 percent, less than or equal to 9 percent, less than or equal to 8 percent, less than or equal to 7 percent, less than or equal to 6 percent, less than or equal to 5 percent, less than or equal to 4.5 percent, less than or equal to 4 percent, less than or equal to 3.5 percent, less than or equal to 3 percent, less than or equal to 2.5 percent, less than or equal to 2 percent, less than or equal to 1.5 percent, or less than or equal to 1 percent. Fertilizers may include, but are not limited to, ammonium sulfate (AMS), ammonium phosphate, ammonium nitrate, solutions of ammonium nitrate and urea which are commonly referred to in the art as 28% N or 32% N or UAN, ammonium thiosulfate, potassium nitrate, potassium phosphate, potassium chloride, potassium carbonate, and the like, and mixtures thereof. In addition to their fertilizer properties, AMS and UAN are commonly used as spray adjuvants or water conditioning agents with glyphosate herbicide treatments in order to improve biological efficacy. Thus, AMS is often mixed with glyphosate and the methods and compositions described herein can be used to improve compatibility when these solutions are combined with aqueous herbicide solutions containing a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, a water soluble salt of an arylcarboxylic acid and/or a water soluble salt of a heteroarylcarboxylic acid.

Micronutrients may include one or more nutrients essential to plant growth and health that are only needed in very small quantities and may contain, among other things, one or more inorganic cations such as, for example, the cations of manganese, copper, iron, molybdenum, and zinc. Such micronutrients may be added to aqueous herbicide spray solutions containing a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, a water soluble salt of an arylcarboxylic acid, a water soluble salt of a heteroarylcarboxylic acid, and/or a water soluble salt of glyphosate for economical delivery to crop plants. Compatibility problems of these aqueous herbicide spray solutions may occur if the conditions for incompatibility of these solutions exist as described herein.

Organo ammonium cations that may cause incompatibility in the aqueous herbicide solutions described herein, particularly in concentrates and pre-mix concentrates, include monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof.

Co-formulation ingredients include those products or ingredients that contain inorganic cations and may be selected from one or more of adjuvants, antifoam agents, antimicrobial agents, buffering agents, corrosion inhibitors, defoaming agents, deposition agents, dispersants, dyes, freezing point depressants, neutralizing agents, penetration aids, sequestering agents, spray drift control agents, spreading agents, stabilizers, sticking agents, suspension aids, viscosity-modifying additives, wetting agents, and the like.

The surface active compatibilizers described herein may be used to improve the compatibility of aqueous herbicide solutions containing a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, a water soluble salt of an arylcarboxylic acid, a water soluble salt of a heteroarylcarboxylic acid, and/or a water soluble salt of glyphosate in spray tank mixtures, concentrates, or pre-mix concentrates. In aqueous spray tank mixtures, the surface active compatibilizer described herein may comprise, with respect to the aqueous herbicide spray solution of improved compatibility, from about 0.01 to about 5 weight percent, from about 0.01 to about 4 weight percent, from about 0.01 to about 3 weight percent, from about 0.01 to about 2 weight percent, from about 0.01 to about 1 weight percent, from about 0.05 to about 2 weight percent, from about 0.05 to about 1 weight percent, from about 0.05 to about 0.5 weight percent, from about 0.1 to about 0.4 weight percent, from about 0.15 to about 0.3 weight percent, or from about 0.15 to about 0.25 weight percent. In aqueous concentrates and aqueous pre-mix concentrates, the surface active compatibilizer described herein may comprise, with respect to the aqueous herbicide solution of improved compatibility, from about 0.05 to about 10 weight percent, from about 0.05 to about 8 weight percent, from about 0.05 to about 6 weight percent, from about 0.1 to about 5 weight percent, from about 0.2 to about 5 weight percent, from about 0.3 to about 5 weight percent, from about 0.4 to about 5 weight percent, from about 0.5 to about 5 weight percent, from about 0.5 to about 4 weight percent, from about 0.5 to about 3 weight percent, from about 1 to about 3 weight percent, or from about 1.5 to about 2.5 weight percent.

In some instances the surface active compatibilizers described herein can contain inorganic ions that could add to the concentration of inorganic ions already present in an aqueous herbicide solution as described herein and may cause incompatibility in such a solution. In such cases, the surface active compatibilizer chosen should be able to compatibilize such a solution containing an increased inorganic ion concentration after addition of the surface active compatibilizer. Alternatively, a surface active compatibilizer that does not contain inorganic cations such as, for example, a lignosulfonate where the sulfonic acid groups are in the acid or organo ammonium salt form or a surface active compatibilizer that does not contain chemical functional groups that can form salts can be used. Such surface active compatibilizers that do not contain inorganic cations may be particularly useful for improving the storage stability of aqueous herbicide concentrates and pre-mix concentrates in ambient and sub-ambient temperature conditions.

Without intending to be bound by theory, the surface active compatibilizers described herein are believed to improve the compatibility of aqueous herbicide solutions comprised of at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, a water soluble salt of an arylcarboxylic acid, a water soluble salt of a heteroarylcarboxylic acid and a water soluble salt of glyphosate, a suitable concentration of one or more inorganic cations, and a pH of less than about 6.5 by preventing or inhibiting the crystallization or precipitation of solids. The relative effectiveness of the surface active compatibilizers in preventing the formation of these solids can be estimated by measuring the on-set pH of crystallization (OSPOC) of the solids in a titration analysis procedure. The OSPOC of a particular composition can be measured, for example, by titrating a solution of an aryloxyalkanoic or a pyridyloxyalkanoic acid salt of an inorganic cation such as, for example, the potassium salt of 2,4-D with a strong acid such as, for example, sulphuric acid until solids or crystals begin forming at a particular pH value (the OSPOC). The lower the OSPOC observed with the use of any particular surface active compatibilizer described herein, the better it may perform at preventing crystallization in, and therefore improving the compatibility of, an aqueous herbicide solution as described herein.

Alternatively, the relative effectiveness of the surface active compatibilizers described herein at improving the compatibility of the aqueous herbicide solutions described herein can be determined by measuring the Critical Crystallization Concentration (CCC) of the aryloxyalkanoic acid salt, the pyridyloxyalkanoic acid salt, the arylcarboxylic acid salt, or the heteroarylcarboxylic acid salt of an inorganic cation such as, for example, the potassium salt of 2,4-D in a tank mix solution. The CCC of a particular composition can be measured by preparing saturated and over saturated solutions or mixtures of the composition and then measuring the concentration of the particular herbicidal carboxylic acid remaining in solution. The higher the CCC observed with the use of a particular surface active compatibilizer, the better it may perform at preventing crystallization in, and therefore improving the compatibility of, the aqueous herbicide solutions described herein.

The aqueous herbicide solutions described herein that may be compatibilized using the surface active compatibilizers described herein include concentrates, pre-mix concentrates, and spray solutions prepared by diluting such a concentrate or pre-mix concentrate, or by tank mixing multiple components of a spray solution. The aqueous herbicide concentrate or pre-mix concentrate may comprise the use of, with respect to the total composition, from about 0.05 to 10 weight percent, from 0.05 to 8 weight percent, from 0.05 to 6 weight percent, from 0.1 to 5 weight percent, from 0.2 to 5 weight percent, from 0.3 to 5 weight percent, from 0.4 to 5 weight percent, from 0.5 to 5 weight percent, from 0.5 to 4 weight percent, from 0.5 to 3 weight percent, from 1 to 3 weight percent, or from 1.5 to 2.5 weight percent of one or more of the surface active compatibilizers described herein and from about 20 to about 60 weight percent on an acid equivalent basis of at least one of a water soluble salt of an aryloxyalkanoic acid (such as 2,4-D), a water soluble salt of a pyridyloxyalkanoic acid (such as triclopyr), a water soluble salt of an arylcarboxylic acid (such as dicamba), a water soluble salt of a heteroarylcarboxylic acid (such as aminopyralid) and a water soluble salt of glyphosate, or a pre-mix containing one or more of these salts. The aqueous herbicide concentrate or pre-mix concentrate of improved compatibility is preferably a solution containing the surface active compatibilizer dissolved or dispersed in the concentrate which upon dilution in water with products or solutions and at conditions that are normally prone to cause incompatibility as described herein, forms a herbicide spray solution of improved compatibility. The herbicide spray solution of improved compatibility may also be prepared by tank mixing the individual components of the spray solution at the point of use. Such a spray solution may also be combined with or diluted with products or solutions and at conditions that are normally prone to cause incompatibility, as described herein, to form a herbicide spray solution of improved compatibility.

Use of the surface active compatibilizers as described herein in aqueous spray solutions containing soluble salts of 2,4-D, soluble salts of glyphosate, and inorganic cations provides solutions of improved compatibility at pH levels below about 6.5. Additionally, improved compatibility can be provided below about pH 5.5. Further, improved compatibility can be provided below about pH 5.

A compatible aqueous spray solution containing the water soluble salts of glyphosate and 2,4-D can be prepared by adding the aqueous soluble concentrates of the salts of glyphosate and 2,4-D to an aqueous solution containing one or more of the described surface active compatibilizers. Other co-formulation ingredients such as water soluble or water dispersible ingredients including, but not limited to, dispersing agents, wetting agents, spray drift reduction agents, fertilizers, and antifoam agents, may optionally be added to the spray solution.

An example of improving the compatibility of a spray solution at a pH below about 6.5 containing water soluble salts of glyphosate and 2,4-D, and inorganic cations using the methods described herein includes:

a) preparing a solution in water containing, with respect to the final spray solution, from about 0.01 to about 5 weight per cent of a surface active compatibilizer, such as, for example, Polyfon®O;

b) adding an aqueous concentrate of 2,4-D DMA to the solution prepared in a) to provide a solution comprising, with respect to the final spray solution, from about 0.3 to about 5 weight per cent of 2,4-D on an acid equivalent (ae) basis;

c) adding an aqueous concentrate of Roundup WeatherMax® herbicide (an aqueous concentrate containing glyphosate potassium salt) (Monsanto, St.Louis, MO) to the solution prepared in b) to provide a solution comprising, with respect to the final spray solution, from about 0.3 to about 5 weight per cent of glyphosate on an acid equivalent (ae) basis where the final pH is less than about 6.5;

d) adding an aqueous solution of ammonium sulfate (AMS) to the solution prepared in c) to give a compatible solution comprising, with respect to the final spray solution, from about 1 to about 5 weight per cent of AMS; and

e) optionally, adding other inert co-formulation ingredients to the solution prepared in d).

In a further example, a compatibilized aqueous herbicide spray solution may be prepared by diluting one or more aqueous herbicide concentrates or by tank mixing the components of the spray solution. Such a spray solution may comprise, with respect to the total spray solution, from about 0.01 to about 5 weight percent, from about 0.05 to about 2 weight percent, or from about 0.05 to about 0.5 weight per cent of one or more surface active compatibilizers described herein, from about 0.3 to about 10 weight percent or from about 0.3 to about 5 weight percent each of a water soluble salt of 2,4-D, and a water soluble salt of glyphosate, and, optionally, any additional ingredients such as fertilizer.

In a further example, a compatibilized aqueous herbicide concentrate can contain one or more of the surface active compatibilizers described herein and a water soluble salt of 2,4-D or a water salt of glyphosate, or a pre-mix containing water soluble salts of 2,4-D and glyphosate. The concentrate may comprise, with respect to the total composition, from about 0.05 to about 10 weight percent, from about 0.1 to about 5 weight percent, or from about 0.5 to about 5 weight per cent of one or more surface active compatibilizers, and from about 20 to about 60 weight percent on an acid equivalent basis of at least one of a water soluble salt of 2,4-D and a water soluble salt of glyphosate. As described herein, a compatibilized aqueous herbicide concentrate is a solution containing the surface active compatibilizer dissolved or dispersed in the concentrate which upon dilution in water with products or solutions and at conditions that are normally prone to cause incompatibility, also as described herein, forms a herbicide spray solution of improved compatibility.

In a typical method for preparing the compatible aqueous herbicide concentrate described herein, the one or more surface active compatibilizers, the water soluble salt of at least one of 2,4-D and glyphosate, and, optionally, any additional ingredients, are mixed together in water to provide the aqueous concentrate. The order of addition of ingredients and the mixing conditions can be determined by one of ordinary skill in the art.

The methods and compositions described herein also include a dry herbicide composition including a water soluble salt of 2,4-D and/or a water soluble salt of glyphosate, and one or more surface active compatibilizers as described above. A dry herbicide composition can include from about 0.05 to about 10 weight percent, from about 0.05 to about 8 weight percent, from about 0.05 to about 6 weight percent, from about 0.1 to about 5 weight percent, from about 0.2 to about 5 weight percent, from about 0.3 to about 5 weight percent, from about 0.4 to about 5 weight percent, from about 0.5 to about 10 weight percent, from about 0.5 to about 5 weight percent, from about 0.5 to about 4 weight percent, from about 0.5 to about 3 weight percent, from about 1 to about 3 weight percent, or from about 1.5 to about 2.5 weight percent of one or more surface active compatibilizers and from about 20 to about 80 weight percent on an acid equivalent basis of a water soluble salt of 2,4-D or a water soluble salt of glyphosate, or a mixture of water soluble salts of 2,4-D and glyphosate. Dry herbicide compositions as described herein form a herbicide spray solution of improved compatibility upon dissolution in water with products or solutions and at conditions that are normally prone to cause incompatibility as described herein.

In a typical method for preparing the dry herbicide composition, the one or more surface active compatibilizers, the water soluble salt of at least one of 2,4-D and glyphosate, and, optionally, any additional ingredients, are mixed together in water to provide an aqueous concentrate. The order of addition of ingredients and the mixing conditions used can easily be determined by one of ordinary skill in the art. The aqueous concentrate may then be concentrated by removal of water and then dried to provide the dry herbicide composition which may also be prepared by dry blending the ingredients described herein. The dry composition can be added to an aqueous spray solution containing products or solutions and at conditions that are normally prone to cause incompatibility, as described herein, to form a herbicide spray solution of improved compatibility. As is commonly known, concentrated or dry formulations may be diluted or dissolved in water at from about 10 to about 500 fold dilution at the point of use depending on the agricultural practices.

The methods and compositions described herein can be used for the control of undesired plant growth. In such a use, a herbicidally effective amount of the aqueous spray solution of improved compatibility is applied to an area of soil or targeted plant foliage to kill or provide suitable control of undesirable weed plants.

The effective amount of the active ingredients used in the methods and compositions described herein to be employed in a typical agricultural application often depends upon, for example, the type of plants, the stage of growth of the plants, the severity of environmental conditions, the weeds to be controlled and application conditions. Typically, a weed plant in need of control is contacted with an aqueous herbicidal spray solution that contains from about 0.01 to about 10 weight percent, preferably from about 0.1 to about 5 weight percent of a herbicide active ingredient on an acid equivalent basis with respect to the total aqueous spray solution. The contacting may be in any effective manner. For example, any exposed part of the plant, e.g., leaves or stems may be sprayed with the active ingredient as a solution in a carrier such as water.

The methods and compositions described herein are especially useful for the control of weeds in crops that are naturally tolerant to or have been made tolerant to or resistant to the herbicides contained in the spray solution by genetic manipulation or by mutation and selection. For example, corn, wheat, rice, soybean, sugar beet, cotton, canola, and other crops that have been made tolerant to or resistant to glyphosate and are naturally tolerant or resistant to or have been made genetically tolerant or resistant to 2,4-D can be treated. The aqueous herbicidal spray solutions of the present invention are also effective in controlling many weeds that have become resistant to glyphosate such as, for example, horseweed (*Conyza canadensis*, ERICA).

Optionally, the methods and compositions described herein may additionally contain one or more surfactants. The surfactants can be anionic, cationic or nonionic in character. Typical surfactants include salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; alkylarylsulfonate salts, such as calcium dodecylbenzenesulfonate; alkyl and/or arylalkylphenol-alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol-alkylene oxide addition products, such as tridecyl alcohol ethoxylate; soaps, such as sodium stearate; alkylnaphthalenesulfonate salts, such as sodium dibutyl-naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl) sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryl trimethylammonium chloride; ethoxylated amines, such as tallowamine ethoxylate; betaine surfactants, such as cocoamidopropyl betaine; polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; salts of mono and dialkyl phosphate esters; and mixtures thereof. The amounts and combinations of these surfactants to be used can easily be determined by one of ordinary skill in the art. As discussed above for surface active compatibilizers, it may be advantageous to avoid the use of surfactants that contain inorganic ions such as, for example, Na^+, K^+, or NH_4^+, at a level that will impact crystallization in order to maintain the physical stability of the described compositions.

In addition to the specific methods and compositions set forth above, the methods and compositions described herein also may include compositions containing one or more additional compatible ingredients. These additional ingredients may include, for example, one or more pesticides or other ingredients, which may be dissolved or dispersed in the composition and may be selected from acaricides, algicides, antifeedants, avicides, bactericides, bird repellents, chemosterilants, defoliants, desiccants, disinfectants, fungicides, herbicide safeners, herbicides, insect attractants, insecticides, insect repellents, mammal repellents, mating disrupters, molluscicides, plant activators, modifiers of plant size and structure, rodenticides, semiochemicals, synergists, and virucides. Also, any other additional ingredients providing functional utility such as, for example, antifoam agents, antimicrobial agents, buffers, corrosion inhibitors, dispersing agents, dyes, fragrants, freezing point depressants, neutralizing agents, odorants, penetration aids, sequestering agents, spray drift control agents, spreading agents, stabilizers, sticking agents, viscosity-modifying additives, and the like, may be included in these compositions.

The following Examples are presented to illustrate various aspects of the compositions and methods described herein and should not be construed as limitations to the claims.

Example 1 Reduction of the On-set pH of Crystallization (OSPOC) of an Aqueous Solution of 2,4-D Potassium With the Surface Active Compatibilizers (SAC) Described Herein

The on-set pH of crystallization (OSPOC; the pH of the solution when crystallization begins) of a 100 mL sample of an aqueous solution of a 3 weight percent (acid equivalent basis) of 2,4-D potassium (2,4-D K) with and without added SAC was determined as the pH was slowly lowered by the addition of 0.2 N aqueous sulfuric acid. As shown in Table 1, the addition of 0.2 weight percent of the SAC, with respect to total solution, to the aqueous solution of the 2,4-D K significantly reduced the OSPOC of the 2,4-D containing solutions when compared to the control example where no SAC was used.

Table 1. Inhibition of 2,4-D Potassium Salt Crystallization from Aqueous Solutions at Low pH With Surface Active Compatibilizers (SAC) as Measured by the OSPOC

2,4-D K Concentration % AE w/w	**SAC Product[1]**	**SAC Concentration % (w/w)**	**On-Set pH of Crystallization (OSPOC)**
3%	control, no SAC	0.0%	6.16
3%	Agrimer® AL 10LC	0.2%	5.84
3%	Agrimer® VA 6	0.2%	5.80
3%	Agrimer® VA 3	0.2%	5.60
3%	Agrimer® 30	0.2%	5.87
3%	Agrimer® ST	0.2%	5.87
3%	Erkol® 05/290 PVA	0.2%	5.75
3%	Erkol M05/190	0.2%	5.71
3%	Atlox™ 4913	0.2%	5.41

3%	Atlox™ 4915	0.2%	5.32
3%	Polyfon® H	0.2%	4.94
3%	Polyfon® O	0.2%	4.68
3%	Polyfon® F	0.2%	5.21
3%	Polyfon® T	0.2%	4.88
3%	KRAFTSPERSE® DD-6	0.2%	5.45
3%	REAX® 85A	0.2%	5.07
3%	REAX® 907	0.2%	5.13
3%	REAX® 910	0.2%	5.28
3%	REAX® 83A	0.2%	5.45
3%	UCAR™ 162 Latex	0.2%	5.69
3%	Tetronic® 304	0.2%	5.76
3%	Pluronic® F-68	0.2%	5.66

[1] Agrimer® products are available from International Specialty Products, a division of Ashland (Wayne, NJ); Erkol® products are available from Celanese (Dallas, TX); Atlox™ and Metasperse™ products are available from Croda Inc. (Edison, NJ); Polyfon®, Kraftsperse®, and REAX® products are available from MeadWestvaco Corp. (Charleston, SC); UCAR™ 162 latex is available from Arkema, Inc. (King of Prussia, PA); Tetronic®, and Pluronic® products are available from BASF (Florham Park, NJ).

Example 2 Determination of the Critical Crystallization Concentration (CCC) of Salts of 2,4-D in Aqueous Solutions of Glyphosate With Added Surface Active Compatibilizers (SAC)

The CCC of 2,4-D compositions were measured using the following method. Spray mixtures were prepared containing 2,4-D, glyphosate, inorganic ions, and a surface active compatibilizer at various over-saturated 2,4-D concentrations where crystallizations were observed. The crystals formed in each mixture were isolated, dried, and weighed. The amount/weight of the crystals isolated from each mixture were plotted versus the 2,4-D wt% AE concentration in the initial mixture to provide a linear function. The CCC was determined by measuring the X-intercept of the extrapolated linear function of the crystal weight vs. 2,4-D wt% AE concentration. For example, the following procedure was used to determine the CCC values exhibited in Table 2:

1. Add appropriate amounts of water of 342 ppm hardness and 2,4-D aqueous concentrate formulation, e.g. DMA salt, with or without built-in 1-2% w/w SAC in a 100ml centrifuge tube and mix until a homogeneous solution is achieved.
2. Add the SAC as a tank-mix additive if not included as a built-in ingredient in the 2,4-D aqueous concentrate in step 1.
3. Add an appropriate amount of glyphosate aqueous concentrate formulation, e.g. the glyphosate K salt found in Roundup PowerMax®, to the centrifuge tube and mix by inversion.
4. Optionally, add other tank mix ingredients such as ammonium sulfate (AMS) to the centrifuge tube.
5. Allow 24 hours for equilibration of the sample at ambient temperature before filtering, collecting, drying, and weighing the crystalline precipitates.
6. The amounts of 2,4-D and glyphosate salts were added to achieve desired AE concentrations of 2,4-D and glyphosate at 1:1 ratio, and the amount of water was calculated as a balance ingredient to achieve the final mixture volume of 100 ml.
7. Typically, a series of mixtures were prepared following the steps above at over-saturated concentrations, such as, 1.8%, 2.4%, and 3.0% on an acid equivalent (AE) basis of each herbicide salt. The weight of the crystalline precipitates collected was plotted against the corresponding AE concentration of 2,4-D in the mixture. The critical crystallization concentration (CCC) can then be determined as the maximum % 2,4-D AE concentration before crystallization occurs by extrapolating the linear function of crystal precipitate weight vs. 2,4-D % AE concentration to the horizontal axis where crystal precipitate weight becomes zero.

Table 2. Determination of the Critical Crystallization Concentration (CCC) of Salts of 2,4-D in Aqueous Compositions Containing Salts of Glyphosate With Added Surface Active Compatibilizers (SAC)

2,4-D Salt[1]	**Glyphosate Salt**[2]	**SAC**[3]	**2,4-D CCC %AE**
2,4-D DMA	Roundup PowerMax®	none, control sample	0.89%

2,4-D DMA	Roundup PowerMax®	1% Polyfon® F, built-in	1.16%
2,4-D DMA	Roundup PowerMax®	2% Polyfon® F, built-in	1.26%
2,4-D DMA	Roundup PowerMax®	1% Polyfon® H, built-in	1.46%
2,4-D DMA	Roundup PowerMax®	2% Polyfon® H, built-in	1.66%
2,4-D DMA	Roundup PowerMax®	0.145% Polyfon® H, tank-mix	1.60%
2,4-D DMA	Roundup PowerMax®	0.12% Polyfon® T, tank-mix	1.72%
2,4-D DMA	Roundup PowerMax®	0.07% Polyfon® O, tank-mix	1.62%
2,4-D DMEA	Roundup PowerMax®	none, control sample	1.04%
2,4-D DMEA	Roundup PowerMax®	0.1% Polyfon® O, tank-mix	1.77%
2,4-D DMEA	Roundup PowerMax®	0.1% Polyfon® H, tank-mix	1.39%

[1] 2,4-D salts used were unsequestered dimethyl ammonium salts supplied as DMA®-4 (an aqueous concentrate containing 456 g ae/L of 2,4-D dimethyl ammonium salt) or DMA®-6 (an aqueous concentrate containing 678 g ae/L of 2,4-D dimethyl ammonium salt), both available from Dow AgroSciences LLC, Indianapolis, IN; and 2,4-D DMEA (aqueous concentrate containing 456 g ae/L of 2,4-D dimethylethanol ammonium salt).

[2] Roundup PowerMax® is an aqueous concentrate containing 540 g ae/L of glyphosate potassium salt (Monsanto Company, St. Louis, MO).

[3] Polyfon® products are available from MeadWestvaco Corp. (Charleston, SC).

Example 3 Preparation of a Compatible Aqueous Concentrate of 2,4-D Choline Salt Containing a Surface Active Compatibilizer (SAC) and Dilution of it in Spray Solutions Containing Glyphosate Salts and Ammonium Sulfate (AMS)

A typical procedure for preparing the spray solutions shown in Table 3 involved the following steps:

1. Add an appropriate amount of water of 342 ppm hardness into a 100 ml centrifuge tube, and then add an appropriate amount of a 2,4-D aqueous concentrate formulation, e.g. 2,4-D choline salt, and mix until a homogeneous solution is achieved.
2. The SAC was incorporated into the above spray mixture either from 2,4-D concentrate formulation with built-in SAC, or by direct addition of the SAC or its concentrate solution into the mixture.
3. Add appropriate amount of glyphosate aqueous concentrate formulation, e.g. glyphosate K salt, to the centrifuge tube and mix by inversion.
4. Optionally, add other tank mix ingredients such as AMS to the centrifuge tube.
5. The amounts of 2,4-D and glyphosate salts were added to achieve the desired AE concentrations of 2,4-D and glyphosate at a 1:1 weight ratio, and the amount of water was calculated as a balance ingredient to achieve the final mixture volume of 100 ml. For example, 15 gal/ac, 10 gal/ac, and 5 gal/ac spray volumes for an 840 gae/ha use rate would be corresponding to about 0.6%, 0.9%, and 1.8% AE of 2,4-D and glyphosate in the tank mixtures, respectively.
6. The spray solutions thus prepared were examined after 24 hours of equilibration at ambient temperature for the presence of any crystals or precipitates

<u>Table 3</u>. Compatibility Evaluations of Spray Solutions Prepared by Mixing a 456 g ae/l Aqueous Concentrate of 2,4-D Dimethyl Ammonium Salt with a 540 g ae/l Aqueous Concentrate of Glyphosate Potassium Salt at Various Conditions With or Without the Presence of a SAC

2,4-D Salt[1]	Glyphosate Salt[2]	SAC[3]	SAC Conc.	Crystallization at Various Spray Volumes		
				15 gal/ac	10 gal/ac	5 gal/ac

DMA-4	Roundup PowerMax®	none	none	no	trace	lots of crystals
DMA-4	Roundup PowerMax®	Polyfon® O	0.07% tank-mix	no	no	trace
DMA-4	Roundup PowerMax®	Polyfon® H	0.145% tank-mix	no	no	trace
DMA-4	Roundup PowerMax®	Polyfon® T	0.12% tank- mix	no	no	trace
DMA-4	Roundup PowerMax®	Polyfon® H	2% built-in	no	no	trace
DMA-4	Roundup PowerMax®	Polyfon® F	2% built-in	no	no	some

[1] 2,4-D salts used were unsequestered dimethyl ammonium salts supplied as DMA®-4 (an aqueous concentrate containing 456 g ae/L of 2,4-D dimethyl ammonium salt) available from Dow AgroSciences LLC (Indianapolis, IN).

[2] Roundup PowerMax® is an aqueous concentrate containing 540 g ae/L of glyphosate potassium salt available from Monsanto Company (St. Louis, MO).

[3] Polyfon® products are available from MeadWestvaco Corp. (Charleston, SC).

The present invention is not limited in scope by the embodiments disclosed herein which are intended as illustrations of a few aspects of the invention and any embodiments which are functionally equivalent are within the scope of this invention. Various modifications of the processes, methods, and compositions in addition to those shown and described herein will become apparent to those skilled in the art and are intended to fall within the scope of the appended claims. Further, while only certain representative combinations of the process and method steps and composition components disclosed herein are specifically discussed in the embodiments above, other combinations of the composition components and process and method steps will become apparent to those skilled in the art and also are intended to fall within the scope of the appended claims. Thus a combination of components or steps may be explicitly mentioned herein; however, other combinations of components and steps are included, even though not explicitly stated. The term comprising and variations thereof as used herein is used synonymously with the term including and variations thereof and are open, non-limiting terms.

What is claimed is:

1. A method of improving the compatibility of an aqueous herbicide solution including at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, and a water soluble salt of glyphosate, comprising adding to the aqueous herbicide solution one or more surface active compatibilizers.

2. The method of claim 1, wherein the aryloxyalkanoic acid is 2,4-D, 2,4-DB, dichlorprop, mecoprop, MCPA, or MCPB.

3. The method of any one of claims 1-2, wherein the pyridyloxyalkanoic acid is triclopyr or fluroxypyr.

4. The method of any one of claims 1-3, further comprising one or more inorganic cations selected from the group consisting of NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}, or one or more organo ammonium cations selected from the group consisting of monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and N,N,N-trimethylethanol ammonium (choline), or mixtures thereof.

5. The method of any one of claims 1-4, wherein the aqueous herbicide solution is a concentrate or a pre-mix concentrate.

6. The method of claim 5, wherein the aqueous herbicide solution is a concentrate containing water soluble salts of 2,4-D and/or glyphosate.

7. The method of any one of claims 1-6, wherein the aqueous herbicide solution is a spray solution.

8. The method of any one of claims 1-7, wherein the surface active compatibilizer is a copolymer or grafted polymer of a polyvinylpyrrolidone or a polyvinyl alcohol, a polyacrylate or a polymethacrylate grafted with polyethylene oxide side chains, a polymeric amphoteric dispersant, an ethylene oxide-propylene oxide block copolymer, a sulfonated lignin, a synthetic latex, or mixtures thereof.

9. The method of claim 8, wherein the surface active compatibilizer is in the form of a salt.

10. The method of claim 8, wherein the surface active compatibilizer is in the form of an acid.

11. The method of claim 9, wherein the salt is an organic amine salt or a salt containing inorganic cations.

12. The method of claim 11, wherein the organic amine salt comprises a cation selected from monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof.

13. An aqueous herbicide solution of improved compatibility including at least one of a water soluble salt of an aryloxyalkanoic acid, a water soluble salt of a pyridyloxyalkanoic acid, and a water soluble salt of glyphosate, and one or more surface active compatibilizers.

14. The aqueous herbicide solution of claim 13, wherein the aryloxyalkanoic acid is at least one of 2,4-D, 2,4-DB, dichlorprop, mecoprop, MCPA, and MCPB.

15. The aqueous herbicide solution of any one of claims 13-14, wherein the pyridyloxyalkanoic acid is triclopyr or fluroxypyr.

16. The aqueous herbicide solution of any one of claims 13-15, further comprising one or more inorganic cations selected from the group consisting of NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}, or one or more organo ammonium cations selected from the group consisting of monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, N,N,N-trimethylethanol ammonium (choline), or mixtures thereof.

17. The aqueous herbicide solution of any one of claims 13-16, wherein the aqueous herbicide solution is a concentrate or a pre-mix concentrate.

18. The aqueous herbicide solution of any one of claims 13-17, wherein the aqueous herbicide solution is a concentrate containing water soluble salts of 2,4-D and/or glyphosate.

19. The aqueous herbicide solution of any one of claims 13-18, wherein the aqueous herbicide solution is a spray solution.

20. The aqueous herbicide solution of any one of claims 13-19, wherein the surface active compatibilizer is a copolymer or grafted polymer of a polyvinylpyrrolidone or a polyvinyl alcohol, a polyacrylate or a polymethacrylate grafted with polyethylene oxide side chains, a polymeric amphoteric dispersant, an ethylene oxide-propylene oxide block copolymer, a sulfonated lignin, a synthetic latex, or mixtures thereof.

21. The aqueous herbicide solution of claim 20, wherein the surface active compatibilizer is in the form of a salt.

22. The aqueous herbicide solution of claim 21, wherein the salt is an organic amine salt or a salt containing inorganic cations.

23. The aqueous herbicide solution of claim 22, wherein the organic amine salt comprises a cation selected from monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof.

24. A dry herbicide composition comprising a water soluble salt of 2,4-D and/or a water soluble salt of glyphosate, and one or more surface active compatibilizers.

25. The dry herbicide composition of claim 24, further comprising one or more inorganic cations selected from the group consisting of NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}, or one or more organo ammonium cations selected from the group consisting of monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, N,N,N-trimethylethanol ammonium (choline), or mixtures thereof.

26. The dry herbicide composition of any one of claims 24-25, wherein the surface active compatibilizer is a copolymer or grafted polymer of a polyvinylpyrrolidone or a polyvinyl alcohol, a polyacrylate or a polymethacrylate grafted with polyethylene oxide side chains, a polymeric amphoteric dispersant, an ethylene oxide-propylene oxide block copolymer, a sulfonated lignin, a synthetic latex, or mixtures thereof.

27. The dry herbicide composition of claim 26, wherein the surface active compatibilizer is in the form of a salt.

28. The dry herbicide composition of claim 27, wherein the salt is an organic amine salt or a salt containing inorganic cations.

29. The dry herbicide composition of claim 28, wherein the organic amine salt comprises a cation selected from monomethyl ammonium, isopropyl ammonium, butyl ammonium, dimethyl ammonium, diethyl ammonium, triethyl ammonium, monoethanol ammonium, diethanol ammonium, dimethylethyl ammonium, diethylethanol ammonium, triethanol ammonium, triisopropanol ammonium, tetramethyl ammonium, tetraethyl ammonium, and *N*,*N*,*N*-trimethylethanol ammonium (choline), or mixtures thereof.

INTERNATIONAL SEARCH REPORT

PCT/US2~~013/057431 15.01.2014~~

International application No.

PCT/US 13/57431

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - A01N 25/00 (2013.01)
USPC - 504/116.1; 504/320; 504/313
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 504/116.1; 504/320; 504/313
IPC: A01N 25/00 (2013.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search Words Below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PATBASE: PGPB, USPT, USOC, EPAB, JPAB
Google: Scholar/Patents: improved compatibility dry aqueous herbicide composition 2,4-D triclopyr mcpa glyphosate surface active copolymer inorganic cation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2012/0053056 A1 (LIU et al) 01 March 2012 (01.03.2012) para [0010];[0013]-[0019]	24-29 ------------ 1-3; 13-15
Y	US 2010/0331182 A1 (ZHANG et al) 30 December 2010 (30.12.2010) para [0007];[0025]	1-3; 13-15

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 25 December 2013 (25.12.2013)	Date of mailing of the international search report 15 JAN 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

International application No.

PCT/US 13/57431

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-12 and 16-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.