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(54) **Title**: THICKENED PARAQUAT AND FERTILIZER COMPOSITIONS

(57) **Abstract**: Aqueous solutions are provided which contain i) paraquat, fertilizer, or mixture thereof, ii) an alkyl amidoamine, and iii) a quaternary ammonium compound. Furthermore the use of such compositions in the preparation of agricultural formulations and the use of such formulations to treat a field, plants, or seeds.

THICKENED PARAQUAT AND FERTILIZER COMPOSITIONS

Field of Invention

The present invention relates to aqueous solutions comprising paraquat, a fertilizer, or combinations of paraquat and fertilizer, an alkylamidoalkylamine surfactant, and a surfactant, hereinafter an electrolyte composition. In the agrochemical field one encounters formulations wherein salts, such as paraquat and/or fertilizers, are dissolved in water and subsequent applied to treat fields or crop. Therefore, the electrolyte compositions of the invention are typically agrochemical formulations. Since the compositions are usually applied using a spraying technique, they are preferably sprayable agrochemical formulations. However, the compositions can also be used in other techniques such as fertigation and such as suspo concentrates, wherein part of the formulation is still in the form of suspended solids, typically because the electrolyte concentration is higher than its solubility in the formulation.

Background and problem description

Electrolyte compositions, such as compositions of certain pesticides, adjuvants and optionally further auxiliary ingredients are conventionally sold as concentrated formulations. They are typically intended to be mixed and diluted with water prior to their end-use. Electrolyte compositions are often encountered in the agrochemical field wherein salts, such as fertilizers and herbicide salts are typically used as an aqueous solution and/or dispersion, which is subsequently applied to treat fields or crop. Typically the compositions are sprayed.

The electrolyte compositions often contain adjuvants to stabilize the formulations, prevent drift during spraying, increase the efficacy of the electrolyte, often with the purpose of creating a better working solution and a better distribution of the electrolyte when applied. Typically, the use of the adjuvant allows a lower dosing rate of the electrolyte.

Surface active compounds are conventionally used as adjuvants, for example to change droplet size during spraying, or in order to allow the electrolyte to adhere on the area where it is functional, for example in foliage fertilizers, sometimes referred to as micronutrients, or to change the epidermal layer of the leaf surface, for example to permit pesticide entry. Fatty-alkyl amidoalkylamines are often used for this purpose.

Regulatory requirements and economic reasons now dictate that electrolyte compositions are to be dealt with more carefully than in the past, particularly with less spillage, which causes a need for formulations that are more easily handled and controlled. It was found that high viscous solutions, with a viscosity >100 mPas, preferably >300 mPas, more preferably >400 mPas, and most preferably >500 mPas provide such required handling improvement. The viscosity can be so high that a gel is formed, which may be desired for certain uses, but in an embodiment the viscosity is <10000 mPas. Suitably the high viscous solutions remain their viscosity, also when the product is diluted.

In WO 2010/057886 electrolyte compositions are disclosed wherein alkoxylated gel forming surfactants are used. They are combined with fatty-alkyl amidoalkylamines to reduce actual gel formation.

In US 2013/0143741 herbicidal compositions are disclosed wherein gel-forming polymers are used and optionally an alkoxylated surfactant is added to improve the efficacy of the herbicide.

US 2010/113274 relates to glyphosate compositions using combinations of amidoalkylamines with alkoxylated tertiary amine, alkoxylated quaternary amine, alkoxylated tertiary etheramine, alkoxylated quaternary etheramine, alkoxylated etheramine oxide, alkoxylated tertiary amine oxide, alkoxylated alcohol, phosphate ester of alkoxylated tertiary amine, phosphate ester of alkoxylated etheramine, phosphate ester of alkoxylated alcohol, or combinations thereof.

WO 2001/032019 relates to pesticide emulsified in water with fatty acid amidoamines and/or their quaternized products with optional co-emulsifiers.

CN 102907422 discloses aqueous thickened paraquat compositions, which comprise a combination of specific amino acid based amphiphilic surfactants, quaternary ammonium salt surfactants, and cosurfactants.

However, the conventional solutions were found to be unsatisfactory for paraquat and/or fertilizer formulations. For example emulsion stability, particularly during storage, dilution, and/or the spraying operation, and handling emulsions is often problematic. Further it is noted that conventional solutions involving the use of alkoxylates, particularly ethoxylates, may be undesired because ethoxylate production involves the

use of ethylene oxide which is an extremely flammable gas and its mixtures with air are explosive.

Further it was found that there is a need for being able to combine paraquat and fertilizers in one aqueous solution. Many prior art formulations were found not to allow such combined formulations, since they would separate upon standing.

Accordingly there is a need for an alternative method to thicken formulations, particularly solutions, comprising paraquat, one or more fertilizers, and mixtures thereof. Suitably such thickened formulations are used for tank mixing by a farmer to make more dilute formulations. Whether diluted or not, suitably the thickened solutions comprising paraquat, one or more fertilizers, and mixtures thereof, are applied to plants or seeds. Application to plants is preferably thru foliar contact, but application to soil, with subsequent uptake through roots is acceptable, particularly for fertilizer-containing compositions. Suitably the solution is sprayed on the seed or the seed and the solution are combined at the planting location.

Description of the Invention

The inventors have surprisingly found alternative thickener formulations for making paraquat and fertilizer compositions addressing the above-mentioned problems. The new formulations are solutions based on the use of a combination of fatty-alkyl amidoalkylamines and quaternary ammonium compounds. Such solutions were found to provide good handling properties and allow accurate dosing and uptake of paraquat when used in agrochemical applications. In an embodiment the fatty-alkyl amidoalkylamines are not alkoxylated. In an embodiment the quaternary ammonium compounds are not alkoxylated.

Such solutions can be used to make the desired high viscous compositions with a viscosity >100 mPas, preferably >300 mPas, more preferably >400 mPas, and most preferably >500 mPas, resulting in compositions with improved handling. In an embodiment the formulations are a gel or have a viscosity <10000, suitably <6000,

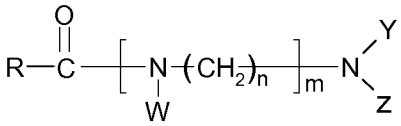
<3000, or <1000 mPas. The viscosity as defined throughout this document is determined at 20°C with a Brookfield® DV-I+ viscometer, equipped with a spindle S-34 and % torque control 10-100%, at 50 rpm. However for extremely viscous poducts the spindle speed may be reduced, e.g. to 20 rpm, or a different spindle may be selected, as is usual in the art.

There is no suggestion in the prior art that the claimed specific combinations of surfactants have beneficial properties allowing high viscosity over a wide concentration range of the paraquat, fertilizer, or combination of paraquat and fertilizer. Also there is no suggestion in the art that paraquat and fertilizers can be combined in such solutions. The combined formulations bring economic advantages but also the efficacy of the paraquat can be improved, presumably, but this is an unproven theory, because the fertilizer increases the plants uptake of the paraquat.

Hence in a first aspect, the present invention relates to an aqueous solution comprising

a) one or more electrolytes selected from paraquat and fertilizer salts,

b) one or more amidoalkylamines of the formula (1)



(1)

wherein R is a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms, m is 1-7, n is 2-6, W and Y are independently chosen from H, hydroxyl, an alkyl group having 1-4 carbon atoms, a benzyl group, -(AO)sH, where AO is an alkyleneoxy group having 2-4 carbon atoms, and s is on the average 1-30, and an acyl (R'C=O) group where R' is a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms,

c) one or more quaternary ammonium compounds having the structure of formula (2):

$R^1R^2R^3R^4N^+ X^-$ (2)

wherein R^1, R^2, R^3, and R^4 are independently selected from saturated or unsaturated, linear or branched, substituted or unsubstituted, alkyl, aralkyl, or alkenyl groups

comprising from 1 to 30 carbon atoms, whereby at least one of R^1, R^2, R^3, and R^4 is a C_4-C_{30} group, and X^- is an anion from an inorganic or organic acid. The fatty amine quaternary may contain ethoxy and/or propoxy groups. One or more of R^1, R^2, R^3, and R^4 may be substituted and contain one or more hydroxyl substituents or ether linkage, including quaternary ammonium compounds derived from C-12 to C-22 fatty amines, and

d) water,

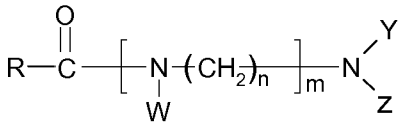
as defined in the claims. Preferably said aqueous solution is a concentrated composition, meaning a product comprising less than 95 % by weight (%w/w) of water. In an embodiment the composition comprises less than 75 %w/w, in another embodiment less than 60 %w/w of water, and in yet another embodiment less than 50 %w/w of water. In an embodiment the amount of water in the aqueous solution is >1, >4, >12, and/or >24 %w/w. The amount of water should be such that the claimed solution is obtained, meaning that all of compounds a), b), and c) are completely dissolved in the aqueous phase at a temperature of 25 °C.

It is noted that an electrolyte composition is herein defined as being aqueous compositions comprising salts, that when contacted with water can dissociate into ions, in a concentration of 1-75 %w/w, in an embodiment 15-65 %w/w, in another embodiment 20-65 %w/w, and yet another embodiment 30-65 %w/w. The salt can be added “as-is” or be formed “in-situ”, for example by adding the acid to an alkaline solution.

In another aspect, the invention relates to aqueous solutions of the previous aspects which further contain one or more acids, bases, and/or salts to control the pH. It was found that the viscosity of some formulations is dependent on pH. Typically a higher pH was found to result in a higher viscosity. For quality control purposes, and to obtain reproducible viscosities, it is therefore advised to add one or more acids, bases, and/or salts to achieve the pH that is desired. Suitably the pH is chosen in the range from 2 or 3 or 4 to 10 or 9 or 8. To achieve the pH a buffer system may be used or created by adding the one or more acids, bases, and/or salts in a conventional way. For comparing products of the invention and materials of the prior art, the pH is suitable kept at 4.

In an embodiment the invention relates to compositions comprising a water-soluble fertilizer. Water-soluble fertilizers include but are not limited to water-soluble nitrates, phosphates, sulfates, chlorides, cyanamides, urea, and mixtures thereof. The major three elements are nitrogen, potassium and phosphorus, the secondary elements, also called micronutrients, are calcium, sulfur, magnesium, and other elements such as boron, manganese, iron, zinc, copper, silicium, and molybdenum. Fertilizers enhance the natural fertility of the soil or replace the chemical elements taken from the soil by harvesting, grazing, leaching or erosion. Suitable artificial fertilizers are inorganic fertilizers formulated in appropriate concentrations and combinations supply three main nutrients: nitrogen, phosphorus and potassium (N, P and K) for various crops and growing conditions. N (nitrogen) promotes leaf growth and forms proteins and chlorophyll. P (phosphorus) contributes to root, flower and fruit development. K (potassium) contributes to stem and root growth and the synthesis of proteins. The common inorganic fertilizers include ammonia (82% nitrogen), NPK combinations, urea (46% nitrogen), superphosphate, mono and dibasic ammonium phosphates (containing nitrogen and phosphate), calcium ammonium nitrate, potassium chloride (muriate of potash). In an embodiment the fertilizer is or comprises a salt selected from nitrates, phosphates, sulfates, particularly ammonium sulfate (AMS) and epson salt, chlorides, cyanamides such as calcium cyanamide, and mixtures thereof. In an embodiment the fertilizer is AMS. Some of these fertilizers may also show herbicidal activity, such as calciumcyanamide.

The amidoalkylamines as used in the invention are compounds of the formula (1)



(1)

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wherein R is a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms, in another embodiment 8-18 carbon atoms; m is 1-7, in another embodiment 1-3, in yet another embodiment, 1-2; n is a number 2-6, in another embodiment 2-3; W and Y are independently chosen from H, hydroxyl, an alkyl group having 1-4 carbon atoms, in another embodiment 1-2 carbon atoms and in still another

embodiment 1 carbon atom, a benzyl group , -$(AO)_sH$, where AO is an alkyleneoxy group having 2-4 carbon atoms, in another embodiment 2 carbon atoms, and s is on the average 1-30, in another embodiment 1-20 and in still another embodiment 5-15; Z is H, hydroxyl, an alkyl group having 1-4 carbon atoms, in another embodiment 1-2 carbon atoms and in another embodiment 1 carbon atom, a benzyl group, $(AO)_sH$, where AO is an alkyleneoxy group having 2-4 carbon atoms, in another embodiment 2 carbon atoms, and s is on the average 1-30, in another embodiment 1-20 and in yet another embodiment 5-15, or an acyl (R'C=O) group, with R' being a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms. R' and R may be the same or different. When Z is the (R'C=O) group, m is preferably 1 to 7, in another embodiment 2-3. In an embodiment W, Y and Z are all not –$(AO)_sH$.

A list of exemplary alkyl amidoamines includes, but is not limited to, C2 (acetic acid) amidoamine (DMAPA, dimethylamidopropylamine), C5 (NEO acid) amidoamine (DMAPA), C6 (butyric acid) amidoamine (DMAPA), C7 (caproic acid) amidoamine (DMAPA), C8 (caprylic acid) amidoamine (DMAPA), C9 (Nonanoic/Pelargonic acid) amidoamine (DMAPA), C10 (capric acid) amidoamine (DMAPA), 2EH (2-ethylhexyl acid) amidoamine (DMAPA), TOFA (toll oil fatty acid) amidoamine (DETA, diethylenetriamine) with 10 – 30EO, C9 (Nonanoic/Pelargonic acid) diethanol amide, and N,N Dimethyl C10 amide. Specific examples of compounds of formula (1) useful in the context of the present invention include, but are not limited to N-[3-(dimethylamino)propyl] (C_{8-10})amide, N-[3-(dimethylamino)propyl] cocoamide and N-[3-(dimethylamino)propyl] (rape-seed)amide. In an embodiment the alkyl amidoamine is coco-amidopropylamine available from AkzoNobel as Adsee® C-70S.

Suitably the alkyl amidoamines of the invention are neutralized before they are used. The inorganic or organic acid used for this purpose is suitably selected from HCl, HCH_3SO_4, H_2SO_4, HBr, HI, H_3PO_4, HNO_3 , H_2CO_3, CH_3CO_2H, and salicylic acid. Neutralization typically involves adding the acid to the alkyl amidoamines until the pH of the amine, or of the water phase of a 50/50 blend of alkyl amidoamine and water which was stirred for 5 minutes at room temperature, is between 6-8. For unknown reasons, it was observed that for glyphosate formulations were most efficiently thickened using alkyl amidoamines that were neutralized with salicylic acid.

The one or more quaternary ammonium compounds in the composition have the structure of formula (2):

$R^1R^2R^3R^4N^+ X^-$ (2)

wherein R^1, R^2, R^3, and R^4 are independently selected from saturated or unsaturated, linear or branched, substituted or unsubstituted, alkyl, aralkyl, or alkenyl groups comprising from 1 to 30 carbon atoms, whereby at least one of R^1, R^2, R^3, and R^4 is a C_4-C_{30} group, and X^- is an anion from an inorganic or organic acid. The compounds may contain one or more of either or both ethoxy and/or propoxy groups. One or more of R^1, R^2, R^3, and R^4 may be substituted and contain one or more hydroxyl substituents or ether linkage. One or more of R^1, R^2, R^3, and R^4 may contain one or more amido linkages.

Any source can be used to provide the R groups of the amidoalkylamine of formula (1) or the quaternary ammonium compound of formula (2). Suitably one or more of the R groups is/are derived from a natural source. Suitably the C_4-C_{30} group is derived from a natural source. Preferred natural sources are oils and fats, such as oils and fats from land animals, marine animals, and plants. Sources of fat and oils from land animals include butterfat, depot fat, lard oil, neat's foot oil, and tallow (such as from beef or mutton). Sources of fat and oils from marine animals include cold-liver oil, herring oil, menhaden oil, sardine oil, sperm oil, and whale oil. Sources of fats and oils from plants include babassu oil, castor oil, cocoa butter, coconut oil, corn oil, cotton seed oil, linseed oil, mustard oil, neem oil, niger-seed oil, oiticica oil, olive oil, palm oil, palm-kernel oil, peanut oil, perilla oil, poppy-seed oil, rapeseed oil, safflower oil, sesame oil, soybean oil, sunflower-seed oil, tall oil, tung oil, and wheat germ oil.

In one embodiment, suitable oils and fats are selected from the group consisting of coconut, soybean (soya), tallow, palm, palm kernel, rapeseed, lard, sunflower, corn, safflower, canola, olive, peanut, and combinations thereof. In another approach, the suitable oils and fats are selected from the group consisting of soybean oil, tallow or coconut oil, such as fully or partially hydrogenated soybean oil, fully or partially hydrogenated tallow, or fully or partially hydrogenated coconut oil. In some approaches, the fatty acid is fully or partially hydrogenated tallow, and in certain approaches, the source of the fatty acid is fully hydrogenated tallow. To make amines from an acid, the

acid is typically conventionally converted into the corresponding nitrile and then conventionally converted to an amine, suitably a tertiary amine. However for products comprising amido linkages the acids can be reacted with alkyldiamines or polyalkylpolyamines in a conventional fashion. To produce quaternary ammonium compounds from the amines, the amines are typically quaternized using conventional means such as alkyl halides and alkyl methosulfates.

Suitable fatty acids may include saturated acids such as isovaleric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, arachidic acid, phytanic acid, behenic acid, lignoceric acid, cerotic acid and montanic acid; or monounsaturated acids such as caproleic acid, palmitoleic acid, oleic acid, vaccenic acid, elaidic acid, brassidic acid, erucic acid, and nervonic acid; diunsaturated acids such as linoleic acid; triunsaturated acids such as eleosteric acid and linolenic acid; and tetraunsaturated acids such as arachidonic acid. In some approaches, the fatty acids are stearic acid, arachidic acid, phytanic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, oleic acid, vaccenic acid elaidic acid, brassidic acid, erucic acid, nervonic acid, linoleic acid, eleosteric acid, linolenic acid, and arachidonic acid. In yet other approaches, the suitable fatty acids are selected from the group consisting of stearic acid, oleic vaccenic acid, elaidic acid, linoleic acid, eleosteric acid, linolenic acid.

One or more, such as two or more, three or more, or all four of R^1, R^2, R^3, and R^4 is/are a linear or branched alkyl or alkenyl radical(s) comprising C1-C30, such as C4-C30, or C10-C30. In some approaches, one or more, such as two or more, three or more, or all four of R^1, R^2, R^3, and R^4 comprise at least C6, at least C8, such as at least C12, or C12-C18. In other approaches, one or more, such as two or more, three or more, or all four of R^1, R^2, R^3, and R^4 comprises a C12-C30 group. In one aspect, at least one, at least two, at least three, or all four of R1,R2, R3, and R4 is/are a C12-C18 linear or branched alkyl or alkenyl radical. In an embodiment at least two of R^1, R^2, R^3, and R^4 are lower alkyl with 1-4 carbon atoms. In one approach, one or more of R^1, R^2, R^3, and R^4 may be an aralkyl group. Such aralkyl group may be derived from non-natural resources, such as a resin or a rosin. Preferably quaternary ammonium compound is free of aryl functionality.

One or more of R^1, R^2, R^3, and R^4 may be saturated or unsaturated. The R^1, R^2, R^3, and R^4 groups each may have an iodine value of 5-30. One or more of R^1, R^2, R^3, and R^4 may be hydrogenated, such as partially or fully hydrogenated. In some approaches, one or more, such as two or more, three or more, or all four of R^1,R^2, R^3, and R^4 may be fully hydrogenated. In yet other approaches, one or more, such as two or more, three or more, or all four of R^1,R^2, R^3, and R^4 may be fully or partially hydrogenated linear or branched alkyl or alkenyl radicals comprising C18, such as fully hydrogenated radicals comprising C18, such as fully hydrogenated C18 radials derived from oleic acid.

One or more of R^1, R^2, R^3, and R^4 may be substituted with an OH function, such as in acids derived from castor oil.

In one embodiment the quaternary ammonium compounds of formula (2) have one or more of R^1, R^2, R^3, and R^4 with an amido function, such as in amidoalkylamines. In an embodiment the quaternary ammonium compound is a product of formula (1) which was quaternized with a compound R^1X in a conventional way. Therefore, in an embodiment the compounds b) and c) of the invention are provided in the form of an amidoalkylamine of formula (1) which is partially quaternized with a compound R^1X. In an embodiment the compounds b) and c) of the invention are provided in the form of an amidoalkylamine of formula (1) which was quaternized for 2%ww, 5%w/w, 10%w/w, 20%w/w, 30%w/w, or more up to 98%w/w, 95%w/w, 90%w/w, 80%w/w, 70%w/w, or less, whereby the percentage is based on the total amount of compounds b) and c). In another embodiment, the quaternary ammonium compounds of formula (2) are not wholly or partially quaternized compounds of formula (1).

The quaternary ammonium compounds of formula (2) may comprise compounds which are ethoxylated, propoxylated and/or butoxylated. In some approaches the fatty amine quaternary comprises about 1 to about 30 alkoxy units, or about 1 to about 20 alkoxy units, such as about 1 to about 15 alkoxy units, or about 1 to about 10 alkoxy units. In one aspect such alkoxy groups are ethoxy groups. In other aspects, the fatty amine quaternary comprises from about 1 to about 10 propoxy units, such as from about 1 to about 5 propoxy units. In one approach, the number of ethoxy and propoxy groups, is between 1 and 40, such as between 2 and 20. The fatty amine quaternary structure may be ethoxylated and/or propoxylated in any order, either randomly or blocky. In one

approach, the fatty amine quaternary is a blocked alkoxylated quaternary ammonium compound. In another embodiment the quaternary ammonium compounds do not comprise alkoxy groups.

In an embodiment R^1 and/or R^2 is linear or branched, substituted or unsubstituted, alkyl group with 12 to 22 carbon atoms, with the remaining groups being lower alkyl groups with 1 to 4 carbon atoms.

In formula (2), X^- is the anion from an alkylating agent. Suitably it is selected from Cl^-, $CH_3SO_4^-$, HSO_4^-, Br^-, I^-, $H_2PO_4^-$, NO_3^-, HCO_3^-, and $CH_3CO_3^-$ groups. Should X be an anion with more than one charge, it can complex with a number of quaternary ammonium groups that correspond to its charge. For instance, one sulfate anion with a 2- charge can be complexed with two quaternary ammonium groups.

The fatty amine based quaternary ammonium compound of formula (2) is suitable an Arquad® product supplied by AkzoNobel. Suitably it is selected from di-fatty di-lower-alkyl quaternary ammonium compounds, such as dimethyl didecyl ammonium chloride, dimethyl dicycloalkyl ammonium chloride, dimethyl dicoco ammonium chloride, dimethyl dilauryl ammonium chloride, dimethyl distearyl ammonium chloride, dimethyl ditallow alkyl ammonium chloride and corresponding salts with other anions.

In an embodiment the quaternary ammonium compound is selected from fatty tri-lower-alkyl quaternary ammonium compounds, such as trimethyl decyl ammonium chloride, trimethyl cycloalkyl ammonium chloride, trimethyl coco ammonium chloride, trimethyl lauryl ammonium chloride, trimethyl stearyl ammonium chloride, trimethyl tallow alkyl ammonium chloride and corresponding salts with other anions.

In an embodiment the quaternary ammonium compound is selected from dimethyl dicoco ammonium chloride and methyl benzyl dicoco ammonium chloride. In another embodiment it is a C16 trimethyl ammonium chloride (sold as Adsee® 1629 by AkzoNobel).

The water can be of any source. In an embodiment it is well water or city water. In another embodiment it is water collected from precipitation.

Depending on the intended way of application of the electrolyte formulation, the electrolyte concentration may differ. In the electrolyte compositions of claim 1 the paraquat and/or fertilizer is suitably present in an amount of from 2.5 to 75 %w/w, or in an amount of from 3 to 70 %w/w, or in an amount of from 4 to 65 %w/w, whereby the amount of electrolyte is calculated as pure electrolyte.

The alkylamidoamines are suitably used in an amount of from 5 to 400, in an embodiment from 10 to 300, in another embodiment from 20 to 200 g/l in the concentrated compositions.

The quaternary ammonium compounds are suitably used in an amount of 5, or 10, or 20, or 30, or 40, or 50 up to 400 or 300 or 250 g/l in the concentrated compositions.

The concentrations of the compounds in the electrolyte composition are preferably such that (i) the concentrated composition is a viscous solution having the desired viscosity, and which can be diluted with water to form viscous agrochemical ready-to-use-formulation, while having an as small as possible volume for transportation and storage purposes, and (ii) that the agrochemical ready-to-use formulation contains the suitable amount of the agrochemically active ingredients.

In another aspect the present invention relates to a method of preparing an agrochemical formulation comprising combining the above-described paraquat and/or fertilizer compositions with a sufficient amount of an aqueous medium to obtain the electrolyte-containing formulation which is suitable for being used, i.e. applied to fields or plants. The aqueous medium is preferably water, for example tap water or rain water. The diluted compositions should have a concentration of the paraquat and/or fertilizer that makes it suitable for end-use, i.e. for fertilizing or treating plants or seeds, preferably for fertilizing or treating plants. In an embodiment an electrolyte formulations is diluted to lower concentration, suitably with water, to obtain viscous agrochemical formulations of paraquat and/or fertilizer containing of from 0.1 to 250, more preferably from 0.5 to 150, even more preferably from 1 to 100 g/l, the amount of electrolyte being

calculated as pure electrolyte. For crop field spray applications, a conventionally used total spray rate is 200 litres/hectar, and the typical recommended treat rate of electrolyte is from 1 to 5 kg electrolyte/ha, resulting in a preferred electrolyte concentration in the agrochemical formulation of from 0.5 to 2.5 wt% (5 to 25 g/l), expressed as the weight of the electrolyte in the spray solution.

The present invention also relates a method of treating a field or a plant or seed by distributing the composition of the invention over said field or contacting said plant or seed with a composition according to the invention, preferably a field or plant is treated. In a further aspect, a part of the plant or seeds is contacted with a composition or agrochemical formulation of the invention, at an amount sufficient for the electrolyte to obtain the desired agrochemical effect on the plant or seed. Preferably, the step of contacting a plant or seed with the agrochemical formulation involves spraying the agrochemical formulation onto the plant or seed.

The electrolyte compositions and agrochemical formulations may comprise further auxiliary ingredients. Auxiliary ingredients include defoamers like the SAG products from Momentive Performance Chemicals, USA, the BC Antifoam products of KCC Brasilon, Foamaster of Cognis, Rhodisol of Rhodia, Break Thru of Degussa, and/or the Surfynol® DF series and the Airase® SSDL™ products of Air Products may be included in the formulation. If used, they are suitably used in an amount of from 0.01 to 10, in an embodiment from 0.05 to 1, in another embodiment from 0.1 to 0.5 g/l in the concentrated compositions. Other auxiliary ingredients include pesticides that are not in the salt form, particularly if they are water-soluble and particularly when they lead to a higher ionic strength in the formulation, such as phenoxy-acid-type herbicides, including a product such as 2,4-D (2,4-dichlorophenoxy). If so desired, the solutions of the invention can be mixed with non-soluble chemicals. The dispersions that are obtainable in this way are to be included in the term “solutions” as used herein.

The invention will now be further illustrated with reference in the following example which is provided for illustrative purposes only. Throughout this document, unless

indicated differently, the weight percentages of the compositions are based on the total weight of the composition, whereby the total weight of the composition is 100 wt%. The term water-soluble is used for materials that dissolve in an amount of at least 1 g per liter of demineralized water at 25 °C. Where used, the term “consisting” also embraces “consisting substantially”, but may optionally be limited to its strict meaning of “consisting entirely”.

Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of the words, for example “comprising” and “comprises”, mean “including but not limited to”, and do not exclude other moieties, additives, components, integers or steps. Moreover the singular encompasses the plural unless the context otherwise requires: in particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Where upper and lower limits are quoted for a property, for example for the concentration of a component, then a range of values defined by a combination of any of the upper limits with any of the lower limits may also be implied.

It will also be appreciated that features from different aspects and embodiments of the invention may be combined with features from any other aspect and embodiment of the invention.

Material and Methods

Adsee 1629 = C-16 fatty amine based quaternary ammonium salt provided by Akzo Nobel, Sweden.

Adsee C70S adjuvant = N-[3-(dimethylamino)propyl] cocoamide (Coco-APA) supplied by AkzoNobel Surface Chemistry, Sweden (provided as 70% active), neutralized with salicylic acid.

Paraquat dichloride 42% samples ex Lu-ba Chemical Company and Hextar Chemicals Company were evaluated.

Ammonium sulfate, potassium nitrate, phosphoric acid (85% purity), and urea were purchased from Merck Chemicals.

Procedure

In the examples solutions as indicated were prepared by measuring the ingredients and combining them with water, whereby the amount of water used was the amount needed to achieve a total volume of 1 liter. Examples marked CE are comparative. Hereafter the mixture was stirred until all solids were fully dissolved, where desired after heating to 40 °C, and subsequent the solution was cooled to room temperature. The viscosity of the resulting solutions was measured at a temperature of 20 °C (unless indicated differently), using a Brookfield viscometer model DV-I with a S34 spindle at a speed of 30 rpm at PH 4. The viscosity observed is noted in the tables.

Example 1, evaluation in formulations comprising Paraquat dichloride ex Lu-ba Chemical Company

Composition	#1 - CE	#2	#3	#4
Paraquat TK 42% (g)	600	600	600	600
Adsee 1629 (g)	100	90	80	75
Adsee C-70S (g)	0	10	20	25
Water	Up to 1L	Up to 1L	Up to 1L	Up to 1L
Viscosity (mPas)	120	630	8,450	>10,000

Example 2, evaluation in formulations comprising Paraquat dichloride ex Hextar Chemicals Company

Composition	#1 - CE	#2 - CE	#3	#4
Paraquat TK 42% (g)	600	600	600	600
Adsee 1629 (g)	0	50	80	100
Adsee C-70S (g)	0	0	20	50
Water	Up to 1L	Up to 1L	Up to 1L	Up to 1L
Viscosity (mPas)	30	120	6,450	>10,000

Example 3, evaluation in formulations comprising 40% Ammonium sulfate solution

Composition	#1 - CE	#2	#3	#4	#5
(NH4)2SO4 (g)	400	400	400	400	400
Adsee 1629 (g)	50	47.5	45.0	42.5	40
Adsee C-70S (g)	0	2.5	5.0	7.5	10
Water	Up to 1L	Up to 1L	Up to 1L	Up to 1L	Up to 1L
Viscosity* (mPas)	20	390	550	1150	2850

* = Measured at 25°C

Example 4, evaluation in formulations comprising a complex fertilizer solution (NPK)

Composition	#1 - CE	#2	#3	#4	#5
KNO3 (g)	100	100	100	100	100
Phosphoric Acid - 85% purity (g)	110	110	110	110	110
Urea (g)	60	60	60	60	60
(NH4)2SO4 (g)	50	50	50	50	50
Adsee 1629 (g)	40	40	40	40	40
Adsee C-70S (g)	0	2.5	5.0	7.5	10
Water	Up to 1L	Up to 1L	Up to 1L	Up to 1L	Up to 1L
Viscosity* (mPas)	300	570	630	750	950

* = Measured at 25°C

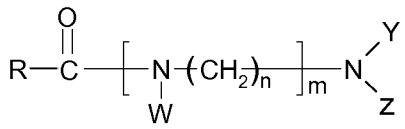
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Claims

1. An aqueous solution comprising

a) one or more electrolytes selected from paraquat and fertilizer salts in a total amount of 2.5 – 75 percent by weight of the total formulation,

b) one or more amidoalkylamines of the formula (1)



(1)

wherein R is a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms, m is 1-7, n is 2-6, W and Y are independently chosen from H, hydroxyl, an alkyl group having 1-4 carbon atoms, a benzyl group, -(AO)sH, where AO is an alkyleneoxy group having 2-4 carbon atoms, and s is on the average 1-30, and an acyl (R'C=O) group where R' is a linear or branched, saturated or unsaturated alkyl group having 2-22 carbon atoms,

c) one or more quaternary ammonium compounds having the structure of formula (2):

$R^1R^2R^3R^4N^+ X^-$ (2)

wherein R^1, R^2, R^3, and R^4 are independently selected from saturated or unsaturated, linear or branched, substituted or unsubstituted, alkyl, aralkyl, or alkenyl groups comprising from 1 to 30 carbon atoms, whereby at least one of R^1, R^2, R^3, and R^4 is a C_4-C_{30} group, and X^- is an anion from an inorganic or organic acid, and

d) water.

2. A solution of claim 1 with a viscosity from 100 to 10000 mPas at 20°C as determined with a Brookfield® DV-I viscometer, equipped with a spindle S34 and % torque control 10-100%,.

3. A solution of claim 1 or 2 comprising from 3 to 75 % by weight of paraquat, fertilizer or mixture of paraquat and fertilizer.

4. A solution of any one of claims 1-3 comprising from 5 to 400 gram per liter of amidoalkylamines of the formula (1).

5. A solution of any one of claims 1-4 comprising from 5 to 400 gram per liter of quaternary ammonium compounds having the structure of formula (2).

6. A solution of any one of claims 1-5 comprising a quaternary ammonium compound which is a quaternized amidoalkylamine of formula (1).

7. A solution of any one of claims 1-6 further comprising one or more acids, bases, or salts to control the pH.

8. Process to make solutions of any one of claims 17 by mixing the ingredients in the indicated amounts

9. Process to make an aqueous agrochemical formulation by diluting a solution of any one of claims 1-7.

10. Agrochemical formulations obtainable with the process of claim 9.

11. Use of an agrochemical formulation of claim 10 to treat a field, plant, or seed.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/052581

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N25/02 A01N25/30 A01P13/00 A01N43/40 C05G3/02
C05G3/06
ADD.
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)
A01N C05G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 01/32019 A1 (COGNIS DEUTSCHLAND GMBH [DE]; SABORIT LUIS [ES]) 10 May 2001 (2001-05-10) page 7; example 4; table 1	1-11
A	CN 101 601 380 A (LIANXIAO YANG [CN]) 16 December 2009 (2009-12-16) page 7; claim 1; table 1	1-11
A	CN 102 907 422 A (JIANGSU ZHONGSHAN CHEMICAL CO LTD) 6 February 2013 (2013-02-06) paragraph [0019]; claim 1	1-11

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 March 2017	21/03/2017

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/052581

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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