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(54) Title: EMULSIFIABLE CONCENTRATE COMPRISING A PHENOXY-ALKANOIC ACID HERBICIDE

(57) Abstract: An emulsifiable concentrate of a phenoxy-alkanoic acid herbicide comprising a phenoxy-alkanoic acid herbicide dis-
solved in an amide solvent and at least one amine.



Emulsifiable concentrate comprising a Phenoxy-alkanoic Acid Herbicide

Field

[1] The invention relates to an emulsifiable concentrate composition comprising a
5 phenoxy-alkanoic acid herbicide a process for preparation of the composition and
method for control of plant growth using the composition.

Background

[2] Auxin herbicides have proven to be effective for control of unwanted plants.
Phenoxy-alkanoic acid herbicides include 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4-
10 DB (4-(2,4-dichlorophenoxy)butanoic acid), dichloroprop (2-(2,4-
dichlorophenoxy)propanoic acid), dicloprop-P, MCPA ((4-chloro-2-
methylphenoxy)acetic acid), MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid),
mecoprop (2-(4-chloro-2-methylphenoxy)propanoic acid) and mecoprop-P.

[3] Phenoxy-alkanoic acid herbicides in the acid form have poor solubility in water
15 and are commonly formulated as an ester, such as the methyl ester or an amine salt
such as the dimethylamine salt. The Phenoxy-alkanoic esters, such as the methyl
ester, are more active than the salts but are more likely to volatilize with the potential
to damage off-target plants. The Phenoxy-alkanoic esters and auxin amine salts are
each converted in the target plants to the acid which is active in controlling plant
20 growth. It is desirable to formulate the acids as a stable concentrate.

[4] Some acid herbicides from the auxin class have been formulated in the form of
the acid. Volgas et al. (US 8,426,341) discloses an acid herbicide concentrate with a
specific alcohol ethoxylate surfactant which forms a microemulsion on dilution with
water.

25 [5] Groenewegen et al. (US 2012/0283103) describes the use of certain fatty acid
amide solvents to form concentrate emulsions (CEs) and emulsifiable concentrates
(ECs) of auxin herbicides. The amide solvents are said to have high solvency for
water insoluble compounds in preparing concentrates in the form of an emulsion
(CEs) and emulsifiable concentrates (ECs).

[6] Concentrated emulsions (CEs) contain water which necessarily reduces the potential loading of the active. We have found that emulsifiable concentrates of Phenoxy-alkanoic acids still have poor solution stability even in amide solvents and on cold storage give rise to crystal formation in the concentrate and/or crystal formation on dilution of the concentrate to form an emulsion. Poor storage stability and the consequential formation of precipitates can disrupt effective use of the herbicide through clogging of spray equipment and/or dosing of the herbicide at a lower rate than desired.

[7] There is a need for a more highly stable emulsifiable concentrate of phenoxy-alkanoic acid herbicides.

[8] The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

Summary

[9] We provide an emulsifiable concentrate of a phenoxy-alkanoic acid herbicide comprising a phenoxy-alkanoic acid herbicide dissolved in an amide solvent and at least one amine.

[10] The amine (which when there is more than one said amine is the total of the amines) is preferably present in an amount of from 0.5% to 5% by weight more preferably from 2% to 5%, still more preferably from 3% to 5% by weight of the amine based on the weight of the emulsifiable concentrate.

[11] There is further provided a method for the preparation of an emulsifiable concentrate of phenoxy-alkanoic acid herbicide comprising combining said phenoxy-alkanoic acid herbicide with an amide solvent and at least one amine (preferably in an amount of from 0.5% to 5% by weight, more preferably from 2% to 5%, still more preferably from 3% to 5% by weight of a tri-alkanolamine based on the weight of the emulsifiable concentrate) and heating the compositions, preferably to a temperature

of at least 40°C, more preferably 50°C, still more preferably at least 60°C and most preferably at least 65°C, to provide a solution of the phenoxy-alkanoic acid herbicide.

[12] There is further provided a method of controlling weeds comprising providing a phenoxy-alkanoic acid emulsifiable concentrate according to the above, diluting the concentrate with water to provide an emulsion and applying the diluted concentrate to the weeds to be controlled.

[13] We have further found that the emulsifiable concentrate may result in formation of a minor proportion of esters and amides of the phenoxyalkanoic acids on storage.

While the esters and amides may be active herbicides, in order to avoid in situ

formation of esters and/or amides it is particularly preferred to include a small amount of water, preferably from 0.5 to 5% by weight water based on the weight of the emulsifiable concentrate more preferably from 0.5% to 3%, still more preferably from 1% to 3%, by weight water based on the weight of the emulsifiable concentrate

Detailed Description

[14] The term “emulsion”, as used herein, refers to a fine dispersion of minute droplets of one liquid in another in which it is not soluble or miscible and includes microemulsions and macroemulsions. The term “emulsifiable concentrates” refers to concentrates which, on dilution, form either microemulsions or macroemulsions.

[15] Throughout the description and the claims of this specification the word

“comprise” and variations of the word, such as “comprising” and “comprises” is not intended to exclude other additives, components, integers or steps.

[16] The reference to a phenoxy-acid herbicide herein, except where the context determines otherwise, refers to the phenoxy-alkanoic acid herbicide in the form of the free acid.

[17] The concentrate composition comprises a phenoxy-alkanoic acid herbicide.

Typically said phenoxy-alkanoic acid herbicide will be present in a total amount of at least 200g acid per litre of emulsifiable concentrate preferably at least 250 g/L, more preferably at least 300 g/L, still more preferably at least 350 g/L and most preferably at least 380 g/L phenoxy-alkanoic acid herbicide. In some embodiments the

concentration of phenoxy acid herbicide is at least 400g/L such as at least 450 g/L or

at least 500g/L of the emulsifiable concentrate. The phenoxy-alkanoic acid herbicide may consist of a single herbicide or mixture of two or more phenoxy-alkanoic acid herbicides.

[18] The preferred phenoxy-alkanoic acid herbicide includes at least one selected from the group consisting of:

phenoxyacetic herbicides including 2,4-D and MCPA;

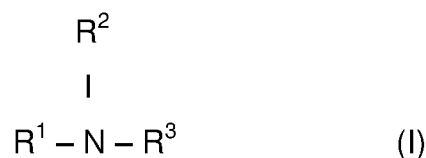
phenoxybutyric herbicides including 4-CPB, 2,4-DB, 3,4-DB, MCPB and 2,4,5-TB;
and

phenoxypropionic herbicides including dichlorprop, dichlorprop-P, fenoprop, mecoprop and mecoprop-P.

[19] The more preferred herbicides are selected from the group consisting of 2,4-D, MCPA, dicloprop, dicloprop-P, mecoprop and mecoprop-P. In a particularly preferred set of embodiments the emulsifiable concentrate comprises 2,4-D in an amount of at least 200g acid per litre of emulsifiable concentrate preferably at least 250 g/L, more preferably at least 300 g/L, still more preferably at least 350 g/L and most preferably at least 380 g/L.

[20] The emulsifiable concentrate composition comprises an amine. The amine is typically a primary secondary or tertiary amine and may comprise aliphatic straight or branched chain substituents, aliphatic ring substituents or may comprise the heteroatom of a aliphatic heterocyclic amine. The amine may comprise a plurality of amine groups and/or mixture of amines.

[21] In one embodiment the amine comprises at least one amine of formula (I)



wherein R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, C_1 to C_{10} alkyl; C_5 or C_6 cycloaliphatic optionally substituted with from one to four C_1 to C_4 alkyl groups and/or an amino- C_1 to C_4 alkyl group; C_1 to C_{10} alkyl substituted with a substituent selected from the group consisting of hydroxyl, C_1 to C_{10}

alkoxy, amino, (C₁ to C₆ alkyl)amino and di-(C₁ to C₆ alkyl)amino; and the group wherein two of R¹, R² and R³ together form a ring of 5 or 6 constituent ring members selected from methylene, -O-, -N- and -N(C₁ to C₆-alkyl)- and the other of R¹, R² and R³ is selected from hydrogen, C₁ to C₆ alkyl and C₁ to C₆ alkyl substituted with a substituent selected from the group consisting of hydroxyl, C₁ to C₆ alkoxy, amino and (C₁ to C₆ alkyl)amino; and wherein at least one of R¹, R² and R³ is other than hydrogen.

[22] In one set of embodiments the amine is of formula I wherein R¹, R² and R³ are independently selected from the group selected from hydrogen and C₁ to C₁₀ alkyl wherein at least one of R¹, R² and R³ is C₁ to C₁₀ alkyl. Preferred amines in this group are mono-, di- and tri-(C₁ to C₆ alkyl)amines and preferably tri-(C₁ to C₄ alkyl)amines such as triethylamine.

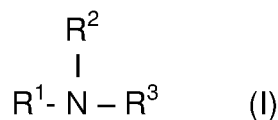
[23] In a further set of amines of formula I R¹, R² and R³ are independently selected from the group consisting of hydrogen, C₁ to C₁₀ alkyl and C₁ to C₁₀ alkyl substituted with a substituent selected from the group consisting of hydroxyl, C₁ to C₁₀ alkoxy, amino, (C₁ to C₆ alkyl)amino and di-(C₁ to C₆ alkyl)amino wherein at least one of R¹, R² and R³ is other than hydrogen and C₁ to C₁₀ alkyl. Examples of amines in this group include compounds of formula I wherein R¹, R² and R³ are independently selected from hydrogen, C₁ to C₆ alkyl and C₁ to C₆ alkyl substituted with a substituent selected from the group consisting of hydroxyl, C₁ to C₆ alkoxy, amino, (C₁ to C₄ alkyl)amino and di-(C₁ to C₄ alkyl)amino wherein at least one of R¹, R² and R³ is other than hydrogen and C₁ to C₆ alkyl. More specific examples of this group of compounds include (C₁ to C₆ alkanol)amines, di-(C₁ to C₆ alkanol)amines, tri-(C₁ to C₆ alkanol)amines di-(C₁ to C₆ alkyl) (C₁ to C₆ alkanol)amines, (amino C₁ to C₆ alkyl)di-(C₁ to C₆ alkyl)amines, di(-amino-C₁ to C₆ alkyl)alkylamines.

[24] In a further set of amines of Formula I two of R¹, R² and R³ together form a ring, incorporating the amine nitrogen, of 5 or 6 constituent ring members selected from the group consisting of methylene and optionally a further heteroatom ring member selected from -O-, -N(H)- and -N(C₁ to C₆-alkyl)-; and the other of R¹, R² and R³ is selected from hydrogen, C₁ to C₆ alkyl and C₁ to C₆ alkyl substituted with a

substituent selected from the group consisting of hydroxyl, C₁ to C₆ alkoxy, amino and (C₁ to C₆ alkyl)amino

[25] The constituent ring members where at least two of R¹, R² and R³ form a heterocyclic ring of 5 or 6 constituent members may, for example, be a ring selected
5 from the group consisting of pyrrolidine, piperidine, morpholine and piperazine.

[26] The preferred amines are of formula I



10 wherein either (i) R¹, R² and R³ are C₂ to C₄ alkanol or (ii) R¹ is C₁ to C₁₀ alkoxy substituted C₂ to C₄ alkyl and R² and R³ are independently hydrogen or C₁ to C₄ alkyl.

[27] More preferably the amines are trialkanolamines and alkoxyamines are of formula (I) wherein (i) R¹, R² and R³ are independently selected from C₂ to C₄ alkanol (more preferably triethanolamine and triisopropanolamine) or (ii) R¹ is selected from
15 C₁ to C₆ alkoxy-substituted alkyl and R² and R³ are hydrogen or C₁ to C₄ alkyl such as methyl (preferably R² and R³ hydrogen).

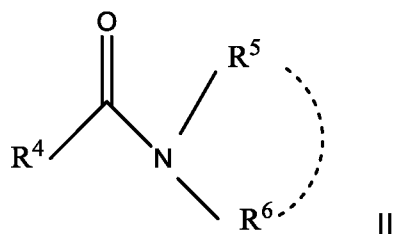
[28] Specific examples of amines selected from trialkanolamines, alkoxyalkylamines and mixtures thereof include triethanolamine, tripropanolamine, methoxypropylamine and hexyloxypropylamine.

20 [29] The trialkanolamine is preferably selected from the group consisting of tri-(C₂ to C₄ alkanol)amines such as triethanolamine, triisopropanolamine and mixtures thereof.

[30] The amine is preferably present in an amount of from 0.5% to 5% by weight more preferably 1% to 5% by weight, still more preferably 2% to 5% by weight, still more preferably from 3% to 5% by weight and most preferably from 4% to 5% by
25 weight of the amine based on the weight of the emulsifiable concentrate.

[31] The emulsifiable concentrate composition comprises an amide solvent. The amide solvent is, in one set of embodiments, present in an amount of from 25% to 60% by weight of the composition, preferably from 25% to 50% and more preferably from 25% to 45% by weight of the emulsifiable concentrate composition.

[32] Examples of suitable amide solvents include compounds of formula II:



wherein

R^4 is selected from the group consisting of hydrogen and C_1 to C_{17} hydrocarbyl;

5 R^5 is selected from the group consisting of C_1 to C_{15} hydrocarbyl;

R^6 is selected from the group consisting of C_1 to C_{15} hydrocarbyl; and

R^5 and R^6 may together form a ring incorporating the nitrogen of the amide comprising 4 or 5 methylene groups; preferred examples of R^5 and R^6 are

independently selected from the group consisting of C_1 to C_6 hydrocarbyl and the

10 group wherein R^5 and R^6 together form a ring incorporating the nitrogen of the amine by a bridging group $R^5 \dots R^6$ of formula $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$ or $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$.

[33] In one embodiment the amide solvent is of formula II wherein

15 R^4 is selected from the group consisting of C_3 to C_{17} alkyl, preferably C_6 to C_{17} aliphatic; and

R^5 and R^6 are independently selected from the group C_1 to C_6 alkyl and the group wherein R^5 and R^6 together form a bridging group of formula selected from the group consisting of $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$ and $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$, preferably R^5 and R^6 are independently selected from C_1 to C_4 alkyl or the group wherein R^5 and R^6 together form a bridging group of formula $-\text{CH}_2 \text{CH}_2 \text{OCH}_2 \text{CH}_2-$, $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$ and $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2-$.

[34] In a preferred set of embodiments, the amide solvent of formula II wherein

R^4 is C_6 to C_{17} alkyl; and

25 R^5 and R^6 are independently selected from C_1 to C_4 alkyl such as methyl, ethyl, n-propyl, isopropyl.

[35] Examples of the amide solvents include

N,N-dimethyl fatty acid amides such as N,N-dimethyl C₈ to C₁₆ fatty acid amide.

[36] The preferred amide “solvents” are fatty acid amides comprising a C₅ to C₁₇ aliphatic group.

[37] Specific examples of amide solvents include:

- 5 N,N-dimethyl-octanamide, N,N-dimethyl-decanamide,
N,N-dimethyl-caprylamide, N,N-dimethyl-2-ethylhexanoamide,
N,N-dimethyl-oleamide N,N-dimethyl-lauricamide (also known as N,N-
dimethyldodecanamide), N,N-dimethyl-myristicamide (also known as N,N-
dimethyltetradecanamide), N,N-dimethyl-9-decenamide and mixtures of two or
10 more thereof.

[38] The emulsifiable concentrate may and preferably will, include a hydrocarbon co-solvent. The hydrocarbon co-solvent preferably has a flash point of at least 60.5 °C. The hydrocarbon co-solvent preferably comprises at least one hydrocarbon selected
15 from alkyl substituted aromatics such as mono-, di- and trialkyl benzenes and alkyl naphthalenes. For example, C₉ alkyl benzene is reported to have a flash point of 42 °C whereas C₁₀ alkylbenzene is reported to have a flash point of 66 °C. A preferred co-solvent is a mixture of C₈ to C₁₂ di- and tri-alkyl benzenes, commercially available from Exxon Mobil as Solvesso 150TM and Solvesso 200TM.

20 [39] The hydrocarbon co-solvent is preferably in the range of from 2% to 25% w/w of the emulsifiable concentrate. Preferably the hydrocarbon co-solvent is present in an amount of from 5% to 20% w/w and more preferably from 5% to 15% w/w of the emulsifiable concentrate.

[40] The emulsifiable concentrate will typically comprise an emulsifier component.
25 The emulsifier component may, for example, comprise from 2% w/w to 25% w/w of the emulsifiable concentrate. The emulsifier component preferably comprises from 5% w/w to 20% w/w and more preferably from 5% w/w to 15% w/w of the concentrate composition.

[41] The emulsifier component may include anionic, non-ionic, cationic or mixed types of emulsifiers. In one embodiment the concentrate comprises an anionic emulsifier (preferably an alkylarylsulfonate) in an amount in the range of from 1% w/w to 10% w/w of the concentrate.

5 [42] The emulsifiable concentrate preferably comprises an alkylarylsulfonate anionic emulsifier. Alkylarylsulfonates are anionic surfactants and are available in compositions containing suitable counterions which may be optionally substituted ammonium and metal counterions. Examples of alkylarylsulfonates include butylnaphthalenesulfonic acid, the di- and tri-isopropylnaphthalenesulfonic acids, the
10 salts of the condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, the salts of the condensation products of sulfonated naphthalene and naphthalene derivatives with phenol and formaldehyde, and the salts of alkylarylbenzenesulfonic acids such as dodecylbenzenesulfonic acid. Benzenesulfonates, such as alkyl- or arylbenzenesulfonates, e.g. (poly)alkyl- and
15 (poly)arylbenzenesulfonates which are acidic and neutralized with suitable bases, for example having 1 to 12 carbon atoms per alkyl radical or having up to 3 styrene units in the polyaryl radical, preferably (linear) dodecylbenzenesulfonic acid and oil-soluble salts thereof, such as, for example, the calcium salt or the isopropylammonium salt of dodecylbenzenesulfonic acid.

20 [43] It is particularly preferred that the composition of the invention contain a salt of dodecylbenzenesulfonic acid and most preferably calcium dodecylbenzenesulfonate.

[44] The emulsifiable concentrate preferably comprises a nonionic surfactant component. Preferred non-ionic surfactants include the condensation products of alkylene oxide with components forming nonpolar groups such as the condensation
25 products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol; the condensation products of ethylene oxide with phenols and alkylphenols such as isooctylphenol, octylphenol and nonylphenol; the condensation products of ethylene oxide with castor oil; the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitan monolaurate, and their condensation products with
30 ethylene oxide; ethylene oxide/propylene oxide block copolymers; lauryl alcohol polyglycol ether acetal.

[45] Examples of nonionic surfactants which may be used alone or in combination in the emulsifier component are listed below, in which EO=ethylene oxide units, such as PO=propylene oxide units and BO=butylene oxide units:

C₁₀-C₂₄-alcohols which may be alkoxyated, e.g. with 1-60 alkylene oxide units, preferably 1-60 EO and/or 1-30 PO and/or 1-15 BO in any order. The terminal hydroxyl groups of these compounds can be terminally capped by an alkyl, cycloalkyl or acyl radical having 1-24 carbon atoms. Examples of such compounds are: Genapol[®] C, L, O, T, UD, UDD, X products from Clariant, Plurafac[®] and Lutensol[®] A, AT, ON, TO products from BASF, Marlipal[®] 24 and O13 products from Condea, Dehypon[®] products from Henkel, Ethylan[®] products from Akzo Nobel, such as Ethylan CD 120.

Copolymers consisting of EO, PO and/or BO units, such as, for example, block copolymers, such as the Pluronic[®] products from BASF and the Synperonic[®] products from Uniquema with a molecular weight of from 400 to 10⁸.

Alkyleneoxy adducts of C₁-C₉ alcohols, such as Atlox[®] 5000 from Uniquema or Hoe[®] -S3510 from Clariant.

Fatty acid and triglyceride alkoxyates, such as the Serdiox[®] NOG products from Condea or alkoxyated plant oils, such as soybean oil, rapeseed oil, corn oil, sunflower oil, cottonseed oil, linseed oil, coconut oil, palm oil, thistle oil, walnut oil, peanut oil, olive oil or ricinus oil (i.e. castor oil), in particular rapeseed oil and castor oil, plant oils also being understood as meaning their transesterification products, e.g. alkyl esters, such as rapeseed oil methyl ester or rapeseed oil ethyl ester, for example the Emulsogen[®] products from Clariant, salts of aliphatic, cycloaliphatic and olefinic carboxylic acids and polycarboxylic acids, and alpha-sulfo fatty acid esters as available from Henkel. Particularly preferred in this group are castor oil ethoxyates such as TERMUL[®] 1284 and TERMUL[®] 1285 from Huntsman.

Fatty acid amide alkoxyates, such as the Comperlan[®] products from Henkel or the Amam[®] products from Rhodia.

Alkyleneoxy adducts of alkynediols, such as the Surfynol[®] products from Air Products. Sugar derivatives, such as amino and amido sugars from Clariant, glucitols from Clariant, alkyl polyglycosides in the form of the APG[®] products from Henkel or such as sorbitan esters in the form of the Span[®] or Tween[®] products from Uniquema
5 or cyclodextrine esters or ethers from Wacker.

Alkyleneoxy adducts based on polyol, such as Polyglycol[®] products from Clariant. Interface-active polyglycerides and derivatives thereof from Clariant. Surface-active compounds based on silicone and/or silane, such as the Tegopren[®] products from Goldschmidt and the SE[®] products from Wacker, and the Bevaloid[®],
10 Rhodorsil[®] and Silcolapse[®] products from Rhodia (Dow Corning, Reliance, GE, Bayer).

Per- or polyfluorinated surface-active compounds, such as Fluowet[®] products from Clariant, the Bayowet[®] products from Bayer, the Zonyl[®] products from Du Pont and products of this type from Daikin and Asahi Glass.

15 Interface-active sulfonamides, e.g. from Bayer.

Surface-active polyvinyl compounds, such as modified polyvinylpyrrolidone, such as the Luviskol[®] products from BASF and the Agrimer[®] products from ISP or the derivatized polyvinylacetates, such as the Mowilith[®] products from Clariant or the butyrates, such as the Lutonal[®] products from BASF, the Vinnapas[®] and the
20 Pioloform[®] products from Wacker or modified polyvinyl alcohols, such as the Mowiol[®] products from Clariant.

Surface-active polymers based on maleic anhydride and/or reaction products of maleic anhydride, and maleic anhydride and/or reaction products of copolymers which include maleic anhydride, such as the Agrimer[®] - VEM A products from ISP.

25 Surface-active derivatives of montane, polyethylene and polypropylene waxes, such as the Hoechst[®] waxes or the Licowet[®] products from Clariant.

Poly- or perhalogenated surfactants, such as, for example Emulsogen[®]-1557 from Clariant.

Phenols which may be alkoxyated, for example phenyl (C₁-C₄)alkyl ethers or (poly)alkoxyated phenols [=phenol (poly)alkylene glycol ethers], for example having 1 to 50 alkyleneoxy units in the (poly)alkyleneoxy moiety, where the alkylene moiety preferably in each case has 1 to 4 carbon atoms, preferably phenol reacted with 3 to 10 mol of alkylene oxide.

(poly)alkylphenols or (poly)alkylphenol alkoxyates [polyalkylphenol (poly)alkylene glycol ethers], for example with 1 to 12 carbon atoms per alkyl radical and 1 to 150 alkyleneoxy units in the polyalkyleneoxy moiety, preferably tri-n-butylphenol or triisobutylphenol reacted with 1 to 50 mol of ethylene oxide,

polyarylphenols or polyarylphenol alkoxyates [=polyarylphenol (poly)alkylene glycol ethers], for example tristyrylphenol polyalkylene glycol ethers with 1 to 150 alkyleneoxy units in the polyalkyleneoxy moiety, preferably tristyrylphenol reacted with 1 to 50 mol of ethylene oxide.

[46] Examples of surfactants from the group of aromatic-based surfactants are the surfactants of the abovementioned groups, preferably phenol reacted with 4 to 10 mol of ethylene oxide, available commercially, for example, in the form of the Agrisol[®] products (Akros), triisobutylphenol reacted with 4 to 50 mol of ethylene oxide, commercially available, for example, in the form of the Sapogenat[®] T products (Clariant), nonylphenol reacted with 4 to 50 mol of ethylene oxide, commercially available, for example, in the form of the Arkopal[®] products (Clariant), tristyrylphenol reacted with 4 to 150 mol of ethylene oxide, for example from the Soprophor[®] series, such as Soprophor[®] FL, Soprophor[®] 3D33, Soprophor[®] BSU, Soprophor[®] 4D-384, Soprophor[®] CY/8 (Rhodia).

[47] The non-ionic emulsifier present in the compositions of the invention may comprise one such surfactant or a blend of two or more non-ionic surfactants.

[48] The emulsifier is more preferably selected from alcohol ethoxylates, fatty acid ethoxylates, fatty amide ethoxylates and EO/PO block copolymers including butyl based block copolymers. The non-ionic emulsifier preferably comprises in the range of from 2% w/w to 25% w/w of the composition. More preferably the non-ionic

emulsifier comprises in the range of from 2% w/w to 20% w/w and more preferably from 2% w/w to 15% w/w of the concentrate.

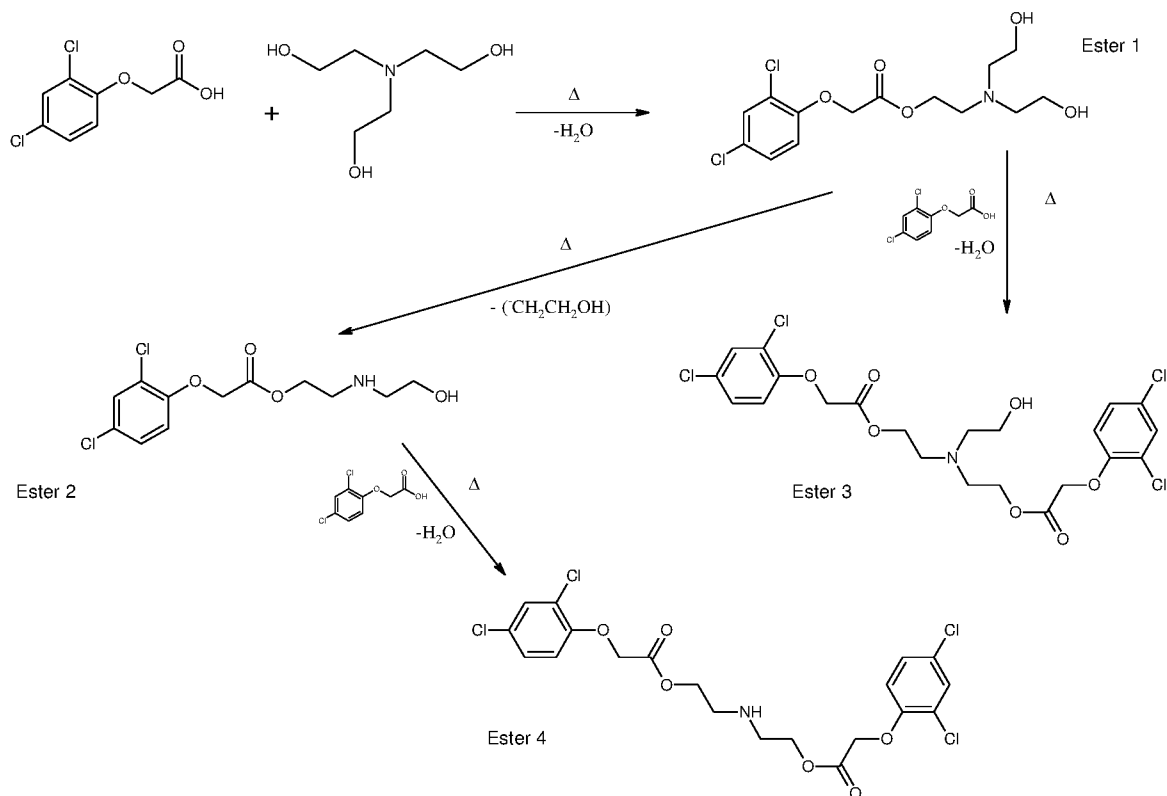
[49] In one embodiment, the anionic emulsifier (preferably an alkylaryl sulfonate) comprises from 1% to 10% w/w of the composition and the non-ionic emulsifier
5 comprises from 2% to 15% w/w of the composition.

[50] We have found that over a period of time the phenoxy-alkanoic acid concentration in the emulsifiable concentrate is reduced by formation of ester and/or amide derivatives of the phenoxy acid. This problem has not previously been recognised but is believed to occur in the presence of amines. The problem
10 regarding loss of active ingredients in acid emulsifiable concentrate (EC) formulations was discovered during the development of the phenoxy-alkanoic acid emulsifiable concentrate compositions, particularly 2,4-D acid EC formulations. Samples of 2,4-D acid EC formulations were initially tested for 2,4-content via a HPLC method specific to free 2,4-D acid. During formulation development and after subjecting formulations
15 to a 2 weeks at 54°C accelerated stability study a decreased level of 2,4-D free acid was found when compared to initial sample assay results. A method which was developed and validated for assaying total 2,4-D content via hydrolysis provided evidence that the loss in free acid content was via the speciation of 2,4-D acid into unknown transformation products. Subsequent work to identify the 2,4-D species was
20 carried out via LCMS (Liquid chromatography with positive electrospray ionization and time of flight mass spectrometry detection). The LCMS technique was successful in the identification and characterisation of a number of 2,4-D transformation species. This methodology was further utilised in the identification of transformation products in MCPA acid EC formulations.

[51] The transformation products were found to be esters and/or amides derived from the phenoxy-alkanoic acid herbicide in the presence of the amine. We have found that under the conditions found in EC formulations the carboxylic acid moiety present in the active ingredients; 2,4-D, MCPA react with base ingredients containing primary and secondary amine groups to produce amides and with alcohol groups to
30 produce esters as shown, for example, in Schemes 1 and 2 relating to 2,4-D. Note not all possible reaction schemes are provided below, as numerous iterations of alkyl,

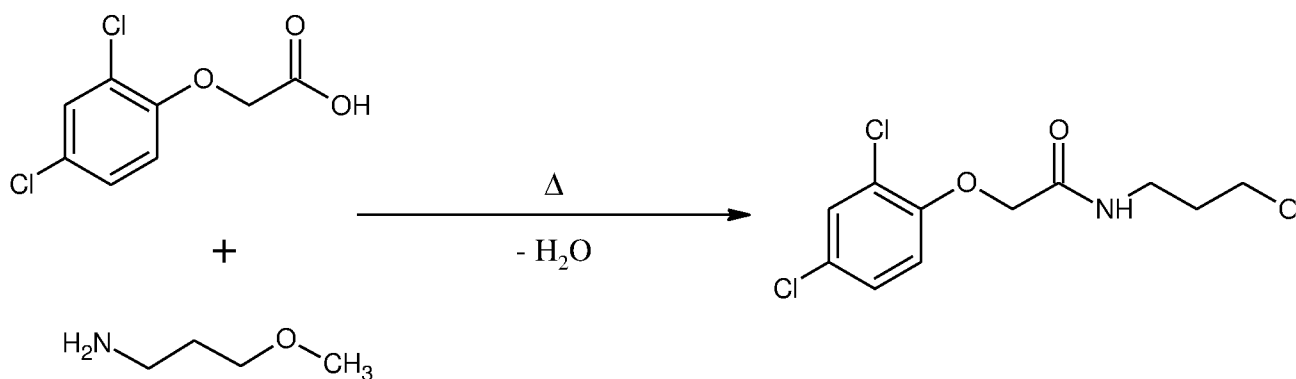
alkoxyl and ethanolamine type bases were tested during the formulation development stage.

Reaction Scheme 1 – Reaction of 2,4-D esters with triethanolamine (TEA)



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Reaction Scheme 2 – Reaction of 2,4-D with methoxypropylamine (MOPA)



[52] The reactions of carboxylic acids with amines are generally considered to proceed via an activation of the carboxylic acid prior to amide formation. It is unclear how these reactions are catalyzed/activated in the EC formulations, however addition

10

of water reduces significantly the formation of these transformed phenoxyalkanoic acid herbicides.

[53] The esters and amides retain a level of herbicidal activity but it is desirable to retain the phenoxy-alkanoic acid as a stable long term active.

- 5 [54] We have found that the addition of small amounts of water maintains the active ingredients predominantly in their acid form. The amount of water can be determined for any composition bearing in mind the desire to avoid formation of ester and amide derivatives.

- 10 [55] Generally speaking the amount of water is at least 0.5% by weight water based on the weight of the emulsifiable concentrate. More preferably the water is present in an amount of from 0.5 % to 3%, still more preferably from 1% to 3% by weight water based on the weight of the emulsifiable concentrate.

[56] In one set of embodiments the concentrate composition comprises:

- 15 Phenoxy-alkanoic acid herbicide selected from the group consisting of 2,4-D, MCPA, dicloprop, dicloprop-P, mecoprop, mecoprop-P, clopyralid and triclopyr (most preferably 2,4-D) in an amount of at least 250 g/L, more preferably at least 300 g/L and still more preferably at least 350 g/L, even more preferably at least 380 g/L (such as in some embodiments where the concentration of phenoxy acid herbicide is at least 400 g/L, at least 450g/L or at least 500g/L of the emulsifiable concentrate);
- 20 amide solvent, preferably fatty acid amide in an amount of from 25% to 60% w/w of the composition, more preferably 25% to 50% w/w and most preferably 25% to 45% w/w of the concentrate;

- 25 hydrocarbon co-solvent preferably selected from the group of C_8 - C_{12} di- and tri-alkylbenzenes in an amount of from 2% to 25% w/w, more preferably 5% to 20% w/w and most preferably 5% to 15% w/w of the concentrate;

anionic emulsifier in an amount of from 1% to 10% w/w of the composition;

non-ionic emulsifier in an amount of from 2% to 25% w/w, more preferably 2% to 20% w/w and still more preferably 2% to 15% w/w of the concentrate composition;
and

trialkanolamine (preferably selected from triethanolamine, triisopropanolamine and mixtures thereof), alkoxyalkylamine (preferably selected from methoxyalkylamine and mixtures of two or more thereof, in an amount of from 0.5% to 20% w/w of the concentrate, more preferably from 3% to 15% w/w of the concentrate and still more preferably from 5% to 15% w/w based on the total weight of said phenoxy-alkanoic acid auxin herbicides.

[57] The composition preferably contains water in an amount of at least 0.5% by weight water based on the weight of the emulsifiable concentrate. More preferably the water is present in an amount of from 0.5 % to 3%, still more preferably from 1% to 3% by weight water

[58] The composition of the invention has been found to provide good storage stability and also forms an emulsion on dilution with water which has good stability to allow effective application to plants.

[59] There is further provided a method for the preparation of an emulsifiable concentrate of auxin acid selected from the group consisting of phenoxy acid auxin herbicides and pyridine auxin herbicides and mixtures thereof (preferably the auxin acid herbicides are selected from the group consisting of 2,4-D, MCPA, dicloprop, dicloprop-P, mecoprop, mecoprop-P, clopyralid and triclopyr and most preferably 2,4-D) comprising combining said phenoxy-alkanoic acid with an amide solvent and amine and heating the compositions, preferably to a temperature of at least 40°C, more preferably 50°C, still more preferably at least 60°C and most preferably at least 65°C, to provide a solution of the auxin acid.

[60] In a further aspect, the invention provides a method of controlling weeds comprising providing an emulsifiable concentrate as hereinbefore described; diluting the concentrate with water to form an emulsion and applying the diluted composition to the weeds.

[61] The composition may comprise one or more further actives selected from the group consisting of herbicides fungicides, insecticides, plant growth regulators and biologicals.

[62] Examples of additional herbicides may be selected from the following classes:

amide herbicides such as allidochlor, beflubutamid, benzadox, benzipram, bromobutide, cafenstrole, CDEA, cyprazole, dimethenamid, dimethenamid-P, diphenamid, epronaz, etniproamid, fentrazamide, flupoxam, fomesafen, halosafen, isocarbamid, isoxaben, napropamide, naptalam, pethoxamid, propyzamide, quinonamid and tebutam;

anilide herbicides such as chloranocryl, cisanilide, clomeprop, cypromid, diflufenican, etobenzanid, fenasulam, flufenacet, flufenican, mefenacet, mefluidide, metamifop, monalide, naproanilide, pentanochlor, picolinafen and propanil;

arylalanine herbicides such as benzoylprop, flamprop and flamprop-M;

chloroacetanilide herbicides such as acetochlor, alachlor, butachlor, butenachlor, delachlor, diethatyl, dimethachlor, metazachlor, metolachlor, S-metolachlor, pretilachlor, propachlor, propisochlor, prynachlor, terbuchlor, thenylchlor and xylachlor;

sulfonanilide herbicides such as benzofluor, cloransulam, diclosulam, florasulam, flumetsulam, metosulam, perfluidone, pyrimisulfan and profluazol;

sulfonamide herbicides such as asulam, carbasulam, fenasulam, oryzalin, penoxsulam and pyroxsulam, see also sulfonylurea herbicides;

thioamide herbicides such as bencarbazone and chlorthiamid;

antibiotic herbicides such as bilanafos;

benzoic acid herbicides such as dicamba, chloramben, 2,3,6-TBA and tricamba;

pyrimidinyloxybenzoic acid herbicides such as bispyribac and pyriminobac;

pyrimidinylthiobenzoic acid herbicides such as pyrithiobac;

phthalic acid herbicides such as chlorthal;

quinolinecarboxylic acid herbicides such as quinclorac and quinmerac;

arsenical herbicides such as cacodylic acid, CMA, DSMA, hexaflurate, MAA, MAMA, MSMA, potassium arsenite and sodium arsenite;

benzoylcyclohexanedione herbicides such as mesotrione, sulcotrione, tefuryltrione and tembotrione;

benzofuranyl alkylsulfonate herbicides such as benfuresate and ethofumesate;

carbamate herbicides such as asulam, carboxazole, chlorprocarb, dichlormate, fenasulam, karbutilate and terbucarb;

carbanilate herbicides such as barban, BCPC, carbasulam, carbetamide, CEPC, chlorbufam, chlorpropham, CPPC, desmedipham, phenisopham, phenmedipham, phenmedipham-ethyl, propham and swep;

cyclohexene oxime herbicides such as alloxydim, butroxydim, clethodim, cloproxydim, cycloxydim, profoxydim, sethoxydim, tepraloxym and tralkoxydim;

cyclopropylisoxazole herbicides such as isoxachlortole and isoxaflutole;

dicarboximide herbicides such as benzfendazole, cinidon-ethyl, flumezin, flumiclorac, flumioxazin, and flumipropyn;

dinitrophenol herbicides such as dinofenat, dinoprop, dinosam, dinoseb, dinoterb,

DNOC, etinofen and medinoterb;

diphenyl ether herbicides such as ethoxyfen;

nitrophenyl ether herbicides such as acifluorfen, aclonifen, bifenox, chlormethoxyfen, chlornitrofen, etniproamid, fluorodifen, fluoroglycofen, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen;

dithiocarbamate herbicides such as dazomet and metam;

halogenated aliphatic herbicides such as alorac, chloropron, dalapon, flupropanat, hexachloroacetone, iodomethane, methyl bromide, monochloroacetic acid, SMA and TCA;

imidazolinone herbicides such as imazamethabenz, imazamox, imazapic,

imazapyr, imazaquin and imazethapyr;

nitrile herbicides such as bromobonil, bromoxynil, chloroxynil, iodonil, ioxynil and pyraclostrobin;

organophosphorus herbicides such as amiprofos-methyl, anilofos, bensulide, bilanafos, butamifos, 2,4-DEP, DMPA, EBEP, fosamine, glufosinate, glyphosate, and piperophos;

oxadiazolone herbicides such as dimefuron, methazole, oxadiargyl and oxadiazon;

phenoxy herbicides such as bromofenoxim, clomeprop, 2,4-DEB, 2,4-DEP, difenopenten, disul, erbon, etniproamid, fenteracol and trifluralin;

aryloxyphenoxypropionic herbicides such as chlorazifop, clodinafop, clofop, cyhalofop, diclofop, fenoxaprop, fenoxaprop-P, fenthiaprop, fluazifop, fluazifop-P, haloxyfop, haloxyfop-P, isoxapyrifop, metamifop, propaquizafop, quizalofop, quizalofop-P and trifop;

phenylenediamine herbicides such as dinitramine, and prodiamine

- phenyl pyrazolyl ketone herbicides** such as benzofenap, pyrasulfotole, pyrazolynate, pyrazoxyfen and topramezone;
- pyrazolylphenyl herbicides** such as fluazolate, nipyraclufen and pyraflufen;
- pyridazine herbicides** such as credazine, pyridafol and pyridate;
- 5 **pyridazinone herbicides** such as brompyrazon, chloridazon, dimidazon, flufenpyr, metflurazon, norflurazon, oxapyrazon and pydanon;
- pyridine herbicides** such as aminopyralid, clodinate, clopyralid, dithiopyr, fluroxypyr, haloxydine, picloram, picolinafen, pyriclor, thiazopyr and triclopyr;
- pyrimidinediamine herbicides** such as iprymidam and tioclorim;
- 10 **quaternary ammonium herbicides** such as cyperquat, diethamquat, difenzoquat, diquat, morfamquat and paraquat;
- thiocarbamate herbicides** such as butylate, cycloate, di-allate, EPTC, esprocarb, ethiolate, isopolinate, methiobencarb, molinate, orbencarb, pebulate, prosulfocarb, pyributicarb, sulfallate, thiobencarb, tiocarbazil, tri-allate and vernolate;
- 15 **thiocarbonate herbicides** such as dimexano, EXD, proxan and eptam (EPTC);
- thiourea herbicides** such as methiuron;
- triazine herbicides** such as dipropetryn; triaziflam and trihydroxytriazine;
- chlorotriazine herbicides** such as atrazine; chlorazine, cyanazine, cyprazine, eglinazone, ipazine, mesoprazine, procyazine, proglinazone, propazine, sebuthylazine,
- 20 **simazine, terbuthylazine and trietazine;**
- methoxytriazine herbicides** such as atraton, methometon, prometon, secbumeton, simeton and terbumeton;
- methylthiotriazine herbicides** such as ametryn, aziprotryne, cyanatryn, desmetryn, dimethametryn, methoprotryne, prometryn, simetryn and terbutryn;
- 25 **triazinone herbicides** such as ametridione, amibuzin, hexazinone, isomethiozin, metamitron and metribuzin;
- triazole herbicides** such as amitrole, cafenstrole, epronaz and flupoxam;
- triazolone herbicides** such as amicarbazone, bencarbazone, carfentrazone, flucarbazone, propoxycarbazone and sulfentrazone ;
- 30 **triazolopyrimidine herbicides** such as cloransulam, diclosulam, florasulam, flumetsulam, metosulam and penoxsulam;
- uracil herbicides** such as butafenacil, bromacil, flupropacil, isocil, lenacil and terbacil;

urea herbicides such as benzthiazuron, cumyluron, cycluron, dichloralurea, diflufenzopyr, isonoruron, isouron, methabenzthiazuron, monisouron and noruron;

phenylurea herbicides such as anisuron, buturon, chlorbromuron, chloreturon, chlorotoluron, chloroxuron, daimuron, difenoxuron, dimefuron, diuron, fenuron,

5 fluometuron, fluothiuron, isoproturon, linuron, methiuron, methyldymron, metobenzuron, metobromuron, metoxuron, monolinuron, monuron, neburon, parafluron, phenobenzuron, siduron, tetrafluron and thidiazuron;

sulfonylurea herbicides including:

pyrimidinylsulfonylurea herbicides such as amidosulfuron; azimsulfuron, 10 bensulfuron, chlorimuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, mesosulfuron, nicosulfuron, orthosulfamuron, oxasulfuron, primisulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron and trifloxysulfuron;

triazinylsulfonylurea herbicides such as chlorsulfuron, cinosulfuron, 15 ethametsulfuron, iodosulfuron, metsulfuron, prosulfuron, thifensulfuron, triasulfuron, tribenuron, triflusulfuron and tritosulfuron; and

thiadiazolylurea herbicides such as buthiuron, ethidimuron, tebuthiuron, thiazafluron and thidiazuron; and

unclassified herbicides such as KIH-485, acrolein, allyl alcohol, azafenidin, 20 benazolin, bentazone, benzobicyclon, buthidazole, calcium cyanamide, cambendichlor, chlorfenac, chlorfenprop, chlorflurazole, chlorflurenol, cinmethylin, clomazone, CPMF, cresol, ortho-dichlorobenzene, dimepiperate endothal, fluoromidine, fluridone, flurochloridone, flurtamone, fluthiacet, indanofan, methyl isothiocyanate, OCH, oxaziclomefone, pentachlorophenol, pentoxazone, 25 phenylmercury acetate, pinoxaden, prosulfalin, pyribenzoxim, pyriftalid, quinoclamine, rhodethanil, sulglycapin, thidiazimin, tridiphane, trimeturon, tripropindan and tritac.

[63] The weight ratio of phenoxy-alkanoic acid to other herbicide will depend on the nature of the other herbicide and desired loading. However, typically the weight ratio of phenoxy-alkanoic acid to other herbicide (or herbicides) is in the range of from 30 : 30 1 to 1 : 10. It is generally preferred that the phenoxy-alkanoic acid herbicide constitutes more than 15% w/w of the total herbicide content and preferably at least 75% w/w of the total herbicide content. In one embodiment the mixture with other

herbicides comprises more than 50% w/w of the total herbicide content of 2,4-D and preferably at least 75% w/w 2,4-D and most preferably at least 80% w/w 2,4-D.

[64] In one set of embodiments the composition comprises a phenoxy-alkanoic acid herbicide and a pyridine auxin herbicide such as picloram, clopyralid, triclopyr, fluroxypyr, aminopyralid or mixtures of two or more thereof. Typically the weight ratio of phenoxy-alkanoic acid to pyridine auxin herbicide (or herbicides) is in the range of from 30 : 1 to 1 : 10. Preferably the pyridine auxin herbicide will be in the form of the acid. In a further set of embodiments the composition comprises a phenoxyalkanoic acid herbicide and glyphosate (preferably in the form of glyphosate acid) in a weight ratio in the range of from 30 : 1 to 1 : 10.

[65] In a further set of embodiments the emulsifiable concentrate comprises a mixture of the phenoxy-alkanoic acid herbicide and an aryloxyphenoxy-alkanoic acid herbicide, preferably selected from the group consisting of fenoxaprop, fenoxaprop-P, haloxyfop and mixtures thereof. The weight ratio of phenoxy-alkanoic acid to aryloxyphenoxyalkanoic acid herbicide (or herbicides) is preferably in the range of from 30 : 1 to 1 : 10.

[66] The emulsifiable concentrate composition is typically in the form of solution, however in some embodiments additional components such as further active agents may be present as may be present as a solid suspension in the concentrate.

[67] The invention will now be described with reference to the following Examples. It is to be understood that the Examples are provided by way of illustration of the invention and that they are in no way limiting to the scope of the invention.

EXAMPLES

Examples 1 to 4 (E1 to E4)

[68] The compositions of these examples were prepared by combining the components shown in Table 1 in accordance with a process comprising the following steps in sequence:

Step 1: Weight all excipients (excluding the Amine) into a 250ml beaker.

Step 2: Add a magnetic flea to the beaker, place beaker on a hot plate, commence stirring and heat to 75 Deg. C.

Step 3: Continue heating at 75 Deg. C while stirring for approximately 1.0 hour or until all solids have dissolved.

5 Step 4: Continue heating at 75 Deg. C while stirring add the Amine slowly.

Table 1

Material name	E1 (g)	E2 (g)	E3 (g)	E4 (g)
2,4-D acid (97.7%)	41	41	41	41
KEMMAT HF60	4	4	4	4
TERMUL 1284	6	6	6	6
TOXIMUL 8320	5	5	5	5
Triethanolamine (TEA) 85%	5	Nil	5	5
Tri-isopropanol-amine (TIPA) 85%	Nil	5	Nil	Nil
Diethanolamine (DEA) 85%	Nil	Nil	Nil	Nil
Mono-ethanol-amine (MEA) 99%	Nil	Nil	Nil	Nil
Surfonic AGM-550	Nil	Nil	5	10
SOLVESCO 200	10	10	10	10
Hallcomid 8-10	To 100g (29g)	To 100g (29g)	To 100g (24g)	To 100g (19g)
Observations	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve. Stable after 24hrs @ RT.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve. Stable after 24hrs @ RT.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve. Stable after 24hrs @ RT.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve. Stable after 24hrs @ RT.
Emulsion Stability (CIPAC MT36.1) (5/95 dilution in CIPAC STD D water)	Very good bloom. 30min: Stable (Nil cream) 2hrs: Stable (Nil cream) 4hrs: Stable (Nil cream) 24hrs: Stable (Nil cream)	Very good bloom. 30min: Stable (Nil cream) 2hrs: Stable (Nil cream) 4hrs: 0.2ml cream 24hrs: 1ml cream	Very good bloom. 30min: Stable (Nil cream) 2hrs: Stable (Nil cream) 4hrs: Stable (Nil cream) 24hrs: Stable (Nil cream)	Very good bloom. 30min: Stable (Nil cream) 2hrs: Stable (Nil cream) 4hrs: Stable (Nil cream) 24hrs: Stable (Nil cream)
Comments	24hrs @ RT & 0 Deg. C. No crystallization occurs after 7days @ 0 Deg. C (with seeding). D(20 Deg. C)=1.128 g/ml	24hrs @ RT & 0 Deg. C. No crystallization occurs after 7days @ 0 Deg. C (with seeding). D(20 Deg. C)=1.222 g/ml	24hrs @ RT & 0 Deg. C. No crystallization occurs after 7days @ 0 Deg. C (with seeding). D(20 Deg. C)=1.137 g/ml	24hrs @ RT & 0 Deg. C. No crystallization occurs after 7days @ 0 Deg. C (with seeding). D(20 Deg. C)=1.139 g/ml

Examples 5 to 9

[69] The compositions of these examples were prepared by combining the components as specified in Table 2 with a process involving the following steps on sequence:

- 5 Step 1: Weigh all excipients (excluding the Amine) into a 250ml beaker.
- Step 2: Add a magnetic flea to the beaker, place beaker on a hot plate, commence stirring and heat to 75 Deg. C.
- Step 3: Continue heating at 75 Deg. C while stirring for approximately 1.0 hour or until all solids have dissolved.
- 10 Step 4: Continue heating at 75 Deg. C while stirring add the Amine slowly.

Table 4

Material name	E5 (g)	E6 (g)	E7 (g)	E8 (g)	E9 (g)
2,4-D acid (97.7%)	41	41	41	41	41
KEMMAT HF60	4	5	3	4	4
TERMUL 1284	4	5	5	6	5
TOXIMUL 8320	4	5	4	5	3
SOLVESSO 200	10	F10	10	10	10
Amine (TIPA 85%)	3	Nil	Nil	Nil	Nil
Amine (TEA 85%)	Nil	3	3	3	3
Hallcomid 8-10	To 100g (34g)	To 100g (31g)	To 100g (34g)	To 100g (31g)	To 100g (34g)
Observations	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve.	After 1.0hr of stirring & heating @ 75 Deg. C all solids dissolve.
Comments	Emulsification stability (5/95 in STD D water) is v. good (V. good bloom). 30min: ~0.2ml cream; 2hrs: ~0.5ml cream; 4hrs: ~1ml cream; 24hrs: ~3ml cream. Easily re-emulsifies after 10 inversions. No crystallization occurs after 24hrs @ RT & 0 Deg. C. No crystallization occurs after 7 days @ 0 Deg. C (with seeding).	Emulsification stability (5/95 in STD D water) is v. good (V. good bloom). 30min: ~0.2ml cream; 2hrs: ~0.5ml cream; 4hrs: ~1ml cream; 24hrs: ~3ml cream. Easily re-emulsifies after 10 inversions. No crystallization occurs after 24hrs @ RT & 0 Deg. C. No crystallization occurs after 7 days @ 0 Deg. C (with seeding).	Emulsification stability (5/95 in STD D water) is v. good (V. good bloom). 30min: stable; 2hrs: stable; 4hrs: stable; 24hrs: ~0.5ml cream. Easily re-emulsifies after 10 inversions. No crystallization occurs after 24hrs @ RT & 0 Deg. C. No crystallization occurs after 7 days @ 0 Deg. C (with seeding).	Emulsification stability (5/95 in STD D water) is v. good (V. good bloom). 30min: stable; 2hrs: stable; 4hrs: stable; 24hrs: stable. No crystallization occurs after 7 days @ 0 Deg. C (with seeding).	Emulsification stability (5/95 in STD D water) is v. good (V. good bloom). 30min: ~0.2ml cream; 2hrs: ~0.5ml cream; 4hrs: ~1ml cream; 24hrs: ~3.5ml cream. Easily re-emulsifies after 10 inversions. No crystallization occurs after 24hrs @ RT & 0 Deg. C. No crystallization occurs after 7 days @ 0 Deg. C (with seeding).

Example 10 - 40% 2,4-D acid EC (4% TEA99% + 2% water)

[70] The composition shown in Table 3 was prepared using the manufacturing method described and resulted in the properties shown in Table 4.

Table 3

40% w/w 2,4-D acid EC.	2,4-D acid 97.6%	205.0 g
	LABS acid	20.0 g
	TOXIMUL 8320	35.0 g
	TEA 99%	20.0 g
	SOLVESSO 200	50.0 g
	Water	10.0g
	Hallcomid 8-10	160.0 g

Manufacturing Method

- Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).
- Step 3: Continue stirring at 40°C for 10min or until a homogenous mixture is obtained.
- Step 4: Weigh the 2,4-D acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.
- Step 6: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained.
Cool the contents of vessel 2 to 50°C.
- Step 7: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.
- Step 8: Continue to cool, stir the contents of vessel 2 for 10min, cool to 20°C and add the water slowly.
- Step 9: Continue stirring for ~10min at 20°C.
- Step 10: Filter the formulation through 100 micron GAF filter.

RESULTS – Table 4

Parameters	INITIAL	2w at 54°C
Appearance	Yellow clear liquid	Yellow clear liquid
Active content (2,4-D), g/kg	395.6	388.6
Density (20°C), g/ml	1.121	1.121
pH (1% dilution in DI water)	3.12	3.14
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h;24hrs) % cream (30min;2h;24hrs) <u>CIPAC STD D water</u> % Oil (30min;2h;24hrs) % cream (30min;2h;24hrs)	Very good emulsification. (0; 0; 0) (0; 0; 0.5) (0; 0; 0) (0; 0; 0.5)	Very good emulsification. (0; 0; 0) (0; 0; 0.5) (0; 0; 0) (0.2; 0.4; 0.8)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

[71] The composition was found to meet all the parameters required for this product with excellent emulsification stability. The active content was found to be within specification initially and after accelerated storage stability (initial: 395.6g/L 2,4-D acid; After 2 weeks @ 54°C: 388.6g/L 2,4-D acid).

Example 11 – 40% 2,4-D acid EC (4% methoxypropylamine (MOPA) + 2% water

[72] The composition shown in Table 5 was prepared using the manufacturing method described and resulted in the properties described in Table 6.

Table 5

40% w/w 2,4-D acid EC.	2,4-D acid 97.6%	205.0 g
	LABS acid	20.0 g
	TOXIMUL 8320	35.0 g
	methoxypropylamine (MOPA)	20.0 g
	Water	10.0 g
	SOLVESSO 200	50.0 g
	Hallcomid 8-10	160.0 g

Manufacturing Method

- Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).
- Step 3: Continue stirring at 40°C for 10min or until a homogenous mixture is obtained.
- Step 4: Weigh the 2,4-D acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.
- Step 6: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained.
Cool the contents of vessel 2 to 50°C.
- Step 7: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.
- Step 8: Mix the contents of vessel 2 for a further 10min and while mixing, add the water slowly.
- Step 9: Continue stirring for ~10min and cool the mixture to 20°C.
- Step 10: Filter the formulation through 100 micron GAF filter.

RESULTS – Table 6

Parameters	INITIAL	2w at 54°C
Appearance	Yellow clear liquid	Yellow clear liquid
Active content (2,4-D), g/kg	400	393
Density (20°C), g/ml	1.11	1.115
pH (1% dilution in DI water)	3.34	3.29
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h;4hrs) % cream (30min;2h;4hrs) <u>CIPAC STD D water</u> % Oil (30min;2h;4hrs) % cream (30min;2h;4hrs)	Very good emulsification. (0; 0; 0) (0.3; 0.5; 0.7) (0; 0; 0) (0.5; 0.6; 1.0)	Very good emulsification. (0; 0; 0) (0; 0.3; 0.5) (0; 0; 0) (0.2; 0.5; 0.6)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

[73] The active content was found to be within specification initially and after the accelerated storage stability (initial: 400.0g/L 2,4-D acid; After 2 weeks @ 54°C: 393.0g/L 2,4-D acid).

Example 12 – 40% 2,4-D acid EC (2% TEA + 2% MOPA + 2% water)

[74] The composition of Example 12 was prepared from components shown in Table 7 using the procedure shown below and provided a composition having the properties detailed in Table 8.

Table 9

40% w/w 2,4-D acid EC.	2,4-D acid 98.78%	202.5 g
	LABS acid	20.0 g
	TOXIMUL 8320	35.0 g
	TEA 99%	10.0 g
	MOPA	10.0 g
	SOLVESSO 200	50.0 g
	Water	10.0 g
	Hallcomid 8-10	162.5 g

Manufacturing Method

- Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amines slowly (exothermic).
- Step 3: Continue stirring at 40°C for 10min or until a homogenous mixture is obtained.
- Step 4: While stirring (at 40°C), add water slowly. Mix for ~20min.
- Step 5: Weigh the 2,4-D acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 6: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.
- Step 7: Continue heating at 65°C while stirring for ~60min or until a homogenous mixture is obtained.
Cool the contents of vessel 2 to 50°C.
- Step 8: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2.

Step 9: Continue stirring for a further 20min and cool to 20°C.

Step 10: Filter the formulation through 100 micron GAF filter.

RESULTS - Table 8

Parameters	INITIAL	2w at 54°C
Appearance	Yellow clear liquid	Yellow clear liquid
Active content (2,4-D), g/kg	392	390
Density (20°C), g/ml	1.119	1.119
pH (1% dilution in DI water)	3.18	3.29
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h;24hrs) % cream (30min;2h;24hrs) <u>CIPAC STD D water</u> % Oil (30min;2h;24hrs) % cream (30min;2h;24hrs)	Very good emulsification. (0; 0; 0) (0; 0; 1.0) (0; 0; 0) (0; 0; 1.0)	Very good emulsification. (0; 0; 0) (0.2; 0.4; 1.5) (0; 0; 0) (0.3; 0.6; 1.6)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

[75] The active content was found to be within specification initially and after the accelerated storage stability (initial: 392.0g/L 2,4-D acid; After 2 weeks @ 54°C:

5 390.0g/L 2,4-D acid).

Example 13 – 40% MCPA acid EC (4% (methoxypropylamine) MOPA + 2% water)

[76] The composition shown in Table 9 was prepared by the manufacturing method described and the resulting properties of the composition are set out in Table 10.

Table 9

40% w/w MCPA acid EC.	MCPA acid 96%	208.3 g
	LABS acid	13.0 g
	TERMUL 1284	20.0 g
	TOXIMUL 8320	17.0 g
	MOPA	20.0 g
	SOLVESSO 200	50.0 g
	Water	10.0 g
	Hallcomid 8-10	161.7 g

Manufacturing Method

- Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid + TOXIMUL 8320 + TERMUL 1284 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).
- Step 3: Continue stirring at 40°C for 30min or until a homogenous mixture is obtained.
- Step 4: While continuing to mix, add the water slowly.
- Step 5: Weigh the MCPA acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 6: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.
- Step 7: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained.
Cool the contents of vessel 2 to 50°C.
- Step 8: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.
- Step 9: Continue stirring for ~10min and cool the mixture to 20°C.
- Step 10: Filter the formulation through 100 micron GAF filter.

RESULTS – Table 10

Parameters	INITIAL	2w at 54°C
Appearance	Yellow/amber coloured liquid.	Yellow/amber coloured liquid.
Active content (MCPA), g/kg	413	402
Density (20°C), g/ml	1.075	1.074
pH (1% dilution in DI water)	3.5	3.52
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h;4hrs) % cream (30min;2h;4hrs) <u>CIPAC STD D water</u> % Oil (30min;2h;4hrs) % cream (30min;2h;4hrs)	Very good emulsification. (0; 0; 0) (0.8; 1.8; 2.0) (0; 0; 0) (0.8; 2.0; 2.2)	Very good emulsification. (0; 0; 0) (1.5; 2.5; 4.0) (0; 0; 0) (1.5; 3.0; 5.0)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

[77] The active content was found to be within specification initially and after the accelerated storage stability (initial: 413.0g/L MCPA acid; After 2 weeks @ 54°C: 402.0g/L MCPA acid).

Examples 14 – 17 2,4-D acid EC concentrates

[78] Emulsifiable concentrate compositions containing 2,4-D in accordance with Table 11 were prepared using the Manufacturing Method described.

Table 11

Material name/Formulation ID	E14 (g)	E15 (g)	E16 (g)	E17 (g)
2,4-D acid (97.6%)	410	410	410	405 (2,4-D acid 98.78%)
Calsogen AR100 (40% CaTetrapropyleneBS + 10% Fatty alcohol polyglycol ether 6-15EO in Solvent Naptha (petroleum), heavy aromatic	Nil	Nil	Nil	Nil
LABS acid (Linear Alkyl Benzene Sulphonic Acid)	40	40	40	40
TOXIMUL 8320 (>=90% Polyethylene-Polypropylene glycol monobutyl ether)	70	70	70	70
Triethanolamine (TEA) 99%	50	40	Nil	20
Methoxypropylamine (MOPA)	Nil	Nil	40	20
SOLVESCO 200 (Solvent Naphtha (petroleum), heavy aromatic)	100	100	100	100
Water	10	20	20	20
Hallcomid 8-10 (N,N-dimethyl-Octamide 40 - 70% + N,N-dimethyl-Decamide 30 - 60%)	to 1000g (320 g)	to 1000g (320 g)	to 1000g (320 g)	to 1000g (325 g)

Manufacturing method	2	2	2
Observations/Comments	Formulated using a different manufacturing method and an alternative emulsifier system and using 5% TEA + 1% water. Formulation meets specification for Emulsifiable Concentrate products. Based on the assay results, transformation reactions are still occurring.	As per E14 but formulated using 4% TEA + 2% water. Formulation meets specification for Emulsifiable Concentrate products, including active content.	Formulated using 4% MOPA + 2% water. Active content remains stable. Meets specification for Emulsifiable Concentrate products.
Appearance (Initial)	Yellow, clear liquid	Yellow, clear liquid	Yellow, clear liquid
Appearance (after 2W @ 54°)	Yellow, clear liquid	Yellow, clear liquid	Yellow, clear liquid
Active content (2,4-D), g/kg (Initial)	390	396	400
Active content (2,4-D), g/kg (after 2W @ 54° C)	381	389	393
Density (20°C), g/ml (Initial)	1.122	1.121	1.11
Density (20°C), g/ml (after 2W @ 54° C)	1.122	1.121	1.115
pH (1% diin in DI water) (Initial)	3.18	3.12	3.34
pH (1% diin in DI water) (after 2W @ 54° C)	3.15	3.14	3.29
INITIAL Emulsion Stability (CIPAC MT36.1)	Very good emulsification	Very good emulsification	Very good emulsification
CIPAC STD A water % Oil (30min; 2h; 24hrs)	(0; 0; 0)	(0; 0; 0)	(0; 0; 0)
% cream (30min; 2h; 24hrs)	(0; 0; 0.1)	(0; 0; 0.5)	(0; 0; 1.0)

<u>CIPAC STD D water</u> % Oil (30min; 2h; 24hrs) % cream (30min; 2h; 24hrs)	(0; 0; 0) (0; 0; 0.1)	(0; 0; 0) (0; 0; 0.5)	(0; 0; 0) (0.5; 0.6; 1.0)	(0; 0; 0) (0; 0; 1.0)
<u>After 2 weeks @ 54°C</u> Emulsion Stability (CIPAC MT36.1)	Very good emulsification.	Very good emulsification.	Very good emulsification.	Very good emulsification.
<u>CIPAC STD A water</u> % Oil (30min; 2h; 24hrs) % cream (30min; 2h; 24hrs)	(0; 0; 0) (0; 0; 0.5)	(0; 0; 0) (0; 0; 0.5)	(0; 0; 0) (0; 0.3; 0.5)	(0; 0; 0) (0.2; 0.4; 1.5)
<u>CIPAC STD D water</u> % Oil (30min; 2h; 24hrs) % cream (30min; 2h; 24hrs)	(0; 0.4; 0.8) (0; 0.4; 0.8)	(0; 0; 0) (0.2; 0.4; 0.8)	(0; 0; 0) (0.2; 0.5; 0.6)	(0; 0; 0) (0.3; 0.6; 1.6)
<u>Low temp storage stab. (CIPAC MT39.3)</u>				
24 hrs:	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.
7 days (seeding):	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.

Manufacturing Method 1

- Step 1: Weight the CALSOGEN AR100, TOXIMUL 8320 & 40% of SOLVESSO 200 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place baker on a stirrer, commence stirring & heat to 40°C.
- Step 3: Continue stirring for 30min or until a homogenous mixture is obtained.
- Step 4: Weigh the 2,4-D acid & the Hallcomid 8-10 & 60% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 75°C.
- Step 6: Continue heating at 75°C while stirring for ~60min or until a homogenous mixture is obtained. Cool the mixture to 40°C.
- Step 7: While stirring vessel 2 (at 40°C), add contents of vessel 1 slowly to vessel 2.
- Step 8: Continue stirring for ~30min or until a homogenous mixture is obtained.
Cool the mixture to 20°C & filter through 100 micron filter.

Manufacturing Method 2

- Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 250ml beaker (vessel 1).
- Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).
- Step 3: Heat to 50°C and continue stirring for 30min or until a homogenous mixture is obtained.
- Step 4: Weigh the 2,4-D acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).
- Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.
- Step 6: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained. Cool the contents of vessel 2 to 50°C.
- Step 7: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.
- Step 8: Continue stirring the contents of vessel 2 for 10min, cool to 20°C and add the water slowly.
- Step 9: Continue stirring for ~10min at 20°C.
- Step 10: Filter the formulation through 100 micron GAF filter.

Examples 18-21 – MCPA EC Compositions

[79] Emulsifiable concentrates containing MCPA were prepared having the composition set out in Table 12 using manufacturing method 1 or 2 shown below the Table.

Table 12

Material name/Formulation ID	E18 (g)	E19 (g)	E20 (g)	E21 (g)
MCPA acid (97.0%)	412	412	417 (MCPA acid 96%)	417 (MCPA acid 96%)
LABS acid (Linear Alkyl Benzene Sulphonic Acid)	26	26	26	26
TERMUL 1284 (>60% Castor Oil Ethoxylate)	40	40	40	40
TOXIMUL 8320 (>= 90% Polyethylene-polypropylene glycol monobutyl ether)	34	34	34	34
Triethanolamine (TEA) 85%	20	30	Nil	Nil
Mono-ethanolamine (MEA) 99%	Nil	Nil	Nil	20
Methoxypropylamine (MOPA) 100%	Nil	Nil	40	20
Water	Nil	Nil	20	20
SOLVESSO 200 (Solvent Naphtha (petroleum), heavy aromatic)	100	100	100	100
Hallcomid 8-10 (N,N-dimethyl-Octamide 40 - 70% + N,N-dimethyl-Decamide 30 - 60%)	to 1000g (368 g)	to 1000g (358 g)	to 1000g (323 g)	to 1000g (323 g)
Manufacturing method	1	1	2	2

Observations/Comments	Formulation meets specification for Emulsifiable Concentrate products, some reduction in active content over 2 weeks.	Formulation meets specification for Emulsifiable Concentrate products, some reduction in active content over 2 weeks.	Formulation meets the specification for Emulsifiable Concentrate products including active content. The emulsification stability of the product is not ideal, however, it is within the specification limits for emulsifiable concentrates as the APVMA guidelines.	Formulation meets specification for Emulsifiable Concentrate products composition shows reduced active content after acc. Storage stability (2 weeks @54°C).
Appearance (Initial)	Yellow, clear liquid	Yellow, clear liquid	Yellow/amber clear liquid	Yellow, slightly hazy liquid
Appearance (after 2W @ 54°C)	Yellow, clear liquid	Yellow, clear liquid	Yellow/amber clear liquid	Yellow, slightly hazy liquid
Active content (2,4-D), g/kg (Initial)	390	389	413	404
Active content (2,4-D), g/kg (after 2W @ 54°C)	383	382	402	376
Density (20°C), g/ml (Initial)	1.066	1.07	1.075	1.074
Density (20°C), g/ml (after 2W @ 54°C)	1.066	1.07	1.074	1.074
pH (1% diin in DI water) (Initial)	3.12	3.2	3.5	3.61
pH (1% diin in DI water) (after 2W @ 54°C)	3.15	3.24	3.52	3.59
(INITIAL) Emulsion Stability (CIPAC MT36.1)	Good emulsification.	Very good emulsification.	Good emulsification.	Good emulsification.

% Oil (30min)	(0)	(0)	(0)	(0)
% cream CIPAC STD A Water (30min)	(1.5)	(0)	(0.8)	(0)
% Oil (30min)	(0)	(0)	(0)	(0)
% cream CIPAC STD D Water (30min)	(0)	(0)	(0.8)	(0)
AFTER 2W @ 54°C Emulsion Stability (CIPAC MT36.1)	Poor emulsification	Poor emulsification	Good emulsification	Good emulsification
<u>CIPAC STD A water</u>	(0)	(0)	(0)	(0)
% Oil (30min)	(5)	(6)	(1.5)	(0)
% cream (30min)				(0.2)
<u>CIPAC STD D water</u>	(0)	(0)	(0)	(0)
% Oil (30min)	(7)	(7)	(1.5)	(0.2)
% cream (30min)				
Low temp storage stab. (CIPAC MT39.3)				
24hrs:	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization. Hazy.
7days (seeding):	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization.	Stable. No crystallization. Hazy.

Manufacturing Method 1

Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid + TOXIMUL 8320 + TERMUL 1284 into a 250ml beaker (vessel 1).

Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).

Step 3: Continue stirring at 40°C for 30min or until a homogenous mixture is obtained.

Step 4: While continuing to mix, add the water slowly.

Step 5: Weigh the MCPA acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).

Step 6: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.

Step 7: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained.

Cool the contents of vessel 2 to 50°C.

Step 8: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.

Step 9: Continue stirring for ~10min and cool the mixture to 20°C.

Step 10: Filter the formulation through 100 micron GAF filter.

Manufacturing Method 2

Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid + TOXIMUL 8320 + TERMUL 1284 into a 250ml beaker (vessel 1).

Step 2: Add a magnetic flea to the beaker, place beaker on a stirrer, commence stirring & add amine slowly (exothermic).

Step 3: Continue stirring at 40°C for 30min or until a homogenous mixture is obtained.

Step 4: While continuing to mix, add the water slowly.

Step 5: Weigh the MCPA acid & the Hallcomid 8-10 & 40% of SOLVESSO 200 into a 1L beaker (vessel 2).

Step 6: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 65°C.

Step 7: Continue heating at 65°C while stirring for ~30min or until a homogenous mixture is obtained.

Cool the contents of vessel 2 to 50°C.

Step 8: While stirring vessel 2 (at 50°C), add contents of vessel 1 slowly to vessel 2. Commence cooling.

Step 9: Continue stirring for ~10min and cool the mixture to 20°C.

Step 10: Filter the formulation through 100 micron GAF filter.

Example 21 and 22 – EC Compositions of 2,4-D plus glyphosate

- [80] Compositions of acid herbicide emulsifiable concentrate containing both 2,4-D and glyphosate in acid form were prepared by combining the components in Table 13 in the parts by weight shown and using the manufacturing method described and were found to be stable.

Table 13

Glyphosate vehicle			
All g/L	A	F	F1
Glyphosate as 100%	262	240	240
Propylene Glycol	900	640	484
MOPA 100%	200	120	276

	E21	E22
Glyphosate	125	100
24D	200	200
Propylene Glycol	125	260
MOPA	10	10
HOPA 100%Tomamine		50
Hallcomid M8-10	225	300
Solvesso 200	25	50
Termul 1284	30	60
Toximul 8320	25	50
Kermat HF60		

emulsification D	Pass	Pass
emulsification C	Pass	Pass
1%pH	4.19	3.55
Viscosity 5°C cp	72	469
Viscosity 20°C cp	38	148
Assay glyphosate g/L		
Assay 24D g/L		

Manufacturing Method –Weigh out Propylene Glycol in a 400mL glass beaker and heat to 75°C whilst stirring with an overhead stirrer.

- 5 1. Maintaining the temperature at 75°C add in Glyphosate and stir vigorously until fully dispersed.
2. Whilst stirring add in MOPA (HOPA in E22) until a clear solution results. Add more MOPA if required to dissolve Glyphosate. Record amount and pH. This is the Glyphosate vehicle.
- 10 3. In a 2L tall glass beaker add in Hallcomid M-8-10 and heat to 75°C whilst stirring with an overhead stirrer.
4. Maintaining the temperature at 75°C add in 24D and stir vigorously until fully dissolved.
5. In a 250ml beaker add in Solvesso 200 followed by Toximul 8320 and Termul 1284 and heat to 50°C and mix until a clear solution results.
- 15 6. While stirring vigorously and maintaining the temperature at 75°C add in the above Solvesso 200 mix to the 24D solution and stir until homogenous and clear.
7. To the clear 24D emulsifier solution add the Glyphosate vehicle solution and mix and allow to cool.
8. Allow to return to RT and make to 1L with Hallcomid.

Examples 23-27 – EC Compositions of 2,4-D and Fluroxypyr

[81] Emulsifiable concentrate compositions containing both 2,4-D acid and fluroxypyr acid were prepared using the components in the parts by weight shown in Table 14 and using the manufacturing method listed. The emulsifiable concentrates were found to have good stability.

Table 14

	E23 (g)	E24 (g)	E25 (g)	E26 (g)	E27 (g)
Fluroxypyr	110	110	110	110	110
24D	200	200	200	200	200
NMP	50	50	50	50	50
MOPA 100%	10	20	30	50	20
HOPA 100%					10
Hallcomid M8-10	480	480	480	480	480
Solvesso 200	50	50	50	50	50
Termul 1284	60	60	60	60	60
Toximul 8320	50	50	50	50	50
Appearance	Clear solution	Clear solution	Clear solution	Clear solution	Clear solution
Low temp stability					
1% pH	3.32	3.55	3.7	4.06	3.76
Density	1.067	1.067	1.067	1.066	1.067
Emulsion A 30min	0.1ml pass	0ml pass	0ml pass	0ml pass	0ml pass
Emulsion D 30min	0.1ml pass	0ml pass	0ml pass	0ml pass	0ml pass
Emulsion A 2hours	0.2ml pass	0ml pass	0ml pass	0ml pass	0ml pass
Emulsion D 2hours	0.2ml pass	0ml pass	0ml pass	0ml pass	0ml pass
Foaming ml	25	25	30	25	

Manufacturing Method - 1L batches with Fluroxypyr and 24D

1. Weigh out Hallcomid M-8-10 and NMP into a 2L glass beaker and add in Fluroxypyr and heat on a hot plate to 75°C whilst stirring with an overhead stirrer until a clear solution results.
2. When the above solution is clear add 2,4D and maintain at 75°C whilst stirring with an overhead stirrer until a clear solution results.

3. To a 400ml glass beaker with a magnetic stirrer add in Solvesso 200, Toximul 1284, and Toximul 8320 and mix at 50°C until homogenous and a clear solution results.
4. To the 2L beaker add in the contents of the 400ml beaker whilst vigorously stirring
5 and maintain the temperature at 75°C.
5. Mix until homogenous and clear and allow to cool.
6. When at 40°C check pH of 1% aqueous solution.
7. Add in Base and mix for ten minutes.
8. Allow to cool to 20°C and fill into a 1L batch and make up to volume with
10 Hallcomid M-8-10.

Examples 28-35 – Mixtures of 2,4-D and Picloram

[82] Emulsifiable concentrate compositions containing both 2,4-D and picloram in acid form were prepared by combining the components in the parts by weight shown in Table 15 and using the manufacturing method described.

Table 15

Picloram/24D 22.5/360g/L		E28	E29	E30	E31	E32	E33	E34	E35
All g/L									
Picloram as 100%		22.5	22.5	22.5	22.5	22.5	64	64	64
2,4D as 100%		360	360	360	360	360	240	240	240
Hallcomid M8-10		520	520	510	510	510	550	550	550
Solvesso 200		50	50	50	50	50	50	50	50
Termul 1284		60	60				60	60	60
Toximul 8320		50	50	110	110	110	50	50	50
MOPA 100%		20	40	10	20	20	10	30	50
Appearance		clear sol	clear sol	clear sol	clear sol	clear sol	clear sol	clear sol	clear sol
Low temp stability		clear sol	clear sol	clear sol	clear sol	clear sol	clear sol	clear sol	clear sol
1% pH		3.32	3.73	3.21	3.67	3.97	3.15	3.56	3.75
Density		1.073	1.073	1.074	1.074	1.074	1.049	1.049	1.049
picloram g/L initial		23.5	22.9	25.6	25.1	24.9	64.7	63.6	62.3
picloram g/L initial HYD		23.4		25	24.6	23.8	64.1	63.3	62.8
24D g/L initial		351		357	350	346	242	238	233
Emulsion A		pass	pass	pass	pass	pass	pass	pass	pass
Emulsion D		pass	pass	pass	pass	pass	pass	pass	pass
Foaming ml		12	12	8	8	8	20		

Manufacturing Method - 1L batches

1. Weigh out Hallcomid M-8-10 into a 2L glass beaker and add in Picloram and heat on a hot plate to 75°C whilst stirring with an overhead stirrer until a clear solution results.
2. When the above solution is clear add 2,4D and maintain at 75°C whilst stirring with an overhead stirrer until a clear solution results.
3. To a 400ml glass beaker with a magnetic stirrer add in Solvesso 200, Toximul 1284, and Toximul 8320 and mix at 50°C until homogenous and a clear solution results.
4. To the 2L beaker add in the contents of the 400ml beaker whilst vigorously stirring and maintain the temperature at 75°C.
5. Mix until homogenous and clear and allow to cool.
6. When at 40°C check 1% pH.
7. Add in Base and mix for ten minutes.
8. Allow to cool to 20°C and fill into a 1L batch and make up to volume with Hallcomid M-8-10.

[83] Example 36 – Comparison of the influence of small amounts of water on stability of the acid form of phenoxy alkanoic acids.

[84] In the absence of water it was generally found that compositions of the invention undergo a small but nonetheless significant reduction in the alkanoic acid herbicide content with ageing as a result of the formation of esters and/or amides as shown in Schemes 1 and 2. While these products formed are herbicidal it is desirable to maintain a highly stable content of the active in the alkanoic acid form.

[85] When the 2,4-D compositions of the invention, in the absence of water, were subject to accelerated aging (2 weeks at 54°C) the content of the 2,4-D herbicide in the acid form compared with the total 2,4-D herbicide in all forms (including acid and ester/amide forms) was determined for a number of compositions.

[86] The loss of 2,4-D in acid form as a result of transformation during accelerated aging was found to be as follows:

	Average % 2,4-D loss	= 10.1%
15	Average g/kg loss	= 41.2 g/Kg
	Maximum % 2,4-D loss	= 15.2%
	Maximum g/kg	= 61.0 g/Kg
	Minimum % 2,4-D loss	=4.3%
	Minimum g/Kg loss	=17.2 g/Kg

[87] The presence of about 2% w/w of water in the identified compositions of the invention identified as containing water provided a significant improvement in the retention and long term stability of the 2,4-D herbicide in acid form.

[88] Composition of the invention comprising about 2% added water were found to undergo an average loss of 2,4-D in acid form with accelerated aging (2 weeks at 54°C) as follows :

[89] Average % 2,4-D loss = 1.5%

Average g/kg loss = 6.0 g/Kg

Maximum % 2,4-D loss = 2.2%

Maximum g/kg = 9.0 g/Kg

Minimum % 2,4-D loss = 0.51%

5 Minimum g/Kg loss = 2 g/Kg

[90] Typical losses of MCPA compositions of the invention in the absence of water addition, when measured via free acid assay, were found to be in the same range as those determined for 2,4-D in the absence of water, as summarised above. The stability of the MCPA compositions of the invention with addition of water were found to follow the above reported trends seen in 2,4-D formulations.

Method - Summary, Free Phenoxy-alkonic Acid Content Analysis:

[91] Acid content and the change in acid content with time was determined for compositions using the following procedure for determine free acid content and total phenoxyalkanoic acid content including acid transformed through ester and/or amide formation.

[92] Samples of the formulations are diluted in a solution of acetonitrile and water (70:30), with internal standard added. The free phenoxy-alkonic acid content of the formulations are determined by HPLC using a C18 column, gradient elution and UV detection. Quantitation is carried out via internal standard calibration. The method is specific only for phenoxyalkonic acids in their free acid form any other species of the phenoxyalkonics are not detected nor are they converted back to their acid form via this analysis.

Method Summary Total Phenoxy-alkonic acid Content Analysis:

[93] Samples of the formulations are dispersed in a solution of sodium hydroxide, with internal standard added. The solutions are then heated at 70°C for 15mins, to convert all transformation products to their acid form. The total phenoxy-alkonic acid content in the formulations is determined by HPLC using a C18 column, gradient elution and UV detection. Quantitation is carried out via internal standard calibration.

The method has been validated and therefore proven to recover/convert all phenoxyalkonic species back to their original input acid form.

Example 37

[94] The following composition of Table 16 was prepared by combining the components in the amounts listed using the manufacturing method described. The composition had properties shown in Table 17.

Table 16: (40% 2,4-D acid EC) - Using Hallcomid M-12-14.

40% w/w 2,4-D acid EC.	2,4-D acid 98%	408.0 g
	LABS acid	40.0 g
	TOXIMUL 8320	70.0 g
	Triethylamine (TEA)	50.0 g
	SOLVESSO 200	100.0 g
	Hallcomid M-12-14	332.0 g

Manufacturing Method

Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 1L beaker (V 1).

Step 2: Commence stirring with an over head stirrer & add the triethylamine slowly (exothermic).

Step 3: Continue stirring for ~30min or until a homogenous mixture is obtained.

Step 4: Weigh the 2,4-D acid & the Hallcomid M-12-14 & 40% of SOLVESSO 200 into a 2L beaker (V2).

Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 70°C.

Step 6: Continue heating at 70°C while stirring for ~30min or until a homogenous mixture is obtained.

Step 7: Cool the contents of V2 to 50°C.

Step 8: While stirring V2 (at 50°C), add contents of V1 slowly to V2.

Step 9: Mix the contents of V2 for a further 10min.

Step 10: Continue stirring for a further ~20min while cooling the mixture to 20°C.

Step 11: Filter the formulation through 100 micron GAF filter.

Table 17

Parameters	INITIAL	2w at 54°C
Appearance	Yellow clear liquid	Yellow clear liquid
Active content (2,4-D), g/kg	398 (436 g/L)	395 (433 g/L)
Density (20°C), g/ml	1.096	1.096
Viscosity (cP) Spindle: S21 Speed: 12RPM Temp.: 20°C	225.4	227.3
Viscosity (cP) Spindle: S21 Speed: 3RPM Temp.: 5°C	862.5	859.2
Persistent Foam test (CIPAC MT47.2) (5% dilution in CIPAC STD C water)	20ml	20ml
pH (1% dilution in DI water)	3.34	3.29
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h; 4hrs) % cream (30min;2h; 4hrs)	Good emulsification. (0; 0; 0) (0.2; 0.5; 0.8)	Good emulsification. (0; 0; 0) (0.2; 0.5; 0.8)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

Example 38

[95] The following composition of Table 18 was prepared by combining the components in the amounts listed using the manufacturing method described. The composition had properties shown in Table 19.

Table 18: (40% 2,4-D acid EC) - Using Hallcomid 1025.

40% w/w 2,4-D acid EC.	2,4-D acid 98%	408.0 g
	LABS acid	40.0 g
	TOXIMUL 8320	70.0 g
	Triethylamine (TEA)	50.0 g
	SOLVESSO 200	100.0 g
	Hallcomid 1025	332.0 g

Manufacturing Method

Step 1: Weigh 60% of the SOLVESSO 200 the LABS acid, TOXIMUL 8320 into a 1L beaker (V 1).

Step 2: Commence stirring with an over head stirrer & add the triethylamine slowly (exothermic).

Step 3: Continue stirring for ~30min or until a homogenous mixture is obtained.

Step 4: Weigh the 2,4-D acid & the Hallcomid 1025 & 40% of SOLVESSO 200 into a 2L beaker (V2).

Step 5: Place beaker on a hot plate, commence stirring with an overhead mixer & heat to 70°C.

Step 6: Continue heating at 70°C while stirring for ~30min or until a homogenous mixture is obtained.

Step 7: Cool the contents of V2 to 50°C.

Step 8: While stirring V2 (at 50°C), add contents of V1 slowly to V2.

Step 9: Mix the contents of V2 for a further 10min.

Step 10: Continue stirring for a further ~20min while cooling the mixture to 20°C.

Step 11: Filter the formulation through 100 micron GAF filter.

Table 19

Parameters	INITIAL	2w at 54°C
Appearance	Yellow clear liquid	Yellow clear liquid
Active content (2,4-D), g/kg	403 (447 g/L)	399 (443 g/L)
Density (20°C), g/ml	1.109	1.109
Viscosity (cP) Spindle: S21 Speed: 12RPM Temp.: 20°C	163.7	164.5
Viscosity (cP) Spindle: S21 Speed: 6RPM Temp.: 5°C	530.5	531.8
Persistent Foam test (CIPAC MT47.2) (5% dilution in CIPAC STD C water)	20ml	20ml
pH (1% dilution in DI water)	3.28	3.25
Emulsion Stability (CIPAC MT36.1) <u>CIPAC STD A water</u> % Oil (30min;2h; 4hrs) % cream (30min;2h; 4hrs) <u>CIPAC STD D water</u> % Oil (30min;2h; 4hrs) % cream (30min;2h; 4hrs)	Good emulsification. (0; 0; 0) (1.5; 2; 4) (0; 0; 0) (1.8; 3; 4)	Good emulsification. (0; 0; 0) (1; 1.5; 2) (0; 0; 0) (1; 1.5; 2)
Low temp storage stab. (CIPAC MT39.3) 24hrs: 7days (seeding):	Stable. No crystallization. Stable. No crystallization.	

In the Examples, the products identified are as follows:

Atlas™ G-5002L – butyl block copolymer polymeric non-ionic oil-in-water emulsifier.

Synperonic™ A11 – polyoxyethylene (11) C₁₂ – C₁₅ alcohol non-ionic emulsifier.

Calsogen™ ARL 100ND – alkyl benzene sulfonate anionic emulsifier.

5 Solvesso™ 200 – alkylbenzene IBP 220°C.

Tomamine™ – PA – 10L is a commercial brand of hexyloxypropylamine available from Air Products and Chemicals, Inc.

KEMMAT™ HF60 – calcium dodecyl benzene sulfonate.

TERMUL™ 1284 – ethoxylated castor oil emulsifier.

10 TOXIMUL™ 8320 – butyl block copolymer, polymeric emulsifier.

HALLCOMID™ M 8-10 N,N-dimethyl decanamide

HALLCOMID™ M-12-14 – mixture of N,N-dimethyl lauricamide and N,N-dimethyl myristicamide

HALLCOMID™ 1025 - N,N-dimethyl 9-decanamide

15 MEA - monoethanolamine
TIPA - triisopropanolamine
MIPA - monoisopropylamine

DEA - diethanolamine

TEA - triethanolamine

20 EDA - ethylenediamine

DETA - diethylenetriamine

MOPA - methoxypropylamine

HOPA - hexyloxypropylamine

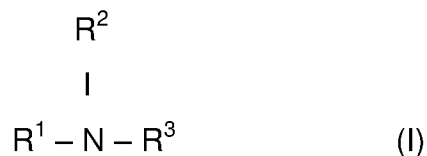
Rhodiasolv™ Match 111 – non-ionic solvent blend

25 BEROL™ 106 – ethoxylated castor oil

Claims

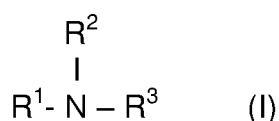
1. An emulsifiable concentrate of a phenoxy-alkanoic acid herbicide comprising a phenoxy-alkanoic acid herbicide dissolved in an amide solvent and at least one amine.

2. An emulsifiable concentrate according to claim 1, wherein the amine comprises at least one amine of formula (I)



wherein R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, C_1 to C_{10} alkyl; C_5 or C_6 cycloaliphatic optionally substituted with from one to four C_1 to C_4 alkyl groups and/or an amino- C_1 to C_4 alkyl group; C_1 to C_{10} alkyl substituted with a substituent selected from the group consisting of hydroxyl, C_1 to C_{10} alkoxy, amino, C_1 to C_6 alkylamino and di-(C_1 to C_6 alkyl)amino; and the group wherein two of R^1 , R^2 and R^3 together form a ring of 5 or 6 constituent ring members selected from methylene, -O-, -N- and -N(C_1 to C_6 -alkyl)- and the other of R^1 , R^2 and R^3 is selected from hydrogen, C_1 to C_6 alkyl and C_1 to C_6 alkyl substituted with a substituent selected from the group consisting of hydroxyl, C_1 to C_6 alkoxy, amino and C_1 to C_6 alkylamino; and wherein at least one of R^1 , R^2 and R^3 is other than hydrogen

3. An emulsifiable concentrate according to claim 1 wherein the amine comprises at least one amine of formula I



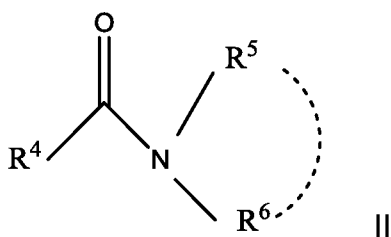
wherein either (i) R^1 , R^2 and R^3 are C_2 to C_4 alkanol or (ii) R^1 is C_1 to C_{10} alkoxy substituted C_2 to C_4 alkyl and R^2 and R^3 are independently hydrogen or C_1 to C_4 alkyl.

4. An emulsifiable concentrate according to claim 2, wherein the amine comprises at least one of formula (I) wherein (i) R^1 , R^2 and R^3 are independently selected from C_2 to C_4 alkanol or (ii) R^1 is selected from C_1 to C_6 alkoxy-substituted alkyl and R^2 and R^3 are hydrogen or C_1 to C_4 alkyl. .

5. An emulsifiable concentrate according to any one of the previous claims, wherein the amine is selected from the group consisting triethanolamine, triisopropanolamine, methoxypropylamine, hexyloxypropylamine and mixtures of two or more thereof.

6. An emulsifiable concentrate according to any one of the previous claims, wherein the amine is present in an amount of from 0.5% to 5% by weight of the amine based on the weight of emulsifiable concentrate.

7. An emulsifiable concentrate according to any one of the previous claims, wherein the amide solvent comprises at least one compounds of formula II:



wherein

R^4 is selected from the group consisting of hydrogen and C_1 to C_{17}

hydrocarbyl;

R^5 is selected from the group consisting of C_1 to C_{15} hydrocarbyl;

R^6 is selected from the group consisting of C_1 to C_{15} hydrocarbyl; and

R^5 and R^6 may together form a ring incorporating the nitrogen of the amide comprising 4 or 5 methylene groups; preferred examples of R^5 and R^6 are

independently selected from the group consisting of C_1 to C_6 hydrocarbyl and the group wherein R^5 and R^6 together form a ring incorporating the nitrogen of the amine by a bridging group $R^5 \dots R^6$ of formula $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 -$ or $-\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 -$.

8. An emulsifiable concentrate according to claim 7, wherein in formula II
R⁴ is selected from the group consisting of C₆ to C₁₇ aliphatic; and
R⁵ and R⁶ are independently selected from the group C₁ to C₆ alkyl and the
group wherein R⁵ and R⁶ together form a bridging group of formula selected
5 from the group consisting of –CH₂CH₂CH₂CH₂– and
–CH₂CH₂CH₂CH₂CH₂–.
9. An emulsifiable concentrate according to claim 7 or claim 8, wherein amide
solvent is of formula II wherein
10 R⁴ is C₆ to C₁₇ alkyl; and
R⁵ and R⁶ are independently selected from C₁ to C₄ alkyl.
10. An emulsifiable concentrate according to any one of the previous claims,
wherein the amide solvent is selected from the group consisting of N,N-
15 dimethyl fatty acid amides.
11. An emulsifiable concentrate according to any one of the previous claims,
wherein the amide solvent is a fatty acid amide comprising a C₆ to C₁₇ aliphatic
group.
- 20 12. An emulsifiable concentrate according to any one of the previous claims,
wherein amide solvent is selected from the group consisting of N,N-dimethyl
octanamide, N,N-dimethyl decanamide, N,N-dimethyl caprylamide, N,N-
dimethyl 2-ethylhexanoamide, N,N-dimethyl oleamide N,N-
25 dimethyl lauricamide, N,N-dimethyl myristicamide, N,N-dimethyl 9-decenamide
and mixtures of two or more thereof.
13. An emulsifiable concentrate according to any one of the previous claims,
wherein the amide solvent is present in an amount of from 25% to 60% by
30 weight of the composition by weight of the emulsifiable concentrate
composition.

14. An emulsifiable concentrate according to any one of the previous claims,
wherein phenoxy-alkanoic acid herbicide comprises at least one selected from
the group consisting of:
phenoxyacetic herbicides including 2,4-D and MCPA;
5 phenoxybutyric herbicides including 4-CPB, 2,4-DB, 3,4-DB, MCPB and 2,4,5-
TB; and
phenoxypropionic herbicides including dichlorprop, dichlorprop-P, fenoprop,
mecoprop and mecoprop-P.
15. An emulsifiable concentrate according to any one of the previous claims,
10 wherein the phenoxy-alkanoic acid herbicide is 2,4-D, MCPA or a mixture
thereof.
16. An emulsifiable concentrate according to any one of the previous claims,
wherein the emulsifiable concentrate comprises a mixture of the phenoxy-
15 alkanolic acid herbicide and an aryloxyphenoxy-alkanoic acid herbicide.
17. An emulsifiable concentrate according to any one of the previous claims,
wherein phenoxy-alkanoic acid herbicide is present in a total amount of at least
200g acid per litre of emulsifiable concentrate.
20
18. An emulsifiable concentrate according to any one of the previous claims
wherein the phenoxy-alkanoic acid is present in a total amount of at least 400g
acid per litre of emulsifiable concentrate.
- 25 19. An emulsifiable concentrate of any one of the previous claims further
comprising a hydrocarbon co-solvent which has a flash point of at least 60.5°C.
20. An emulsifiable concentrate according to claim 18 wherein the hydrocarbon co-
solvent comprises at least one hydrocarbon selected from alkyl substituted
30 aromatics.

21. An emulsifiable concentrate according to claim 19 or claim 20, wherein the hydrocarbon co-solvent is present in an amount in the range of from 2% to 25% w/w of the emulsifiable concentrate.
- 5 22. An emulsifiable concentrate according to any one of the previous claims comprising emulsifier in an amount in the range of from 5% w/w to 25% w/w of the emulsifiable concentrate composition.
- 10 23. An emulsifiable concentrate according to claim 22 wherein the emulsifier comprises an alkylaryl sulfonate such as calcium dodecylbenzene sulfonate.
- 15 24. An emulsifiable concentrate according to claim 22 or claim 23 wherein the emulsifier comprises a non-ionic emulsifier selected from alcohol ethoxylates, fatty acid ethoxylates, fatty amide ethoxylates and EO/PO block copolymers including butyl based block copolymers, in an amount in the range of from 2% w/w to 20% w/w of the emulsifiable concentrate composition.
- 20 25. An emulsifiable concentrate according to any one of claims 21 to 24 comprising anionic emulsifier in an amount of from 1% to 10% w/w of the composition and non-ionic emulsifier in an amount of from 2% to 15% w/w of the composition.
- 25 26. An emulsifiable concentrate according to any one of the previous claims comprising water in an amount amount of from 0.5 % to 5% based on the weight of the emulsifiable concentrate.
- 30 27. A method for the preparation of an emulsifiable concentrate of phenoxy-alkanoic acid herbicide comprising combining said phenoxy-alkanoic acid herbicide with an amide solvent and amine of formula 1 according to claim 2 or claim 3, to provide a solution of the phenoxy-alkanoic acid herbicide.

- 5 28. A method of controlling weeds comprising providing a phenoxy-alkanoic acid emulsifiable concentrate according to any one of claims 1 to 25, diluting the concentrate with water to provide an emulsion and applying the diluted concentrate to the weeds to be controlled.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2016/050336

A. CLASSIFICATION OF SUBJECT MATTER

A01N 25/22 (2006.01) A01N 25/02 (2006.01) A01N 25/04 (2006.01) A01N 25/30 (2006.01) A01N 27/00 (2006.01)
A01N 39/00 (2006.01)

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)

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)

Databases: EPOQUE (EPODOC, WPIAP), STN (CAPLUS, REGISTRY), Espacenet, Google Patents, Google Scholar; Keywords: phenoxies, phenoxy acid/herbicide/emulsion, phenoxy-acetic/propionic/butyric acid, amides/solvents, amines, stabilisation (and like terms, and used in various combinations); IPC/CPC: A01N, A01N25, A01N2300/00; Applicant/Inventors: Nufarm, Aristos Panayi, Claudio Silva, Chad Sayer, Sumit Sharma

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"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 10 June 2016	Date of mailing of the international search report 10 June 2016
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaaustralia.gov.au	Authorised officer Callen Puah AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832209

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. PCT/AU2016/050336
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8044059 B2 (HOPKINS et al.) 25 October 2011 Abstract, col. 2-4, col. 3 lines 3-16, col. 4 lines 1-24	1-28
X	US 8426341 B2 (VOLGAS et al.) 23 April 2013 claims 1-3, 11, 12, Example 1	1-28
X	US 2010/0016163 A1 (KEIPER et al.) 21 January 2010 Abstract; paragraphs [0001, 0004, 0036-0038, 0045, 0066, 0086]	1-28
A	US 4213776 A (GIILCK et al.) 22 July 1980	
A	WO 2013/126947 A1 (HUNTSMAN CORPORATION AUSTRALIA PTY LIMITED) 06 September 2013	
A	WO 2015/054561 A1 (DOW AGROSCIENCES LLC) 16 April 2015	

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2016/050336	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
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		BR 102014025328 A2	29 Sep 2015
		CA 2925389 A1	16 Apr 2015
		CN 105592705 A	18 May 2016
		US 2015105254 A1	16 Apr 2015
	UY 35779 A	29 May 2015	
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			