FORMULATIONS

The present invention relates to formulations, particularly to agrochemical formulations, more particularly to emulsifiable concentrates (ECs) and agrochemical compositions formulated as emulsifiable concentrates.

The present invention is based on the determination that certain components of agrochemical compositions exhibit incompatibilities which can lead to undesirable properties when formulated, such as cloudiness and, in some examples, formation of precipitates.

Certain established agrochemical compositions include components having higher levels of toxicity, such as eye toxicity, than would be permissible for new compositions. Whilst alternative formulation ingredients are available, the alternative ingredients may exhibit incompatibilities with other ingredients. For example, CaDDBS (Calcium dodecylbenzene sulfonate, CAS No 26264-06-2) is an emulsifier commonly used in emulsifiable concentrates of herbicidally active compounds, but shows Category 1 eye toxicity (causing serious and irreversible effects on the eye). In contrast, 2-propanamine DDBS, (CAS registry number 84961-74-0), available under the trade mark Zephrym 3300B is Category 2 eye irritant emulsifier. Category 2 requires that any eye irritation is reversible within no more than 21 days. However, 2-propylamine DDBS is incompatible with certain conventional solvent systems, giving rise to cloudiness and precipitation.

Such incompatibilities are particularly likely in combination agrochemical compositions in which two or more active ingredients, each of which may have different formulation requirements, are combined. One active ingredient may require formulating with anionic excipients or adjuvants, whereas another active ingredient may require formulating with non-ionic excipients or adjuvants. Formulations involving multiple active ingredients may also differ from the individual formulations for each active ingredient as a result of seeking to formulate the combination with a common solvent, compatible with all active ingredients. .

It is with these problems in mind that the present invention has been devised.

In a first aspect, the present invention provides an agrochemical composition comprising at least one active ingredient and a carrier composition; wherein the carrier composition comprises an organic solvent, at least one anionic component, at least one non-ionic component and a phosphate ester.

In preferred embodiments, the phosphate ester is present in an amount of 0.5 to 3.0 % w/w based on the total weight of the composition, more preferably from 1.0 to 2.5 % w/w.

In a second aspect, the present invention also provides a carrier composition for at least one agrochemically-active ingredient, the carrier composition comprising an organic solvent, at least one anionic component, at least one non-ionic component and a phosphate ester.

In preferred embodiments, the phosphate ester is present in ratio to the combined amount of anionic component and non-ionic component of from 1:5 to 1:25 by weight.

The at least one anionic component may be selected from anionic surfactants, dispersants, emulsifiers, wetting agents and solvents.

In some embodiments, the at least one anionic component is selected from alkylbenzene sulfonic acids; optionally 4-alkylbenzene sulfonic acids, further optionally 4-C_{10}-C_{13}-sec-alkyl benzene sulfonic acids.

In a preferred embodiment, the at least one anionic component is an alkylbenzene sulfonic acid 2-propanamine salt, optionally benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0).

The at least one non-ionic component may be selected from non-ionic surfactants, emulsifiers and solvents.

In some embodiments, the at least one non-ionic component is selected from alkylated C_{10}-C_{20} fatty acids and alkoxylated C_{10}-C_{20} fatty acids.

In certain examples, the at least one non-ionic component is selected from: i) alkylated seed oils, optionally methylated seed oils, ii) alkoxylated castor oils, optionally ethoxylated castor oil; and iii) amides of formula R^1-C(=O)NR^2R^3 wherein R^1-is C_8 to C_{14}, optionally C_{11} and/or C_{13} and R^2 and R^3 are C_1 to C_3 and may be the same or different, further optionally wherein R^2 and R^3 are both methyl.

In preferred embodiments, the phosphate ester is a polyether phosphate, optionally a styrene oxide polyether phosphate.

In preferred embodiments, the organic solvent comprises at least one solvent selected from alkyl benzoates, optionally methyl benzoate, and C_{10}-C_{13} aromatic hydrocarbons.

In particularly preferred embodiments, the organic solvent is methyl benzoate, the anionic component is benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0), and the phosphate ester is a polyether phosphate, optionally oxirane, phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ethers (CAS 308336-53-0).

In certain embodiments, the compositions further comprise one or more of an antifoam, a safener and a thickener.

In certain embodiments, the compositions further comprise water, preferably deionised water, in an amount of from 0.1 to 1.0 % w/w, optionally from 0.2 to 0.8 % w/w.

The compositions of the present invention may be used to formulate in a variety of end use applications, including agrochemical formulations, such as herbicide, fungicide, acaricide, insecticide, nematicide, insecticide and plant growth regulator formulations. The compositions are particularly advantageous for formulating agrochemical formulations as emulsifiable concentrates (EC), which forms a third aspect of the present invention. More specifically, the compositions are particularly useful for formulating agrochemical emulsifiable concentrates having more than one active ingredient.

In one example, the at least one active ingredient is 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide, or an agrochemically-acceptable salt thereof.

In a further example, the at least one active ingredient is 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid, or an agrochemically-acceptable salt thereof, optionally benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate.

Advantageously, preferred embodiments of the composition comprise two or more active ingredients.

In one example, the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide and 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid or agrochemically-acceptable salts thereof. Optionally, the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide and benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate.

In certain examples, the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide in an amount of from 20 to 40% w/w, optionally in an amount of from 25 to 30% w/w.

In some examples, the composition comprises benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate in an amount of from 0.4 to 2.0% w/w, optionally about 0.8%, 0.9% or 1.0% w/w.

Accordingly, in a fourth aspect, the present invention further provides agrochemical compositions, and methods of preparing agrochemical compositions, comprising two or more active ingredients.

In a first example, the method comprises: i) formulating a first active ingredient in a first solvent with at least one anionic component to form a first active composition; ii) formulating a second active ingredient in a second solvent with at least one non-ionic component to form a second active composition; and combining the first and second active compositions to form a combination active composition. The method further comprises mixing the combination active composition with a phosphate ester as defined above.

In a second example, the method comprises: i) formulating a first active ingredient in a first solvent with at least one anionic excipient or adjuvant to form a first active composition; ii) formulating a second active ingredient in a second solvent with at least one non-ionic excipient or adjuvant to form a second active composition; and combining at least one of the first and second active compositions with a phosphate ester as defined above. The method further comprises combining the first and second active compositions.

Optionally, the first solvent and the second solvent are the same.

In a third example, the method comprises mixing a first active ingredient in an organic solvent as defined above; adding a second active ingredient to the mixture of the first active ingredient and the organic solvent; adding an anionic component as defined above to the mixture; adding a phosphate ester as defined above to the mixture; and adding a non-organic component as defined above to the mixture.

In a further aspect, the present invention provides the use of an alkylbenzene sulfonic acid 2-propanamine salt, optionally benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0), and a phosphate ester, optionally a polyether phosphate, further optionally a styrene oxide polyether phosphate, preferably oxirane, phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ethers (CAS 308336-53-0), as a replacement for calcium dodecylbenzene sulfonate in agrochemical compositions.

The above and other aspects of the present invention will now be illustrated in further detail, by way of example only, with reference to the following examples and the accompanying figures, in which:

Figure 1 is a photograph showing a bottle containing a first reference mixture of components of compositions of the present invention;

Figure 2 is a photograph showing a bottle containing a second reference mixture of components of compositions of the present invention;

Figure 3 is a photograph showing a bottle containing a first comparative mixture of components of compositions of the present invention;

Figure 4 is a photograph showing a bottle containing a second comparative mixture of components of compositions of the present invention;

Figure 5 is a photograph showing a bottle containing a first mixture in accordance with an embodiment of the present invention;

Figure 6 is a photograph showing a bottle containing a third comparative mixture of components of compositions of the present invention;

Figure 7 is a photograph showing a bottle containing a second mixture in accordance with the present invention; and

Figure 8 is a photograph showing, on the right, a first comparative agrochemical formulation and, on the left, a first inventive agrochemical formulation in accordance with the present invention.

Examples

Unless otherwise stated, weights and concentrations are expressed as percentages by weight.

The skilled reader will understand that certain compounds or compositions as used in the compositions of the present invention are well known as showing multiple In the present application, certain components of the compositions have multiple functionalities within agrochemical compositions. Certain components may function as emulsifiers and as wetting agents, for example, or a dispersants or surfactants.

The present invention has been devised based on the determination that certain anionic components show an incompatibility with certain non-ionic components. In particular, it has been determined that certain anionic alkylbenzene sulfonic acids show an incompatibility with certain non-ionic components such as non-ionic emulsifiers and solvents. For example, Zephrym 3300B (IUPAC name - Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.-, compd. with 2-propanamine (1:1), CAS registry number 84961-74-0) gives rise to cloudiness in methyl benzoate formulations with non-ionic emulsifiers such as Emulsogen EL360, an ethoxylated castor oil, and non-ionic solvents such

Hallcomid M-12-14, an amide of formula R-C(=O)NMe_2, in which R is C_{11} or C_{13}. After a period of time, the cloudy precipitate of the mixture settles to the bottom of the container.

Investigations have shown this incompatibility to be independent of the active ingredients themselves and that the cloudiness can be removed by inclusion in the composition of a phosphate ester.

Specific examples of anionic excipients or adjuvants include alkylbenzene sulfonic acids such as benzenesulfonic acid, 4-C_{10}-C_{13}-sec-alkyl derivatives with 2-propanamine in a 1:1 combination (CAS registry number 84961-74-0), available under the trade names Atlas G-3300B, Maxemul 7201, Atlox 3300B and Zephrym 3300B. These compositions are known for their dispersant, surfactant and wetting agent properties.

Examples of non-ionic components include alkylated and alkoxylated C_{10} to C_{20} fatty acids, such as ethoxylated castor oil sold under the trade marks Emulsogen EL360, Alkamuls EL-620 and Agnique CSO35, Hallcomid M-12-14 identified above, and methylated seed oils.

Examples of suitable phosphate esters include polyether phosphates, including styrene oxide polyether phosphate such as oxirane, 2-phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ether (CAS: 308336-53-0) (for example, that sold under the trade mark Break-Thru DA 655 and commonly used as a dispersing agent in oil dispersions in amounts of about 5 to 10 wt.%, or as a wetting agent); ethoxylated phosphate esters such as Stepfac 8181, polyethylene glycol monotridecyl ether phosphate (CAS: 9046-01-9, 73038-25-2; 78330-24-2), a surfactant; and Silsense PE-100, a dimethicone polyethylene glycol phosphate used as an emulsifier and dispersant.

Examples of the solvent for the compositions of the present invention include methyl benzoate, 2-ethylhexyl benzoate, and C10 to C13 aromatic hydrocarbons such as Solvesso 200ND, Kocosol 200ND and Garosol 200.

Reference Examples

Reference Example 1

Zephrym 3300B (6.5% w/w) and methyl benzoate (34.5% w/w) were mixed. A clear solution was formed (Fig 1).

Reference Example 2

Zephrym 3300B (6.5% w/w) and Hallcomid M-12-14 (18% w/w) mixed, and also formed a clear solution (Fig 2).

Comparative Examples

Comparative Example 1

Zephrym 3300B (6.5% w/w), methyl benzoate (34.5% w/w) and Hallcomid M-12-14 (18% w/w) were mixed. A highly cloudy mixture was formed (Fig 3).

Comparative Example 2

Comparative Example 1 was repeated with the amount of Hallcomid M-12-14 being halved to 9% w/w. The mixture remained cloudy (Fig 4), but was less cloudy than that of Comparative Example 1.

Comparative Example 3

Zephrym 3300B (9.5 % w/w) and Emulsogen EL360 (12% w/w) were mixed with Kocosol 200ND as a solvent/filler. A hazy mixture was formed (Fig 6).

Inventive Examples

Inventive Example 1

Break-Thru DA 655 was added to the mixture of Comparative Example 1 in an amount of 1.95% w/w. The cloudiness of the mixture disappeared, leaving a clear solution (Fig 5).

Inventive Example 2

Break-Thru DA 655 was added to the mixture of Comparative Example 3 in an amount of 1.3% w/w. The cloudiness of the mixture disappeared, leaving a clear solution (Fig 7).

Similar results were seen with mixtures of Zephrym 3300B or Atlox 3300B at 6.6% w/w with 6.8 % w/w Alkamuls EL-620 (a polyethylene glycol ethoxylated castor oil) in methyl benzoate, which gave a cloudy mixture which, on standing, precipitated to the bottom of the mixing bottle. Addition of Break-Thru DA 655 at 2% w/w cleared the cloudiness. It is believed that the cloudiness arises from an incompatibility between the anionic component and the non-ionic component. Preliminary experiments showed a linear relationship between the non-ionic component content of the mixture and the minimum amount of Break-Thru DA655 required to remove the cloudiness. For example, an

emulsifier combination of 30 wt.% Zephrym 3300B and 70 wt.% Emulsogen EL360 in a solvent required about 1.2 wt.% of Break-Thru DA655 to achieve clarity of the solution whereas an equal mixture of the two components required about 0.2 wt.% of Break-Thru to achieve clarity of the solution.

The compositions of the present invention are particularly useful in combination agrochemical compositions, comprising two or more active ingredients, and overcoming incompatibilities between the formulation materials used for each active ingredient.

Agrochemical compositions comprising two or more active ingredients may be prepared as follows.

In a first example, a first active ingredient is formulated with at least one anionic component in a first solvent to form a first active composition. A second active ingredient is formulated with at least one non-ionic component in a second solvent, which may be the same as or different from the first solvent, to form a second active composition.

In one alternative, the first and second active compositions are combined to form a combination active composition and the phosphate ester described above is mixed with the combination active composition.

In an alternative procedure, one or both first and second active compositions are combined with a phosphate ester as described above and the compositions then combined.

In a third example, the method comprises the steps of: i) mixing a first active ingredient in the organic solvent; ii) adding a second active ingredient to the mixture of the first active ingredient and the organic solvent; iii) adding an anionic component as described above to the mixture; iv) adding a phosphate ester as described above to the mixture; and v) adding a non-organic component as described above to the mixture.

The methods may further include the steps of adding safeners, antifoams and other excipients and adjuvants as required.

Example Herbicidal Compositions

Comparative Example 4 - c*omparative herbicidal composition*

A composition was prepared by combining Alkamuls EL-620 LIE (ethoxylated castor oil) in an amount of 6.8 % w/w, Zephrym 3300B as emulsifier (6.6 % w/w), pretilachlor technical (30 % w/w),

florpyrauxifen-benzyl (1.33 % w/w) and fenclorim (7.5 % w/w). The mixed composition was cloudy (Figure 8, right-hand bottle) and, after time, a precipitate settled to the bottom of the bottle.

Inventive Example 3 - *first inventive herbicidal composition*

The comparative herbicidal composition preparation was repeated and a cloudy mixture formed. Break-Thru DA 655 was added at 1.95 % w/w and the sample became clear (Figure 8, left-hand bottle).

Inventive Example 4 - s*econd inventive herbicidal composition*

An example Emulsifiable Concentrate (EC) composition was prepared having the following composition:

Component	CAS No	Amount (% w/v)	Amount (% w/w)	Function
Pretilachlor technical (2-chloro-2',6'-diethyl-N-(2-propoxyethyl)-acetanilide)	51218-49-6	30	27.3473	Active ingredient
Florpyrauxifen-benzyl (4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid)	1390661-72-9	1	0.9116	Active ingredient
Fenclorim (4,6-dichloro-2-phenyl-pyrimidine)	3740-92-9	7.5	6.8368	Safener
ATLOX 3300B (alkylaryl sulfonate isopropylamine salt)	26264-05-1	7.1305	6.5	Emulsifier
EMULSOGEN EL 360 (condensation product of castor oil and ethylene-oxide)	61791-12-6	14.261	13	Emulsifier
SAG 1572 SILICONE ANTIFOAM EMULSION	159002-21-8	0.01	0.0091	Antifoam

BREAK-THRU DA 655 (Oxirane, polymer with phenyloxirane, mono(dihydrogen phosphate), decyl ether (9CI))	308336-53-0	2.194	2	
Methyl benzoate	93-58-3	37.9045 (to 100%)	43.3952 (to 100%)	Solvent

At a temperature in the range of about 25-32 °C, florpyrauxifen-benzyl technical was added to methyl benzoate with mixing to obtain a clear solution, and filtered. Fenclorim technical was added with mixing until a clear solution was obtained and the solution was filtered. Pretilachlor technical was added and mixed homogeneously followed by SAG 1572 antifoam. The speed of mixing was increased to ensure homogenous mixing. Emulsifier Atlox 3300B was warmed to about 40 °C and added to the mixture, with homogeneous mixing until a clear solution was obtained. Break-Thru DA 655, also warmed to about 40 °C, was added with mixing until a clear solution was obtained. Emulsifier Emulsogen EL360, was added, having also been warmed to about 40 °C prior to addition, with mixing to form a clear solution. The clear solution obtained was filtered with a 50 micron sieve.

The resultant solution remained stable over 4, 8 and 12 week periods with storage at 5°C, 0°C and -10°C, with no precipitation or crystal growth; and each satisfied FAO specifications for emulsion stability and re-emulsification after 24 hours (MT 36.3, CIPAC Handbook K, p.137, 2003) when diluted at 1.5 wt.% dilution in water (CIPAC A).

CLAIMS

1. A carrier composition for at least one agrochemically-active ingredient, the carrier composition comprising an organic solvent, at least one anionic component, at least one non-ionic component and a phosphate ester.

2. A carrier composition as claimed in claim 1 wherein the phosphate ester is present in ratio to the combined amount of anionic component and non-ionic component of from 1:5 to 1:25 by weight, preferably from 1:8 to 1:18.

3. A composition as claimed in claim 1 or claim 2 wherein the at least one anionic component is selected from alkylbenzene sulfonic acids; optionally 4-alkylbenzene sulfonic acids, further optionally 4-C_{10}-C_{13}-sec-alkyl benzene sulfonic acids.

4. A composition as claimed in claim 3 wherein the at least one anionic component is an alkylbenzene sulfonic acid 2-propanamine salt, optionally benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0).

5. A composition as claimed in any preceding claim wherein the at least one non-ionic component is selected from alkylated C_{10}-C_{20} fatty acids and alkoxylated C_{10}-C_{20} fatty acids.

6. A composition as claimed in claim 5 wherein the at least one non-ionic component is selected from alkylated seed oils, optionally methylated seed oils, alkoxylated castor oil, optionally ethoxylated castor oil, or amides of formula R^1-C(=O)NR^2R^3 wherein R^1-is C_8 to C_{14}, optionally C_{11} and/or C_{13} and R^2 and R^3 are C_1 to C_3 and may be the same or different, further optionally wherein R^2 and R^3 are both methyl.

7. A composition as claimed in any preceding claim wherein the phosphate ester is a polyether phosphate, optionally a styrene oxide polyether phosphate, further optionally oxirane, phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ethers (CAS 308336-53-0).

8. A composition as claimed in any preceding claim wherein the organic solvent comprises at least one solvent selected from alkyl benzoates and C_{10}-C_{13} aromatic hydrocarbons, optionally wherein the organic solvent is or comprises methyl benzoate.

9. A composition as claimed in any preceding claim wherein the organic solvent is methyl benzoate, the anionic component is benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0), and the phosphate ester is a polyether phosphate, optionally oxirane, phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ethers (CAS 308336-53-0).

10. An agrochemical composition comprising at least one active ingredient and a carrier composition as claimed in any one of claims 1 to 9; optionally comprising at least two active ingredients.

11. An agrochemical composition as claimed in claim 10 wherein the phosphate ester is present in an amount of 0.5 to 3.0 % w/w based on the total weight of the composition, preferably from 1.0 to 2.5 % w/w.

12. A composition as claimed in claim 10 or claim 11 wherein the at least one active ingredient is 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide, or an agrochemically-acceptable salt thereof, or 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid, or an agrochemically-acceptable salt thereof, optionally benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate.

13. A composition as claimed in any one of claims 10 to 12 wherein the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide and 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylic acid or agrochemically-acceptable salts thereof. Optionally, the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide and benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate.

14. A composition as claimed in claim 12 or claim 13 wherein the composition comprises 2-chloro-N-(2,6-diethylphenyl)-N-(2-propoxyethyl)acetamide in an amount of from 20 to 40% w/w, optionally in an amount of from 25 to 30% w/w.

15. A composition as claimed in any one of claims 12 to 14 wherein the composition comprises benzyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-5-fluoropyridine-2-carboxylate in an amount of from 0.4 to 2.0% w/w, optionally about 0.8%, 0.9% or 1.0% w/w.

16. Use of an alkylbenzene sulfonic acid 2-propanamine salt, optionally benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., compds. with 2-propanamine (CAS 84961-4-0), and a phosphate ester, optionally a polyether phosphate, further optionally a styrene oxide polyether phosphate, preferably oxirane, phenyl-, polymer with oxirane, mono(dihydrogen phosphate), decyl ethers (CAS 308336-53-0), as a replacement for calcium dodecylbenzene sulfonate in agrochemical compositions.

17. An emulsifiable concentrate comprising a composition as claimed in any one of claims 1 to 15.

18. A method of preparing a composition as claimed in claim 10, the method comprising formulating a first active ingredient in a first solvent with at least one anionic excipient or adjuvant

to form a first active composition; formulating a second active ingredient in a second solvent with at least one non-ionic excipient or adjuvant to form a second active composition; and i) combining the first and second active compositions to form a combination active composition; and mixing the combination active composition with a phosphate ester or ii) combining at least one of the first and second active compositions with a phosphate ester and combining the first and second active compositions.