(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
13 April 2006 (13.04.2006)

PCT

(10) **International Publication Number**
WO 2006/038019 A1

(51) **International Patent Classification:**
A01N 25/30 (2006.01)

(21) **International Application Number:** PCT/GB2005/003860

(22) **International Filing Date:** 7 October 2005 (07.10.2005)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**

0422470.5	9 October 2004 (09.10.2004)	GB
0506617.0	1 April 2005 (01.04.2005)	GB

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** NON-IONIC SURFACTANT AGGREGATES

(57) **Abstract:** A non-ionic surfactant aggregate comprises a water insoluble biocidally active ingredient, a non-ionic surfactant system, and water. The non-ionic surfactant system comprises first and second non-ionic surfactants.

NON-IONIC SURFACTANT AGGREGATES

This invention relates to non-ionic surfactant aggregates. More particularly, but not exclusively, the invention relates to mixed non-ionic surfactant aggregates. The invention also relates to methods of solubilising water insoluble ingredients, and the packaging of products incorporating such aggregates. Embodiments of the invention relate to formulations and methods whereby specific aggregate structures can be made in order to accommodate water containing mixtures into packaging made from water soluble films such as polyvinyl alcohol (PVA).

Pesticide formulations are normally prepared as concentrated products which are then diluted in water prior to their application by a variety of techniques (e.g. spray, mist, fog etc.), onto a variety of surface types (e.g. plants, hard surfaces, fabrics etc) to give protection against a wide range of target pests (eg. insects, fungal infections, weeds etc). In the majority of cases the actual active component is not soluble in water to any appreciable extent and a number of formulation types are required in order to achieve active ingredient concentrations at appreciable, and as a consequence commercially viable, levels.

Traditionally the formulations used can be of three main general types:

(a) Emulsifiable Concentrates and Oil in Water Emulsions

The active ingredient is dissolved in hydrocarbon solvent with a blend of surfactants to produce the emulsifiable concentrate (EC) which is then diluted with water prior to use to produce an oil in water emulsion. Alternatively the EC can be partially diluted to give an oil in water emulsion concentrate (EW) which is then further diluted with water prior to use.

(b) Suspension Concentrates (Flowables)

The **ai** is ground into a fine form and suspended in a liquid base (oil or water) using a range of additives such as dispersants (surfactants), thickening agents, preservatives and anti freeze (water based) so that when added to water the **ai** is in the form of finely suspended particles. These types of formulation can be combined with emulsions (EW) to form suspo-emulsions.

c) Solid Formulations

Wettable Powders (WP) consist of an inert powder impregnated with the active ingredient which is then milled to a small and evenly distributed paticle size. The dispersion of the powder upon dilution in water is aided by the incorporation of wetting agents and dispersants (surfactants) into the formulation. There are a number of variations on this basic theme (e.g. water dispersible granules etc).

Whilst the use of these formulation types is well established for a diverse range of application types (eg. crop protection, vector control, public hygiene and pest control, timber treatment, home and garden, professional grounds care, termite control etc) there are inherent weaknesses with all formulation types. The Suspension Concentrates (SC) and Wettable Powders require significant processing costs associated with the milling of the solid component, the EC and EW formulations contain organic solvents which can be hazardous both to the user and the Environment. Moreover, all these formulations, when diluted with water, show a propensity to phase separate either by sedimentation (SC and WP) or by creaming (EC and EW) and in the case of the SC and EW types this phase separation can also occur in the concentrates.

The degree of phase separation can be very significant and this is illustrated in table 1 below where the level of separation was determined analytically by HPLC, for a range of conventional formulations containing synthetic pyrethroid insecticides as the active ingredient following their dilution with water.

Dilutions were prepared and mixed thoroughly at which point samples were taken and the nominal active ingredient content determined analytically. The dilutions were then allowed to stand for four hours and further samples taken from the top, middle and bottom 10% fractions and the active ingredient content determined and expressed as a fraction of the nominal value.

Table 1: Phase Separation following dilution

	EC Formulation	EW Formulation
nominal ai content (wt%)	0.067	0.0127
ai content in Top 10%	0.119	0.0044
(ai) actual/nominal	**1.78**	**0.35**
ai content in Middle 10%	0.030	0.0045
(ai) actual/nominal	**0.45**	**0.35**
ai content in Bottom 10%	0.025	0.0500
(ai) actual/nominal	**0.30**	**3.94**

This phase separation can give rise to problems in two different aspects of performance:

(a) where (ai) actual/nominal is <<1 the level of biological control of the pest is low; and

(b) where (ai) actual/nominal is >>1 the toxicological risk to both operator and environment is high.

According to one aspect of this invention, there is provided a non-ionic surfactant aggregate comprising a water insoluble ingredient, a non-ionic surfactant system and water. The preferred embodiment of the non-ionic surfactant aggregate comprises a mixed non-ionic surfactant aggregate.

According to another aspect of this invention there is provided a method of solubilising a water insoluble ingredient comprising mixing a water insoluble ingredient with a non-ionic surfactant system and water to provide a non-ionic surfactant aggregate in which the water insoluble ingredient is solubilised therein.

The non-ionic surfactant aggregate may comprise one or more water insoluble ingredients. The, or each, water insoluble ingredient is preferably an organic substance. The water insoluble ingredient is preferably an active ingredient, preferably a biologically active ingredient, such as a biocide. The active ingredient may comprise a pesticide. The active ingredient may comprise one or more of a herbicide, a fungicide, an insecticide, a nematicide and a miticide.

One advantage of the preferred embodiments of this invention is that mixed non-ionic surfactant aggregates containing high levels of active ingredient or ingredients can be diluted with water to produce a thermodynamically stable mixed non-ionic surfactant aggregate. Such mixed non-ionic surfactant aggregates have no tendency to phase separate across a broad range of temperatures (typically 0-50°C) at a wide range of water hardness (typically 0-1000ppm calcium carbonate).

The active ingredient may comprise an insecticide, which may comprise one or more of: pyrethroids, such as a synthetic pyrethroid; an organophosphate compound, such as chlorpyrifos-ethyl, chlorpyrifos-methyl, pirimiphos-methyl, fenitrothion; a phenyl ether such as pyriproxyfen; a benzoylurea, such as flufenoxuron; a carbamate, such as fenoxycarb, carbosulfan; nicotinoids, such as acetamiprid; pyridinecarboxamides, such as flonicamid; and/or others.The pyrethroid may be selected from one or more of bifenthrin, zeta-cypermethrin, alpha-cypermethrin, tetra-methrin, lambda-cyhalothrin, fenvalerate, cyfluthrin, bio-resmethrin, permethrin, delta-methrin.

The active ingredient may comprise a fungicide which may be selected from one or more of a conazole compound, such as azaconazole, cyproconazole, propiconazole, tebuconazole; carbamates such as IPBC (3-iodo-2-propynyl-butyl-carbamate); and/or others.

The active ingredient may comprise a herbicide which may be selected from the triazolinone compounds such as carfentrazone-ethyl, the aryl triazolinone compounds such as sulfentrazone or the phosphonic acid compounds such as glyphosate. These can be mixed with plant growth regulators such as Ethephon.

The non-ionic surfactant system may comprise a single non-ionic surfactant, but preferably, the non-ionic surfactant system comprises first and second non-ionic surfactants. The first non-ionic surfactant may be more soluble in oil than in water, (having a low hydrophilic-lipophilic balance [HLB]) and the second non-ionic surfactant may be more soluble in water than in oil (having a high HLB).

Preferably, the first and second non-ionic surfactants have different hydrophilic-lipophilic balances to each other.

The non-ionic surfactant system may comprise greater than two non-ionic surfactants.

In some embodiments where there are mixtures of water insoluble active ingredients, the blend of non-ionic surfactants required to provide the desired level of stability (as a concentrate or as a dilution in water) can be complex.

The non-ionic surfactant system may comprise one or more of alkoxylated alcohols, amine ethoxylate, ester ethoxylate, castor oil ethoxylate, fatty acid ethoxylate, amide ethoxylate, ethylene oxide-propylene oxide block copolymers, alkoxylated oils, such as alkoxylated vegetable oils, alkoxylated fatty acids, alkylomide ester or food ester.

The aggregate may be substantially free of ionic surfactants. As used herein the term "substantially free of" is intended to encompass the situation where small amounts are present, but these amounts do not substantially affect the properties or characteristics of the aggregate.

The alkoxylated alcohols may comprise an alcohol ethoxylate. The alkoxylated alcohol may have a straight or branched chain. The alkoxylated alcohol may be any chain length but preferred chain lengths, are 8 to 18 carbon atoms, more preferably 9 to 13 carbon atoms. The alkoxylated alcohol may comprise 1 to 50 moles of ethylene oxide per molecule, preferably 1 to 20 moles ethylene oxide per molecule, and more preferably 2 to 12 moles ethylene oxide per molecule.

The ethylene oxide-propylene oxide block copolymer may have an ethylene oxide content in the range of 10wt% to 80wt%. Preferably, the ethylene oxide-propylene oxide block copolymer has an ethylene oxide content in the range of 10wt% to 40wt%, more preferably in the range of 10wt% to 20wt%. Ethylene oxide propylene oxide block copolymers having a higher ethylene oxide than propylene oxide content are more soluble in water than in oil, (ie. have a high HLB value). Conversely, ethylene oxide-propylene oxide block copolymers having a higher propylene oxide than ethylene oxide content are more soluble in oil than in water (ie. have a low HLB value).

The ethylene oxide-propylene oxide block copolymers used in the preferred embodiment of this invention may comprise molecules with a propylene oxide backbone with ethylene oxide end groups. With such block copolymers, the size of the propylene oxide backbone and the amount of ethylene oxide in the molecule allow for a wide range of variations in terms of water solubility (as shown by aqueous Cloud Points). Hence, they can be used either as primary surfactants (where the ethylene oxide content is 20% or above) or cosurfactants (where the ethylene oxide content is typically 10%).

In the preferred embodiment, ethylene oxide-propylene oxide block copolymers having an ethylene oxide content of less than substantially 20wt% have a low HLB value. Such block copolymers have, in the preferred embodiments, a propylene oxide backbone, and the HLB value can be modified by altering the molecular weight of the propylene oxide backbone.

The alkoxylated vegetable oil may comprise alkoxylated castor oil. The alkoxylated castor oil may comprise an ethoxylated castor oil. The ethoxylated castor oil may have an ethylene oxide content of 5 to 200 moles ethylene oxide per molecule, preferably 5 to 100 moles ethylene oxide per molecule, more preferably 5 to 60 moles ethylene oxide per molecule.

The non-ionic surfactant aggregate may be provided in one of a plurality of structures, such as a micellar solution, (which may comprise normal or inverted micelles), an oil in water ("water external") microemulsion, a water in oil ("oil external") microemulsion, or a molecular cosolution. These mixed non-ionic surfactant aggregates can also take the form of viscous gels which may be comprised of liquid crystals, and may contain hexagonal, lamella, cylindrical or spherical structures.

The preferred embodiments of the invention have the advantage of enabling a water insoluble ingredient eg. a pesticide, to be solubilised in water, by means of a non-ionic surfactant system, to form a mixed non-ionic surfactant aggregate.

The water insoluble ingredient may be present in the aggregate in an amount in the range of 0.001wt% to 50wt%, preferably 0.001wt% to 40wt%.

In a first embodiment, the water insoluble ingredient may be present in the non-ionic surfactant aggregate in an amount in the range of 0.1wt% to 40wt%, preferably 1wt% to 40wt%, more preferably 2wt% to 40wt%. This embodiment may comprise a water in oil aggregate such as a lipophilic mixed non-ionic surfactant aggregate, which may comprise a water in oil microemulsion, a micellar solution or a cosolution.

In a second embodiment, the water soluble ingredient may be present in the aggregate in an amount in the range of 0.1wt% to 35wt%, preferably 1wt% to 30wt%, more preferably 2wt% to 25wt%. This embodiment may comprise a mixed non-ionic surfactant aggregate, which may comprise a hexagonal, lamella, cylindrical or spherical structure.

In a third embodiment, the water insoluble ingredient may be present in the aggregate in an amount in the range of 0.001wt% to 20wt%, preferably 0.001wt% to 15wt%. This embodiment may comprise an oil in water aggregate, such as a hydrophilic mixed non-ionic surfactant aggregate, which may comprise an oil in water microemulsion, a micellar solution or a cosolution.

The non-ionic surfactant system may be present in the aggregate in the range of 0.1wt% to 80wt%, preferably 0.2wt% to 60wt%, more preferably 0.2wt% to 40wt%.

The mass fraction of any given surfactant in a mixture of surfactants can vary within the range 0.01 to 0.99 although typically it will be in the range 0.10 to 0.80 depending on the degree of complexity of both the water soluble ingredient and the surfactant system.

In the first embodiment which may comprise the water in oil aggregate, such as a lipophilic mixed non-ionic surfactant aggregate in the form of water in oil microemulsions, a micellar solution or a cosolution the surfactant system may be present in the non-ionic surfactant aggregate in an amount in the range of 10wt% to 90wt%, preferably 10wt% to 60wt% and more preferably 10wt% to 40wt%.

In the second embodiment which may comprise the hexagonal, lamella, cylindrical or spherical aggregate structures, the surfactant system may be present in the aggregate in an amount in the range of 10wt% to 60wt%, preferably 10wt% to 40wt% and more preferably 10wt% to 30wt%.

In the third embodiment which may comprise the oil in water aggregate, such as a hydrophilic mixed non-ionic surfactant aggregate in the form of an oil in water microemulsion, a micellar solution or a cosolution the surfactant system may be present in the non-ionic surfactant aggregate in an amount in the range of 0.2wt% to 40wt%, preferably 0.2wt% to 35wt%, more preferably 0.2wt% to 25wt%.

The water may be present in the non-ionic surfactant aggregate in amount in the range of 0.1wt% to 99.5wt%, preferably 5wt% to 99.5wt%, more preferably 10wt% to 99.5wt%.

In the first embodiment, which may comprise a water in oil aggregate, such as a lipophilic non-ionic surfactant aggregate in the form of a water in oil microemulsion, a micellar solution or a cosolution the water may be present in the non-ionic surfactant aggregate in an amount 0.1wt% to 35wt%, preferably 5wt% to 35wt%, more preferably 10wt% to 35wt%.

In the second embodiment, which may comprise hexagonal, lamella, cylindrical or spherical aggregate structures, the water may be present in an amount in the range of 20wt% to 55wt%, preferably 30wt% to 55wt%, more preferably 35wt% to 55wt%.

In the third embodiment, which may comprise an oil in water aggregate, such as a hydrophilic non-ionic surfactant aggregate in the form of an oil in water microemulsion, a micellar solution or a cosolution the water may be present in the non-ionic surfactant aggregate in the range of 50wt% to 99.5wt%, preferably 55wt% to 99.5wt%, more preferably 60wt% to 99.5wt%.

The non-ionic surfactant aggregate may further comprise additives which may comprise one or more of the following: a synergist; a growth regulator, for example an insect growth regulator; a pH modifier; a wetting agent.

The synergist may be used with insecticides, such as synthetic pyrethroids, and may be in the form of an organic oil, such as piperonyl butoxide. Other types of oils may include natural oils such as canola oil, which may provide adjuvant effects when used in herbicidal formulations. The growth regulator may comprise a phenyl ether, such as pyriproxifen. The pH modifier may comprise an acid or an alkali which may be inorganic acids or inorganic alkalis. The pH modifier may be hydrochloric acid. Other suitable pH modifiers may comprise an amine such as triethanolamine. The wetting agent may comprise additional surfactants, which may comprise cationic, anionic, non-ionic or amphoteric substances. An example of a suitable wetting is an alkyl aryl sulphonate such as Nansa SSA, and/or a quaternary ammonium, such as Surfac DDAC. The wetting agents have the advantage of enhancing the wetting, spreading, or sticking of spray applications on target substrates.

Under the correct conditions, as would be appreciated by persons skilled in the art, at least one of the preferred embodiments form non-ionic surfactant aggregate structures, which may be lipophilic, and which can solubilise high concentrations of water insoluble organic compounds such as biocide active ingredients.

By selecting and balancing the surfactant chemistry correctly, as would be appreciated by persons skilled in the art, the lipophilic mixed non-ionic surfactant aggregates can take the form of discrete water in oil microemulsion droplets. The formation of such discrete droplets allow for the incorporation of significant quantities of water in liquid formulations contained in packaging members such as sachets formed from water soluble films such as polyvinylacohol (PVA).

According to another aspect of this invention, there is provided a packaged product comprising a water soluble packaging member containing a non-ionic aggregate as described above.

The water soluble packaging member may comprise a sealed sachet. The water soluble packaging member may be formed of a water soluble plastics material such as polyvinylalcohol (PVA).

Embodiments of the invention will now be described by way of example only.

A first embodiment of this invention comprises lipophilic mixed non-ionic surfactant aggregate which may be in the form of a water in oil microemulsion, a micellar solution or a cosolution. The non-ionic water in oil aggregate comprises a water insoluble active ingredient, such as an organic biocide. A suitable such biocide is a pesticide. The organic biocide is present in the water in oil aggregate in an amount in the range of 2wt% to 40wt%.

The water in oil aggregate further includes a surfactant system comprising at least first and second non-ionic surfactants to solubilise the biocide. The first non-ionic surfactant comprises at least one water soluble primary surfactant. The second non-ionic surfactant comprises at least one water insoluble cosurfactant. The first non-ionic surfactant has a high hydrophilic-lipophilic balance (HLB) relative to the second non-ionic surfactant, which has a relatively low HLB.

The surfactant system is present in the mixed non-ionic surfactant aggregate in an amount in the range 10wt% to 90wt% where the cosurfactant mass fraction, (Pcos)m, is in the range of 0.07 to 0.787. The mass fraction, (Psurf)m, for any individual non-ionic surfactant is of the order of 0.04 - 0.9. Water is also present in an amount in the range 0.1wt% to 35wt%. The system may also include other additives which do not contribute to the formation of the mixed non-ionic surfactant aggregates themselves, but which can provide enhanced properties. The other additives may be present in an amount in the range of 0.1wt% to 20wt%. These additives could include wetting agents, synergists, pH modifiers etc. The mixed non-ionic surfactant aggregates can be formed by any suitable method known in the art and such methods will immediately be known to persons skilled in the art on reading this specification. Specific examples of lipophilic mixed non-ionic surfactant aggregates which may be in the form of water in oil microemulsion droplets, a micellar solution or a cosolution are as follows:

Example 1 : Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.237$, $[\mathrm{Psurf}]_m=0.763$, $[\mathrm{Pcos}]_m=0.07$

Component	wt%
Alpha-cypermethrin (synthetic pyrethroid insecticide)	5
Tetramethrin (synthetic pyrethroid insecticide)	5
Piperonyl Butoxide (organic oil as synergist)	10
Pyriproxifen (phenyl ether insect growth regulator)	2
Neodol 91-2.5 (alcohol ethoxylate cosurfactants, CP<0ºC)	5
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	46
Pluronic PE10400 (EO-PO copolymer primary surfactant, CP=75ºC)	20

Hydrochloric Acid, 28% (pH modifier)	0.2
Water	6.8

Example 2 : **Oil External Pesticide Concentrate** $[\text{Pact}]_m=0.182$, $[\text{Psurf}]_m=0.818$, $[\text{Pcos}]_m=0.565$	
Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	2.5
Propiconazole (triazole fungicide)	11.25
Surfac UN90 (alcohol ethoxylate primary surfactant, CP=82ºC)	27
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC	35
Water	24.25

Example 3 : **Oil External Pesticide Concentrate** $[\text{Pact}]_m=0.143$, $[\text{Psurf}]_m=0.857$, $[\text{Pcos}]_m=0.5$	
Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	10
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	30
Pluronic PE10100 (EO-PO copolymer cosurfactant CP~10ºC)	30
Water	30

Example 4 : **Oil External Pesticide Concentrate** $[\text{Pact}]_m=0.093$, $[\text{Psurf}]_m=0.907$, $[\text{Pcos}]_m=0.582$	
Component	**wt%**
IPBC (carbamate fungicide)	7.5
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	20
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	22.5

Surfac UN90 (alcohol ethoxylate primary surfactant, CP=82ºC)	30.5
Water	19.5

Example 5 : Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.04$, $[\mathrm{Psurf}]_m=0.96$, $[\mathrm{Pcos}]_m=0.381$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	3.16
Neodol 91-5 (alcohol ethoxylate primary surfactants, CP=35º)	46.6
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	28.74
Water	21.5

Example 6 : Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.345$, $[\mathrm{Psurf}]_m=0.655$, $[\mathrm{Pcos}]_m=0.787$

Component	**wt%**
IPBC (carbamate fungicide)	15
Propiconazole (triazole fungicide)	15.1
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	26.88
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	18
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	12.15
Hydrochloric Acid, 28% (pH modifier)	0.2
Fluorad FC171 (fluorinated alkyl alkoxylate wetting agent	0.1
Water	12.57

<u>Example 7</u> : Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.344$, $[\mathrm{Psurf}]_m=0.656$, $[\mathrm{Pcos}]_m=0.071$

<u>Component</u>	<u>wt%</u>
IPBC (carbamate fungicide)	15
Propiconazole (triazole fungicide)	15.1
Flufenoxuron (Benzoylurea insect growth regulator)	1.1
Alkamuls 719E (castor oil ethoxylate primary surfactant, CP>100ºC)	50.5
Surfac UN90 (alcohol ethoxylate primary surfactant, CP=82ºC)	4.7
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	4.2
Surfac DDAC (quarternary ammonium wetting agent)	1.5
Hydrochloric Acid, 28% (pH modifier)	0.1
Water	7.8

<u>Example 8</u> : Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.358$, $[\mathrm{Psurf}]_m=0.642$, $[\mathrm{Pcos}]_m=0.226$

<u>Component</u>	<u>wt%</u>
Alpa-cypermethrin (synthetic pyrethroid insecticide)	5
Tetramethrin (synthetic pyrethroid insecticide)	5
Piperonyl Butoxide (organic oil as synergist)	20
Pyriproxifen (phenyl ether insect growth regulator)	2
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	13
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	44.5
Nansa SSA (alkyl aryl sulphonic acid pH modifier)	0.25
Water	10.25

Example 9: Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.105$, $[\mathrm{Psurf}]_m=0.895$, $[\mathrm{Pcos}]_m=0.385$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	8.43
Lutensol XL70 (alcohol ethoxylate primary surfactant, CP~60ºC)	44
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	27.57
Water	20

Example 10: Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.303$, $[\mathrm{Psurf}]_m=0.697$, $[\mathrm{Pcos}]_m=0.351$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	26.32
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	38.11
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	20.57
Water	13

Example 11: Oil External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.141$, $[\mathrm{Psurf}]_m=0.859$, $[\mathrm{Pcos}]_m=0.5$

Component	wt%
Zeta-cypermethrin (synthetic pyrethroid insecticide)	11.5
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP~10ºC)	35
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	35
Nansa SSA (alkyl aryl sulphonic acid pH modifier)	0.2
Water	18.3

Example 12 : **Oil External Pesticide Concentrate**

$[Pact]_m=0.125$, $[Psurf]_m=0.875$, $[Pcos]_m=0.25$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	5.25
Flonicamid (pyridinecarboxamide insecticide)	5.05
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	27
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	18
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	27
Water	17.7

Example 13 : **Oil External Pesticide Concentrate**

$[Pact]_m=0.23$, $[Psurf]_m=0.77$, $[Pcos]_m=0.341$

Component	**wt%**
Carfentrazone ethyl (triazolone herbicide)	13.3
Canola Oil (vegetable oil adjuvant)	6
Surfac UN90 (alcohol ethoxylate primary surfactant, CP=82ºC)	17
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	22
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	25.5
Water	16.2

Example 14 : Oil External Pesticide Concentrate

$[Pact]_m$=0.431, $[Psurf]_m$=0.569, $[Pcos]_m$=0.267

Component	**wt%**
Carfentrazone ethyl (triazolone herbicide)	22.1
Canola Oil (vegetable oil adjuvant)	12
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	12
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	33
Water	20.9

The term "EO-PO copolymer" means an ethylene oxide-propylene oxide copolymer."

The formation of discrete water in oil microemulsion droplets can be demonstrated experimentally by following the conductivity during water enrichment of systems containing a hydrocarbon (e.g. pesticide ai) and two surfactants. In Tables 2 and 3 the conductivity as a function of the water mass fraction, [Paq]m, given by:

[Paq]m = mass of water / total mass of system

is compared for two systems in which the only difference is the cosurfactant mass fraction, (Pcos)m, given by:

[Pcos]m = mass of cosurfactant / total surfactant mass

Table 2 : Conductivity vs [Paq]m at [Pcos]m 0.575	
(Paq)m	Conductivity (mu.S)
0	0
0.025	11
0.05	17
0.065	33
0.09	67
0.11	100
0.15	210
0.2	535
0.25	2000
0.27	3200
0.3	5330

Table 3 : Conductivity vs [Paq]m at [Pcos]m 0.575	
(Paq)m	Conductivity (mu.S)
0.	0
0.01	1
0.025	4
0.05	8
0.06	12
0.07	14
0.09	13.5
0.10	13
0.13	8
0.15	7
0.175	5
0.20	4
0.225	3
0.25	2.5

0.30	2.5
0.32	80
0.34	400
0.35	550

At [Pcos]m 0.575 as [Paq]m increases conductivity increase dramatically showing percolative behaviour. This type of system is best described as being due to the presence of either a bicontinuous (cosolubilised) system or aggregation units with very flexible interfaces and short life times.

At (Pcos)m 0.65 the conductivity remains very low and varies in a non-monotonous manner as [Paq]m increases. Initially there is an increase in conductivity as water is added due to the formation of hydrated surfactant aggregates. At some point, (Paq)m 0.06 to 0.1, conductivity begins to decrease as more water is added due to the replacement of hydrated surfactant aggregates with water in oil microemulsion droplets having definite water cores. As more water is added conductivity remains more or less constant as more and more discrete droplets are formed until a further critical point is reached at (Paq)m 0.3 - 0.32 where conductivity begins to increase rapidly as more water is added. This change is brought about by either a change from spherical to non-spherical droplets or an aggregation of water droplets or indeed a degree of phase inversion brought about by the increase in the mass fraction of dispersed (water) phase.

The above examples of the invention can be packed into standard plastic bottles made from materials such as heavy density polyethylene (HDPE) plastics. Alternatively, in some case, where the water is encapsulated within the mixed surfactant aggregate, thereby preventing contact between the water and the water soluble film, they can be incorporated into water soluble sachets made from materials such as PVA.

The above embodiments are concentrates in the form of lipophilic mixed non-ionic surfactant aggregates which are thermodynamically stable and contain high levels of active ingredient. They are intended for dilution in water whereupon the aggregates spontaneously invert to thermodynamically stable hydrophilic mixed non-ionic surfactant aggregates which can be in the form of oil in water microemulsions, micellar solutions etc. These diluted systems can then be used in a variety of applications.

The stability of these diluted concentrates is best shown by the following examples where dilutions were prepared in waters of various degrees of hardness (expressed as ppm calcium carbonate) and the turbidity measured as a function of time and temperature using an Orbeco-Hellige Digital Turbidimeter.

Table 4 : Turbidity vs Water Hardness @ RT
(Example 3 above diluted @ 1 in 200)

Water Hardness	**Turbidity vs Time**		
	Initial	4 hours	24 hours
0 ppm	12.8	11.6	13.1
100 ppm	13.6	11.4	12
342 ppm	14	11.9	12.4
500 ppm	13	11.8	12

Table 5 :

Turbidity (24 hours) vs Water Hardness vs Temperature (Example 5 above diluted @ 1 in12.5)

Water Hardness	**Turbidity vs Temperature**		
	Initial	**4 hours**	**24 hours**
	4°C	RT	35°C
0 ppm	2	2.6	4.9
100 ppm	2	2.8	4.7
342 ppm	1.8	2.7	4.6
500 ppm	1.9	2.6	4.8

These can be compared to results obtained with a similar system based on a combination of an anionic surfactant and a non-ionic surfactant as given below:

Component	**wt%**
Propiconazole (triazole fungicide)	5.63
Solvesso 150 (naphthenic hydrocarbon solvent)	4.61
Nansa SSA (dodecyl benzene sulphonic acid - anionic surfactant)	7.14
Pluronic PE10100 (EO-PO block copolymer surfactant)	9.72
Sodium Hydroxide	0.25
Water	72.65

The turbidity of dilutions at 1 in 12.5 were prepared in a range of hard waters and measured as a function of time at RT, the results are given in Table 6 below:

Table 6 :

Turbidity (24 hours) vs Water Hardness vs Temperature (Anionic - Non-ionic surfactant combination)

Water Hardness	**Turbidity vs Temperature**		
	Initial	4 hours	24 hours
0 ppm	0.7	1.1	0.8
100 ppm	60.7	163.0*	195.0*
342 ppm	240.0	263.0*	282.0*
500 ppm	281.0	310.0*	505.0*

Note: * these samples showed signs of sedimentation upon standing.

Another technique which can be used to look at effects such as water hardness on the diluted systems is that of Photo Correlation Spectroscopy which uses light scattering as a means of determining particle size. Particles suspended in a medium such as water are subjected to random Brownian Diffusion such that small particles will move much faster than larger ones. The rate of diffusion can be measured by examining the change in intensity of laser light that is scattered at 90° and the radius of the particles, Rh, is given by the equation:

$$\underline{Rh = \qquad kT / 6 \ \pi \eta D}$$

where

k = Boltzmann's constant

T = absolute temperature

η = viscosity of the fluid medium

D = diffusion constant

Using this technique samples were prepared and the particle size determined as a function of water hardness and temperature, results are shown in tables 7 and 8 below:

Table 7 :
Particle Size (nm) vs Water Hardness @ RT
(Example 3 above @ 1 in 200 dilution)

Water Hardness	**Particle Diameter (nm)**	
	Initial	**24 hours**
0 ppm	23.6	22
100 ppm	23.4	22.3
342 ppm	22.4	21.9
500 ppm	22.1	23.5

These dilutions showed a very small degree of translucency indicative of oil in water systems which are in the form of microemulsions and this is confirmed by a typical particle size in the range of 10 to 100 nm.

Table 8 :
Particle Size (24 hours) vs Water Hardness vs Temperature
(Example 5 above @ 1 in 25 dilution)

Water Hardness	**Particle Diameter (nm)**			
	25°C	30°C	40°C	45°C
0 ppm		12.1		
100 ppm		10.4		
342 ppm		10.8		
500 ppm	11.7	11.3	14.2	15.2

All of these samples have the appearance of "water" as confirmed by the turbidity readings, the particle size distribution includes a significant number of particles with diameters below 10 nm and they are probably best described as micellar solutions.

A second embodiment of this invention comprises liquid crystalline "gels" having for example hexagonal, lamella, cylindrical or spherical aggregate structures which will contain water insoluble organic biocide(s) which may be a pesticide active ingredient. The biocide(s) will be present in these structures in an amount in the range 0.1wt% to 35.0wt%. The surfactant system will comprise a mixture of at least two non-ionic surfactant molecules with a total surfactant concentration in the range 10.0wt% to 60.0wt% with the cosurfactant mass fraction, [Pcos]m, of the order 0.04 to 0.65. Water will also be present in these structures at a concentration in the range 20.0wt% to 55.0wt%. The system may also include other additives which do not contribute to the formation of the mixed non-ionic surfactant aggregate, themselves, but can provide enhanced properties and which may be present in an amount in the range 0.1wt% to 20wt%. These other additives may include wetting agents, synergists, pH modifiers etc.

The mixed non-ionic surfactant aggregates can be formed by any suitable method known in the art and such methods will immediately be known to persons skilled in the art on reading this specification. Specific examples of these liquid crystalline "gels" are as follows:

Example 15 : Pesticide Gel

$[Pact]_m$=0.041, $[Psurf]_m$=0.959, $[Pcos]_m$=0.636

Component	**wt%**
IPBC (carbamate fungicide)	2.13
Lutensol TO 8 (alcohol ethoxylate primary surfactant, CP=60ºC)	18.31
Pluronic PE8100 (EO-PO copolymer cosurfactant, CP~15ºC)	32.06
Water	47.5

Example 16 : Pesticide Gel

$[\mathrm{Pact}]_m=0.043$, $[\mathrm{Psurf}]_m=0.957$, $[\mathrm{Pcos}]_m=0.636$

Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	0.5
Propiconazole (triazole fungicide)	2
Lutensol ON 70 (alcohol ethoxylate primary surfactant, CP~60ºC)	20
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	35
Aerosol OT100 (di-octyl sulphsuccinate wetting agent)	0.15
Water	42.35

Example 17 : Pesticide Gel

Component	**wt%**
Flufenoxuron (Benzoylurea insect growth regulator)	0.1
Lutensol AO7 (alcohol ethoxylate primary surfactant, CP=43ºC)	18.5
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	20
Pluronic PE10400 (EO-PO copolymer primary surfactant, CP=75ºC)	10.5
Fluorad FC171 (Fluorinated alkyl alkoxylated wetting agent)	0.1
Water	50.8

These types of system are intended for use without dilution and can supply high active ingredient loadings at highly targeted areas. They have significant potential in the treatment of large dimensional structural timbers where they can be injected into pre-drilled holes providing very good active ingredient distribution throughout the timber which is not possible using conventional spray or brush applications to exposed surfaces.

The viscosity of these "gels" thus formed by these mixed non-ionic surfactant blends can vary significantly in the range of 1000 cPs to >100,000 cPs and will depend to a large extend on the ratio of the various non-ionic surfactants.

If the cosurfactant mass fraction, ([Pcos]m is high (>0.3) medium viscosity "gels" corresponding to an hexagonal array of aggregates tend to form adjacent to the region of lipophilic mixed surfactant aggregates. If this mass fraction is low (<0.2) high viscosity "gels" corresponding to a lamella structures tend to form adjacent to the region of hydrophilic mixed surfactant aggregates.

The flow properties of both types of "gel" are best described by pseudoplastic behaviour. When injected into 1cm pre-drilled holes in timber the mass uptake of these "gels" appears to be quite significant with movement of the active ingredient in some cases exceeding 20cm. Moreover, analytical studies indicate that diffusion of the "gel" through the timber occurs without phase separation.

A third embodiment of this invention comprises hydrophilic mixed non-ionic surfactant aggregates, which may be in the form of micellar solutions or oil in water microemulsions, which contain water insoluble organic biocide(s) which may be a pesticide active ingredient.

The organic biocide(s) will be present in these aggregates in an amount in the range 0.001wt% to 20wt%. The surfactant system comprises at least one water soluble primary surfactant, and at least one water insoluble cosurfactant with the total surfactant concentration being in the range of 0.2wt% to 40wt%. The mass fraction of the cosurfactant [Pcos]m is of the order of 0.17 - 0.47. Water will also be present in the aggregate in an amount in the range 50wt% to 99.5wt%. The system may also include other additives which do not contribute to the formation of the mixed non-ionic surfactant aggregates themselves, but which can provide enhanced properties. These other may be present in an amount in the range 0.1wt% to 20wt%, these may include wetting agents, synergists, pH modifiers etc.

The mixed non-ionic surfactant aggregates can be formed by any suitable method known in the art and such methods will immediately be known to persons skilled in the art on reading this specification. Specific examples of hydrophilic mixed non-ionic surfactant aggregates are as follows:

Example 18 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.048$, $[\mathrm{Psurf}]_m=0.952$, $[\mathrm{Pcos}]_m=0.333$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	0.3
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	4 2
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	2
Water	93.7

Example 19 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.068$, $[\mathrm{Psurf}]_m=0.932$, $[\mathrm{Pcos}]_m=0.421$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	8.43
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	24
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	17.57
Water	50

Example 20 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.169$, $[\mathrm{Psurf}]_m=0.831$, $[\mathrm{Pcos}]_m=0.423$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	2.1
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	16.74
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	12.16
Water	69

Example 21 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.067$, $[\mathrm{Psurf}]_m=0.933$, $[\mathrm{Pcos}]_m=0.214$

Component	**wt%**
Zeta-cypermethrin (synthetic pyrethroid insecticide)	2.5
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	17.5
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	7.5
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	10
Nansa SSA (alkyl aryl sulphonic acid pH modifier)	0.2
Water	62.3

Example 22 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.256$, $[\mathrm{Psurf}]_m=0.744$, $[\mathrm{Pcos}]_m=0.172$

Component	**wt%**
Carfentrazone-ethyl (triazolone herbicide)	5
Canola Oil (vegetable oil adjuvant)	5
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	5

Lutensol XL70 (alcohol ethoxylate primary surfactant, CP~60ºC)	4
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	20
Water	61

Example 23 : Water External Pesticide Concentrate

$[Pact]_m=0.185$, $[Psurf]_m=0.815$, $[Pcos]_m=0.273$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	1.25
Flonicamid (pyridinecarboxamide insecticide)	1.25
Piperonyl Butoxide (organic oil as synergist)	5
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	12
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	9
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	12
Aerosol OT100 (di-octyl sulphosuccinate wetting agent)	0.5
Water	59

Example 24 : Water External Pesticide Concentrate

$[Pact]_m=0.185$, $[Psurf]_m=0.815$, $[Pcos]_m=0.475$

Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	5
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	13
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	14.5
Water	67.5

Example 25 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.197$, $[\mathrm{Psurf}]_m=0.803$, $[\mathrm{Pcos}]_m=0.425$

Component	**wt%**
Propiconazole (triazole fungicide)	2.82
IPBC (carbamate fungicide)	2.82
Permethrin (synthetic pyrethroid insecticide)	1.25
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	16.17
Pluronic PE8100 (EO-PO copolymer cosurfactant, CP~15ºC)	11.95
Fluorad FC171 (fluorinated alkyl alkoxylate wetting agent)	0.2
Water	64.79

Example 26 : Water External Pesticide Concentrate

$[\mathrm{Pact}]_m=0.158$, $[\mathrm{Psurf}]_m=0.842$, $[\mathrm{Pcos}]_m=0.25$

Component	**wt%**
Propiconazole (triazole fungicide)	5.63
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	7.5
Lutensol XL90 (alcohol ethoxylate primary surfactant, CP~90ºC)	22.5
Water	64.37

The specific examples above (18 to 26) are all comprised of hydrophilic mixed non-ionic surfactant aggregates which may be in the form of cosolubilised systems, micellar solutions or oil in water microemulsions. They are all thermodynamically stable and are designed for further dilution with water prior to application for a range of uses and moreover upon further dilution in water the systems maintain their thermodynamic stability.

Given that the external phase of these systems is in all cases water they are not suitable for incorporation into sachets made from water soluble PVA films and would be generally supplied as concentrates in conventional plastic (HDPE) containers.

The stability of both the concentrates and dilutions can be studied by techniques already described above for the study of oil external pesticide concentrates.

The preferred embodiments of the non-ionic surfactant aggregates can be considered as being comprised of three main components, as follows:

(a) an active ingredient phase which comprises the biocidal active ingredient plus any synergists, adjuvants etc;

(b) a surfactant phase which comprises at least one non-ionic surfactant which is soluble in water (having an aqueous Cloud Point > 25ºC and designated as the "primary surfactant") and at least one non-ionic surfactant which is insoluble in water (having an aqueous Cloud Point < 25ºC and designated as the "cosurfactant") where the Cloud Point is determined by any suitable method such as the German standard method (DIN 53917); and

(c) an aqueous phase which comprises water and any additives such as pH modifiers, wetting agents, preservatives, colourants etc.

The active ingredient phase and the surfactant phase collectively can be considered as the organic phase.

The formation and stabilisation of these mixed non-ionic surfactant aggregates, which can be in the form of:

(a) a lipophilic surfactant aggregate which is in the form of a concentrated active ingredient composition which of itself is thermodynamically stable and is diluted with water prior to use to spontaneously form thermodynamically stable hydrophilic surfactant aggregates which can be in the form of microemulsions, micellar solutions etc.;

(b) a hydrophilic surfactant aggregate which is in the form of a concentrated active ingredient compositon which of itself is thermodynamically stable and is diluted with water prior to use whilst retaining the thermodynamically stability of the aggregates which can be in the form of microemulsions, micellar solutions etc.; and

(c) a hydrophilic surfactant aggregate which is in the form of a thermodynamically stable Ready to Use (RtU) active ingredient composition.

is governed by the relationship between the various three component phases defined above.

The key relationships can be defined by the mass fraction ratio of the various phases where the key mass fraction ratios are:

(a) active ingredient mass fraction [Pact]m, given by
[Pact]m = mass of active ingredient phase/mass of organic phase

(b) total surfactant mass fraction, [Psurf]m, given by:

[Psurf]m = mass of non-ionic surfactants/mass of organic phase

(c) cosurfactant mass fraction, [Pcos]m, given by:

[Pcos]m – mass of cosurfactant(s)/mass of non-ionic surfactants.

Whilst all three mass fractions will exert an influence on the formation and stabilisation of thermodynamically stable, single phase surfactant aggregates it is [Pcos]m,the cosurfactant mass fraction which is the overriding driver for this process.

Combinations of water soluble primary surfactant(s) with water insoluble cosurfactant(s) can be varied in order to change the overall hydrophilic- lipophilic nature of the surfactant blend. The optimum stability of the aggregate system is achieved when [Pcos[m matches as closely as possible the Required Hydrophilic Lipophilic Balance (Required HLB) of the active ingredient phase.

The Required HLB of the active ingredient phase will be dependent of the surfactant system used. Consider the above examples 1 and 8 below where the active ingredient phase is a mixture of four components, alpha-cypermethrin, tetramethrin, piperonyl butoxide and pyriproxifen. To determine the Required HLB we need to calculate the Contribution to HLB, (Con-HLB), for each surfactant by multiplying an individual surfactant mass fraction, [Psurf-I]m, by the actual HLB of that surfactant, where:

$[\text{Psurf-I}]_m$ = mass of individual non-ionic surfactant/total mass of non-ionic surfactants

and the Required HLB is the sum of all the Con-HLB values.

Example 1			
Surfactant/type	HLB	$[\text{Psurf-I}]_m$	Con-HLB
Neodol 91-2.5/cosurfactant	8.1	5.0/71.0	0.57
Neodol 91-5/prim.surfactant	11.6	46.0/71.0	7.52
Pluronic PE10400/prim.surfactant	13.0	20.0/71.0	3.66
Required HLB			**11.75**

Example 8			
Surfactant/type	HLB	$[\text{Psurf-I}]_m$	Con-HLB
Neodol 91-2.5/cosurfactant	8.1	13.0/57.5	1.83
Emulan EL40/prim.surfactant	13.0	44.0/57.5	9.95
Required HLB			**11.69**

Consider now the above examples 13 and 14 below where the active ingredient phase is a mixture of two components, carfentrazone-ethyl and canola oil:

Example 13			
Surfactant/type	HLB	$[\text{Psurf-I}]_m$	Con-HLB
Neodol 91-2.5/cosurfactant	8.1	22.0/64.5	2.76
Surfac UN90/prim.surfactant	13.7	17.0/64.5	3.61
Emulan EL40/prim.surfactant	13.0	25.5/64.5	5.14
Required HLB			**11.51**

Example 14			
Surfactant/type	HLB	$[\text{Psurf-I}]_m$	Con-HLB
Neodol 91-2.5/cosurfactant	8.1	12.0/45.0	2.16
Emulan EL40/prim.surfactant	13.0	33.0/45.0	9.53
Required HLB			**11.78**

Now consider the examples 20 and 12 below:

Example 20

The active ingredient phase comprises a single component, bifrenthrin, which is an extremely lipophilic molecule and this is reflected in the much lower value for **Required HLB**:

Surfactant/type	HLB	[Psurf-I]$_m$	Con-HLB
Pluronic PE10100/cosurfactant	1.0	17.57/41.57	0.42
Neodol 91-5/prim.surfactant	11.6	24.0/41.57	6.70
Required HLB			**7.12**

Example 12

Here we have a 50:50 mixture of bifenthrin and flonicamid as the active ingredient phase where the flonicamid is considerably more hydrophilic in nature and the change in the nature of the active ingredient phase is reflected in the Required HLB.

Surfactant/type	HLB	[Psurf-I]$_m$	Con-HLB
Pluronic PE10100	1.0	18.0/72.0	0.25
Neodol 91-5/prim.surfactant	11.6	27.0/72.0	4.35
Emulan EL40/prim.surfactant	11.6	27.0/72.0	4.86
Required HLB			**9.46**

As an alternative these hydrophilic mixed non-ionic surfactant aggregates can be used in the preparation of Ready to use (Rtu), pesticide formulations with specific examples as follows:

Example 27 : Water External Pesticide Rtu

$[Pact]_m=0.034$, $[Psurf]_m=0.966$, $[Pcos]_m=0.167$

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	0.003
Flonicamid (pyridinecarboxamide insecticide)	0.003
Piperonyl Butoxide (organic oil as synergist)	0.015
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	0.4
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	0.1
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	0.1
Aerosol OT 100 (di-octyl sulphosuccinate wetting agent)	0.1
Water	99.349

Example 28 : Water External Pesticide Rtu

$[Pact]_m=0.141$, $[Psurf]_m=0.859$, $[Pcos]_m=0.5$

Component	**wt%**
Pyrethrum 25% (natural pyrethrins insecticide)	0.02
Piperonyl Butoxide (organic oil as synergist)	0.22
Myclobutanil (conazole fungicide)	0.006
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	0.75
Surfac UN90 (alcohol ethoxylate primary surfactant, CP=82ºC)	0.25
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	0.5
Water	98.254

Example 29 : Water External Pesticide Rtu

$[\text{Pact}]_m=0.284$, $[\text{Psurf}]_m=0.716$, $[\text{Pcos}]_m=0.441$

Component	**wt%**
Zeta-cypermethrin (synthetic pyrethroid insecticide)	0.015
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	0.4
Pluronic PE10100 (EO-PO copolymer surfactant, CP~10ºC)	0.1
Emulan EL40 (castor oil ethoxylate primary surfactant, CP>100ºC)	0.1
Nansa SSA (alkyl aryl sulphonic acid pH modifier)	0.02
Water	99.365

Example 30 : Water External Pesticide Rtu

$[\text{Pact}]_m=0.284$, $[\text{Psurf}]_m=0.716$, $[\text{Pcos}]_m=0.441$

Component	**wt%**
Natural pyrethrums, 25% (natural pyrethrin insecticide)	1.2
Piperonyl Butoxide (organic oil as synergist)	1.5
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	0.3
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	3.8
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	2.7
Water	90.5

Example 31 : Water External Pesticide Rtu

$[Pact]_m$=0.186, $[Psurf]_m$=0.814, $[Pcos]_m$=0.333

Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	0.1
Propiconazole (triazole fungicide)	0.225
IPBC (carbamate fungicide)	0.225
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	0.8
Neodol 91-5 (alcohol ethoxylate primary surfactant CP=35ºC)	0.8
Pluronic PE10400 (EO-PO copolymer primary surfactant CP=75ºC)	0.8
Aerosol OT100 (di-octyl sulphosuccinate wetting agent)	0.05
Water	97

Example 32 : Water External Pesticide Rtu

$[Pact]_m$=0.006, $[Psurf]_m$=0.994, $[Pcos]_m$=0.3

Component	**wt%**
Bifenthrin (synthetic pyrethroid insecticide)	0.003
Neodol 91-5 (alcohol ethoxylate primary surfactant CP=35ºC)	0.35
Pluronic PE10100 (EO-PO copolymer cosurfactant, CP~10ºC)	0.15
Water	99.497

5

Example 33 : Water External Pesticide Rtu

Component	**wt%**
Permethrin (synthetic pyrethroid insecticide)	0.2
Neodol 91-2.5 (alcohol ethoxylate cosurfactant, CP<0ºC)	1.3
Neodol 91-5 (alcohol ethoxylate primary surfactant, CP=35ºC)	2
Neodol 91-8 (alcohol ethoxylate primary surfactant, CP=82ºC)	0.9
Emulan EL40 (castor oil ethoxylate primary surfactant CP>100ºC)	1
Water	94.6

The formulations of examples 27 to 33 above are not designed for further dilution and they are thermodynamically stable hydrophilic mixed non-ionic surfactant aggregates which can be in the form of cosolubilised sytems, micellar solutions or oil in water microemulsions. They are to be supplied in conventional plastic bottles made from HDPE or PET and would be expected to have stability allowing for a two year shelf-life under UK ambient conditions.

According to another aspect of this invention certain thermodynamic and physical properties, for example lack of phase separation, small particle size and low surface tension, of the hydrophilic mixed non-ionic surfactant aggregates can result in a significant improvement in the biological effectiveness of the applied active ingredient when compared to that achieved with more conventional types of formulation. This enhancement is best demonstrated by reference to the following examples given below.

Example A : Use of Insecticide by Soil Application

In certain instances the insect pest attacking a particular plant species does so by attacking the roots of the plant which are embedded in the soil substrate. In these cases the insecticide has to be applied directly to the soil and the criteria which determines the level of control of the pest is depth of penetration into the soil and eveness of distribution within sub-levels within the soil substrate.

In laboratory studies columns of soil were prepared in such a manner that 230 gms of soil having a moisture content of 5wt% were tamped to give a column height of 8 inches within a 10 inch plastic tube of 1.25 inch internal diameter. The formulation shown in example 10 above, which is in the form of a lipophilic mixed non-ionic surfactant aggregate, was diluted to 0.08% bifenthrin in water and 2mls of this dilution applied by pipette to the surface of the soil column described above, this was followed immediately by application of 20mls of double distilled water as an eluent. After standing for 24 hours the plastic tube was split and the column of soil exposed. The soil was then split into 1 inch segments which were then placed in sealed glass jars with 20ml of HPLC grade methanol and placed in an ultrasonic bath for 30 minutes to extract the bifenthrin. Following the ultrasonication a 2ml sample of each extraction was placed in a centrifuge vial and centrifuged for 10 minutes at 10,000rpm to sediment out any extraneous particulate material. The clear supernatant liquid was then injected on to an HPLC column (reverse phase) and the concentrate of bifenthrin present in each 1 inch section of soil determined. In parallel to this a commercial Emulsifiable Concentrate, (EC), formulation of bifenthrin was also diluted in water to 0.08% active ingredient and columns of soil treated in an identical manner to that described above.

The results, which are the mean of five replicates analysed in duplicate with external standard solutions used for calibration of bifenthrin level, are given in tables 9 and 10 below where the results are expressed as % of applied bifenthrin present in each 1 inch segment.

Table 9 :

Distribution of bifenthrin in soil columns

Effect of formulation type : MNSA vs EC

Soil Depth (inches)	**% of total bifenthrin in soil**	
	MNSA	**EC**
0-1	17.97	33.7
1-2	22.81	31.34
2-3	26.67	21.03
3-4	22.64	10.61
4-5	8.66	3.32
5-6	1.25	0

Table 10 :

Cumulative distribution of bifenthrin in soil columns

Effect of formulation type : MNSA vs EC

Cumulative Depth (inches)	**% of total bifenthrin in soil**	
	MNSA	**EC**
0-1	17.97	33.70
0-2	40.78	65.04
0-3	67.45	86.07
0-4	90.09	96.68
0-5	98.75	100
0-6	100	

These results clearly demonstrate that the hydrophilic mixed non-ionic surfactant aggregates deposit the active ingredient much more evenly throughout the soil following topical application to the surface when compared to a conventional EC formulation. Moreover, the active ingredient is deposited to much greater depths (32.45% of total active ingredient with

MNSA vs 13.93% of total active ingredient with EC into the 3 to 6 inch segment) and this would be expected to give much better control of soil borne insect pests.

In a second experiment the formulation given in Example 5 and contained within a water soluble sachet [PVA film] was diluted in water to give a bifenthrin concentration of 0.08% and this solution used to treat a column of soil as described in the methodology above. The distribution of bifenthrin throughout the column of soil is given in tables 11 & 12 where it is again compared to the standard EC formulation.

Table 11 :
Distribution of bifenthrin in soil columns
MNSA example 5 vs EC

Cumulative Depth (inches)	**% of total bifenthrin in soil**	
	MNSA	**EC**
0-1	8.21	33.7
1-2	13.16	31.34
2-3	16.21	21.03
3-4	21.37	10.61
4-5	24.15	0
5-6	15.13	
6-7	1.56	
7-8	0.21	

Table 12 :
Distribution of bifenthrin in soil columns
MNSA example 5 vs EC

Cumulative Depth (inches)	**% of total bifenthrin in soil**	
	MNSA	**EC**
0-1	8.21	33.7
0-2	21.37	65.04
0-3	37.58	86.07
0-4	58.95	96.68
0-5	83.1	100
0-6	98.23	
0-7	99.79	
0-8	100	

With this formulation with an increased surfactant: bifenthrin ratio we see even better distribution of the active ingredient within the soil to greater depths with the potential for much improved control of soil borne insect pest.

Example B: Topical application to timbers

Traditionally timbers have been treated **in situ** by the spray or brush application of solutions of insecticide or fungicide in a petroleum based solvent. Although conventional water based systems such as dilutions (in water) of SC and EC type systems have been examined these proved ineffectual with respect to their poor penetration into the sub surface layers of the timber. In the treatment of timbers by surface application there is a need to have some of the active ingredient deposited at or near the surface in order to protect against infestation of the timber by freshly laid eggs and also to provide a “toxic envelope” extending to a depth of 5-6mm into the timber in order to eradicate larvae present in the timber. Solvent based systems give this type of deposition pattern when applied to timbers in this manner.

The structure of timber includes an array of capillary tubes with diameters typically in the range of 1-10 microns through which fluids are transported into the wood. Failure of the SC and EC systems will be due, in the main, to the relatively large particle size of the dispersed phase containing the insecticide active ingredient which will be of an order of magnitude that is similar to these capillary tubes.

The mixed non-ionic surfactant aggregates described herein have typical aggregate diameters in the range 10-100nm (0.01-0.1 microns) and as a consequence we might expect them to behave in a manner similar to a solvent particularly if the surfactant can also allow for effective wetting of the timber surfaces.

In an initial study a bifenthrin mixed non-ionic aggregate formulation as given in example 9 was diluted in water to give a bifenthrin concentration of 0.03% w/w and this was applied to the radial face of blocks of Scots pine sapwood at the rate of 240 mls per square metre. At the same time a commercial sample of an 8% bifenthrin SC formulation was also diluted to the same in use level and applied to Scots pine sapwood blocks at the same rate.

The treated blocks were then left at ambient conditions for 7 days. Thin sections (ca 0.125mm) of timber were then removed from the timber blocks using a hand plane (sections were weighed and the exact thickness determined using the density of wood in a particular block). These sections were then extracted by ultrasonication for 1 hour in 2 mls of methanol (HPLC grade) and the concentration of insecticide determined analytically by an HPLC method.

In this study the proportion of the applied active ingredient found in the top 0.25mm if the timber (surface layer) were determined and the results were as shown in Table 13 below.

Table 13 :

Distribution of bifenthrin in surface layer of timbers treated by topical application

MNSA example vs SC

Sample	**% of bifenthrin in surface layer**
MNSA	33.2
SC	72.4

Clearly, as expected, the SC formulation deposits a much greater proportion of its active ingredient into the surface layer and therefore does not penetrate the sub surface of the timber.

In a second study a permethrin based MNSA formulation as given in example 3 above along with a commercial EC formulation were diluted in water to give a permethrin concentration of 0.1% w/w and applied to timber blocks as described above. As a control a solution of 0.1% w/w permethrin dissolved in Shellsol A (naphthenic solvent) was also tested. Sections were taken down to 6mm and the % of the permethrin in each section determined, the results are given in Table 14 below.

Table 14 :

Deposition profile of permethrin in Scots pine sapwood following topical application

Effect of formulation type

Section Depth (mm)	**% permethrin in section**		
	Solvent	**EC**	**MNSA**
0-1	61.2	81.9	53.5
1-2	15.5	15.2	24.2
2-3	10.7	2.9	12.0
3-4	7.8		7.3
4-5	3.9		2.2
5-6	0.9		0.4

The MNSA formulation gives a very similar profile as the solvent based solution whereas the EC system gives a much shallower deposition with more than 80% of the ai in the top 1mm layer.

There is thus described a non-ionic surfactant aggregate, which in the preferred embodiments, allows water insoluble active ingredients to be solubilised or emulsified into a water carrier for delivery, eg. by spraying, as desired, e.g. to a surface or plant. Moreover the preferred embodiments provide the advantage of a lack of phase separation. This lack of phase separation is demonstrated in Table 15 below using results generated as per Table 1 above with an MNSA formulation containing a synthetic pyrethroid insecticide as the active ingredient.

Table 15 :

Phase Separation following dilution

	MNSA Formulation	
nominal active ingredient content (wt%)	0.0127	
ai content in Top 10%	0.0129	
active/ingredient actual/nominal		**1.01**
active ingredient content in Middle 10%	0.013	
active ingredient actual/nominal		**1.02**
active ingredient content in Bottom 10%	0.0127	
active ingredient actual/nominal		**1.00**

Whilst endeavouring in the foregoing specification to draw attention to those features of the invention believed to be of particular importance it should be understood that the Applicant claims protection in respect of any patentable feature or combination of features hereinbefore referred to and/or shown in the drawings whether or not particular emphasis has been placed thereon.

CLAIMS

1. A non-ionic surfactant aggregate comprising a water insoluble biocidally active ingredient, a non-ionic surfactant system, and water, wherein the non-ionic surfactant system comprises first and second non-ionic surfactants.

2. A non-ionic surfactant aggregate according to claim 1 wherein the first non-ionic surfactant comprises at least one primary non-ionic surfactant, being soluble in water, and the second non-ionic surfactant comprises at least one non-ionic cosurfactant, being insoluble in water.

3. A non-ionic surfactant aggregate according to claim 2 wherein the primary non-ionic surfactant has an aqueous cloud point greater than 25°C and the non-ionic cosurfactant has an aqueous cloud point less than 25°C.

4. A non-ionic surfactant aggregate according to any preceding claim and wherein the mass fractions of the active ingredient [Pact]m, total non-ion surfactant [Psurf]m, non-ionic cosurfactant [Pcos]m are as follows:

active ingredient mass fraction, [Pact]m: 0.002 to 0.431
total non-ionic surfactant mass fraction [Psurf]m: 0.569 to 0.998
non-ionic cosurfactant mass fraction [Pcos]m: 0.07 to 0.787

5. A non-ionic surfactant aggregate according to any preceding claim substantially free of organic solvent.

6. A non-ionic surfactant aggregate according to any preceding claim substantially free of ionic surfactants.

7. A non-ionic surfactant aggregate according to any preceding claim wherein the biocide is selected from one or more of an insecticide, a fungicide, a herbicide, a nematicide, a miticide.

8. A non-ionic surfactant aggregate according to Claim 7 wherein the insecticide is selected from one or more of a pyrethroid, an organophosphate compound, a phenyl ether, a benzoylurea, a carbamate, a nicotinoid, a pyridinecarboxamide.

9. A non-ionic surfactant aggregate according to Claim 8 wherein: where the insecticide comprises a pyrethroid, the pyrethroid is selected from one or more of bifenthrin, zeta-cypermethrin, alpha-cypermethrin, tetra-methrin, lambda-cyhalothrin, fenvalerate, cyfluthrin, bio-resmethrin, permethrin, delta-methrin; where the insecticide comprises an organophosphate compound, the organophosphate compound is selected from one or more of chlorpyrifos-ethyl, chlorpyrifos-methyl, pirimiphos-methyl, fenitrothion; where the insecticide comprises a phenyl ether, the phenyl ether comprises pyriproxyfen where the insecticide comprises a benzoylurea; the benzoylurea comprises flufenoxuron where the insecticide comprises a carbamate; the carbamate comprises fenoyxcarb, carbosulfan; where the insecticide comprises a nicotinoid, the nicotinoid comprises acetamiprid; where the insecticide comprises a pyridinecaboxamide, the pyridinecaboxamide comprises flonicamid.

10. A non-ionic surfactant aggregate according to Claim 7 wherein the fungicide is selected from one or more of a conazole compound and a carbamate.

11. A non-ionic surfactant aggregate according to Claim 10 wherein: the conazole compound is selected from one or more of azaconazole, cyproconazole, propiconazole, tebuconazole; the carbamate comprises IPBC (3-iodo-2-propynyl-butyl-carbamate).

12. A non-ionic surfactant aggregate according to Claim 7 wherein the herbicide is selected from one or more of a triazolinone, an aryl triazoline, a phosphonic acid.

13. A non-ionic surfactant aggregate according to Claim 12 wherein: where the herbicide comprises a triazolinone, the triazolinone comprises carfentrazone-ethyl; where the herbicide comprises an aryl triazolinone, the aryl triazolinone comprises sulfentrazone; where the herbicide comprises a phosphonic acid, the phosphonic acid comprises glyphosate.

14. A non-ionic surfactant aggregate according to any preceding claim wherein the non-ionic surfactant system comprises one or more of alkoxylated alcohols, amine ethoxylate, ester ethoxylate, castor oil ethoxylate, fatty acid ethoxylate, amide ethoxylate, ethylene oxide-propylene oxide block copolymers, alkoxylated oils, alkoxylated vegetable oils, alkoxylated fatty acids, alkylomide ester or food ester.

15. A non-ionic surfactant aggregate according to Claim 14 wherein the alkoxylated alcohols comprise an alcohol ethoxylate, and have a straight or branched chain.

16. A non-ionic surfactant aggregate according to Claim 14 or 15 wherein the alkoxylated alcohol has a chain length of 8 to 18 carbon atoms, preferably 9 to 13 carbon atoms, and comprises 1 to 50 moles of ethylene oxide per molecule, preferably 1 to 20 moles ethylene oxide per molecule, and more preferably 2 to 12 moles ethylene oxide per molecule.

17. A non-ionic surfactant aggregate according to claim 14 wherein the ethylene oxide-propylene oxide block copolymer has an ethylene oxide content in the range of 10wt% to 90wt%, preferably, in the range of 10wt% to 40wt%, more preferably in the range of 10wt% to 20wt%.

18. A non-ionic surfactant aggregate according to Claim 14 wherein the alkoxylated vegetable oil comprises an alkoxylated castor oil.

19. A non-ionic surfactant aggregate according to Claim 18 wherein the alkoxylated castor oil comprises an ethoxylated castor oil, having an ethylene oxide content of 5 to 200 moles ethylene oxide per molecule, preferably 5 to 100 moles ethylene oxide per molecule, more preferably 5 to 60 moles ethylene oxide per molecule.

20. A non-ionic surfactant aggregate according to any preceding claim wherein the water insoluble ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.001wt% to 50wt%, preferably 0.001wt% to 40wt%.

21. A non-ionic surfactant aggregate according to Claim 20 wherein the water insoluble ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.1wt% to 40wt%, preferably 1wt% to 40wt%, more preferably 2wt% to 40wt%.

22. A non-ionic surfactant aggregate according to Claim 21 wherein the non-ionic surfactant aggregate comprises a lipophilic mixed non-ionic surfactant aggregate, in the form of a water in oil microemulsion, a micellar solution or cosolution.

23. A non-ionic surfactant aggregate according to Claim 20 wherein the water insoluble biocidally active ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.1wt% to 35wt%, preferably 1wt% to 30wt%, more preferably 2wt% to 25wt%.

24. A non-ionic surfactant aggregate according to Claim 23 wherein the non-ionic surfactant aggregate comprises a hexagonal, lamella, cylindrical or spherical structure.

25. A non-ionic surfactant aggregate according to Claim 20 wherein the water insoluble biocidally active ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.001wt% to 20wt%, preferably 0.001wt% to 15wt%.

26. A non-ionic surfactant aggregate according to Claim 25 wherein the non-ionic surfactant aggregate comprises a hydrophilic mixed non-ionic surfactant aggregate, in the form of an oil in water microemulsion, a micellar solution or a cosolution.

27. A non-ionic surfactant aggregate according to any preceding claim wherein the non-ionic surfactant system is present in the non-ionic surfactant aggregate in the range of 0.1wt% to 80wt%, preferably 0.2wt% to 60wt%, more preferably 0.2wt% to 40wt%.

28. A non-ionic surfactant aggregate according to Claim 27 wherein the total surfactant mass fraction ratio [Psurf]m is in the range 0.5 to 0.998, preferably in the range 0.569 to 0.96, and the cosurfactant mass fraction ratio, (Pcos)m, is in the range 0.02 to 0.9, preferably in the range 0.07 to 0.787.

29. A non-ionic surfactant aggregate according to Claim 27 or 28 wherein the surfactant system is present in the non-ionic surfactant aggregate in an amount in the range of 10wt%to 90wt%, preferably 10wt% to 60wt% and more preferably 10wt% to 40wt%.

30. A non-ionic surfactant aggregate according to Claim 27 or 28 wherein the surfactant system is present in the non-ionic surfactant aggregate in an amount in the range of 10wt% to 60wt%, preferably 10wt% to 40wt% and more preferably 10wt% to 30wt%.

31. A non-ionic surfactant aggregate according to Claim 27 or 28 wherein the surfactant system is present in the non-ionic surfactant aggregate in an

amount in the range of 0.2wt% to 40wt%, preferably 0.2wt% to 35wt%, more preferably 0.2wt% to 25wt%.

32. A non-ionic surfactant aggregate according to any preceding claim wherein the water is present in the non-ionic surfactant aggregate in amount in the range of 0.1wt% to 99.5wt%, preferably 5wt% to 99.5wt%, more preferably 10wt% to 99.5wt%.

33. A non-ionic surfactant aggregate according to Claim 32 wherein the water is present in the non-ionic surfactant aggregate in an amount 0.1wt% to 35wt%, preferably 5wt% to 35wt%, more preferably 10wt% to 35wt%.

34. A non-ionic surfactant aggregate according to Claim 32 wherein the water is present in the non-ionic surfactant aggregate in the range of 50wt% to 99.5wt%, preferably 55wt% to 99.5wt%, more preferably 60wt% to 99.5wt%.

35. A non-ionic surfactant aggregate according to Claim 32 wherein the water is present in the non-ionic surfactant aggregate in the range of 50wt% to 99.5wt%, preferably 55wt% to 99.5wt%, more preferably 60wt% to 99.5wt%.

36. A method of solubilising a water insoluble ingredient comprising mixing a water insoluble biocidally active ingredient with a non-ionic surfactant system and water to provide a non-ionic surfactant aggregate in which the water insoluble ingredient is solubilised therein, wherein the non-ionic surfactant system comprises first and second non-ionic surfactants.

37. A method according to claim 36 wherein the first non-ionic surfactant comprises at least one primary non-ionic surfactant, being soluble in water, and the second non-ionic surfactant comprises at least one non-ionic cosurfactant, being insoluble in water.

38. A method according to claim 37 wherein the first non-ionic surfactant has a cloud point greater than 25ºC and the second non-ionic surfactant has a cloud point less than 25ºC.

39. A method according to any of claims 36 to 38 wherein the mass fractions of the active ingredient (Pact)m, total non-ionic surfactant (Psurf)m, non-ionic cosurfactant (Pcos)m are as follows:

active ingredient mass fraction (Pcos)m: 0.002 to 0.431
total non-ionic surfactant mass fraction (Psurf)m: 0.569 to 0.998
non-ionic cosurfactant mass fraction (Pcos)m: 0.07 to 0.787

40. A method according to any of claims 36 to 39 substantially free of organic solvent.

41. A method according to any of claims 36 to 40 substantially free of ionic surfactants.

42. A method according to any of claims 36 to 41 wherein the biocide is selected from one or more of an insecticide, a fungicide, a herbicide, a nematicide, a miticide.

43. A method according to Claim 42 wherein the insectide is selected from one or more of a pyrethroid, an organophosphate compound, a phenyl ether, a benzoylurea, a carbamate, a nicotinoid, a pyridinecarboxamide.

44. A method according to Claim 43 wherein: where the insecticide comprises a pyrethroid, the pyrethroid is selected from one or more of bifenthrin, zeta-cypermethrin, alpha-cypermethrin, tetra-methrin, lambda-cyhalothrin, fenvalerate, cyfluthrin, bio-resmethrin, permethrin, delta-methrin; where the insecticide comprises an organophosphate compound, the organophosphate compound is selected from one or more of chlorpyritos-

ethyl, chlorpyritos-methyl, pirimphos-methyl, fenitrothian; where the insecticide comprises a phenyl ether, the phenyl ether comprises pyriproxyfen; where the insecticide comprises a benzoylurea, the benzoylurea comprises flufenoxuron; where the insecticide comprises a carbamate, the carbamate comprises fenoxycarb, carbosulfan; where the insecticide comprises a nicotinoid, the nicotinoid comprises acetamiprid; where the insecticide comprises a pyridenecarboxamide, the pyridine carboxamide comprises flonicamid.

45. A method according to Claim 42 wherein the fungicide is selected from one or more of a conazole compound and a carbamate.

46. A method according to Claim 45 wherein: where the fungicide comprises a conazole compound, the conazole compound is selected from one or more of azaconazole, cyproconazole, propiconazole, tebuconazole; where the fungicide comprises a carbamate, the carbamate comprises IPBC (3-iodo-2-propynyl-butyl-carbamate).

47. A method according to Claim 42 wherein the herbicide is selected from one or more of a triazolinone compound, an aryl triazolinone compound, a phosphonic acid.

48. A method according to Claim 47 wherein: where the herbicide comprises a triazolinone compound, the triazolinone compound comprises carfentrazone-ethyl; where the herbicide comprises an aryl triazolinone compound, the aryl triazolinone compound comprises sulfentrazone; where the herbicide comprises a phosphonic acid, the phosphonic acid comprises glyphosate.

49. A method according to any of Claims 36 to 48 wherein the non-ionic surfactant system comprises one or more of a alkoxylated alcohols, amine ethoxylate, ester ethoxylate, castor oil ethoxylate, fatty acid ethoxylate, amide

ethoxylate, ethylene oxide-propylene oxide block copolymers, alkoxylated oils, alkoxylated vegetable oils, alkoxylated fatty acids, alkylomide ester or food ester.

50. A method according to Claim 49 wherein the alkoxylated alcohols comprise an alcohol ethoxylate, and have a straight or branched chain.

51. A method according to Claim 49 or 50 wherein the alkoxylated alcohol has a chain length of 8 to 18 carbon atoms, preferably 9 to 13 atoms, and comprises 1 to 50 moles of ethylene oxide per molecule, preferably 1 to 20 moles ethylene oxide per molecule, and more preferably 2 to 12 moles ethylene oxide per molecule.

52. A method according to Claim 49 wherein the ethylene oxide-propylene oxide block copolymer has an ethylene oxide content in the range of 10wt% to 80wt%, preferably in the range of 10wt% to 40wt%, more preferably in the range of 10wt% to 20wt%.

53. A method according to Claim 49 wherein the alkoxylated vegetable oil comprises an alkoxylated castor oil.

54. A method according to Claim 53 wherein the alkoxylated castor oil comprises an ethoxylated castor oil, having an ethylene oxide content of 5 to 200 moles ethylene oxide per molecule, preferably 5 to 100 moles ethylene oxide per molecule, more preferably 5 to 60 moles ethylene oxide per molecule.

55. A method according to any of claims 36 to 54 wherein the water insoluble ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.001wt% to 50wt%, preferably 0.001wt% to 40wt%.

56. A method according to Claim 55 wherein the water insoluble ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.1wt% to 40wt%, preferably 1wt% to 40wt%, more preferably 2wt% to 40wt%.

57. A method according to Claim 56 wherein the non-ionic surfactant aggregate comprises a lipophilic mixed non-ionic surfactant aggregate, in the form of a water in oil microemulsion.

58. A method according to Claim 55 wherein the water soluble biocidally active ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.1wt% to 35wt%, preferably 1wt% to 30wt%, more preferably 2wt% to 25wt%.

59. A method according to Claim 58 wherein the non-ionic surfactant aggregate comprises hexagonal, lamella, cylindrical or spherical structure.

60. A method according to Claim 55 wherein the water soluble ingredient is present in the non-ionic surfactant aggregate in an amount in the range of 0.001wt% to 20wt%, preferably 0.001wt% to 15wt%.

61. A method according to Claim 60 wherein the non-ionic surfactant aggregate comprises a hydrophilic mixed non-ionic surfactant aggregate, in the form of an oil in water microemulsion, a micellar solution or a cosolution.

62. A method according to any of claims 36 to 61 wherein the total non-ionic surfactant mass fraction ratio (Psurf)m is in the range of 0.4 to 0.998, preferably 0.4 to 0.95 for lipophilic aggregates or 0.5 to 0.95 for hydrophilic aggregates, and the cosurfactant mass fraction ratio (Pcos)m is in the range 0.05 to 0.8 for hydrophilic and lipophilic aggregates.

63. A method according to Claim 62 wherein the mass fraction of any given surfactant in a mixture of surfactants varies within the range of 0.01 to 0.99, preferably in the range 0.10 to 0.80.

64. A method according to Claim 62 or 63 wherein the surfactant system is present in the non-ionic surfactant aggregate in an amount in the range of 10wt% to 90wt%, preferably 10wt% to 60wt% and more preferably 10wt% to 40wt%.

65. A method according to Claim 62 or 63 wherein the surfactant system is present in the non-ionic surfactant aggregate in an amount in the range of 10wt% to 60wt%, preferably 10wt% to 40wt% and more preferably 10wt% to 30wt%.

66. A method according to Claim 62 or 63 wherein the surfactant system is present in the non-ionic surfactant aggregate in an amount in the range of 0.2wt% to 40wt%, preferably 0.2wt% to 35wt%, more preferably 0.2wt% to 25wt%.

67. A method according to any of claims 36 to 66 wherein the water is present in the non-ionic surfactant aggregate in amount in the range of 0.1wt% to 99.5wt%, preferably 5wt% to 99.5wt%, more preferably 10wt% to 99.5wt%.

68. A method according to Claim 67 wherein the water is present in the non-ionic surfactant aggregate in an amount 0.1wt% to 35wt%, preferably 5wt% to 35wt%, more preferably 10wt% to 35wt%.

69. A method according to Claim 67 wherein the water is present non-ionic surfactant aggregate in an amount in the range of 20wt% to 55wt%, preferably 30wt% to 55wt%, more preferably 35wt% to 55wt%.

70. A method according to Claim 67 wherein the water is present in the non-ionic surfactant aggregate in the range of 50wt% to 99.5wt%, preferably 55wt% to 99.5wt%, more preferably 60wt% to 99.5wt%.

71. A packaged aggregate comprising a water soluble packaging member containing a non-ionic aggregate as claimed in any of claims 1 to 35.

72. A packaged product according to Claim 71 wherein the water soluble packaging member comprises a sealed sachet.

73. A packaged product according to Claim 71 or 72 wherein the water soluble packaging member is formed of a water soluble plastics material such as polyvinylalcohol (PVA).

74. A non-ionic surfactant aggregate according to Claim 1 substantially as herein described.

75. A method of solubilising a water soluble ingredient according to Claim 36 substantially as herein described.

76. A packaged product according to Claim 71 substantially as herein described.

77. Any novel subject matter or combination including novel subject matter disclosed herein, whether or not within the scope of or relating to the same invention as any of the preceding claims.

INTERNATIONAL SEARCH REPORT

ternational Application No
CT/GB2005/003860

A. CLASSIFICATION OF SUBJECT MATTER
A01N25/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 045 816 A (NARAYANAN ET AL) 4 April 2000 (2000-04-04) the whole document -----	1-77
X	US 5 283 229 A (NARAYANAN ET AL) 1 February 1994 (1994-02-01) the whole document -----	1-77
X	US 2003/125211 A1 (WOZNICA ZENON J ET AL) 3 July 2003 (2003-07-03) the whole document ----- -/--	1-77

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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Date of the actual completion of the international search 11 January 2006	Date of mailing of the international search report 20/01/2006
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Marie, G

INTERNATIONAL SEARCH REPORT

ernational Application No
CT/GB2005/003860

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199505 Derwent Publications Ltd., London, GB; Class C07, AN 1995-032795 XP002362219 & JP 06 316502 A (SUMIKA TAKEDA NOYAKU KK) 15 November 1994 (1994-11-15) abstract -----	1-77
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X	WO 99/49008 A (RECKITT & COLMAN INC; LU, ROBERT, ZHONG; KLOEPPEL, ANDREW, ARNO) 30 September 1999 (1999-09-30) the whole document -----	1-77
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INTERNATIONAL SEARCH REPORT

Information on patent family members

ernational Application No
CT/GB2005/003860

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