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FULLY WATER-DILUTABLE MICROEMULSIONS

This invention relates to microemulsions of water-insoluble active ingredients having microbicial, herbicidal, insecticidal, plant growth regulating or pharmaceutical activity.

5 Microemulsions containing water-insoluble biocidal or pesticidal agents have been proposed in, for example:

US 5,013,748, which discloses aqueous biocidal microemulsions useful for the protection of wood. The biocidal components employed contain at least one triazole fungicide, at least one quaternary ammonium fungicide and at least one benzimidazole fungicide in a liquid carrier
1) comprising at least two necessary polar solvents. This patent does not teach fully water dilutable systems.

US 4,954,338, which teaches oil-in-water microemulsions of isothiazolones with low water solubility with EO/PO copolymer/anionic sulfates or sulfonates as microemulsifier. The solvents are alkyl alcohols or alkylalkoxylated alcohols. This patent requires the use of EO/PO (ethylene oxide/propylene oxide) copolymer to maintain the microemulsion with dilution by water.

US 4,567,161, which discloses transparent microemulsions with active ingredients (e.g. pesticides, herbicides, pharmaceuticals) together with a phospholipid and a coemulsifier (glycerin ester).

0 CA 1209361, which discloses cold stable aqueous microemulsions of agrochemical pesticides, household pest control agents, and pharmaceuticals using an emulsifier which is a mixture of alkylaryl polyglycol and an alkylarylsulfonate salt.

US 4,973,352, which discloses aqueous microemulsions for only herbicidal use containing a combination of a herbicide, one or more emulsifiers or wetting agents such as
5 calcium dodecylbenzenesulfonate, one or more organic solvents and water. This patent also does not teach fully water dilutable microemulsions.

US 4,904,695, which discloses an aqueous based insecticidal microemulsion comprising a synthetic pyrethroid/organophosphate, surfactant blend, adjuvants, such as antifoamers, thickeners and preservatives, and water. The microemulsions of this patent are not fully water
10 dilutable.

US 4,995,900 discloses only water/oil microemulsion formulations of water-insoluble herbicides and are, therefore, not fully water dilutable.

35 Fully water dilutable microemulsions, especially of certain insoluble biocidal active ingredients, have not been previously known and available. By fully water dilutable is meant a microemulsion which is water-dilutable from water-free concentrates (referred to as microemulsion concentrates) to microemulsion containing large concentrations of water.

The present invention provides in one aspect a composition comprising <Insert new claim 1>

~~(A) an active ingredient which has a solubility in water of less than 1% at room temperature and a melting point of less than 100°C;~~

- ~~with a non-polar, water immiscible solvent capable of dissolving at least 5% by weight of~~
 (A) at room temperature;
 (C) a surfactant system comprising:
 (C1) at least one sulfated or sulfonated anionic surfactant having about 3-17%
 sulfation or sulfonation; and
 (C2) at least one ethoxylated surfactant; and
 (D) 0 to 99.9 % by weight water;
 the weight ratio of (C1) to (C2) being from 10/90 to 90/10;
 the weight ratio of said (A) to (B) being from 95/5 to 1/99, and
 the weight ratio of said (A) to (C) being from 1/99 to 86/14;
 said composition being thermodynamically stable and clear, opalescent, or only
 slightly cloudy at all levels of water dilution up to 99.9%.

In another aspect, the invention ^{provides} a method for inhibiting the growth of bacteria, fungi, and algae. A further aspect of the invention comprises the use of such compositions to control bacteria, fungi and/or algae.

By "active ingredient" is meant any compound having microbicidal, herbicidal, insecticidal, plant growth regulating or pharmaceutical activity. ^{selected from} Preferred active ingredients are microbicides. Especially preferred are 4,5-dichloro-2n-octyl-3-isothiazolone and 2-n-octyl-3-isothiazolone. ^{selected from} Other preferred active ingredients are agricultural fungicides, for example 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene, 2,4-dinitro-6-octyl-phenylcrotonate, and alpha-butyl-alpha-(4-chlorophenyl)-1H-1,2,4-triazole-1-propanenitrile.

The microemulsions of the invention are useful in many areas of preservation and agricultural applications, depending on the activity of the active ingredient. The isothiazolones, for example, are active as disinfectants, sanitizers, cleaners, deodorizers, liquid and powder soaps, skin removers, oil and grease removers, food processing chemicals, wood preservation, polymer latices, paint, lazures, stains, mildewcides, hospital and medical antiseptics, medical devices, metal working fluids, cooling water, air washers, petroleum protection, paper treatment, pulp and paper slurries, paper mill slimicides, petroleum products, adhesives, textiles, pigment slurries, latexes, leather and hide treatment, petroleum fuel, jet fuel, laundry sanitizers, agricultural formulations, inks, mining, nonwoven fabrics, petroleum storage, rubber, sugar processing, tobacco, swimming pools, photographic rinses, cosmetics, toiletries, pharmaceuticals, chemical toilets, household laundry products, diesel fuel additives, waxes and polishes, oil field applications, and many other applications where water and organic materials come in contact under conditions which allow the growth of undesired microorganisms. Other active ingredients are useful as fungicides, miticides, herbicides, insecticides, and plants growth regulators.

In general, one or more active ingredient compounds which are less than 10000 ppm soluble in water at room temperature and having a melting point of less than 100°C can be used in the invention.

⊗ <, in particular a method of controlling bacteria or fungal growth in a pulp or paper making process comprising employing a composition as described in the immediately preceding paragraph in the process in an amount sufficient to control the growth.>

3 < pine oil / xylene or pine oil / benzyl alcohol >

The non-polar, water immiscible solvent is preferably selected from the group consisting of benzyl alcohol, benzyl acetate, pine oil, phenethyl alcohol, xylene, phenoxyethanol, butyl phthalate, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and alkylbenzene, said solvent being capable of dissolving at least 5% by weight of (A) at room temperature, is used to dissolve the active ingredient(s).

A surfactant system comprising two different surfactants is used. The first surfactant comprises ~~one or more~~ ^{at least one} sulfated or sulfonated anionic surfactants having about 3-17% sulfation or sulfonation, preferably selected from the group consisting of sulfated and/or sulfonated castor oil, sulfated and/or sulfonated ethoxylated alkylphenols, sulfated and/or sulfonated ethoxylated fatty alcohols, sulfated and/or sulfonated fatty acids, and sulfated alkanolamides. The second surfactant comprises ~~one or more~~ ^{at least one} ethoxylated surfactants, which ~~are~~ ^{is} preferably selected from the group consisting of ethoxylated (C₁₀-C₁₈)alkyl phosphate monoesters and/or diesters and/or triesters, ethoxylated (C₁₀-C₁₈)alkaryl phosphated monoesters and/or diesters, ethoxylated (C₈-C₂₀)monoalkyl- or dialkylphenols, ethoxylated alkylamides, ethoxylated alkanols, and ethoxylated castor oil, but excluding a polyoxyethylene/polyoxypropylene block copolymer.

Microemulsion concentrates without water can be prepared according to the invention, as can microemulsions comprising up to 99.9% by weight water. As mentioned above, the compositions of the invention remain microemulsions at all levels of water dilution, one of the important novel features of the invention. The composition remains thermodynamically stable and clear, opalescent, or only slightly cloudy at all levels of water dilution up to 99.9%.

Weight ratios of the first surfactant to the second surfactant are from 10/90 to 90/10. Weight ratios of the active ingredient(s) to solvent(s) are from 95/5 to 1/99. Weight ratios of active ingredient(s) to surfactant system are from 1/99 to 86/14.

Various adjuvants including antifoam agents, such as the commercially available silicone antifoam emulsions, and the like can be included, for example antifreeze agents such as propylene glycol, urea, and the like; water soluble inorganic salts, such as sodium chloride, magnesium sulfate, and the like which are used to optimize the action of the surfactant because it increases the concentration of the surfactant at the interface of the microemulsion; wetting agents; thickeners; defoamers; and the like.

) The microemulsion concentrates of the invention can be prepared by dissolving solid active ingredient in an organic solvent to form the oil phase. The surfactants can then be added to the oil phase, either individually or in combination. The resulting mixture is gently stirred or agitated to give a microemulsion concentrate. Alternatively, if the solid active ingredient is heat stable, all the components may be added together in a single vessel and the vessel heated slightly to form the microemulsion concentrate. This has the advantage that it is a one step addition. When the active ingredient is a liquid, either approach will work. A liquid active ingredient may be used itself as the oil phase without the addition of an organic solvent. It is preferred that an organic solvent be used to dissolve the active ingredient to form the oil phase. It is further preferred that the oil phase be formed first and the surfactants added to it.

CLAIMS: A

1. Composition comprising

(A) an active ingredient which has a solubility in water of less than 1% at room temperature and a melting point of less than 100°Cx selected from <Insert claim 8>;

(B) a non-polar, water immiscible solvent capable of dissolving at least 5% by weight of (A) at room temperaturex and selected from <Insert claim 2>;

(C) a surfactant system comprising:

(C1) at least one sulfated ^{or} sulfonated anionic surfactant having about 3-17% sulfation or sulfonation and selected from <Insert claim 3>; and

(C2) at least one ethoxylated surfactant and selected from <Insert claim 4> but not including a polyoxyethylene/polyoxypropylene block copolymer; and

(D) 0 to 99.9 % by weight water;

the weight ratio of (C1) to (C2) being from 10/90 to 90/10;

the weight ratio of said (A) to (B) being from 95/5 to 1/99, and

the weight ratio of said (A) to (C) being from 1/99 to 86/14;

said composition being thermodynamically stable and clear, opalescent, or only slightly cloudy at all levels of water dilution up to 99.9%.

Insert new claims 2 & 3

~~2. Composition according to claim 1 wherein the water-immiscible solvent comprises~~

<benzyl alcohol, benzyl acetate, pine oil, phenethyl alcohol, xylene, phenoxyethanol, butyl phthalate, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, ^{and mixtures of} alkylbenzene, ^{preferably a} mixture of benzyl alcohol and pine oil, benzyl acetate, pine oil/xylene or pine oil/benzyl alcohol>

~~3. Composition according to claim 1 or 2 wherein the sulfated or sulfonated anionic~~

~~surfactant (C1) comprises~~ sulfated and/or sulfonated castor oil, sulfated and/or sulfonated ethoxylated alkylphenols, sulfated and/or sulfonated ethoxylated fatty alcohols, sulfated and/or sulfonated fatty acids, ^{and} sulfated alkanolamides > preferably sulfated and/or sulfonated castor oil

~~4. Composition according to any preceding claim wherein the ethoxylated surfactant~~

~~(C2) comprises~~ ethoxylated (C₁₀-C₁₈)alkyl phosphate monoesters and/or diesters and/or triesters, ethoxylated (C₁₀-C₁₈)alkaryl phosphated monoesters and/or diesters, ethoxylated (C₈-C₂₀)monoalkyl- or dialkylphenols; ethoxylated alkylamides, ethoxylated alkanols, ^{and} ethoxylated castor oil > preferably an anionic, ethoxylated (C₁₀-C₁₈)alkyl phosphate or a nonionic, ethoxylated (C₈-C₂₀)mono- and/or dialkyl phenol

4. ^A Composition according to any ^{one of the} preceding claim^s wherein the weight ratio of (A) to (C)

is from 1/99 to 30/70.

5. ^A Composition according to any ^{one of the} preceding claim^s wherein the weight ratio of (C1) to

(C2) is from 30/70 to 70/30, preferably from 50/50 to 70/30

2. A composition according to claim 1 wherein the sulfated or sulfonated anionic surfactant (C1) comprises sulfated and/or sulfonated castor oil.

3. A composition according to claim 1 or 2 wherein the ethoxylated surfactant (C2) comprises an anionic ethoxylated (C₁₀-C₁₈) alkyl phosphate or a nonionic ethoxylated (C₈-C₂₀) mono- and/or dialkyl phenol.

~~B. Composition according to any preceding claim wherein (A) comprises~~ 4,5-dichloro-
2n-octyl-3-isothiazolone, 2n-octyl-3-isothiazolone, 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-
(trifluoromethyl)benzene, 2,4-dinitro-6-octyl-phenyl-crotonate, ^{and} ~~of~~ ^{but} alph-butyl-alpha-(4-
chlorophenyl)-1H-1,2,4-triazole-1-propanenitrile)

9. ^A~~10.~~ Composition according to any ^{one of the} preceding claim^s in the form of a microemulsion concentrate having 0% water.

12. Method of controlling bacteria or fungal growth in a pulp or paper making process comprising employing a composition as defined in ^{one of the} preceding claims in said process in an amount sufficient to control said growth.

-11. A composition according to claim 1 wherein the active ingredient (A) is selected from 4,5-dichloro-2-n-octyl-3-isothiazolone or 2-n-octyl-3-isothiazolone.

ABSTRACTFULLY WATER-DILUTABLE MICROEMULSIONS

Fully water-dilutable microemulsions are disclosed comprising ~~comprising~~ <Insert new claim 1>.

~~(A) an active ingredient which has a solubility in water of less than 1% at room temperature and a melting point of less than 100°C;~~

(B) a non-polar, water immiscible solvent capable of dissolving at least 5% by weight of (A) at room temperature;

(C) a surfactant system comprising:

(C1) at least one sulfated or sulfonated anionic surfactant having about 3-17% sulfation or sulfonation; and

(C2) at least one ethoxylated surfactant; and

(D) 0 to 99.9 % by weight water;

the weight ratio of (C1) to (C2) being from 10/90 to 90/10;

the weight ratio of said (A) to (B) being from 95/5 to 1/99, and

the weight ratio of said (A) to (C) being from 1/99 to 86/14;

said composition being thermodynamically stable and clear, opalescent, or only slightly cloudy at all levels of water dilution up to 99.9%.

The microemulsions are particularly useful in areas where preservation is required.