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GEL FORMULATION

The present invention relates to a water dispersible agrochemical gel formulation.

Gels comprising a surfactant, an agrochemical, an acrylic acid polymer or copolymer and water are disclosed in W092/01377.

The present invention provides a water dispersible gel comprising (a) an effective amount of an ionic, water soluble agrochemical, (b) an effective amount of a crosslinked polyacrylic acid, (c) water, and (d) an amount of a base sufficient to cause a mixture of (a), (b) and (c) to gel.

The water dispersible gels of the present invention are suitable for packaging in standard containers or for containment in a water-soluble or water dispersible bag. The gels of the present invention are able to be dispersed in water, and the rate of dispersion depends on the degree agitation the gel water mixture is subjected to and also the amount of water present.

The ionic, water soluble agrochemical, is, for example, a herbicide (such as a paraquat salt (for example paraquat dichloride or paraquat bis(methylsulphate)), a diquat salt (for example diquat dibromide or diquat alginate) or glyphosate or a salt or ester thereof (such as glyphosate isopropylammonium, glyphosate sesquisodium or glyphosate trimesium (also known as sulfosate)), an insecticide or a fungicide. It is preferred that the ionic, water soluble agrochemical is paraquat dichloride, diquat dibromide, glyphosate isopropylammonium or glyphosate trimesium (also known as sulfosate).

Crosslinked polyacrylic acids preferably have a molecular weight in the range 5×10^5 to 5×10^6 , especially in the range 1×10^6 to 4×10^6 . They are available commercially, for example as CARBOPOLs marketed by B F Goodrich (such as CARBOPOLs 5984, 2984, 940, 5984, 910, 941, 934, 934P or ETD 2050).

Suitable bases include ammonium or alkali metal (such as sodium or potassium) hydroxides, carbonates or bicarbonates (for example sodium hydroxide, sodium carbonate or sodium bicarbonate); or amines of formula $R^1R^2R^3N$ (wherein R^1 , R^2 and R^3 are, independently, hydrogen or C_{1-6} alkyl [optionally substituted by C_{1-6} alkoxy, hydroxy, halogen, C_{1-6} haloalkoxy (such as OCF_3), C_{1-6} hydroxyalkoxy (such as $HOCH_2CH_2O$) or C_{1-4} alkoxy(C_{1-6})alkoxy (such as $CH_3O(CH_2)_2O$ or $CH_3O(CH_2)_5O$] such as $HOCH_2CH_2$).

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It is preferred that R^1 , R^2 and R^3 are, independently, C_{1-6} alkyl or C_{1-6} alkyl monosubstituted with hydroxy. An amine of formula $R^1R^2R^3N$ is, for example, triethylamine or triethanolamine.

Alkyl and the alkyl part of alkoxy groups is straight or branched chain and preferably contains from 1 to 4 carbon atoms. It is, for example, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl or *tert*-butyl.

In one aspect the present invention provides a water dispersible gel comprising (a) 1-60% (especially 5-60%) by weight of an ionic, water soluble agrochemical, (b) 1-4% by weight of a crosslinked polyacrylic acid, (c) 30-80% by weight of water, and (d) 2-20% by weight of a base.

In another aspect the present invention provides a water dispersible gel comprising (a) 20-60% by weight of an ionic, water soluble agrochemical, (b) 1-4% by weight of a crosslinked polyacrylic acid, (c) 30-80% by weight of water, and (d) 2-20% by weight of a base.

In a further aspect the present invention provides a water dispersible gel comprising (a) 20-60% by weight of an ionic, water soluble agrochemical, (b) 1-4% by weight of a crosslinked polyacrylic acid, (c) 30-80% by weight of water, (d) 2-20% by weight of a base, and (e) 1-40% of an electrolyte.

When a gel of the present invention is going to be held in a water-soluble or water dispersible sachet and when the ionic strength of said gel is low it is preferred that said gel comprises a suitable electrolyte in addition to the ionic agrochemical present. The electrolyte helps to improve the insolubility of the material from which the sachet is made in the gel. (See Polyvinyl Alcohol - Properties and Applications pages 38-43, edited by C. A. Finch, published by J Wiley & Sons in 1973 and EP-A1-0518689.) Suitable electrolytes may, for example, comprise a cation or mixtures of cations selected from the list comprising: ammonium, copper, iron, potassium and sodium; and an anion or mixture of anions selected from the list comprising: sulphate, nitrate, fluoride, chloride, bromide, iodide, acetate, tartrate, ammonium tartrate, benzenesulphonate, benzoate, bicarbonate, carbonate, bisulphate, bisulphite, sulphate, sulphite, borate, borotartrate, bromate, butyrate, chlorate, camphorate, chlorite, cinnamate, citrate, disilicate, dithionate, ethylsulphate, ferricyanide, ferrocyanide, fluorosilicate, formate, glycerophosphate, hydrogenphosphate, hydroxostannate, hypochlorite, hyponitrite, hypophosphite, iodate,

isobutyrate, lactate, laurate, metaborate, metasilicate, methionate, methylsulphate, nitrite, oleate, orthophosphate, orthophosphite, orthosilicate, oxalate, perborate, perchlorate, phosphate, polyfluoride, polychloride, polyiodide, polybromide, polysulphide, polysulphate, polysulphite, salicylate, silicate, sorbate, stannate, stearate, succinate or valerate. Preferred electrolytes are ammonium sulphate, sodium sulphate, potassium sulphate, copper sulphate, ammonium nitrate, sodium nitrate, potassium nitrate, sodium chloride or potassium chloride.

It is preferred that sufficient base is added cause the pH of the water dispersible gel to be in the range 6 to 10, especially 6 to 8. If too much base is added the pH of the mixture will be too high and the gel formed will break down. Thus, in another aspect the present invention provides a water dispersible gel comprising (a) an effective amount of an ionic, water soluble agrochemical, (b) an effective amount of a crosslinked polyacrylic acid, (c) water, and (d) an amount of a base sufficient to cause the pH of the resulting gel to lie in the range 6 to 10 (especially 6 to 8, particularly 6 to 7).

In a further aspect the present invention provides a water dispersible gel which comprises 2-5% by weight of an alkali metal hydroxide, carbonate or bicarbonate.

A Bohlin VOR rheometer may be used to measure the elasticity and viscosity of the gel formulation of the present invention under low shear conditions. Here a sinusoidally varying strain (at a frequency of 1Hz) is applied to a sample of a formulation maintained at 25°C. The resultant stress, which also varies sinusoidally with time, is observed. The ratio of the maximum stress to the maximum strain is known as the complex modulus (G^*). By using the phase shift, δ , between the stress and strain wave forms the complex modulus may be split into two components - the storage (elastic) modulus (G') and the loss (viscous) modulus (G''). The storage and loss moduli are a measure of the energy stored and the energy lost respectively, in an oscillatory cycle. The relative magnitude of the loss and storage moduli ($G''/G' = \tan \delta$) provides information on the elasticity of the gel. The lower the value of $\tan \delta$ the greater the degree of gelation. Similarly, gels are characterised by their non-Newtonian flow behaviour, exhibiting, for example, yield values and shear thinning. Yield values can be measured using a Haake Rotovisco RV20 under high shear

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conditions.

In a still further aspect the present invention provides a water dispersible gel as hereinbefore described having a storage modulus (G') in the range 1-1000Pa, preferably 20-500Pa, more preferably in the range 100-200Pa.

In another aspect the present invention provides a water dispersible gel as hereinbefore described having a $\tan \delta$ (ratio of loss modulus to storage modulus) of less than 1, preferably less than 0.5, more preferably less than 0.2, especially less than 0.1. (Rheological measurements are carried out at a temperature of 25°C. Oscillation measurements are carried out within the linear viscoelastic region as determined by strain sweep measurements made at a frequency of 1Hz (6.28 rad/s)).

In another aspect the present invention provides a water dispersible gel comprising 10-20% by weight of a base of formula $R^1R^2R^3N$ (wherein R^1 , R^2 and R^3 are as defined above).

In another aspect the present invention provides a water dispersible gel comprising 1.5 to 3, especially 2 to 2.75 by weight of a crosslinked polyacrylic acid.

When the gel of the invention is to be contained in a water soluble or water dispersible sachet it is preferred that a plasticiser is included in the gel. The plasticiser is preferably present in the range 0.1 to 1% (especially 0.3 to 0.75%) by weight. Suitable plasticisers include glycols (for example ethylene glycol), glycerine and dibutylphthalate.

Depending on the nature of the ionic, water soluble agrochemical present, one or more adjuvants or co-formulants (such as a wetter or anti-freezing agent) may also be comprised in the gel of the present invention. Adjuvants include a neutral or anionic surfactant [such as a soap, a salt of an aliphatic monoester of sulphuric acid (for example, sodium lauryl sulphate), a salt of a sulphonated aromatic compound (for example, sodium dodecylbenzenesulphonate, an alkyl glucoside or a polysaccharide)].

In a further aspect the present invention provides a gel of the present invention as defined above which also comprises a chelating or sequestering agent for calcium ions. A suitable chelating or sequestering agent is ethylenediaminetetraacetic acid.

Over and above the components already mentioned, a water dispersible

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gel of the present invention may also comprise an adhesive, an antifoaming agent, a buffer, a deodorant, a dye, an emetic, a preservative, an odourant, a perfume, a safener, a further solvent, a stabiliser, a synergist, a thickener or a wetting agent.

A gel of the invention can be made simply by initially mixing all the components other than the base, and then adding the base to form the gel. Thus it can be appreciated that a gel of the present invention is made by a pH switching process.

In a further aspect the present invention provides a containerisation system comprising a water soluble or water dispersible bag containing a water dispersible gel of the present invention, provided the gel has sufficient ionic strength.

The water soluble or water dispersible bag can be made from a variety of materials and preferred materials are polyethylene oxide, methyl cellulose or, especially, polyvinylalcohol (PVA). The PVA is generally partially or fully alcoholysed or hydrolysed, for example 40-100%, especially 80-100%, alcoholysed or hydrolysed polyvinyl-acetate film. It is preferred that the PVA film is a laminate of two or more thicknesses of film, a surface modified film or a co-extruded film (such as is described in WO 94/29188).

In another aspect the containerisation system comprises a bag-in-bag arrangement comprising a water-soluble or water dispersible bag holding a gel of the present invention and a second water-soluble or water dispersible bag also holding a gel of the present invention. This bag-in-bag arrangement can be used, for example, to contain a gel of the present invention comprising an ionic, water soluble agrochemical in the inner bag and a gel of the present invention comprising adjuvant, synergist or penetrating agent in the outer bag.

In a further aspect the containerisation system provides two water-soluble or water dispersible bags joined at a common seal, one containing a gel of the present invention comprising one ionic, water soluble agrochemical, the other bag containing a gel of the present invention comprising a different ionic, water soluble agrochemical.

In a still further aspect the containerisation system comprises a bag-in-bag arrangement comprising a first water-soluble or water dispersible bag holding a gel of the present invention and a second

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water-soluble or water dispersible bag surrounding the first water-soluble or water dispersible bag. The advantage of this system is that the second bag presents a barrier to any matter leaking from the first bag.

In another aspect the containerisation system comprises a bag-in-bag arrangement comprising a first water-soluble or water dispersible bag holding a gel of the present invention and a second water-soluble or water dispersible bag holding an agrochemical composition (such as a liquid, granule, powder or gel composition comprising a fungicide, herbicide, insecticide, adjuvant, synergist or penetrating agent).

In a further aspect the containerisation system comprises a bag-in-bag arrangement comprising a first water-soluble or water dispersible bag holding an agrochemical composition (such as a liquid, granule, powder or gel composition comprising a fungicide, herbicide, insecticide, adjuvant, synergist or penetrating agent) and a second water-soluble or water dispersible bag holding a gel of the present invention.

In another aspect the containerisation system provides two water-soluble or water dispersible bags joined at a common seal, one containing a gel of the present invention comprising a fungicide, herbicide, insecticide, adjuvant, synergist or penetrating agent the other bag containing an agrochemical composition (such as a liquid, granule, powder or gel composition comprising a fungicide, herbicide, insecticide, adjuvant, synergist or penetrating agent).

The water soluble or water dispersible sachet can be formed and filled using standard techniques (such as thermoforming or vertical form-fill-sealing).

In use the containerisation system can be mixed with water to give a sprayable solution or dispersion of the ionic chemical. The containerisation system is especially useful in agriculture.

The following Examples illustrate the invention. CARBOPOL is a Trade Mark of B F Goodrich.

EXAMPLE 1

A solution of sulfosate in water (61.4% w/w, 34.19g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (35.04g), and water (0.88g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.48g) was

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then added to neutralize the acid and bring the pH of the system up to 6.45. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 2

A solution of sulfosate in water (61.4% w/w, 34.16g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (21.00g), and water (14.89g) and ethylene glycol (0.36g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.27g) was then added to neutralize the acid and bring the pH of the system up to 6.65. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 3

A solution of sulfosate in water (61.4% w/w, 34.17g) was added to a 6% (w/w) aqueous solution of CARBOPOL 2984 (35.00g), and water (0.90g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.48g) was then added to neutralize the acid and bring the pH of the system up to 6.23. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 4

A solution of sulfosate in water (61.4% w/w, 34.18g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (24.50g), and water (11.36g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.28g) was then added to neutralize the acid and bring the pH of the system up to 6.59. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 5

A solution of sulfosate in water (61.4% w/w, 34.14g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (31.49g), and water (4.37g) and ethylene glycol (0.38g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.39g) was then added to neutralize the acid and bring the pH of the system up to 6.35. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 6

A solution of sulfosate in water (61.4% w/w, 39.81g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (17.51g), and water (12.77g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.70g) was then added to neutralize the acid and bring the pH of the system up to

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6.52. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 7

A solution of sulfosate in water (61.4% w/w, 39.81g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (20.42g), and water (9.93g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.80g) was then added to neutralize the acid and bring the pH of the system up to 6.48. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 8

A solution of sulfosate in water (61.4% w/w, 39.80g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (23.34g), and water (6.95g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.88g) was then added to neutralize the acid and bring the pH of the system up to 6.48. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 9

A solution of sulfosate in water (61.4% w/w, 39.89g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (26.23g), and water (4.09g) and ethylene glycol (0.36g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.81g) was then added to neutralize the acid and bring the pH of the system up to 6.38. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 10

A solution of sulfosate in water (61.4% w/w, 39.78g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (29.17g), and water (1.10g) and ethylene glycol (0.36g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.85g) was then added to neutralize the acid and bring the pH of the system up to 6.36. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 11

A solution of sulfosate in water (61.4% w/w, 39.81g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (24.63g), and water (5.82g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.82g) was then added to neutralize the acid and bring the pH of the system up to 6.23. This resulted in the CARBOPOL 2984 swelling.

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EXAMPLE 12

A solution of sulfosate in water (61.4% w/w, 39.79g) was added to a 5% (w/w) aqueous solution of CARBOPOL 2984 (22.56g), and water (7.79g) and ethylene glycol (0.35g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.82g) was then added to neutralize the acid and bring the pH of the system up to 6.23. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 13

CARBOPOL 2984 (2.12g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.50g) after which and water (12.34g) and ethylene glycol (0.34g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.01g) was then added to neutralize the acid and bring the pH of the system up to 6.66. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 14

CARBOPOL 2984 (1.94g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.51g) after which water (12.57g) and ethylene glycol (0.35g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.01g) was added to neutralize the acid and bring the pH of the system up to 6.71. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 15

CARBOPOL 2984 (1.75g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.58g) after which water (12.89g) and ethylene glycol (0.35g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.05g) were added to neutralize the acid and bring the pH of the system up to 6.81. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 16

CARBOPOL 2984 (1.41g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.53g) after which water (13.12g) and ethylene glycol (0.35g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.05g) was added to neutralize the acid and bring the pH of the system up to 6.81. This resulted in the CARBOPOL 2984 swelling.

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EXAMPLE 17

CARBOPOL 2984 (1.58g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.55g) after which water (13.07g) and ethylene glycol (0.34g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.05g) was added to neutralize the acid and bring the pH of the system up to 6.78. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 18

CARBOPOL 2984 (1.23g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.67g) after which water (13.22g) and ethylene glycol (0.36g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.08g) was added to neutralize the acid and bring the pH of the system up to 6.87. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 19

CARBOPOL 2984 (1.05g) was mixed with a solution of sulfosate in water (61.4% w/w, 45.62g) after which water (13.43g) and ethylene glycol (0.37g) were added. The mixture was shaken and left on rollers to ensure thorough mixing. Triethanolamine (10.13g) was added to neutralize the acid and bring the pH of the system up to 6.93. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 20

A solution of sulfosate in water (61.4% w/w, 40.02g) was added to a 6% (w/w) aqueous solution of CARBOPOL 2984 (26.23g), and water (20.00g) was then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.77g) was then added to neutralize the acid and bring the pH of the system up to 6.49. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 21

A solution of sulfosate in water (61.4% w/w, 40.02g) was added to a 6% (w/w) aqueous solution of CARBOPOL 2984 (26.67g), and water (13.33g) was then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.99g) was then added to neutralize the acid and bring the pH of the system up to 6.47. This resulted in the CARBOPOL 2984 swelling.

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EXAMPLE 22

A solution of sulfosate in water (61.4% w/w, 40.07g) was added to a 6% (w/w) aqueous solution of CARBOPOL 2984 (30.00g), and water (10.00g) was then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.97g) was then added to neutralize the acid and bring the pH of the system up to 6.40. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 23

A solution of sulfosate in water (61.4% w/w, 40.02g) was added to a 6% (w/w) aqueous solution of CARBOPOL 2984 (33.34g), and water (6.68g) was then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (3.59g) was then added to neutralize the acid and bring the pH of the system up to 6.86. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 24

A solution of sulfosate in water (61.4% w/w, 250.14g) was added to a mixture of a 4.7% (w/w) aqueous solution of CARBOPOL 2984 (33.34g) and ethylene glycol (1.27g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (15.51g) was then added to neutralize the acid and bring the pH of the system up to 6.28. This resulted in the CARBOPOL 2984 swelling.

A sample of the gel formed (25g) was placed into a sachet made of polyvinylalcohol (Chris Craft M7030) and the sachet's opening was heat sealed. After storage at 25°C for 3 months the sachet remained supple and, when put in contact with water, the sachet and its contents readily dispersed.

EXAMPLE 25

A solution of sulfosate in water (61.4%, 20.02g) was added to a 6.25% (w/w) aqueous solution of CARBOPOL 941 (15.02g) and water (5.00g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (1.68g) was then added to neutralize the acid and bring the pH up to 6.57. This resulted in the CARBOPOL 941 swelling.

EXAMPLE 26

A solution of sulfosate in water (61.4%, 20.06g) was added to a 6.22% (w/w) aqueous solution of CARBOPOL 910 (15.02g) and water (5.14g). The mixture was then shaken and left on rollers to ensure thorough mixing.

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Sodium hydroxide (1.53g) was then added to neutralize the acid and bring the pH up to 6.44. This resulted in the CARBOPOL 910 swelling.

EXAMPLE 27

A solution of sulfosate in water (61.4%, 26.04g) was added to a 6.18% (w/w) aqueous solution of CARBOPOL 2984 (30.02g) and water (24.06g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (3.11g) was then added to neutralize the acid and bring the pH up to 6.72. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 28

A solution of sulfosate in water (61.4%, 32.50g) was added to a 6.17% (w/w) aqueous solution of CARBOPOL 2984 (30.00g) and water (17.52g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (3.01g) was then added to neutralize the acid and bring the pH up to 6.57. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 29

A solution of sulfosate in water (61.4%, 45.55g) was added to a 6.17% (w/w) aqueous solution of CARBOPOL 2984 (30.00g) and water (4.50g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (3.16g) was then added to neutralize the acid and bring the pH up to 6.51. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 30

A solution of sulfosate in water (61.4%, 40.09g) was added to a 5.99% (w/w) aqueous solution of CARBOPOL 2984 (30.00g) and water (10.00g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium bicarbonate (6.45g) was then added to neutralize the acid and bring the pH up to 6.66. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 31

A solution of sulfosate in water (61.4%, 39.99g) was added to a 6.18% (w/w) aqueous solution of CARBOPOL 2984 (30.00g) and water (10.02g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium carbonate (4.80g) was then added to neutralize the acid and bring the pH up to 6.59. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 32

A solution of sulfosate in water (61.4%, 40.00g) was added to a 6.15% (w/w) aqueous solution of CARBOPOL 5984 (30.00g) and water (10.50g). The mixture was then shaken and left on rollers to ensure thorough mixing.

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Sodium hydroxide (3.03g) was then added to neutralize the acid and bring the pH up to 6.55. This resulted in the CARBOPOL 5984 swelling.

EXAMPLE 33

A solution of sulfosate in water (61.4%, 20.00g) was added to a 6.19% (w/w) aqueous solution of CARBOPOL ETD 2050 (16.68g) and water (3.44g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (1.71g) was then added to neutralize the acid and bring the pH up to 6.71. This resulted in the CARBOPOL ETD 2050 swelling.

EXAMPLE 34

A solution of glyphosate isopropylammonium in water (61.5%, 20.21g) was added to a (w/w) aqueous solution of 6.17% CARBOPOL 2984 (15.00g) and water (5.01g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.86g) was then added to neutralize the acid and bring the pH up to 6.49. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 35

A solution of diquat dibromide in water (26.3% w/v, 32.50g) was added to a 6.09% (w/w) aqueous solution of CARBOPOL 2984 (11.67g) and water (8.35g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (0.30g) and a 40% aqueous solution of sodium hydroxide in water (0.14g) were then added to neutralize the acid and bring the pH up to 6.42. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 36

A solution of paraquat dichloride in water (32.3% w/w, 20.01g) was added to a 6.10% (w/w) aqueous solution of CARBOPOL 2984 (11.68g) and water (8.45g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (0.24g) and a 40% aqueous solution of sodium hydroxide (0.16g) were then added to neutralize the acid and bring the pH up to 6.57. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 37

A solution of paraquat dichloride in water (32.3% w/w, 25.01g) was added to a 6.10% (w/w) aqueous solution of CARBOPOL 2984 (15.00g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (0.37g) and a 40% aqueous solution of sodium hydroxide (0.10g) were then added to neutralize the acid. This resulted in the CARBOPOL 2984 swelling.

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EXAMPLE 38

A solution of paraquat dichloride in water (32.3% w/w, 20.02g) was added to a 6.13% (w/w) aqueous solution of CARBOPOL 2984 (17.50g), sodium chloride (1.00g) and water (2.38g). The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (0.45g) was then added to neutralize the acid. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 39

A solution of sulfosate in water (61.4%, 20.05g) was added to a 6.10% (w/w) aqueous solution of CARBOPOL 2984 (15.03g) and water (1.02g). The mixture was then shaken and left on rollers to ensure thorough mixing. Triethylamine (4.04g) was then added to neutralize the acid and raise the pH up to 7.29. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 40

A solution of sulfosate in water (57.6% w/w, 30.41g) was added to a 6.55% (w/w) aqueous solution of CARBOPOL 2984 (22.03g), and water (6.57g) and ethylenediaminetetraacetic acid (1.51g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (2.29g) was then added to bring the pH of the system up to 6.16. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 41

A solution of sulfosate in water (57.6% w/w, 30.35g) was added to a 6.55% (w/w) aqueous solution of CARBOPOL 2984 (21.97g), and water (5.03g) and ethylenediaminetetraacetic acid (3.05g) were then added. The mixture was then shaken and left on rollers to ensure thorough mixing. Sodium hydroxide (3.05g) was then added to bring the pH of the system up to 6.29. This resulted in the CARBOPOL 2984 swelling.

EXAMPLE 42

The rheological properties of the products of the foregoing Examples were measured on a Bohlin rheometer using a cup and bob or cone and plate geometry. The measurements were primarily carried out at a temperature of 25°C. Oscillation measurements were carried out within the linear viscoelastic region as determined by strain sweep measurements made at a frequency of 1Hz (6.28 rad/s).

The values for the moduli at 1 Hz are presented in TABLE I, where G^* is the complex modulus; G' the storage modulus; G'' the loss modulus; δ the phase angle between the loss and storage moduli; and $\tan \delta$ is G''/G' .

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TABLE I

EXAMPLE No	G^* (Pa)	G' (Pa)	G'' (Pa)	$\tan \delta$
1	282	281	16.4	0.058
2	37.3	37.2	2.95	0.079
3	390	389	20.6	0.053
4	72.6	72.4	4.67	0.065
5	215	215	11.9	0.055
6	28.0	27.9	2.47	0.088
7	60.9	60.8	4.44	0.073
8	112	112	5.90	0.053
9	167	167	8.34	0.050
10	255	254	13.2	0.052
11	424	423	28.1	0.066
12	343	343	19.2	0.056
13	407	404	43.5	0.107
14	458	452	74.8	0.165
15	378	373	62.2	0.167
16	125	123	21.9	0.178
17	199	196	35.2	0.179
18	63.0	60.9	16.1	0.264
19	23.3	21.9	8.12	0.37
20	35.8	35.6	3.58	0.10
21	130	130	8.07	0.062
22	154	154	10.0	0.065
23	241	240	15.4	0.061
24	189	188	11.0	0.058
25	88.8	86.7	19.4	0.224
26	53.8	50.0	19.8	0.400
27	359	359	16.5	0.046
28	212	212	9.69	0.046
29	172	172	8.58	0.050
30	204	204	9.38	0.046
31	216	215	10.8	0.050
32	205	205	13.8	0.067

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TABLE I (Continued)

EXAMPLE No	G^* (Pa)	G' (Pa)	G'' (Pa)	$\tan \delta$
33	279	272	59.5	0.219
34	132	130	18.3	0.141
35	242	242	10.7	0.044
36	201	200	10.2	0.051
37	212	211	14.2	0.067
38	158	158	8.95	0.057
39	223	222	18.2	0.082
40	-	129	9.55	0.074
41	-	117	9.97	0.085



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REPLACEDCLAIMS

1. A water dispersible gel comprising:
 - (a) an effective amount of an ionic, water soluble agrochemical;
 - (b) an effective amount of a cross-linked polyacrylic acid;
 - (c) water; and,
 - (d) an amount of a base sufficient to cause a mixture of (a), (b) and (c) to gel.
2. A water dispersible gel as claimed in claim 1, said gel comprising:
 - (a) an effective amount of an ionic, water soluble agrochemical;
 - (b) an effective amount of a crosslinked polyacrylic acid;
 - (c) water; and,
 - (d) an amount of a base sufficient to cause the pH of the resulting gel to lie in the range 6 to 10.
3. A water dispersible gel as claimed in claim 1 or 2, said gel comprising:
 - (a) 1-60% by weight of an ionic, water soluble agrochemical;
 - (b) 1-4% by weight of a crosslinked polyacrylic acid;
 - (c) 30-80% by weight of water; and,
 - (d) 2-20% by weight of a base.
4. A water dispersible gel as claimed in claim 1, 2 or 3 wherein the crosslinked polyacrylic acid has a molecular weight in the range 5×10^5 to 5×10^6 .
5. A water dispersible gel as claimed in claim 1, 2, 3 or 4 wherein the base is an ammonium or alkali metal hydroxide, carbonate or bicarbonate; or an amine of formula $R^1R^2R^3N$ wherein R^1 , R^2 and R^3 are, independently, hydrogen or C_{1-6} alkyl [optionally substituted by C_{1-6} alkoxy, hydroxy, halogen, C_{1-6} haloalkoxy, C_{1-6} hydroxyalkoxy or C_{1-4} alkoxy(C_{1-6})alkoxy].
6. A water dispersible gel as claimed in claim 1, 2, 3, 4 or 5 wherein the ionic, water soluble agrochemical is a paraquat salt, a diquat

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salt, or a salt or ester of glyphosate.

7. A water dispersible gel as claimed in claim 1, 2, 3, 4 or 5 wherein the ionic, water soluble agrochemical is paraquat dichloride, diquat dibromide, glyphosate isopropylammonium or glyphosate trimesium.
8. A containerisation system comprising a water dispersible gel, as claimed in any one of the preceeding claims, contained in a water-soluble or water dispersible bag.
9. A process for preparing a water dispersible gel as claimed in claim 1, the process comprising mixing components (a), (b) and (c) and then adding component (d) until the pH of the mixture is in the range 6-10.

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PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PDD 40228X/WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 95/ 01605	International filing date (day/month/year) 06/07/1995	Priority date (day/month/year) 28/07/1994
International Patent Classification (IPC) or national classification and IPC A01N25/04		
Applicant ZENECA LTD et al.		

RTMP's copy

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consists of a total of 4 sheets.

3. This report contains indications and corresponding pages relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 08/01/1996	Date of completion of this report 04. 11. 96
Name and mailing address of the IPEA  European Patent Office, P.B. 5818 Patentaan 2 NL-2280 HV Rijswijk - Netherlands Tel. (+31-70) 340-2040, Tx. 31 851 epo nl, Fax: (+31-70) 340-3018	Authorized officer  Telephone No. 3289 Mullers W.

I. Basis of the report

1. This report has been drawn up on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*

☐ the international application as originally filed

☒ the description, pages 1-16

, as originally filed

pages

, filed with the demand

pages

, filed with the letter of

☐ the claims, Nos.

, as originally filed

Nos.

, as amended under Article 19

Nos.

, filed with the demand

Nos.

1-6

, filed with the letter of

10.09.96

☐ the drawings, sheets / fig.

, as originally filed

sheets / fig.

, filed with the demand

sheets / fig.

, filed with the letter of

2. The amendments have resulted in the cancellation of:

☐ the description, pages:

☐ the claims, Nos.

☐ the drawings, sheets / fig.

3. ☐ This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2 (c)).

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Claims	1 - 6	YES
	Claims		NO.
Inventive Step	Claims	1 - 6	YES
	Claims		NO
Industrial Applicability	Claims	1 - 6	YES
	Claims		NO

2. Citations and Explanations

The following documents (D1 and D2) have been considered for the purposes of this report:

D1 EP,A,518689
D2 WO,A,9201377

Novelty

The cited prior art does not disclose (see below) containerisation systems according to the claims of the present application.

Therefore the application satisfies the criterion set forth in Article 33(2) PCT because the subject-matter of the claims, insofar they are clear (see below under point VIII), is new in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

Inventive Step

The problem underlying the invention can be seen in the provision of a containerisation system comprising a water dispersible aqueous gel comprising a ionic, water-soluble agrochemical (see page 1, lines 5-14 and page 5, paragraph 3).

The proposed solution according to independent claim 1 is characterised by the use of a gel comprising as the essential features certain amounts of the ionic water-soluble agrochemical, a cross-linked polyacrylic acid, water and a base causing gelation.

Document D1, which is considered to be the closest prior art, provides solutions to the same problem for hazardous agrochemicals in general (see D1, column 3, lines 37-42; claims 1 and 28). This solution is characterised by the addition of an electrolyte to an aqueous formulation which is preferably in gel form (see column 5, lines 9-13 ; claim15 and column 4, line 44-

column 5, line 8). Therefore it contains preferably beside the agrochemical also one or two thickeners (see column 3, line 47- column 4, line 22 and claims 12 and 13). The agrochemical may be ionic and water-soluble (see column 4, lines 38-43); the pH is preferably between 6 and 9 (see claim 12). The rheological properties are in principal those required for the gels of the present application, i.e. a $\tan \delta \leq 1.5$ is required (see claim 18).

The gelling agent may be an inorganic or an organic thickener like e.g. xanthan gum (see example 4 and 6). Polyacrylic acid is also mentioned as a suitable thickener (see column 8, lines 34-49). A second thickener which may again be i.a. polyacrylic acid (see column 11, lines 32-46) may be present too. The hazardous product is for instance an agrochemical (column 8, line 53- column 9, line 12 and claims 2 and 3), specified are i.a. diquat, paraquat and glyphosate and salts thereof (see column 10, lines 20, 29, 23 and 35-54). Polyvinyl alcohol is the preferred polymeric material for the bags (see column 12, lines 3-6, 24-25 and 36-41 and claim 24).

The proposed thickening agents seem to form gels by a process of solvation which is influenced by the presence of electrolytes. There is no incentive for the skilled person to investigate gelation using a neutralised form of a crosslinked polyacrylic acid.

Document D2 provides another solution to the problem of providing containerisation systems by disclosing dispersible formulations suitable to be packaged into water-soluble bags. The formulations comprise a hazardous chemical, a surfactant, an acrylic acid polymer or copolymer or its salt and 0.05-5% of water (see D2, page 1- page 4, line 9). The acrylic acid polymer or copolymer has a molecular weight of 5000-5,000,000 and may be cross-linked (see page 4, line 26 - page 5, paragraph 1). It is present in an amount of preferably 0.5-5% while the active agent is present at preferably 10-90% (see page 6, paragraph 2). $\tan \delta$ should be ≤ 1.5 (see page 6, penultimate paragraph). Herbicides are among the hazardous material specified among these glyphosate and paraquat are mentioned. The film forming material constituting the bags is preferably polyvinyl alcohol (see page 10, paragraph 2).

The skilled person when trying to solve the above mentioned problem would probably not consider this teaching, because it relates to substantially non-aqueous gels.

There is nothing in the teaching of either document nor in their combined teaching that would have suggested to the skilled person to solve the problem defined above by modifying the gels disclosed in these two documents in such a way that he would arrive at the solution proposed in the present application; i.e. by choosing polyacrylic acid as the thickener in a gel according to document D1 and neutralise it or by adding more water to the gel according to document D2 and at the same time omitting the surfactant, which is an essential feature of formulations according to D2.

Therefore the present application satisfies the criterion set forth in Article 33(3) PCT; the subject-matter of claims 1 to 6 involves an inventive step (Rule 65(1)(2) PCT).

Industrial Applicability

The claimed invention is considered to be industrially applicable; the claims therefore satisfy the criterion set forth in Article 33(4) PCT.

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

The description should have been brought into conformity with the amended claims. The requirements of Rule 5.1 (a)(ii)(iii) PCT are, thus, not fulfilled.



CLAIMS

1. A containerisation system comprising a water dispersible gel contained in a water-soluble or water dispersible bag; the water dispersible gel comprising:
 - (a) 1-60% by weight of an ionic, water-soluble agrochemical;
 - (b) 1-4% by weight of a crosslinked polyacrylic acid;
 - (c) 30-80% by weight of water; and,
 - (d) 2-20% by weight of a base.
2. A containerisation system as claimed in claim 1, wherein the pH of the gel is in the range 6 to 10.
3. A containerisation system as claimed in claim 1 or 2 wherein the crosslinked polyacrylic acid has a molecular weight in the range 5×10^5 to 5×10^6 .
4. A containerisation system as claimed in claim 1, 2 or 3 wherein the base is an ammonium or alkali metal hydroxide, carbonate or bicarbonate; or an amine of formula $R^1R^2R^3N$ wherein R^1 , R^2 and R^3 are, independently, hydrogen or C_{1-6} alkyl [optionally substituted by C_{1-6} alkoxy, hydroxy, halogen, C_{1-6} haloalkoxy, C_{1-6} hydroxyalkoxy or C_{1-4} alkoxy(C_{1-6})alkoxy].
5. A containerisation system as claimed in claim 1, 2, 3 or 4 wherein the ionic, water-soluble agrochemical is a paraquat salt, a diquat salt, or a salt or ester of glyphosate.
6. A containerisation system as claimed in claim 1, 2, 3 or 4 wherein the ionic, water-soluble agrochemical is paraquat dichloride, diquat dibromide, glyphosate isopropylammonium or glyphosate trimesium.

REPLACEMENT SHEET

10 SEP 1996

AMENDED SHEET
IPEA/EP

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: A01N 25/04, 25/34, 57/20, 43/90, 43/40 // (A01N 57/20, 25:34, 25:04) (A01N 43/90, 25:04) (A01N 43/40, 25:04)	A1	(11) International Publication Number: WO 96/03038 (43) International Publication Date: 8 February 1996 (08.02.96)
(21) International Application Number: PCT/GB95/01605 (22) International Filing Date: 6 July 1995 (06.07.95) (30) Priority Data: 9415290.7 28 July 1994 (28.07.94) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): TADROS, Tharwat, Fouad [GB/GB]; 89 Nash Grove Lane, Wokingham, Berkshire RG11 4HE (GB). TAYLOR, Philip [GB/GB]; April Cottage, 1 North Dean, Maidenhead, Berkshire SL6 7JD (GB). (74) Agents: TIERNEY, Francis, John et al.; Zeneca Agrochemicals, Intellectual Property Dept., Jealott's Hill Research Station, P.O. Box 3538, Bracknell, Berkshire RG12 6YA (GB).	(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MW, MX, NO, NZ, PL, RO, RU, SD, <u>SG</u> , SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> RTMP's copy + ISA + IPER + amendt. SG 96/2130-G	
(54) Title: GEL FORMULATION		
(57) Abstract		
A water dispersible gel comprising: a) an effective amount of an ionic, water soluble agrochemical; b) an effective amount of a cross-linked polyacrylic acid; c) water; and, d) an amount of a base sufficient to cause a mixture of (a), (b) and (c) to gel.		

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