(12) STANDARD PATENT (11) Application No. **AU 2006327936 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
Formulation

(51) International Patent Classification(s)
A01N 25/28 (2006.01) ***A01N 51/00*** (2006.01)
A01N 25/04 (2006.01) ***A01P 7/04*** (2006.01)

(21) Application No: **2006327936** (22) Date of Filing: **2006.12.22**

(87) WIPO No: **WO07/072046**

(30) Priority Data

(31) Number	(32) Date	(33) Country
0526416.3	**2005.12.23**	**GB**

(43) Publication Date: **2007.06.28**
(44) Accepted Journal Date: **2013.05.02**

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(56) Related Art
WO 2005/063016 A1 (BAYER TECHNOLOGY SERVICES GMBH) 14 July 2005
WO 1997/027939 A1 (FRAUNHOFER GES FORSCHUNG [DE] et al.) 07 August 1997
WO 2002/060573 A2 (HENKE: KGAA [DE] et al.) 08 August 2002
WO 1996/003041 A1 (CIBA-GEIGY AG [CH/CH]) 8 February 1996
WO 2000/048465 A1 (THIES TECHNOLOGY [US/US]) 24 August 2000
US 5 788 991 (NASTKE et al.) 4 August 1998
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WO 1995/008322 A1 (MINNESOTA MINING AND MANUFACTURING COMPANY [US/US])
30 March 1995
US 5 221 535 A (DOMB) 22 June 1993

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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 June 2007 (28.06.2007)

PCT

(10) International Publication Number
WO 2007/072046 A2

(51) International Patent Classification:
A01N 25/28 (2006.01) *A01N 51/00* (2006.01)
A01N 25/04 (2006.01) *A01P 7/04* (2006.01)

(21) International Application Number:
PCT/GB2006/004902

(22) International Filing Date:
22 December 2006 (22.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0526416.3 23 December 2005 (23.12.2005) 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, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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:
— *without international search report and to be republished upon receipt of that 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: FORMULATION

(57) Abstract: A product comprising microcapsules which themselves comprise (a) a polymeric shell; and (b) a core comprising an agrochemical which has a melting point greater than or equal to 25°C characterised in that the agrochemical is dispersed as a solid in a hydrophobic material which has a melting point greater than or equal to 25°C but which does not exhibit a glass transition temperature.

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FORMULATION

This invention relates to novel microcapsules which comprise a biologically active compound and processes for the preparation and for the use of such microcapsules. In particular it relates to a product comprising microcapsules which themselves comprise

(a) a polymeric shell; and

(b) a core which comprises an agrochemical which has a melting point above 25°C characterised in that the agrochemical is dispersed as a solid in a hydrophobic material which has a melting point greater than or equal to 25°C but which does not exhibit a glass transition temperature.

Microcapsule technology has been in existence for a number of years. Microcapsules have a variety of uses, especially for containing dyes, inks, chemical reagents, pharmaceuticals, flavouring materials, and more especially agrochemicals, that is fungicides, bactericides, insecticides, herbicides and the like.

Microencapsulated formulations of agrochemicals may be exploited in a wide range of applications both in crop protection and professional products outlets, and may be applied via a variety of methods such as foliar sprays, soil application and as seed treatments. Such formulations allow the release rate of the agrochemical to be controlled over a desired period of time and find applications for weed, fungal or insect control, as termiticides, residual sprays, turf treatments and as seed treatments (amongst others).

In commercial use, agrochemical products are subject to a range of environmental factors which result in a reduction in efficacy of the formulation, including run-off and leaching from soil (which may lead to groundwater contamination), rainfastness and wash-off from seeds; water-soluble active compounds are particularly susceptible to such losses.

The microcapsules of this invention are useful for controlling the release rate of the solid water-soluble biologically active compound, where the biologically active compound is a pesticide [agrochemical], and are particularly useful for controlling the release into any medium where water is present, eg. release of pesticidally active compounds into soil. The microcapsules are even more particularly useful for controlling the release of water-soluble pesticidally active compounds into soil with a high moisture content as a result of heavy rainfall or excessive irrigation. A further advantage is that such products can also

reduce the amount of water soluble product that is leached to lower soil levels by heavy rainfall or irrigation.

Such uses may include application of these products in crop protection for the use of insecticides in vegetable crops to extend the performance of a product in soil; use of such a product to provide long term release characteristics in specific market sectors such as control of termites; use of such a product to increase the period of performance on turf, when formulated together with fertilisers as a granule, or applied directly to turf by an appropriate application method and which is then subjected to high levels of irrigation (as commonly employed on golf-courses); use of such products for the protection of seeds where applied prior to sowing and combined with appropriate inerts to provide efficient coating of the seeds; and use of such a product to provide a longer lasting residual deposit where a long lasting deposit may be required.

Several technologies are commonly known as being useful in the production of microcapsules (for example as described in chapter 4 of "Controlled Delivery of Crop Protection Agents", pub. Taylor and Francis, London 1990). One such technology of particular utility for the encapsulation of agrochemicals is interfacial polymerisation in which the walls of the microcapsules are generally formed of polymeric material produced by a polymerisation reaction which preferably takes place at the interface between two phases, usually an aqueous phase and a water-immiscible organic phase. Thus, they may be produced from a water-in-oil emulsion or more usually an oil-in-water emulsion.

Microcapsules which comprise, in the organic phase, suspensions of solid biologically active compounds in organic solvents or liquid biologically active compounds are known (e.g. as described in patent documents WO 95/13698, EP 0730406, US 5993842 and US 6015571, the contents of which are fully incorporated herein by reference).

Processes for the microencapsulation of water-soluble biologically active compounds are also known, but in these the biologically active compound is generally dissolved in water or a water-miscible solvent prior to encapsulation.

It has now been found that it is possible to encapsulate solid agrochemical compounds which are dispersed in a substantially water-immiscible phase, in which the agrochemical

is dispersed in a hydrophobic material which ha a melting point greater than or equal to 25°C but which does not exhibit a glass transition temperature.

In our co-pending application (which claims priority from the same patent application as this application) one particular method of producing a similar effect of having an agrochemical dispersed in a diffusion limiting structure is to produce an at least partially solid matrix in which the agrochemical is retained more effectively. In that particular case, the (non-continuous) matrix is formed via an interfacial polymerisation of an oil-in-water emulsion, in which the solid water-soluble biologically active material is dispersed within the oil. Surprisingly, in that invention carrying out said interfacial polymerisation results in the formation of a polymer (non-continuous) matrix which is distributed throughout the microcapsules, rather than being restricted to the interface, as is commonly taught in the prior art.

There are several problems which must be overcome for the successful encapsulation of a suspension of solid particles within a microcapsule formed by interfacial polymerisation of an oil-in-water emulsion.

Firstly, a stable suspension of the solid in a substantially water-immiscible liquid must be produced. If dispersants or surfactants are used, they must not interfere with any further processes of dispersion used in making microcapsules.

Secondly, the suspension must be dispersed in water to produce stable, well dispersed droplets. For biologically active substances, it is preferable to have very small droplets of liquid dispersed in water so as to present a high surface area of the resulting microcapsules. To produce very small droplets requires high shear forces which would tend to break down the droplets and/or release the solid from suspension. Surfactants are usually required to achieve good dispersion and stable droplets.

Thirdly, the presence of one or more surfactants may make the dispersed droplet system unstable and the phenomenon of phase inversion may occur, i.e. water forms small droplets within the liquid; a water-in-oil emulsion.

Fourthly, the solid suspended in the water-immiscible liquid is liable to migrate to the aqueous phase, particularly when emulsifying surfactants are used.

The last three of these problems is even more challenging to overcome for the encapsulation of water-soluble biologically active compounds, and it has been found that modifications are required to the procedures described in patent documents WO 95/13698, EP 0730406, US 5993842, US 6015571, US 2003/0119675 and JP 2000247821 for the encapsulation of suspensions of water-insoluble compounds.

It has now been found that it is possible to produce microcapsules which comprise a solid water-soluble, biologically active compound dispersed in a (non-continuous) matrix which is at least partially solid and which is distributed throughout the microcapsules. Moreover it has been found that the release rate of the biologically active compound can be varied over an extremely wide range; surprisingly very slow release rates into aqueous media are possible despite the water-solubility of the compound. This confers useful benefits to products utilising such technology.

One very suitable technique for the formation of said microcapsules is interfacial polymerisation via an oil-in-water emulsion; surprisingly, this results in the formation of a polymer (non-continuous) matrix which is distributed throughout the microcapsules, rather than being restricted to the interface, as is commonly taught in the prior art.

The microcapsules may be produced using the following methodology:

Step 1 – producing the solid water-soluble, biologically active compound with the required particle size, suitably by a milling process. A suitable Volume Median Diameter [VMD] particle size of the solid is 0.01-50μm; more suitably the lower limit is 0.5μm and even more suitably the lower limit is 1.0μm; more suitably the upper limit is 10μm and even more suitably the upper limit is 5μm.

Step 2 – suspending the solid water-soluble, biologically active compound in a substantially water-immiscible liquid. The liquid is preferably a poor solvent for the solid, i.e. it will not dissolve significant quantities of the solid.

The liquid preferably contains a dispersant capable of keeping the solid in the liquid but which does not allow the solid to be extracted into the water when the suspension is dispersed into water. In addition, when the suspension is added to water, the dispersant must not allow phase inversion to occur.

Alternatively, the procedures of steps 1 and 2 may be varied by performing a milling process to reduce the particle size of the solid water-soluble, biologically active compound, after the compound has been suspended in the substantially water-immiscible liquid (media milling).

Step 3 – a physical dispersion of the organic phase in an aqueous phase is prepared. To obtain the appropriate dispersion, the organic phase is added to the aqueous phase, with stirring. A suitable dispersing means is employed to disperse the organic phase in the aqueous phase. Selection of dispersion process and apparatus will depend upon the desired particle size of the emulsion (and ultimate product) to be produced. One suitable means of dispersion is typically a high shear rotor/stator device (such as a laboratory Silverson ™ machine) for small (<10 micron VMD products) but other means can be employed such as Cowles ™ dissolvers, simple mixing devices for larger particle sizes and even high pressure homogenisation equipment. Choice of such equipment is within the scope of one skill in the art. A suitable means may be any high shear device so as to obtain a desired droplet (and corresponding microcapsule particle) size within the range from about 1 to about 200μm; suitably from about 1 to 150μm; more suitably from about 1 to about 50μm; and most suitably from about 3 to about 50μm, VMD. Once the desired droplet size is obtained, the dispersion means is discontinued. Only mild agitation is required for the remainder of the process. The organic phase comprises the solid water-soluble, biologically active compound suspended in the substantially water-immiscible liquid to be encapsulated prepared as described above in steps 1 and 2. The aqueous phase comprises water and at least one emulsifier and/or protective colloid.

Clearly there is a relationship between the particle size of the solid water-soluble, biologically active compound and the particle size of the microcapsules; in order to obtain control over the release rate of the biologically active compound, the VMD ratio of the

particle size of this compound to that of the microcapsules will be typically of the value 1:5; suitably in the range 1:3 to 1:100; more suitably 1:5 to 1:20.

In order to obtain the microcapsules, the organic phase and/or the aqueous phase must contain one or more materials which can react to form a polymer. In one preferred embodiment, the organic phase contains at least one diisocyanate and/or polyisocyanate, whilst the aqueous phase contains at least one diamine and/or polyamine. In the situation where at least one diamine and/or polyamine is included in the aqueous phase, this component is added to the aqueous phase after the formation of the oil-in-water emulsion as described above in step 3.

Step 4 – at least one diamine and/or polyamine is added to the oil-in-water emulsion through the aqueous phase, maintaining mild agitation throughout. Stirring is continued typically for 30 minutes to 3 hours until the formation of the (non-continuous) matrix is complete. The reaction temperature is generally in the range from about 20°C to about 60°C. In the situation where approximately equimolar amounts of isocyanate and amino groups are present, the reaction temperature is preferably from about 20°C to about 40°C, and even more preferably from about 20°C to about 30°C. In the situation where an excess of isocyanate groups are present, the reaction temperature is preferably from about 30°C to about 60°C, and even more preferably from about 40°C to about 50°C. Reaction times in excess of 3 hours combined with temperatures of 60°C or above are not recommended; such conditions have been utilised for the encapsulation of suspensions of water-insoluble compounds (US 2003/0119675 and JP 2000247821) but it has been found that such conditions are not suitable for the formation of the microcapsules of this invention, as they result in poor encapsulation efficiency (the water-solubility of the active compounds increases with increasing temperature, resulting in excessive quantities of the active compound transferring into the aqueous phase).

To form a (non-continuous) matrix, many other microencapsulation techniques are possible, including:

(i) Preparation of a microcapsule in which a monomer is present in the disperse phase and is caused to undergo polymerisation to form the (non-continuous) matrix. Such monomers should be essentially water immiscible and typically comprise a vinyl reactive monomer,

for example, C1-C16 alkyl esters of acrylic and methacrylic acid such as ethyl hexyl acrylate and ethyl hexyl methacrylate. Cross-linking may also be introduced by choice of an appropriate acrylate or methacrylate monomer such as glycidyl methacrylate;

(ii) preparation of a microcapsule in which the solid water-soluble, biologically active compound is dispersed within a liquid in which a reagent is dissolved, and in which the liquid and reagent are caused to react to form the (non-continuous) matrix. Such effects may be achieved by two reactive species, as are required to produce a polyurethane. These include organic liquid soluble polyols to react with a suitable isocyanate. When the isocyanate reactive species has sufficient functionality, the polyol may contain just one polymerisable hydroxyl group. Many chemistries qualify including alcohols and surfactant products derived from alkoxylation processes (including ethylene oxide, propylene oxide and butylene oxide or mixtures thereof. When the isocyanate has less functionality or where high degress of cross linking are desired within the (non-continuous) matrix, the polyol component may comprise more than one polymerisable OH (hydroxyl) functional compounds, suitably comprising two or more hydroxyl groups, per molecule on average. The polymerisable, hydroxyl functional compounds may be aliphatic and/or aromatic. The polymerizable, hydroxyl functional compounds may be straight, cyclical, fused, and/or branched. Particular polymerizable hydroxyl functional compounds include at least one diol, at least one triol, and/or at least one tetrol. Any of these polyol compounds may be monomeric, oligomeric, and/or polymeric as desired. If oligomeric and/or polymeric, the polyol(s) may be selected from one or more hydroxyl functional polyethers, polyesters, polyurethanes, polyacrylics, epoxy resins, polyamides, polyamines, polyureas, polysulfones, combinations of these, or the like. Polyether polyols such as the polyalkylene ether and polyester polyols are also suitable and these are commercially available at relatively low cost and are hydrolytically stable.

Suitable polyalkylene ether polyols include poly(alkylene oxide) polymers which are essentially water immiscible and organic soluble, such as poly(ethylene oxide) and poly(propylene oxide) polymers and copolymers with terminal hydroxyl groups derived from polyhydric compounds, including diols and triols; for example, ethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, pentaerythritol, glycerol, diglycerol, trimethylol propane and similar low molecular weight polyols. Suitable commercially available

polyether polyols include those sold under the trade name Voranol® (The Dow Chemical Company).

The polyester polyols which are suitable in accordance with the invention include known polycondensates of organic dihydroxy and optionally polyhydroxy (trihydroxy, tetrahydroxy) compounds and dicarboxylic and also optionally polycarboxylic (tricarboxylic, tetracarboxylic) acids or hydroxycarboxylic acids or lactones. Instead of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols to prepare the polyesters such as, for example, phthalic anhydride. Examples of suitable diols are ethylene glycol, 1,2-butanediol, diethylene glycol, triethylene glycol, polyalkylene glycols, such as polyethylene glycol, and also 1,2- and 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol or neopentyl glycol hydroxypivalate. Examples of polyols having 3 or more hydroxyl groups in the molecule, which may be used additionally, if desired, include trimethylolpropane, trimethylolethane, glycerol, erythritol, pentaerythritol, di-trimethylolpropane, dipentaerythritol, trimethylol-benzene and trishydroxyethyl isocyanurate.

A particularly suitable class of polyols useful in the compositions, coatings and methods of the invention are the water insoluble phthalic anhydride based polyester-ether polyols which are described, for example, in US 6,855,844 which is incorporated by reference herein. Suitable commercially available phthalic anhydride based polyester-ether polyols include the "Stepanpols"® (Stepan Company).
Other relatively simple feedstocks include natural products that contain reactive hydroxyl groups such as castor oil These systems require the addition of a suitable catalyst that may be added as needed to any of the phases in the formulation. Suitable catalysts are well known in the art but include organometal catalysts such as dibutyl tin dilaurate and tertiary amines such as triethylamine and triisopropanolamine; and

(iii) preparation of a microcapsule wherein a (non-continuous) matrix-forming compound is caused to separate within the microcapsule by removal of a volatile solvent for that compound. This may be achieved by firstly preparing a dispersion of the solid water-soluble biologically active compound in a solution of a water insoluble (non-continuous) matrix forming polymer and a water immiscible volatile solvent for that water insoluble

(non-continuous) matrix forming polymer, secondly forming an emulsion of this water-immiscible mixture in water, stabilising that emulsion by an appropriate technique and then removing the volatile solvent by a suitable evaporation process, yielding a dispersion in water of microcapsules containing the water-soluble biologically active compound distributed throughout a (non-continuous) matrix of the water insoluble polymer. The stabilisation of the intermediate emulsion may be achieved by any suitable microencapsulation process, such as an interfacial polycondensation by the routes well known and outlined above but also by such routes as identified in US 5460817, where the technology is identified as being useful for water insoluble (and oil soluble) biologically active compounds such as chlorpyrifos and trifluralin but does not refer to utility for dispersions in an oil or polymer of a solid water-soluble biologically active compound.

In this present invention, the matrix is provided by a hydrophobic solid with a melting point greater than 25C and which does not exhibit a glass transition temperature. This involves the preparation of a microcapsule in which the agrochemical is dispersed within a hydrophobic solid which is held above its melting point during processing, and is subsequently allowed to solidify by cooling. Further embodiments are possible whereby the hydrophobic solid is mixed with water immiscible organic liquids such that the combination mixture still shows a melting point above 25C. Such products encompass the use of waxes with a melting point above ambient temperature (25°C) and include paraffin wax, carnauba wax, beeswax, and other natural, synthetic or semi-synthetic waxes. The encapsulation process may be carried out in a dispersion in water of the molten material at a suitable temperature during which a polymer shell is caused to separate at the interface between the dispersed oil phase and water and where the dispersion in water of the molten material itself contains the dispersed solid water-soluble biologically active compound. This dispersion of solid in a molten material can be prepared by typical techniques of grinding technical biologically active compound in the molten material or by dispersing previously ground dry technical biologically active compound into molten material. Other techniques for achieving this would be apparent to a skilled person.

In the preparation of such microcapsules, it is naturally assumed that any substantially water immiscible liquid (or hydrophobic solid) used for the preparation of the dispersion of the solid water-soluble biologically active compound will be essentially retained within the microcapsule (unless removed deliberately by evaporation as discussed above).

Undesired loss of solvent (or hydrophobic solid) may alter (or destabilise) the capsule structure and release characteristics. One preferred embodiment of the capsule is where the water-immiscible liquid (and/or hydrophobic solid) does not migrate into the water phase and, moreover, is involatile such that drying operations on the aqueous compositions do not result in solvent loss and thus alteration of the desired capsule composition.

The microcapsules of this invention may be produced using the following methodology:

Step 1 – producing the solid agrochemical with the required particle size, suitably by a milling process. A suitable Volume Median Diameter [VMD] particle size of the solid is 0.01-50μm; more suitably the lower limit is 0.5μm and even more suitably the lower limit is 1.0μm; more suitably the upper limit is 10μm and even more suitably the upper limit is 5μm.

Step 2 – suspending the solid agrochemical in a substantially water-immiscible liquid (or molten mixture with hydrophobic solid or molten hydrophobic solid). The liquid (or molten mixture with hydrophobic solid or molten hydrophobic solid) is preferably a poor solvent for the solid, i.e. it will not dissolve significant quantities of the solid.

The liquid preferably contains a dispersant capable of keeping the solid in the liquid but which does not allow the solid to be extracted into the water when the suspension is dispersed into water. In addition, when the suspension is added to water, the dispersant must not allow phase inversion to occur.

Alternatively, the procedures of steps 1 and 2 may be varied by performing a milling process to reduce the particle size of the solid agrochemical, after the compound has been suspended in the substantially water-immiscible liquid (or molten mixture with hydrophobic solid or or molten hydrophobic solid) (media milling).

In this case, the hydrophobic meltable solid is held above its melting point and the milling operation is carried out at such an elevated temperature. Alternatively, the agrochemical may be separately milled to the required size in a dry milling operation and added to a

molten hydrophobic solid, or it may be milled in a water immiscible organic liquid and added to molten hydrophobic solid. In exceptional circumstances, it is possible to mill in an aqueous medium and with appropriate selection of surfactants, disperse the aqueous mill base as a water-in-oil emulsion to the molten hydrophobic solid.

Step 3 – a physical dispersion of the organic phase in an aqueous phase is prepared. To obtain the appropriate dispersion, the organic phase is added to the aqueous phase, with stirring. Clearly to achieve this part of the process, the temperature at which the process is conducted is above the melting point of the hydrophobic solid (or mixture of hydrophobic solid with suitable water-immiscible liquid). A suitable dispersing means is employed to disperse the organic phase in the aqueous phase. Selection of dispersion process and apparatus will depend upon the desired particle size of the emulsion (and ultimate product) to be produced. One suitable means of dispersion is typically a high shear rotor/stator device (such as a laboratory Silverson ™ machine) for small (<10 micron VMD products) but other means can be employed such as Cowles ™ dissolvers, simple mixing devices for larger particle sizes and even high pressure homogenisation equipment. Choice of such equipment is within the scope of one skill in the art. A suitable means may be any high shear device so as to obtain a desired droplet (and corresponding microcapsule particle) size within the range from about 1 to about 200μm. Preferably the droplet size is from about 3 to about 150μm, and most preferably from about 5 to about 120μm. Once the desired droplet size is obtained, the dispersion means is discontinued. Only mild agitation is required for the remainder of the process. The organic phase comprises the solid water-soluble, biologically active compound suspended in the substantially water-immiscible liquid to be encapsulated prepared as described above in steps 1 and 2. The aqueous phase comprises water and at least one emulsifier and/or protective colloid.

Suitably the core also comprises a water-immiscible liquid.

Suitably the hydrophobic material is a wax.

Suitably the core is fully or partially solid; more suitably it is partially solid.

Clearly there is a relationship between the particle size of the solid agrochemical and the particle size of the microcapsules; in order to obtain control over the release rate of the biologically active compound, the VMD ratio of the particle size of this compound to that

of the microcapsules will be typically of the value 1:5; suitably in the range 1:3 to 1:100; more suitably 1:5 to 1:20.

In order to obtain the microcapsules, the organic phase and/or the aqueous phase must contain one or more materials which can react to form a polymer. In one preferred embodiment, the organic phase contains at least one diisocyanate and/or polyisocyanate, whilst the aqueous phase contains at least one diamine and/or polyamine. In the situation where at least one diamine and/or polyamine is included in the aqueous phase, this component is added to the aqueous phase after the formation of the oil-in-water emulsion as described above in step 3.

Step 4 – at least one diamine and/or polyamine is added to the oil-in-water emulsion through the aqueous phase, maintaining mild agitation throughout. This part of the process may be conducted at a temperature above the melting point of the hydrophobic solid (or mixture of hydrophobic solid with suitable water-immiscible liquid). In one embodiment, however, the reaction product at this stage of the process can be cooled (by a range of techniques) and thereafter a reactive monomer added to the cooled reaction mixture. This cooling at this stage of the process allows the meltable hydrophobic solid to solidify. In one embodiment, an oil soluble or water-dispersible isocyanate may be added at this stage and allowed to equilibrate onto the surface of the solidified emulsion. Thereafter, a further reactant (such as a diamine) can be added. Stirring is continued typically for 30 minutes to 3 hours until the formation of the capsule polymer wall is complete. The reaction temperature is generally in the range from about 20°C to about 80°C. In the situation where approximately equimolar amounts of isocyanate and amino groups are present, the reaction temperature is preferably from about 20°C to about 60°C, and even more preferably from about 20°C to about 40°C. In the situation where an excess of isocyanate groups are present, the reaction temperature is preferably from about 30°C to about 60°C, and even more preferably from about 40°C to about 50°C. Reaction times in excess of 3 hours combined with temperatures of 60°C or above are not recommended; such conditions have been utilised for the encapsulation of suspensions of water-insoluble compounds (US 2003/0119675 and JP 2000247821) but it has been found that such conditions are not suitable for the formation of the microcapsules of this invention, as they result in poor encapsulation efficiency (the water-solubility of the active compounds

increases with increasing temperature, resulting in excessive quantities of the active compound transferring into the aqueous phase).

This invention includes solid agrochemicals. Where the term water-soluble as used when referring to the solid agrochemcial to be encapsulated, this is defined as a water-solubility in the range of 0.1-100 g/l, preferably in the range 0.5-50g/l, at 20°C. This may be any such compound from the group comprising pharmaceuticals and agrochemicals such as insecticides, herbicides, fungicides, acaricides, rodenticides, molluscicides and plant growth regulators.

Suitable herbicides include 2,3,6-TBA, 2,4-D, 2-chloro-6'-ethyl-N-isopropoxymethylaceto-o-toluidide, acifluorfen, alachlor, ametryn, amicarbazone, amidosulfuron, asulam, azimsulfuron, benazolin, benfuresate, bensulfuron-methyl, bentazone, bromacil, carbetamide, chloridazon, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, clomazone, cloransulam-methyl, cyanizine, cyclosulfamuron, dicamba, dichlorprop, dichlorprop-P, diflufenzopyr, dimethachlor, dimethipin, diphenamid, ethametsulfuron-methyl, ethoxysulfuron, fenoxaprop-P, flazasulfuron, florasulam, flucetosulfuron, flumioxazin, fluometuron, flupyrsulfuron-methyl-sodium, fluroxypyr, fomesafen, foramsulfuron, halosulfuron-methyl, haloxyfop-P, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazethapyr, imazasulfuron, iodosulfuron-methyl-sodium, isouron, MCPA, MCPB, mecoprop, mecoprop-P, mesosulfuron-methyl, mesotrione, metamitron, metazachlor, methyldymron, metosulam, metoxuron, metribuzin, metsulfuron-methyl, monolinuron, naptalam, oxasulfuron, penoxsulam, pethoxamid, primisulfuron-methyl, prometon, propachlor, propanil, propham, propoxycarbazone-sodium, prosulfuron, pyroxyfen, quinmerac, rimsulfuron, simetryn, sulcotrion, sulfentrazone, sulfometuron-methyl, sulfosulfuron, tebuthiuron, tepraloxydim, terbacil, terbumeton, thifensulfuron-methyl, tralkoxydim, triasulfuron, tribenuron-methyl, triclopyr and trisulfuron-methyl.

Suitable fungicides include 2-phenylphenol, azaconazole, azoxystrobin, carboxin, cymoxanil, cyproconazole, dodemorph acetate, dodine, epoxyconazole, etridiazole, fenfuram, ferimzone, flusilazole, flutriafol, fuberidazole, furalaxyl, furametpyr, imazalil, metalaxyl, methasulfocarb, metominostrobin, myclobutanil, ofurace, oxadixyl,

oxycarboxin, phenylmercury acetate, propiconazole, prothioconazole, pyrimethanil, pyroquilon, tetraconazole, thiabendazole and tricyclazole.

More suitable fungicides include 2-phenylphenol, azaconazole, carboxin, cymoxanil, dodemorph acetate, dodine, etridiazole, fenfuram, ferimzone, flusilazole, flutriafol, fuberidazole, furalaxyl, furametpyr, imazalil, metalaxyl, methasulfocarb, metominostrobin, myclobutanil, ofurace, oxadixyl, oxycarboxin, phenylmercury acetate, prothioconazole, pyrimethanil, pyroquilon, tetraconazole, thiabendazole and tricyclazole.

Suitable insecticides include abamectin, acetamiprid, aldicarb, azadirachtin, azamethiphos, bendiocarb, carbaryl, carbofuran, clothianidin, cryolite, dazomet, dimethylvinphos, DNOC, emamectin benzoate, ethiofencarb, ethylene dibromide, fenamiphos, fenobucarb, fipronil, flonicamid, imidacloprid, isoprocarb, lufenuron, methidathion, methyl isothiocyanate, metlocarb, pirimicarb, propoxur, pymetrozine, pyridaphenthion, chloranthraniliprole (Renaxapyr™), sabadilla, spinosad, sulcofuron-sodium, thiacloprid, thiamethoxam, thiofanox, triazamate, XMC and xylylcarb.

More suitable insecticides include acetamiprid, aldicarb, azadirachtin, azamethiphos, bendiocarb, carbaryl, carbofuran, clothianidin, cryolite, dazomet, dimethylvinphos, DNOC, ethiofencarb, ethylene dibromide, fenamiphos, fenobucarb, fipronil, flonicamid, imidacloprid, isoprocarb, methidathion, methyl isothiocyanate, metlocarb, pirimicarb, propoxur, pymetrozine, pyridaphenthion, sabadilla, spinosad, sulcofuron-sodium, thiacloprid, thiamethoxam, thiofanox, triazamate, XMC and xylylcarb.

Suitable rodenticides include chloralose, chlorophacinone, coumatetralyl and strychnine.

Suitable molluscicides include metaldehyde and niclosamide.

Suitable plant growth regulators include 1-naphthylacetic acid, 4-indol-3-ylbutyric acid, ancymidol, cloxyfonac, ethychlozate, flurprimidol, gibberellic acid, indol-3-ylacetic acid, maleic hydrazide, mefluidide, prohexadione-calcium and trinexapac-ethyl.

Particularly suitable insecticides are the neonicotinoids such as acetamiprid, clothianidin, imidacloprid, thiacloprid and thiamethoxam. An especially suitable insecticide is thiamethoxam.

In a further aspect, the present invention provides use of a product to combat or control an agricultural pest which comprises applying to the pest or to a locus of the pest, a pesticidally effective amount of the product. The pests may include [fungal] diseases, insects and weeds. Suitably the pest is a termite.

The concentration of the solid agrochemical is suitably from 0.1 - 80%, more suitably 0.1 - 70% [most suitably 0.1 - 65%] by weight of the microcapsule.

For those cases in which the solid agrochemical is suspended in a substantially water-immiscible liquid, said liquid may be any liquid which does not dissolve the compound to any appreciable extent but is a sufficiently good solvent to form a solution with the hydrophobic solid above the melting point of the hydrophobic solid. Suitably the water-solubility of the liquid under ambient conditions [typically 20°C] is approximately 5000ppm by weight or less.

Suitable examples of such liquids are aromatic organic compounds such as xylenes or naphthalenes, eg. Solvesso® 200; aliphatic organic compounds such as alkyl esters, eg. Exxate® 700 – Exxate® 1000, Prifer® 6813; paraffinic compounds, eg. the Norpar® & Isopar® ranges of solvents; alkyl phthalates, such as diethyl phthalate, dibutylphthalate and dioctylphthalate; alcohols, such as isopropyl alcohol; ketones, such as acetophenone and cyclohexanone; mineral oils, eg. Cropspray® 7N or 11N; vegetable or seed oils, such as rapeseed oil; and alkylated seed oils. The liquid may be a mixture of more than one compound.

Furthermore the liquid in which the agrochemical is suspended may in itself be or comprise a second biologically active compound. Moroever, the hydrophobic solid with a melting point above 25C may also be a second (or more) biologically active compound

The phase volumes of the disperse organic phase and the continuous aqueous phase may be varied within a wide range; typically the organic phase is present at 5 to 70% by

weight; suitably from 15 to 70% by weight; and more suitably from 15 to 50% by weight based on the entire formulation.

The hydrophobic meltable solid with a melting point greater than or equal to 25C is the means by which a matrix can be produced to retain the solid agrochemical more effectively within a microcapsule. This meltable solid should not display a glass transition temperature so that it is effectively not a polymer. Such products encompass the use of waxes with a melting point above ambient temperature (25°C). This meltable hydrophobic solid can be a single component or derived form mixtures of products designed to produce a desired melting point. This will include combinations with water immiscible liquids or low melting point hydrophobic solids that produce a mixture with a reduced melting point. These include waxes, C26 and higher, paraffin waxes, cholesterol, fatty alcohols, such as cetyl alcohol, mono-, di- and triglycerides of animal and vegetable origin such as tallow , hydrogenated fat, hydrogenated castor oil, fat derivatives such as fatty acids, soaps, esters, hydrophobic starches such as ethyl cellulose, lecithin, metal soaps of fatty acids such as zinc, calcium or magnesium stearate, palmitate or oleate.

The waxes may be of natural origin, meaning they may be animal, vegetable or mineral. Animal waxes include beeswax, lanolin, shellac wax and Chinese insect wax. Vegetable wax includes carnauba, candelilla, bayberry and sugar cane waxes. Mineral waxes include fossil or earth waxes including ozokerite, ceresin and montan or petroleum waxes, including paraffin and microcrystalline waxes. Alternatively the waxes may be synthetic or mixtures of natural and synthetic waxes. For instance, these can include low molecular weight partially oxidised polyethylene, which can be preferentially co-melted with paraffin.

The fatty derivatives may be either fatty acids, fatty metallic salts of these fatty acids, fatty acid amides, fatty alcohols and fatty esters or mixtures of these. In particular, the acid may be a carboxylic acid and the salts may be calcium, magnesium, zinc or aluminium salts. The acid amide may be stearamide.

Sterols or long chain sterol, esters may also be such as cholesterol or ergosterol. Preferred compounds are waxes such as hydrogenated castor oil, lanolin, beeswax and mixtures of vegetable oils and waxes such as the product PB3™. To determine the preferred composition of the organic phase (either a complete wax or mixture of wax and water-immiscible liquid), phase diagrams can be easily constructed of the likely components to determine optimal melting points for the composite organic phase. Such compositions may

be solid solutions of wax in an oil, eutectic mixtures or even mixtures where the wax and water-immiscible oil are homogeneous above the melting point of the hydrophobic solid but on cooling the hydrophobic solid separates from the water immiscible liquid to produce domains of solid hydrophobic material that can introduce a tortuous path to retard the release of a solid agrochemical from the ultimate microcapsule. In a specific embodiment, the water immiscible liquid (and separately the hydrophobic meltable solid) may be an agrochemical or the hydrophobic organic phase in which the solid agrochemical is dispersed can be a eutectic mixture or solid solution of at least one meltable agrochemical in combination with a second component that may be a water immiscible liquid and which may separately also be an agrochemical.

The liquid (held above the melting point of the hydrophobic meltable solid) containing the solid agrochemical suitably contains a dispersant. The exact choice of dispersant(s) will depend on the choice of solid and the liquid but particularly suitable dispersants are those which act by steric hindrance and are active only at the solid/organic liquid interface and do not act as emulsifying agents. Such dispersants are suitably made up of (i) a polymeric chain having a strong affinity for the liquid and (ii) a group which will adsorb strongly to the solid.

Examples of dispersants which may be used in microcapsules containing a solid biologically active compound suspended in a liquid [and which are generally polymeric] are given in WO 95/13698, and include products available under the tradenmaes Hypermer®, Atlox®, Agrimer® and Solsperse®.

In general, the range of dispersant concentration used is from about 0.01 to about 10% by weight based on the organic phase, but higher concentrations may also be used.

For the successful encapsulation of suspensions of solid agrochemical according to the present invention the choice of the liquid / dispersant combination within the microcapsules is particularly critical. Suitable systems include Solvesso® 200 and Solsperse®17000; rapeseed oil and Solsperse® 17000; a Norpar® 15/Prifer® 6813 mixture with Z190-165™; and Cropspray® 7N or 11N with a one or more dispersants selected from Atlox® 4912, Atlox® LP1, Agrimer® AL22 and Agrimer® AL30. Such combinations are particularly suitable when the biologically active compound is thiamethoxam.

In general, the surfactant or surfactants in the aqueous phase of the microcapsule suspension are selected from anionic, cationic and non-ionic surfactants with an HLB range from about 10 to about 16 that is high enough to form a stable oil-in-water emulsion; non-ionic surfactants are particularly suitable. If more than one surfactant is used, the individual surfactants may have HLB values lower than 10 or higher than 16. However, when combined together the overall HLB value of the surfactants may be in the range 10-16. Suitable surfactants include polyethylene glycol ethers of linear alcohols, ethoxylated nonylphenols, tristyrylphenol ethoxylates, block copolymers of propylene oxide and ethylene oxide, and polyvinyl alcohols. Polyvinyl alcohols are particularly suitable.

In general, the range of surfactant concentration in the process is from about 0.01 to about 10% by weight, based on the aqueous phase, but higher concentrations of surfactant may also be used.

Additionally, a protective colloid may also be present in the aqueous phase. This must adsorb strongly onto the surface of the oil (molten) droplets. Suitable protective colloids include polyalkylates, methyl cellulose, polyvinyl alcohols, mixtures of polyvinyl alcohols and gum arabic, and polyacrylamides. Polyvinyl alcohols are particularly suitable.

There should be sufficient colloid present to afford complete coverage of the surfaces of all the droplets of the molten organic liquid. The amount of protective colloid employed will depend on various factors, such as molecular weight and compatibility. The protective colloid may be added to the aqueous phase prior to the addition of the organic phase, or can be added to the overall system after the addition of the organic phase or the dispersion of it. The protective colloid is generally present in the aqueous phase in an amount of from about 0.1 to about 10% by weight of the aqueous phase.

Where separate emulsifiers and colloid stabilisers are used in the aqueous phase, the emulsifier should not displace the protective colloid from the surface of the droplets of the organic liquid.

In one preferred embodiment, the organic phase contains at least one diisocyanate and/or polyisocyanate, whilst the aqueous phase contains at least one diamine and/or polyamine.

Any diisocyanate or polyisocyanate, or mixtures thereof, may be employed, provided that it is soluble in the liquid chosen for the organic phase. Where aromatic liquids are used, aromatic isocyanates such as isomers of tolylene diisocyanate, isomers and derivatives of phenylene diisocyanate, isomers and derivatives of biphenylene diisocyanates, and/or polymethylenepolyphenyleneisocyanates (PMPPI) are suitable. Where aliphatic liquids are used, aliphatic isocyanates are suitable, for example aliphatic acyclic isocyanates such as hexamethylenediisocyanate (HMDI), cyclic aliphatic isocyanates such as isophoronediisocyanate (IPDI) or 4,4'methylenebis(cyclohexyl isocyanate), and/or trimers of HMDI or IPDI.and the like. Polymeric polyisocyanates, biurets, blocked polyisocyanates, and mixtures of polyisocyanates with melting point modifiers may also be used. MDI is a particularly preferred polyisocyanate. Should other properties be desired from the isocyanate such as increased flexibility, then pegylated derivatives may be employed wherein part of the isocyanate is reacted with a suitable polyol. Such techniques and chemistries are well known in the art. In one embodiment, the isocyanate may be added directly to a cooled (and therefore solidified) emulsion of a solid agrochemical dispersed in a hydrophobic solid. The isocyanate is allowed to equilibrate with the solidified emulsion before addition of further reactants (such as a diamine).

The concentration of the isocyanate(s), and the ratio(s) where more than one isocyanate is used, is/are chosen so as to obtain the desired release rate profile for the particular end application. The concentration of the isocyanate(s) must also be high enough to form a (non-continuous) matrix dispersed throughout the microcapsules. In general, the isocyanate(s) will comprise from about 5 to about 75%, more suitably from about 7 to about 30%, even more suitably from about 10 to about 25% and most suitably from about 10 to about 20%, by weight of the microcapsule.

The diamine or polyamine, or mixtures thereof, may be any such compound(s) which is/are soluble in the aqueous phase. Aliphatic or alicyclic primary or secondary diamines or polyamines are very suitable, such as ethylene-1,2-diamine, diethylenetriamine, triethylenetetramine, bis-(3-aminopropyl)-amine, bis-(2-methylaminoethyl)-methylamine, 1,4-diaminocyclohexane, 3-amino-1-methylaminopropane, N-methyl-bis-(3-

aminopropyl)amine, 1,4-diamino-n-butane, 1,6-diamino-n-hexane and tetraethylenepentamine. Polyethyleneimines are also suitable.

The molar ratio of amine moieties to isocyanate moieties may be varied from about 0.1:1 to about 1.5:1. Suitably either (i) approximately equimolar concentrations of amine and isocyanate moieties are employed, with the molar ratio of amine to isocyanate moieties ranging from about 0.8:1 to about 1.3:1, in which case the wall formation reaction is suitably carried out at a temperature above the melting point of the hydrophobic solid or, when a separate cooling step in introduced to the process to reduce the temperature to below the melting point of the hydrophobic solid, from about 20°C to about 40°C, even more preferably from about 20°C to about 30°C; or (ii) a significant excess of isocyanate is present, with the ratio of amine to isocyanate moieties ranging from about 0.1:1 to about 0.35:1, in which case the wall formation reaction is preferably carried out at a temperature from about 30°C to about 60°C, even more preferably from about 40°C to about 50°C.

Other wall chemistries may be used, for example polyurethanes and polyamides, by appropriate selection of wall forming components. Suitable glycols for addition through the aqueous phase include those taught above and which are water soluble. These may also include simple polyhydroxylic glycols, for example, suitable diols are ethylene glycol, 1,2-butanediol, diethylene glycol, triethylene glycol, polyalkylene glycols, such as polyethylene glycol, and also 1,2- and 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol or neopentyl glycol hydroxypivalate. Examples of polyols having 3 or more hydroxyl groups in the molecule, which may be used additionally, if desired, include trimethylolpropane, trimethylolethane, glycerol, erythritol, pentaerythritol, di-trimethylolpropane, dipentaerythritol, trimethylol-benzene and trishydroxyethyl isocyanurate. Higher functionality may be employed by use of the various sugars such as fructose, dextrose, glucose and derivatives thereof. Mixtures of water soluble and oil soluble reactive hydroxyl containing compounds are also contemplated. Polyamides may be produced in a similar manner by selection of an appropriate acid feedstock (such as sebacoyl chloride). Mixtures, in any ratio, of polyureas, polyurethanes and polyamides are also part of the present invention.

Therefore suitably the polymeric shell is a polymer which is a polyurea, a polyamide or a polyurethane or is a mixture of two or more of these polymers; more suitably it is a polyurea.

In a similar manner, oil soluble amines may be contemplated as being added to the oil phase prior to preparation of the aqueous dispersion and thereafter a suitable water dispersible isocyanate reactant may be added to complete the interfacial reaction.

In another aspect, the present invention provides a process of making a product as herein described comprising the steps
(i) melting the hydrophobic material to form a hydrophobic liquid;
(ii) dispersing the agrochemical in the hydrophobic liquid;
(iii) emulsifying the hydrophobic liquid into an aqueous phase;
(iv) optionally cooling the resultant emulsion;
(v) causing an interfacial polymerisation reaction to occur at the interface between the hydrophobic liquid and the aqueous phase to produce a capsule suspension; and
(vi) optionally allowing or causing the capsule suspension to cool.
Suitably the process comprises the step of rapidly cooling an emulsion to below the melting point of the hydrophobic material.
Suitably the process involves a step where an isocyanate is introduced through the aqueous phase.

By selection of microcapsule size, isocyanate chemistry and concentration, amine identity and the ratio of different isocyanate monomers and/or amines when more than one isocyanate monomer and/or amine is present, the release rate of the solid agrochemical can be varied from a half-life [T50; the time taken for 50% of the active ingredient to be lost from the capsule (i.e. released)] value of a few hours up to several months or years. It is surprising that such a wide range of release rates is achievable for a solid agrochemical, and it is particularly unexpected that extremely slow release rates into an aqueous sink are obtained.

Furthermore, mixtures of microcapsules with different release rates may be combined in a single formulation, to provide a tailored release profile.

The capsule compositions, as produced, will be dispersions in water. These microcapsules may be post-formulated, to stabilise them for long term shelf life storage, with anti-settling agents, which include water-soluble polysaccharides such as xanthan gum, water-insoluble polysaccharides such as microcrystalline cellulose and structured clays such as bentonites. Microcrystalline cellulose is a particularly suitable anti-settling agent.

Furthermore, it is possible to add additional agrochemicals to the aqueous phase, either as solids, emulsions (either as an emulsion of a compound that is liquid at ambient temperature or as an emulsion of a solution of an agrochemical in a suitable essentially water immiscible solvent) or as a solution in water or mixtures of the above. The agrochemical added directly to the external aqueous phase may be the same compound as within the microcapsule.
Therefore suitably the aqueous phase comprises an agrochemical. Suitably an agrochemical in the aqueous phase has a water-solubility in the range of 0.1 to 100 g/l at 20°C; more suitably it is a neonictinoid insecticide; even more suitably it is acetamiprid, clothianidin, imidacloprid, thiacloprid or thiamethoxam; and most suitably it is thiamethoxam.

Where an additional agrochemical is present in the aqueous phase, the concentration of this compound may be varied within a relatively wide range. Generally the concentration of this compound will be between 0 and 50% by weight, based on the total aqueous phase.

Furthermore, it is possible to dry such water based compositions. This can be achieved by concentration of the water based composition (e.g. sedimentation, centrifugation) followed by a suitable drying technique such as drum drying. It may also be achieved by techniques such as spray-drying [including fluid bed agglomeration techniques and similar granulation processes] or, if the compounds are heat sensitive, freeze drying or atmospheric freeze drying. Spray drying techniques are preferred as they are fast and may conveniently be applied to dispersions such as the microcapsules of this invention. Production of dry product from a water based dispersion usually requires the addition of further inert components to protect the integrity of the capsules during the drying stage, or during storage and also to allow easy complete re-dispersion of the dry product back into water for application. Such inerts include, but are not limited to, essentially water soluble film-forming agents such as polyvinyl alcohols, polyvinylpyrrolidones and polyacrylic

acids. Other ingredients may include surfactants, dispersants, sugars, lignosulfonates, disintegrants such as cross-linked polyvinylpyrrolidones and maltodextrins.

The dried products moreover, may contain other agrochemicals that are not encapsulated as described above for the solid agrochemical.

It is also possible to use a dried product directly without dilution into water. Such use may be as a granular product in rice cultivation, for use on cultivated turf and also as a feedstock for blending into fertiliser mixtures for subsequent application to soil, turf or other targets such as rice.
Suitably the dry product is granular.
Suitably the dry product is water-dispersible.

The wide range of release rates achievable with the technology of the present invention allows exploitation in several applications, including traditional crop protection outlets both as a foliar or a soil applied product, for use on cultivated turf, as a seed treatment and numerous other applications such as protection against termites and as a long-lasting residual spray for general pest control.
In a still further aspect of the invention there is provided the use of a composition as described herein for the protection of industrial materials [referred to as "materials protection"]. Suitably the industrial material to be protected is selected from the group consisting of: wood; plastic; wood plastic composite; paint; paper; and wallboards. The protection may be in the form of a product that deters, repels or kills an attack of a target, such as in the area of termite protection, or house protection against invasive insect species, a barrier can be places between the article to be protected (eg a building) and the external environment in which the pest species normally resides.

The term "Industrial Material" includes those materials used in construction and the like. For example, Industrial Material may be structural timber, doors, cupboards, storage units, carpets, particularly natural fibre carpets such as wool and hessian, plastics, wood (including engineered wood) and wood plastic composite.

In a particular embodiment the Industrial Material is a coating. "Coating" includes compositions applied to a substrate, for example, paints, stains, varnishes, lacquers,

primers, semi-gloss coatings, gloss coatings, flat coatings, topcoats, stain-blocking coatings, penetrating sealers for porous substrates, concrete, marble, elastomeric coatings, mastics, caulks, sealants, board and panelling coatings, transportation coatings, furniture coatings, coil coatings, bridge and tank coatings, surface marking paints, leather coatings and treatments, floor care coatings, paper coatings, personal care coatings [such as for hair, skin or nails], woven and non-woven fabric coatings, pigment printing pastes, adhesive coatings [such as, for example, pressure sensitive adhesives and wet- or dry-laminating adhesives] and plaster.

Suitably "coating" means paint, varnish, stain, lacquer or plaster; more suitably "coating" is a lacquer or alternatively "coating" may mean paint. Paint may comprise, for example, a film former and a carrier (which carrier can be water and/or an organic solvent) and optionally a pigment.

In addition to this, "Industrial Material" includes adhesives, sealants, joining materials, joints and insulation material.

"Wood" is to be understood to include wood and wood products, for example: derived timber products, lumber, plywood, chipboard, flakeboard, laminated beams, oriented strandboard, hardboard, particle-board, tropical wood, structural timber, wooden beams, railway sleepers, components of bridges, jetties, vehicles made of wood, boxes, pallets, containers, telegraph-poles, wooden fences, wooden lagging, windows and doors made of wood, plywood, chipboard, joinery, or wooden products which are used, quite generally, for building houses or decks, in building joinery or wood products that are generally used in house-building including engineered wood, construction and carpentry.

"Industrial Material" also includes wallboards such as gypsum based wallboards.

In a still further aspect of the invention there is provided "Industrial Materials" comprising a composition as herein described. In a particular embodiment said Industrial materials are selected from the group consisting of: wood; wood plastic composite; paint; paper; and wallboards. In a particular embodiment said Industrial materials comprise wood.

Examples of ways in which an Industrial Material can be treated with a product according to the invention are: by including said product in the Industrial Material itself, absorbing, impregnating, treating (in closed pressure or vacuum systems) said material with said fungicide, dipping or soaking the building material, or coating the building material for

example by curtain coating, roller, brush, spray, atomisation, dusting, scattering or pouring application.

The use of slow releasing microcapsules allows for an extended period of biological control compared to non-encapsulated formulations, and for soil applied products the extent of leaching may also be reduced by the use of such microcapsules; the latter is particularly relevant for those active compounds with appreciable water solubility disclosed within this invention, whereby their substantial water solubility renders them prone to leaching when applied in an non-encapsulated form. In the particular embodiment where the microcapsules are suspended in an aqueous medium comprising a suspension of non-encapsulated agrochemical, both rapid knockdown activity and an extended period of biological control may be achieved, particularly for insecticides. Other utilities include incorporation of such products into materials where a slow release of a water soluble material is desired, such as for treatment of water bodies and addition to centre pivot irrigation systems where high volumes of water rapidly leach active materials.

The microcapsule suspensions thus produced may be utilized in the normal fashion of such products, i.e. by packaging the suspension and ultimately transferring the suspension into a spray tank or other spray equipment, in which it is mixed with water to form a sprayable suspension. A range of application techniques may be utilised for the soil application of such microcapsules, including pre-planting and post-planting applications either as a dilute spray or as a more concentrated drench, including direct application into the planting hole. Application may also be made to seedling trays etc. prior to transplant. For termite protection, the microcapsules of this invention may be applied as a soil drench underneath the foundations, as a perimeter 'trench and treat' barrier around the outside of the foundations, or applied directly onto concrete. Alternatively, the suspension of microcapsules may be converted into a dry microcapsule product by spray drying or other known techniques and the resulting material packaged in dry form.

It will be appreciated that there are many aspects to the present invention. In one aspect, it relates to a product comprising microcapsules which themselves comprise

(a) a polymeric shell; and

(b) a core which comprises an agrochemical which has a melting point above 25°C characterised in that the agrochemical is dispersed as a solid in a hydrophobic material

which has a melting point greater than or equal to 25°C but which does not exhibit a glass transition temperature.

Further aspects and preferences are given below. Throughout this invention, where the term "water immiscible liquid" is employed this also includes hydrophobic meltable solids above their melting point and mixtures of such hydrophobic solids (above their melting point) with water immiscible liquids

A microcapsule formulation in which microcapsules comprise a solid agrochemical dispersed in a (non-continuous) matrix which is at least partially solid and which is distributed throughout the microcapsules, in which the microcapsules are suspended in an aqueous phase during their formation.

A microcapsule formulation as described above wherein agrochemical is a solid at ambient temperature and is dispersed in an organic non-solvent within the capsules.

A microcapsule formulation as described above and a process as described above for making it in which a monomer is present in the disperse phase and is caused to undergo polymerisation to form the (non-continuous) matrix.

A microcapsule formulation as described above wherein a water immiscible liquid is a vinyl containing reactive monomer.

A microcapsule formulation as described above and a process as described above for making it in which the solid agrochemical is dispersed within a liquid in which a reagent is dissolved, and in which the liquid and reagent are caused to react to form the (non-continuous) matrix.

A microcapsule formulation as described above wherein a water immiscible liquid is a reactant with a second reactive species by which a (non-continuous) matrix is formed.

A microcapsule formulation as described above in which the solid agrochemical is dispersed within a substantially water-immiscible liquid which is retained within the microcapsule.

A microcapsule formulation as described above in which the solid agrochemical is dispersed within a material which is held above its melting point during processing, and is subsequently allowed to solidify.

A microcapsule formulation as described above wherein the water immiscible liquid is a solid at ambient temperature and the process is operated above the melting point of the water immiscible liquid, forming a matrix on cooling below the melting point. For example, when using a wax to form a matrix.

A microcapsule formulation as described above in which the substantially water-immiscible liquid is or comprises a second agrochemical .

A microcapsule formulation as described above in which one or more agrochemical(s) is/are present in the continuous aqueous phase [either as a solid dispersion, a liquid dispersion or as a solution in the aqueous phase].

A microcapsule formulation as described above in which the solid agrochemical which is present in the continuous aqueous phase is the same solid agrochemical as the one which is dispersed in the microcapsules.

A microcapsule formulation as described above in which the pesticide is thiamethoxam.

The use of a microcapsule formulation as described above to control the release rate of a pesticide thereby providing an extended period of biological control.

The use of a microcapsule formulation as described above to control the release rate of a pesticide thereby providing a reduction in leaching of the pesticide.

A microcapsule formulation as described above wherein the formulation is water based (capsules dispersed in water).

A microcapsule formulation as described above where the formulation is a dry product, produced by a drying process such as spray drying or freeze drying or by a suitable concentration procedure and final drying.

A microcapsule formulation as described above where a (non-continuous) matrix-forming compound (suitably a polymer) is caused to separate within the microcapsule by removal of a volatile solvent for that compound.

The use of a microcapsule formulation as described above to improve safety of an agrochemcial either to the manufacturer, user or the environment.

A process for forming a microcapsule formulation as described above in which the (non-continuous) matrix is prepared either before the capsule, during capsule preparation or after capsule preparation.

A process for forming a microcapsule formulation as described above in which the (non-continuous) matrix is formed by an interfacial polycondensation reaction.

A process as described above in which at least one reagent for the polycondensation reaction is present in the dispersed [organic] phase and at least one reagent for the polycondensation reaction is present in the continuous [aqueous] phase.

A process as described above in which the reagents for the polycondensation reaction are only present in the dispersed phase.

The following examples are given by way of illustration and not by way of limitation of the invention, in which many capsule samples are characterised by their VMD [Volume Median Diameter].

Examples 1a-1j

The following examples demonstrate that thiamethoxam can be suspended in a meltable hydrophobic solid, followed by encapsulation within a polyurea wall, wherein isocyanate moieties for the formation of the polyurea wall are dissolved in the meltable hydrophobic

solid. Such formulations are not trivial to prepare successfully due to the high water-solubility of thiamethoxam (4.1g/l at 20°C) which means there is a tendency for the particles of thiamethoxam to migrate into the aqueous phase during the emulsification process and/or before the meltable hydrophobic solid has solidified and the formation of the microcapsule wall is complete. Preventing excessive migration of thiamethoxam particles into the aqueous phase is particularly challenging for this type of formulation due to the elevated temperatures employed during the emulsification process.

Thiamethoxam was encapsulated using the following process according to the recipes given in Table 1. Initially thiamethoxam (pre-ground in an air jet mill or similar) was dispersed into a meltable hydrophobic solid (wax) in the presence of an oil-soluble dispersant; this dispersion was carried out using high shear at a temperature typically 10-20°C above the melting point of the meltable hydrophobic solid. An isocyanate was subsequently dissolved into the thiamethoxam suspension. This suspension was then emulsified into an aqueous solution of polyvinyl alcohol (emulsification being carried out at temperature typically 10-20°C above the melting point of the wax). Additional water was added to reduce the temperature of the emulsion, and rapid cooling was effected by immersion of the emulsion in an ice/water bath (maintaining agitation throughout). An aqueous solution of a polyfunctional amine was added immediately after initiation of the cooling process, and cooling was continued until the wax had solidified. The resultant capsule formulations were characterised by their VMDs.

Paraffin wax (melting point 53-57°C) and beeswax (synthetic, melting point 61-65°C) are supplied by Aldrich.

Lanolin (melting point 38-44°C) is supplied by Acros.

PB3™ (melting point 38-44°C) is a blend of vegetable oil and hydrogenated vegetable oil supplied by Aarhus.

Docosane (melting point 42°C) is available from Sigma-Aldrich.

Solvesso® 100 is an aromatic hydrocarbon solvent supplied by Exxon.

Rapeseed oil (from Brassica rapa) was sourced from Fluka.

Cropspray® 7N is a mineral oil supplied by Sun Oil Company.

Agrimer® AL22 and AL30 are alkylated vinylpyrrolidone copolymers supplied by ISP.

Solsperse® 17000 is a polymeric dispersant supplied by Lubrizol.

Desmodur® Z4470 is the trimer of isophoronediisocyanate supplied by Bayer as a 70% solution in naphtha 100.

Desmodur® W is 4,4'-methylenebis(cyclohexyl isocyanate) supplied by Bayer.

Gohsenol® GL05 is a polyvinylalcohol supplied by Nippon Gohsei.

Table 1

Component (%w/w)	1a	1b	1c	1d	1e	1f
Thiamethoxam	10	10	10	10	10	10
Agrimer AL-30	0.8	0.8	0.8	0.8	0.8	0.8
Beeswax	9.2	9.2	9.2	-	-	-
Lanolin	-	-	-	9.2	9.2	9.2
Desmodur Z4470 SN	1.5	3.2	7.1	1.5	3.2	7.1
Gohsenol GL05	2.7	2.7	2.7	5.4	5.4	5.4
Diethylenetriamine	0.16	0.33	0.74	0.16	0.33	0.74
Water (for emulsification)	44	44	44	41.3	41.3	41.3
Water (for cooling)	To 100%	To 100%	To 100%	To 100%	To 100%	To 100%
VMD (μm)	31.7	29.0	39.7	22.1	23.6	20.14

Component (%w/w)	1g	1h	1i	1j
Thiamethoxam	10	10	10	10
Agrimer AL-30	0.8	0.8	0.8	0.8
PB3	9.2	9.2	9.2	-
Paraffin wax	-	-	-	9.2
Desmodur Z4470 SN	1.5	3.2	7.1	-
Desmodur W	-	-	-	2.2
Gohsenol GL05	2.7	2.7	2.7	2.7
Diethylenetriamine	0.16	0.33	0.74	0.64
Water (for emulsification)	44	44	44	44
Water (for cooling)	To 100%	To 100%	To 100%	To 100%
VMD (μm)	21.1	28.2	19.7	84.1

Examples 2a-2c

The following examples demonstrate that a meltable hydrophobic solid contained within the capsules may consist of a mixed wax/solvent system.

Thiamethoxam was encapsulated according to the recipes given in Table 2 using the same methodology as in Examples 1, but with the additional step of dissolving a solvent in the suspension of thiamethoxam in wax prior to emulsification.

Table 2

Component (%w/w)	2a	2b	2c
Thiamethoxam	9.1	9.1	9.1
Agrimer AL-30	0.73	0.73	0.73
PB3	-	-	8.37
Paraffin wax	8.37	-	-
Beeswax	-	8.37	-
Solvesso 100	1.7	1.7	1.7
Desmodur Z4470 SN	3.2	3.2	3.2
Gohsenol GL05	2.7	2.7	2.7
Diethylenetriamine	0.33	0.33	0.33
Water (for emulsification)	44	44	44
Water (for cooling)	To 100%	To 100%	To 100%
VMD (μm)	63.3	36.9	25.8

Examples 3a-3b

The following examples demonstrate that a meltable hydrophobic solid contained within the capsules may consist of a mixed wax/solvent system; in these examples the internal content of the capsules comprises a mixture of millbases, in each of which thiamethoxam had been dispersed prior to mixing of the millbases.

Thiamethoxam was encapsulated using the following process according to the recipes given in Table 3. A finely ground suspension of thiamethoxam in a substantially water immiscible solvent was mixed with a suspension of thiamethoxam in a wax at a temperature above the melting point of the wax. Encapsulation was then carried out according to the process described in Examples 1.

Table 3

Component (%w/w)	Millbase 1	Millbase 2	Millbase 3	3a	3b

Thiamethoxam	50	50	50	-	-
Agrimer AL-30	4	-	-	-	-
Agrimer AL-22	-	5	-	-	-
Solsperse 17000	-	-	5	-	-
Lanolin	46	-	-	-	-
Cropspray 7N	-	45	-	-	-
Rapeseed oil	-	-	45	-	-
Millbase 1	-	-	-	16	12
Millbase 2	-	-	-	4	-
Millbase 3	-	-	-	-	8
Desmodur W	-	-	-	2.2	-
Desmodur Z4470 SN	-	-	-	-	3.2
Gohsenol GL05	-	-	-	5.4	5.4
Diethylenetriamine	-	-	-	0.64	0.33
Water (for emulsification)	-	-	-	41.3	41.3
Water (for cooling)	-	-	-	To 100%	To 100%
VMD (μm)	-	-	-	10.7	15.0

Example 4

The following example demonstrates that thiamethoxam can be suspended in a wax, followed by encapsulation within a polyurea wall, wherein the isocyanate moieties for the formation of the polyurea wall are added to an aqueous emulsion of the dispersed thiamethoxam in wax after solidification of the wax. This example also uses a novel cooling method which allows a higher concentration of thiamethoxam to be obtained in the final formulation.

Thiamethoxam was encapsulated using the following process according to the recipe given in Table 4. Initially thiamethoxam (pre-ground in an air jet mill or similar) was dispersed into the wax in the presence of an oil-soluble dispersant; this dispersion was prepared using high shear at a temperature typically 10-20°C above the melting point of the wax. This dispersion (suspension) was then emulsified into an aqueous solution of polyvinyl alcohol (emulsification being carried out at temperature typically 10-20°C above the melting point of the wax). The emulsion was then cooled rapidly to below the

melting point of the wax by the addition of carbo-ice to the emulsion, stirring throughout with a low shear mixer.

Once the emulsion was at ambient temperature, an isocyanate was added under low shear stirring.

After 35 minutes, an aqueous solution of a polyfunctional amine was added still under stirring.

Table 4

Example	4
Thiamethoxam technical	13.73
Agrimer AL30	1.10
Docosane	12.63
Gohsenol GL05	3.66
Water (for emulsification)	To 100%
Desmodur W	6.4
Diethylene triamine	2.1
VMD (μm)	10.0

Example 5

The following example demonstrates that the microcapsules prepared according to examples 1-3 are stable upon high temperature storage.

Formulations prepared according to examples 1-3 were stored for up to 3 weeks at 50°C, during which they showed essentially no changes in particle size; the results are given in Tables 5 & 6 below.

Table 5

Example	1a	1b	1c	1d	1e	1f
Initial VMD (μm)	31.7	29.0	39.7	22.1	23.6	20.14
VMD after 3 weeks storage at 50°C (μm)	32.6	27.9	37.1	24.6	24.8	23.8

Table 6

Example	1g	1h	1i	2a	2c	3b
Initial VMD (μm)	21.1	28.2	19.7	63.3	25.8	15.0
VMD after 1 weeks storage at 50°C (μm)	21.7	29.3	20.8	63.5	26.3	16.9

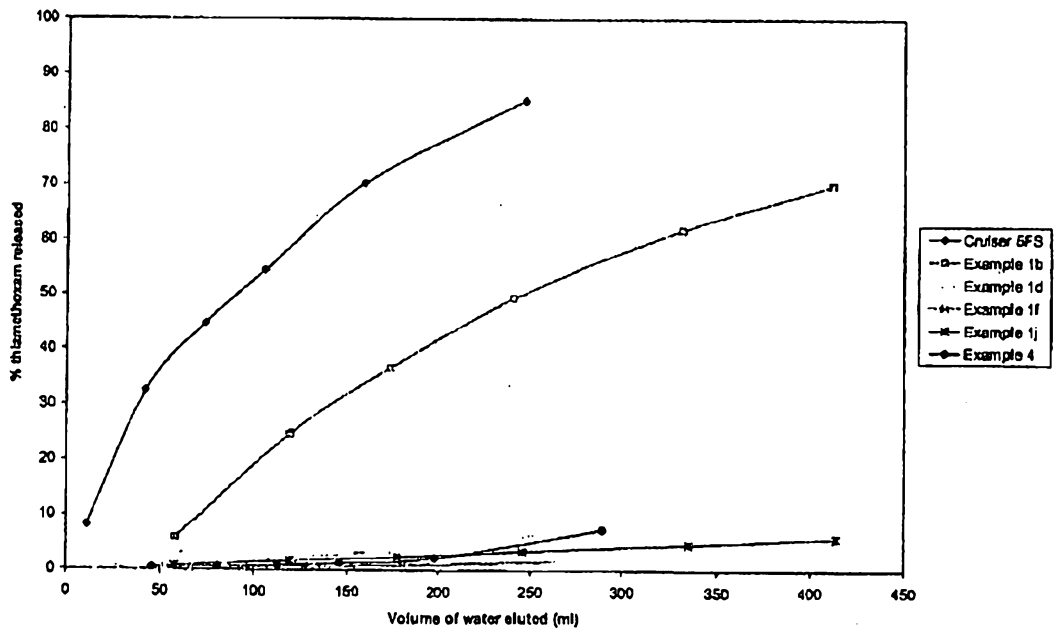
Example 6

This example demonstrates that seed treatments comprising encapsulated suspensions of thiamethoxam in a wax show extended control of release of thiamethoxam compared to unencapsulated thiamethoxam in the form of Cruiser™ 5FS (a suspension concentrate containing 500g/l thiamethoxam).

Encapsulated suspensions of thiamethoxam in wax were mixed with a coating polymer SpectrumTM 300C and applied to maize seeds in a seed treater so as to give a loading of 1.25mg thiamethoxam and 0.625mg Spectrum 300C per seed.

Ten treated seeds were placed on approximately 80g soil in a Buchner funnel (pore size 2, 11cm diameter) and covered with an additional 35g soil and a filter paper. Fixed amounts of water were sprayed onto the filter paper, and the eluent was collected, weighed and analysed for thiamethoxam content. The release rate data obtained is shown in Figure 1.

Figure 1



Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A product comprising microcapsules which themselves comprise
(a) a polymeric shell; and
(b) a core comprising an agrochemical which has a melting point greater than or equal to 25°C characterised in that the agrochemical is dispersed as a solid in a hydrophobic material which has a melting point greater than or equal to 25°C but which does not exhibit a glass transition temperature.

2. A product as claimed in claim 1 where the agrochemical has a water-solubility in the range of 0.1 to 100 g/l at 20°C.

3. A product as claimed in claim 2 where the agrochemical is a neonictinoid insecticide.

4. A product as claimed in claim 3 where the agrochemical is acetamiprid, clothianidin, imidacloprid, thiacloprid or thiamethoxam.

5. A product as claimed in claim 4 where the agrochemical is thiamethoxam.

6. A product as claimed in any one of claims 1 to 5 where the microcapsules are dispersed in an aqueous phase.

7. A product as claimed in any one of claims 1 to 5 where the product is a dry product.

8. A product as claimed in claim 7 where the dry product is granular.

9. A product as claimed in claim 7 or 8 where the dry product is water-dispersible.

10. A product as claimed in claim 6 where the aqueous phase comprises an agrochemical.

11. A product as claimed in claim 10 where the agrochemical in the aqueous phase has a water-solubility in the range of 0.1 to 100 g/l at 20°C.

12. A product as claimed in claim 11 where the agrochemical in the aqueous phase is a neonictinoid insecticide.

13. A product as claimed in claim 12 where the agrochemical in the aqueous phase is acetamiprid, clothianidin, imidacloprid, thiacloprid or thiamethoxam.

14. A product as claimed in claim 13 where the agrochemical in the aqueous phase is thiamethoxam.

15. A product as claimed in any one of the preceding claims where the core also comprises a water-immiscible liquid.

16. A product as claimed in any one of the preceding claims where the hydrophobic material is a wax.

17. A product as claimed in any one of the preceding claims where the core is fully or

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partially solid.

18. A product as claimed in any one of the preceding claims where the core is partially solid.

19. A product as claimed in any one of the preceding claims where the polymeric shell is a polymer which is a polyurea, a polyamide or a polyurethane or is a mixture of two or more of these polymers.

20. A product as claimed in claim 19 where the polymeric shell is a polyurea.

21. A process for preparing a product as claimed in any one of claims 1 to 20 comprising the steps

(i) melting the hydrophobic material to form a hydrophobic liquid;

(ii) dispersing the agrochemical in the hydrophobic liquid;

(iii) emulsifying the hydrophobic liquid into an aqueous phase;

(iv) optionally cooling the resultant emulsion;

(v) causing an interfacial polymerisation reaction to occur at the interface between the hydrophobic liquid and the aqueous phase to produce a capsule suspension; and

(vi) optionally allowing or causing the capsule suspension to cool.

22. A process as claimed in claim 21 which comprises the step of rapidly cooling an emulsion to below the melting point of the hydrophobic material.

23. A process as claimed in claim 21 or 22 where an isocyanate is introduced through the aqueous phase.

24. Use of a product as claimed in any one of claims 1 to 20 to combat or control an agricultural pest which comprises applying to the pest or to a locus of the pest, a pesticidally effective amount of the product.

25. Use of a product as claimed in claim 19 where the pest is a termite.

26. Use of a product as claimed in any one of claims 1 to 20 to control the release rate of an agrochemical.

27. Use of a product as claimed in any one of claims 1 to 20 to reduce the amount of agrochemical that is leached through soil.

28. Use of a product as claimed in any one of claims 1 to 20 in seed treatment.

29. Use of a product as claimed in any one of claims 1 to 20 to provide materials protection

30. A product as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.