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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 February 2018 (22.02.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/032387 A1

(51) International Patent Classification:
B01J 13/16 (2006.01) *A01N 25/28* (2006.01)
B01J 13/02 (2006.01) *C08G 18/10* (2006.01)

(21) International Application Number:
PCT/CN2016/095618

(22) International Filing Date:
17 August 2016 (17.08.2016)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **JIANGSU ROTAM CHEMISTRY CO., LTD.** [CN/CN]; No. 88, Rotam Road, Economic & Technical Development Zone, Kunshan, Jiangsu 215301 (CN).

(72) Inventors: **WU, Yifan**; Unit 6, 26/F, Trend Centre, 29 Cheung Lee Street, Chai Wan, Hong Kong (CN). **BRISTOW, James Timothy**; Unit 6, 26/F, Trend Centre, 29 Cheung Lee Street, Chai Wan, Hong Kong (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/032387 A1

(54) Title: HERBICIDE COMPOSITION COMPRISING CLOMAZONE AND USE THEREOF

(57) Abstract: A microcapsules polymer wall material comprising crosslinked polyurethane–polyurea copolymer and its preparation, as well as a composition comprising a water-immiscible and/or highly volatile material encapsulated within a microcapsule having a wall comprising the microcapsules polymer wall material, and the use of the composition in the control of unwanted plant growth are provided.

HERBICIDE COMPOSITION COMPRISING CLOMAZONE AND USE THEREOF

BACKGROUND OF THE INVENTION

Field of Invention

This invention concerns an improved microcapsules polymer wall material consisting of crosslinked polyurethane-polyurea copolymer and its preparation and use.

Description of Related Art

Capsules of this character have a variety of uses, as for encapsulating dyes, chemical reagents, pharmaceuticals, flavoring materials, pesticides (for example, herbicides, insecticides and fungicides) and the like. Once encapsulated, the liquid or other forms is preserved until it is released by means or instrumentalities that break, crush, melt, dissolve, or remove the capsule wall or until release by diffusion under suitable conditions. The process of the invention is particularly suitable for the production of water-immiscible material inside microcapsules which are of very small in particle size, and suspended in an aqueous solution.

Producing of aqueous dispersions of microcapsules having water-immiscible materials are particularly useful in formulating controlled release of water-immiscible material formulations. It is because they can be diluted with water or liquid fertilizer and then sprayed using conventional equipment to produce uniform coverage of the water-immiscible material in fields. Additives, such as film forming agents, can be added directly to the finished formulation to improve the adhesion of microcapsules to foliage. Reduced toxicity and extended activity of the encapsulated water-immiscible material have been reported.

Various encapsulation techniques have been used or proposed. One of the techniques is known as "simple coacervation". A polymer is separated from a

solvent solution of the polymer by the use of a precipitating agent which reduces the solubility of the polymer in the solvent (e.g., a salt or a non-solvent for the polymer). Patents describing such techniques and their wall material for examples U.S. Pat. Nos. 2,800,458, 3,069,370, 3,116,216, 3,137,631, 3,418,250.

Another technique bases on the interfacial condensation polymerization. British Pat. No. 1,371,179 discloses a process which consists of dispersing an organic pesticide phase containing a polymethylene polyphenylisocyanate or toluene diisocyanate monomer into an aqueous phase. The wall-forming reaction is initiated by elevating temperature to the point which the isocyanate monomers are hydrolyzed at the interface to form amines, which in turn react with unhydrolyzed isocyanate monomers to form the polyurea wall. One difficulty of this technique is the possibility of continued reaction of monomer after packaging. Unless all monomers are reacted during the preparation, there will be continued hydrolysis of the isocyanate monomer together with the evolution of carbon dioxide that will result building up pressure after packaging.

Various methods of encapsulation by interfacial condensation between direct-acting, complimentary reactions are known. Within these methods are reactions for producing various types of polymers as the walls. Many of such reactions to produce the coating substance occur between an amine, which must be of at least difunctional character and a second reactant intermediate, which for producing a polyurea is a difunctional or polyfunctional isocyanate. The amines chiefly used or proposed in these methods are typified by ethylene diamine, having at least 2 primary amino groups. U.S. Pat. No. 3,577,515 is illustrative of encapsulation by interfacial condensation.

SUMMARY OF THE INVENTION

The present invention provides a new and improved encapsulation process which is rapid and effective and avoids the necessity of separation of the encapsulated material from a continuous phase. The present invention also eliminates the necessity of the use of a strong solvent in an organic phase resulting in saving energy, packaging and equipment. In addition, direct

combination of water-based pesticide formulations are possible with other water-based pesticides.

The compositions of the present invention are particularly suitable for formulating water immiscible and/or highly volatile material, such as clomazone, abamectin, pendimethalin, lambda cyhalothrin, spinosad, emamectin benzoate, deltamethrin, cypermethrin, acetochlor, alachlor, metolachlor and combinations thereof. Experiments indicate that conventional oil/water emulsifiers fail to produce sufficiently stable emulsions to attain microencapsulation of concentrated amounts of water immiscible materials and avoid solidification of the oil/water mass when amine is added. Additionally, attempts to encapsulate concentrated amounts of active ingredients (water immiscible and/or highly volatile material) using the interfacial polymerization techniques. For example, as disclosed in U.S. Pat. No. 3,577,515, it resulted in unsatisfactory formulations because of the problems of herbicide crystal growth, agglomeration and solidification of the finished formulations. It was suggested that the herbicide crystal growth results from either incomplete encapsulation of the herbicide or from the passage of small amounts of herbicide through the polymeric wall.

Crystal growth is very undesirable because once it occurs, the finished formulations cannot be used directly. The microcapsules must be separated from the aqueous solution and resuspended in water before they can be sprayed in by conventional agricultural spraying apparatus.

This invention provides a process to encapsulate more than 480 grams of water immiscible material in a polyurethane-polyurea copolymer wall of microcapsules and to suspend the microcapsules in the original aqueous solution. The suspended microcapsules can be stored for an extended period of time and can be exposed for short-terms of elevated temperatures without the occurrence of agglomeration or solidification of the aqueous, capsule mass or herbicide crystal growth.

This invention also provides a method of controlling plant growth at a locus, comprising applying the composition to the locus.

This invention also provides the use of the composition in the control of unwanted plant growth.

DETAILED DESCRIPTION OF THE INVENTION

This invention concerns an improved microcapsules polymer wall material consisting of crosslinked polyurethane-polyurea copolymer. The invention comprises an isocyanate-terminated polyurethane prepolymers. Preferred isocyanate includes polymethylene polyphenyl isocyanates (PMPPI). The prepolymer then forms polyurethane-polyurea copolymer when it is added to a polyfunctional amine. Preferred polyfunctional amine is 1,6-hexamethylene diamine.

In this invention, a water-immiscible (organic) phase, which consists of a water-immiscible material (the material to be encapsulated) and isocyanate-terminated polyurethane prepolymers, is added to an aqueous phase, with agitation, to form a dispersion of small droplets of water-immiscible phase within the aqueous phase. Thereafter, the polyfunctional amine, preferably 1,6-hexamethylene diamine, is added, with continued agitation, to the dispersion. The polyfunctional amine reacts with isocyanate-terminated polyurethane prepolymers to form a capsular polyurethane-polyurea copolymer wall containing the water-immiscible material.

The water-immiscible material, which is the material to be encapsulated, can be clomazone, abamectin, pendimethalin, lambda cyhalothrin, spinosad, emamectin benzoate, deltamethrin, cypermethrin, acetochlor, alachlor, metolachlor and the mixture thereof. The material to be encapsulated can be a combination of two or more various types of water-immiscible materials. The combination can be a herbicide with another herbicide; a herbicide with an insecticide; a herbicide with a fungicide; or a herbicide with a nematicide. The combination can also be any pesticides (for example herbicide) with an inactive ingredient (for example, a solvent or adjuvant).

The organic solvents can be xylene and chlorobenzene.

The isocyanate-terminated polyurethane prepolymers can be prepared by reacting a molar excess of organic polyisocyanate with one or more polyols.

The organic polyisocyanate can be either aliphatic, cycloaliphatic, araliphatic or aromatic. Suitable organic polyisocyanates include meta-phenylene diisocyanate, paraphenylene diisocyanate, 2,4'-diphenylmethane diisocyanate, benzidine diisocyanate, naphthalene-1,5-diisocyanate, hexamethylene diisocyanate, 4,4'4"-triphenylmethane triisocyanate, decamethylene diisocyanate, poly phenylmethylene polyisocyanates that are produced by phosgenation of aniline/formaldehyde condensation products, dianisidine diisocyanate, xylylene diisocyanate, bis(2-isocyanatoethyl)fumarate, bis(2-isocyanatoethyl)cyclohex-4-ene-1,2-dicarboxylate, bis(2-isocyanatoethyl)carbonate, and many other organic polyisocyanates known in the art, which as those disclosed by Siefken, Annalen, 565, 122-135 (1949).

In producing the isocyanate-terminated polyurethane prepolymers of the present invention, one or more polyhydroxy compounds or polyols can be employed in the reaction with the organic polyisocyanate.

Illustrative polyhydroxy compounds include the following classes of compounds:

(a) lactone polyols and alkylene oxide adducts thereof;

(b) polyester polyols, and alkylene oxide adducts thereof;

(c) polyoxyalkylene polyols and polyoxycycloalkylene polyols, and alkylene oxide adducts thereof;

(d) non-reducing sugars and sugar derivatives and alkylene oxide adducts thereof;

(e) alkylene oxide adducts of polyphenols;

(f) polytetramethylene glycols;

(g) functional glycerides, such as castor oil;

(h) polyhydroxy polysulfide polymers;

(i) hydroxyl-terminated extended lactone polyesters prepared by phosgenation of a lactone polyester with a polyol such as bisphenol A (BPA), and the like.

The term "alkylene oxide" includes, for example, ethylene oxide, 1,2-epoxypropane, 1,2-epoxybutane, 2,3-epoxybutane, isobutylene oxide,

epichlorohydrin, and the like, and mixtures thereof.

Lactone polyols are prepared by reacting a lactone, such as epsilon-caprolactone or a mixture of epsilon-caprolactone and an alkylene oxide, with a polyfunctional initiator, such as polyhydric alcohol. The term "lactone polyols" also includes various "copolymers", such as lactone copolyesters, lactone polyester/polycarbonates, lactone polyester/polyethers, lactone polyester/polyether/polycarbonates, and the like.

Polyester polyols are esterification products which range from liquids to non-crosslinked solids, *i.e.,* solids which are insoluble in many of the more common inert normally liquid organic media, and which are prepared by the reaction of monocarboxylic acids and/or polycarboxylic acids, their anhydrides, their esters, or their halides, with a stoichiometric excess of a polyol. Illustrative of the polycarboxylic acids which can be employed to prepare the polyester polyols preferably included dicarboxylic acids and tricarboxylic acids, such as maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, chlorendic acid, 1,2,4-butanetricarboxylic acid, phthalic acid, and the like.

Polyoxyalkyene polyols include alkylene oxide adducts of, for example, water, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, gycerol, 1,2,6-hexanetriol, 1,1,1-trimethylol ethane or propane pentaerythritol, sorbitol, sucrose, lactose, alpha-methylglucoside, alpha-hydroxyalkylgluocoside, and the like. Alkylene oxides employed in producing polyoxyalkylene polyols normally have from 2 to 4 carbon atoms. Ethylene oxide, propylene oxide and mixtures of propylene oxide with ethylene oxide are preferred. Such polyalkylene polyols are well known in the art.

Illustrative of the non-reducing sugars and sugar derivatives contemplated are sucrose, the alkyl glucosides such as methylglucoside, ethyl glucoside, and the like; the polyol glucosides such as ethylene glycol glucoside, propylene glycol glucoside, glycerol glucoside, 1,2,6-hexanetriol glucoside, and the like; and the alkylene oxide adducts thereof.

Alkylene oxide adducts of polyphenols include those in which the polyphenol can be bisphenol A (BPA); bisphenol F(BPF); the condensation

products of phenol and formaldehyde, more particularly the novolac resins; the condensation products of various phenolic compounds and acrolein, the simplest members of this class being the 1,1,3-tris(hydrophenyl)propanes; the condensation products of various phenolic compounds and glyoxal, glutaraldehyde, and other dialdehydes, the simplest members of this class being the 1,1,2,2-tetrabis(hydroxyphenyl)ethanes, and the like.

Another useful class of polyols is the polytetramethylene glycols, which are prepared by polymerizing tetrahydrofuran in the presence of the acidic catalyst. Also, useful are castor oil and alkylene oxide adducts of castor oil.

Suitable polyhydroxy polysulfide polymers have the formula:

HO--R--SS(R'SS)n R—OH

wherein R and R' are divalent aliphatic radicals;

wherein the carbon chain may be interrupted by oxygen atoms and n is an integer having a value of from 1 to 100, which can be prepared by reacting a dihalo-organic compound such as Cl--R'--Cl, a chlorohydrin such as Cl—R'--OH and an inorganic polysulfide.

The polyol or polyol mixture employed can have hydroxyl numbers which vary over a wide range. In general, the hydroxyl numbers of the polyols employed in the invention can range from about 20, and lower, to about 1000, and higher, preferably, from about 30 to about 800, and more preferably from about 35 to about 700. The hydroxyl number is defined as the number of milligrams of potassium hydroxide required for the complete neutralization of the hydrolysis product of the fully acetylated derivative prepared from 1 gram of polyol. The hydroxyl number can also be defined by the equation:

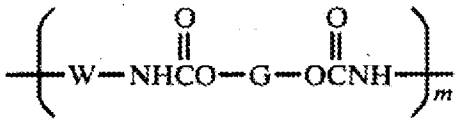
$$\mathrm{OH} = \frac{56.1 \times 1000 \times f}{\mathrm{M.W.}}$$

Where, OH is the hydroxy number of the polyol; *f* is the average functionality, this is average number of hydroxyl groups per molecule of polyol; and M.W. is the average molecular weight of the polyol.

The most preferred polyisocyanates are alkylene diisocyanates and aromatic diisocyanates, especially polymethylene polyphenyl isocyanates

(PMPPI), while the most preferred polyols are the diols of polyalkylene glycols and the diols of polycaprolactones.

As pointed out above to prepare the isocyanate terminated polyurethane prepolymers useful in this invention, at least a slight mole excess of --NCO equivalents (groups) with respect to the hydroxyl equivalents (groups) is employed to end-block the polymer chain with isocyanate groups. Of course, it should be understood that as well as employing a single type of polyisocyanate compound and a single type of polyol compound mixtures of various isocyanates as well as mixtures of various polyols may be used if desired. Furthermore, it should also be clear that the backbone of the isocyanate terminated prepolymers comprises at least one unit and more preferably repeating units of the formula



wherein G represents the residue on removal of the terminal OH groups from the hydroxy terminal polyol employed; wherein W represents a divalent hydrocarbon radical and wherein m is an integer of at least one. Thus, the backbone of said prepolymers are essentially free from other types of repeating units such as urea and the like.

For purposes of the present invention, useful isocyanate-terminated polyurethanes will have a molecular weight that is governed by their intended end use. In solvent-free systems, the polymers should not be too viscous and generally have a molecular weight from 2,000 to about 20,000, preferably from about 4,000 to about 14,000. In solvent systems, viscosity problems can be avoided and molecular weights of the polymers greater than 20,000 can be used provided there is a sufficient concentration of hydrolyzable end groups to form a three-dimensional, cross-linked network upon curing. Where a solvent is employed, it should be inert with respect to the polymer and volatile under the curing conditions.

The polyfunctional amines suitable for use in the present invention are those amines which are capable of reacting with isocyanate-terminated

polyurethane prepolymers to form polyurethane-polyurea copolymer wall. The polyfunctional amines should be water-soluble per se or in water soluble salt form. The usable polyfunctional amines can be selected from a wide range of such materials. Suitable examples of polyfunctional amines which may be used in this invention include, but are by no means limited to the following: ethylenediamine, propylenediamine, isopropylenediamine, hexamethylenediamine, toluenediamine, ethenediamine, triethylenetetraamine, tetraethylenepentamine, pentaethylenehexamine, diethylenetriamine, bis-hexamethylenetriamine and the like. The amines may be used alone or in combination with each other, preferably in combination with 1,6-hexamethylenediamine (HMDA). 1,6-hexamethylenediamine is preferred for use in the process of the present invention.

Isocyanate-terminated polyurethane prepolymers and the polyfunctional amine form the wall which ultimately encapsulates the water-immiscible material. The wall content of the capsules formed by the present process may vary from about 5% to about 30%, preferably 8% to 20% and more particularly, 10% by weight, of the water-immiscible material.

The amount of isocyanate-terminated polyurethane prepolymers and polyfunctional amine used in the process is determined by the percent wall content produced. Generally, there will be present in the reaction, from about 3.5% to about 21.0% isocyanate-terminated polyurethane prepolymers and from about 1.5% to about 9.0% amine, relative to the weight of the water-immiscible material. Preferably, there will be from about 5.6% to about 13.9% isocyanate-terminated polyurethane prepolymers and from about 2.4% to about 6.1% amine and more particularly, 7.0% isocyanate-terminated polyurethane prepolymers and 3.0% amine relative to the weight of the water-immiscible material, present in the reaction. Although a stoichiometric amount of polyfunctional amine relative to the amount of isocyanate-terminated polyurethane prepolymers has been used herein, it should be recognized that excess polyfunctional amine may be used without departing from the spirit or scope of the present invention.

The emulsifying agents, being generally referred to herein as emulsifiers, which are critical for use in the practice of the present invention are

the salts of lignin sulfonate, *e.g.,* sodium, potassium, magnesium, calcium or ammonium salts. In the practice of the process of the present invention, the sodium salt of lignin sulfonate is the preferred emulsifier. Any commercially available emulsifier of the type previously described which does not contain added surfactant, may be conveniently employed and many are described in McCutcheon's Detergents and Emulsifier's, North American Edition 1978 (McCutcheon Div., MC Publishing Co., Glen Rock, N.J.). Commercially available emulsifiers which may be mentioned are: Treax®, LTS, LTK and LTM, respectively, potassium, magnesium and sodium salts of lignosulfonate (50% aqueous solutions), Scott Paper Co., Forest Chemical Products; Marasperse CR® and Marasperse CBOS-3®, sodium lignosulfonate, American Can Co.; Polyfon O®, Polyfon T®, Reax 88B®, Reax 85B®, sodium salts of lignin sulfonate and Reax C-21®, calcium salt of lignin sulfonate, Westvaco Polychemicals, Emulsogen® EL360.

Concentration of emulsifier should vary from about 0.1% to about 15% and preferably from about 0.5% to about 6%, based on the weight of the water-immiscible material. Sodium lignosulfonate emulsifier is preferentially employed at a concentration of 0.5% relative to the weight of the water-immiscible material. Higher concentrations of emulsifier may be used without increased ease of dispersability.

The microcapsules of the present invention require no additional treatment such as separation from the aqueous liquid, but may be directly utilized or combined with, e.g., liquid fertilizers, insecticides or the like to form aqueous solutions which may be conveniently applied in agricultural uses. Most often it is most convenient to bottle or can the aqueous suspension containing the encapsulated water-immiscible material, in which case, it may be desirable to add formulation ingredients to the finished aqueous solution of microcapsules. Formulation ingredients such as thickeners, biocides, surfactants, dispersants, salts, anti-freezing agents and the like can be added to improve stability and ease of application.

The process of the present invention is capable of satisfactory performance and production of encapsulated material without adjustment to a specific pH value. That is, no adjustment of the pH of the system need be

made during the encapsulation process. If it is desired to adjust the pH of the finished microcapsule formulation, as, for example, when the aqueous solution of finished microcapsule is combined with other herbicides, pesticides, etc., conventional cooperating reagents or additions for adjustment of acidity or alkalinity, or like characteristics, may be used, e.g., such substances as hydrochloric acid, sodium hydroxide, sodium carbonate, sodium bicarbonate and the like.

The agitation employed to establish the dispersion of water-immiscible phase droplets in the aqueous phase may be supplied by any means capable of providing suitably high shear, that is, any variable shear mixing apparatus (e.g., blender) can be usefully employed to provide the desired agitation.

The desired condensation reaction at the interface between the water-immiscible phase droplets and the aqueous phase occurs very rapidly and complete within minutes. That is, the formation of the polyurethane-polyurea copolymer capsule wall has been completed, thereby encapsulating the water-immiscible material within a wall of polyurethane-polyurea copolymer and there exists a useable encapsulated product suspended in the aqueous phase.

The particle size of the microcapsules can be ranged from about 1 micron to about 100 microns in diameter. In general, the smaller the particle size the better. The particle size of from about 1 to about 10 microns is the optimum range. The particle size of from about 5 to about 50 microns can obtain a satisfactory formulation.

The particle size is controlled by the emulsifier used and the degree of agitation employed. One convenient manner of controlling the size of the microcapsules is by adjusting the speed of agitation employed, which is supplied to form the dispersion of the water-immiscible phase droplets in the aqueous phase. The greater the speed of agitation at this stage, the smaller the capsules would be obtained. Control of capsule size by adjustment of the rate of agitation is well known in the art.

In order that the concept of the present invention may be more completely understood, the following examples are set forth in which all parts

are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation in the present case.

EXAMPLE 1

General Procedure

An isocyanate-terminated polyurethane prepolymers was prepared from polymethylene polyphenylisocyanate (PMPPI), a polyoxypropylene glycol of OH Number 56 (Union Carbide NIAX Polyol PPG-2025) and a polyoxypropylene triol of OH Number 42 (Union Carbide NIAX Polyol LHT-42). The molar ratio of diol to triol was 2/1 and enough excess PMPPI was used to give an oligomer with 1.8 wt.% NCO. polyurethane-polyurea copolymer was formed by adding polyfunctional amine.

Prepolymer Synthesis Procedure

The following procedure was emphasized to prepare the prepolymer. Prior to use, the polyols were dried under vacuum for four hours at 50°C., cooled, and stored under dry nitrogen.

A five liter, three-neck, round bottom reaction flask equipped with a stirrer and heating mantle, and continuously purged with dry nitrogen, was charged with the following ingredients in the order listed:

Polyoxypropylene glycol (OH No. 56) (PPG 2025)	2000 g
Polymethylene polyphenyl isocyanate (PMPPI)	396.8 g
Stannous octoate catalyst	0.03 g

The mixture was heated for four hours at 60°C under continuous agitation. After the initial 4 hour reaction period, 1327g of LHT 240 triol and 0.03 grams of stannous octoate were added. The temperature was maintained at 60°C until the NCO concentration was about 1.8% by weight. This typically took about 16 to 20 hours.

The isocyanate content of the polyurethane was determined by the di-n-butyl amine method using bromocresol green indicator.

The resulting isocyanate-terminated prepolymer, having an NCO content of 1.78% by weight, was cooled to about 25°C and placed in a low humidity chamber.

EXAMPLE 2

200 g of technical clomaznoe containing 13.9 g of isocyanate-terminated polyurethane prepolymers (from example 1) was emulsified into 141.3 g of water containing 4.0 g of Emulsogen® EL360. Technical clomazone and isocyanate-terminated polyurethane prepolymers were maintained at 50°C; the aqueous solution containing the sodium lignosulfonate emulsifier was at 50°C. The emulsion was formed with a Waring® blender operated at high shear. To the emulsion was added 15.1 g of 40% HMDA with concurrent reduction of shear. After 20 minutes, 132.0 g of ammonium sulfate was added and the formulation was bottled. The particle size of the resulting microcapsules ranged from 1 to 10 microns in diameter. The resulting formulation contains 500 g of encapsulated technical clomazone per liter of aqueous solution.

EXAMPLE 3

200g of technical lambda cyhalothrin maintained at 50°C, containing 15.0g of isocyanate terminated polyurethane prepolymers (from example 1) was poured into 168.0g of water containing 3.8g of Emulsogen® EL360 emulsifier. An emulsion was formed in a square beaker utilizing a Brinkman Polytron® Homogenizer, at high shear (the temperature inside the beaker rose to 60° C as a result of the shear rate). To the emulsion was added 20.0 g of 35% HMDA with simultaneous reduction of shear to a slow rate. The resulting formulation contained 527g of encapsulated technical abamectin per liter of aqueous solution. The resulting microcapsules were 1-10 microns in diameter, particle size. About 20% liquid layer occurred with time but was re-suspended with gentle shaking.

EXAMPLE 4

200.0g of technical abamactin containing 15.0g of isocyanate terminated polyurethane prepolymers (from example 1) was emulsified into 155.9 g of water containing 3.8g of Emulsogen® EL360. Technical abamectin and isocyanate-terminated polyurethane prepolymers (from example 1) were maintained at 50°C; the aqueous solution containing the sodium lignosulfonate emulsifier was at room temperature. The emulsion was formed with a Waring® blender operated at high shear. To the emulsion was added 16.5g of 40% HMDA with concurrent reduction of shear. After 20 minutes, 17.1g of ethylene glycol was added and the formulation was bottled. Settling occurred with time but gentle agitation fully re-suspended the settled layer. Only a trace of material greater than 45 microns was observed when the formulation was passed through a 325 mesh screen (45 micron opening).

The procedure of Example 2 was repeated using various lignin sulfonate emulsifiers in place of Emulsogen® EL360 ; the lignin sulfonate emulsifiers were: Reax 85A®, Reax C-21®, Marasperse CB®, Polyfon H®, Polyfon O®, Polyfon T®, Reax 84A and Marasperse CBOS-3®.

EXAMPLE 5

All starting materials and the Waring® blender cups were maintained at 70°C. 100.0g of technical emamectin benzoate (96.6%) containing 7.5g of isocyanate-terminated polyurethane prepolymers (from example 1) was emulsified into 96.6 g of water containing 2.0 g of Emulsogen® EL360 using a Waring® blender operating at high shear. To the emulsion was added 9.3 g of 35.8% HMDA with concurrent reduction of shear. Capsules ranging from 1 to 60 microns in diameter, with the majority being 1 to 20 microns, were produced.

EXAMPLE 6

100.0g of technical spinosad (90%) containing 7.5g of isocyanate terminated polyurethane prepolymers (from example 1) was emulsified into 152.4 g of

water containing 2.0g of Emulsogen® EL360 emulsifier using high shear. To the emulsion was added 9.3 g of 35.8% HMDA with concurrent reduction of shear. Spherical and irregularly-shaped particles ranging in size of from 1 to 30 microns in diameter, with the majority being 1-20 microns, were observed.

Claims

1. A microcapsules polymer wall material comprising crosslinked polyurethane–polyurea co-polymer.

2. The microcapsules polymer wall material according to claim 1, wherein the crosslinked polyurethane–polyurea copolymer is formed by reacting isocyanate-terminated polyurethane prepolymers with polyfunctional amine.

3. The microcapsules polymer wall material according to claim 2, wherein the isocyanate-terminated polyurethane prepolymers are prepared by reacting a molar excess of organic polyisocyanate with one or more polyols.

4. The microcapsules polymer wall material according to claim 3, wherein the organic polyisocyanate is aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanate, preferably alkylene diisocyanates and aromatic diisocyanates, especially polymethylene polyphenyl isocyanates.

5. The microcapsules polymer wall material according to claim 3, wherein the organic polyisocyanate is selected from the group consisting of meta-phenylene diisocyanate, paraphenylene diisocyanate, 2,4'-diphenylmethane diisocyanate, benzidine diisocyanate, naphthalene-1,5-diisocyanate, hexamethylene diisocyanate, 4,4'4"-triphenylmethane triisocyanate, decamethylene diisocyanate, poly phenylmethylene polyisocyanates that are produced by phosgenation of aniline/formaldehyde condensation products, dianisidine diisocyanate, xylylene diisocyanate, bis(2-isocyanatoethyl)fumarate, bis(2-isocyanatoethyl)cyclohex-4-ene-1,2-dicarboxylate, bis(2-isocyanatoethyl)carbonate and the like.

6. The microcapsules polymer wall material according to claim 3, wherein the polyols are selected from lactone polyols and alkylene oxide adducts thereof; the polyester polyols, and alkylene oxide adducts thereof; polyoxyalkylene polyols and polyoxycycloalkylene polyols, and alkylene oxide adducts thereof; non-reducing sugars and sugar derivatives and alkylene oxide adducts thereof; alkylene oxide adducts of polyphenols;

polytetramethylene glycols; functional glycerides, such as castor oil; polyhydroxy polysulfide polymers; hydroxyl terminated extended lactone polyesters prepared by phosgenation a lactone polyester with a polyol such as bisphenol A (BPA); preferably, the diols of polyalkylene glycols and the diols of polycaprolactones.

7. The microcapsules polymer wall material according to claim 2, wherein the polyfunctional amines are those amines which are capable of reacting with isocyanate-terminated polyurethane prepolymers to form polyurethane- polyurea copolymer, preferably, ethylenediamine, propylenediamine, isopropylenediamine, hexamethylenediamine, toluenediamine, ethenediamine, triethylenetetraamine, tetraethylenepentamine, pentaethylenehexamine, diethylenetriamine, bis-hexamethylenetriamine, most preferably 1,6-hexamethylenediamine.

8. A composition comprising a water-immiscible and/or highly volatile material encapsulated within a microcapsule having a wall comprising the microcapsules polymer wall material according to any of claims 1-7.

9. The composition according to claim 8, the water-immiscible and/or highly volatile material is selected from clomazone, abamectin, pendimethalin, lambda cyhalothrin, spinosad, emamectin benzoate, deltamethrin, cypermethrin, acetochlor, alachlor, metolachlor and combinations thereof.

10. The composition according to claim 8, the water-immiscible and/or highly volatile material is clomazone.

11. The composition according to any of claims 8-10, the content of the microcapsules polymer wall material is about 5% to about 30%, preferably 8% to 20% and more particularly, 10% by weight, of the water-immiscible and/or highly volatile material.

12. The composition according to any of claims 8-11, the particle size of the microcapsules is ranged from about 1 micron to about 100 microns in diameter.

13. The composition according to any of claims 8-12, wherein the composition comprises one or more thickeners, one or more biocides, one or more surfactants, one or more dispersants, one or more salts, one or more

anti-freezing agents.

14. A method of controlling plant growth at a locus, comprising applying to the locus a composition according to any of claims 8-13.

15. A use of the composition according to any of claims 8-13 in the control of unwanted plant growth.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2016/095618

A. CLASSIFICATION OF SUBJECT MATTER

B01J 13/16(2006.01)i; B01J 13/02(2006.01)i; A01N 25/28(2006.01)i; C08G 18/10(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J13/02;B01J13/16; A01N25/28;C08G18/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,WPI,EPODOC,CNKI:immiscible, urea, polyurea, polyurethane, microcapsul+, prepolymer?, herbicide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1400203 A (FUJI PHOTO FILM CO. LTD.) 16 July 1975 (1975-07-16) claims 1 and 3-4; description, page 1, lines 19-25; page 2, lines 77-81; page 3, lines 26-78 and 115-120; page 4, lines 8-14 and 50-54	1-8, 11-12
Y	GB 1400203 A (FUJI PHOTO FILM CO. LTD.) 16 July 1975 (1975-07-16) claims 1 and 3-4; description, page 1, lines 19-25; page 2, lines 77-81; page 3, lines 26-78 and 115-120; page 4, lines 8-14 and 50-54	9-10, 13-15
Y	US 2012220456 A1 (CASAÑA GINER VICTOR, ET AL.) 30 August 2012 (2012-08-30) claim 1; description, paragraph [0023]	9-10, 13-15
X	CN 105076129 A (GUANGDONG HUARUN PAINTS CO. LTD.) 25 November 2015 (2015-11-25) description, example 2; paragraphs [0046]-[0056]	1-15
X	CN 101688812 A (FUJI PHOTO FILM CO. LTD.) 31 March 2010 (2010-03-31) description, example 1	1-8, 11-13
X	US 4409201 A (HOECHST AKTIENGESELLSCHAFT) 11 October 1983 (1983-10-11) claims 1-18	1-15

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 March 2017	**20 April 2017**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China**	**HUANG,Junsheng**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)82246774**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2016/095618

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
GB 1400203 A	16 July 1975	US 4021595 A	03 May 1977
		US 3886085 A	27 May 1975
		DE 2242910 A1	15 March 1973
US 2012220456 A1	30 August 2012	CN 102548413 A	04 July 2012
		US 9320270 B2	26 April 2016
		AR 080604 A1	25 April 2012
		WO 2011015220 A1	10 February 2011
		ZA 201201047 B	31 October 2012
		EP 2461689 A1	13 June 2012
		MX 2012001635 A	20 April 2012
		US 2014010854 A1	09 January 2014
		US 9295249 B2	29 March 2016
CN 105076129 A	25 November 2015	None	
CN 101688812 A	31 March 2010	CN 101688812 B	09 November 2011
		JP 2009014674 A	22 January 2009
		US 8314050 B2	20 November 2012
		WO 2009008269 A1	15 January 2009
		US 2010323188 A1	23 December 2010
		TW 200906642 A	16 February 2009
		TW I370772 B	21 August 2012
		KR 20100054796 A	25 May 2010
		JP 4986749 B2	25 July 2012
		KR 101497737 B1	02 March 2015
US 4409201 A	11 October 1983	IL 62994 A	31 December 1984
		EP 0041210 B1	09 January 1985
		DE 3020781 A1	10 December 1981
		AR 229837 A1	30 December 1983
		PH 17491 A	04 September 1984
		CA 1180608 A	08 January 1985
		IL 62994 D0	31 July 1981
		DE 3020781 C2	18 November 1982
		AU 7116381 A	10 December 1981
		JP S5721932 A	04 February 1982
		PT 73107 A	01 June 1981
		PT 73107 B	21 October 1982
		AU 540890 B2	06 December 1984
		ES 502509 D0	01 April 1982
		DD 159147 A5	23 February 1983
		EP 0041210 A1	09 December 1981
		TR 21304 A	22 March 1984
		NZ 197236 A	12 April 1983
		ZA 8103611 B	30 June 1982
		ZA 8103611 A	30 June 1982
		ES 8203233 A1	01 July 1982
		BR 8103370 A	16 February 1982