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(54) Title: AGROCHEMICAL FORMULATION, METHOD FOR ITS PREPARATION AND USE THEREOF

(57) Abstract: A composition comprising microencapsulated clomazone is provided, the clomazone being contained within microcapsules having a microcapsule wall formed by the coacervation of a plurality of amphoteric polymer electrolytes. In particular, the microcapsules wall is formed from a cellulose derivative, for example carboxymethyl cellulose,a natural gum, for example gum arabic, and gelatin. The microcapsule wall preferably comprises a cross- linking agent, in particular a glycoluril resin. A method for encapsulating comazone by coacervation is also provided.

AGROCHEMICAL FORMULATION, METHOD FOR ITS PREPARATION AND USE THEREOF

The present invention relates to an agrochemical formulation, in particular to a formulation comprising a microencapsulated active ingredient, especially to a formulation comprising microencapsulated clomazone. The present invention further relates to a method of preparing such a formulation and to its use.

It is known formulate agrochemical products in a range of different manners. One method employed is to microencapsulate one or more active ingredients, with the active ingredients held within microcapsules formed of a polymer wall. The microcapsules may be further formulated, for example suspending the microcapsules in a suitable carrier liquid, for application to the locus to be treated.

One such active ingredient that is known to be formulated in this manner is clomazone. Clomazone, (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone) is a well-known for controlling soybean, cotton, cassava, corn, rapeseed, sugar cane, tobacco and other crops. Clomazone has a strong inhibitory effect on the growth of such plants as barnyard grass, green foxtail, crabgrass, Solanum nigrum, Elsholtzia water spine needle, Thlaspi arvense, willow thorn smartweed, cocklebur, pigweed,wild watermelon seedlings, wolf grass and other annual grass and broadleaf weeds, perennial Cephalanoplos Daji, horsetail, Sonchus Caideng.

Currently, the commercially available Clomazone formulation is an emulsion concentrate (EC), with a number of disadvantages. First, the formulation contains significant amounts of organic solvents, such as toluene or xylene. The application of such solvents to plants being treated is both a waste and is harmful to the environment. Second, clomazone has a relatively

high vapour pressure, resulting in high rates of application being required to realize effective plant control, in turn leading to higher costs. Third, as a consequence of its high vapour pressure, clomazone tends to drift from the locus of application, causing damage to crops or other plants in adjacent areas. In particular, the drift of clomazone droplets or vapour is phytotoxic to sensitive plants. Avoiding such drift requires vary careful and accurate spraying techniques, which are difficult to employ. For example, spraying must employ low pressures, use larger amounts of water, be limited to low wind conditions, be limited to certain directions of prevailing wind, and be repeated, for example twice in a day. Particularly sensitive crops, such as fruit trees and vegetables, cannot be subjected to aerial spraying.

The microencapsulation of clomazone can be used to address and overcome the aforementioned drawbacks of the EC formulations. As noted, such microencapsulation is known in the art.

For example, CN 1491540 relates to a method to produce a microencapsulated clomazone herbicide composition employing interfacial polymerization. The microcapsules are formed with a shell of polyethylene to reduce clomazone volatility. However, the preparation process is very complicated and the reaction time is very long. Further, the resulting wall material of the microcapsules is slow to degrade and has a high persistency once applied.

The microencapsulation of agrochemically active components is described in EP 1 840 145, in particular the microencapsulation and formulation of clomazone. The microencapsulation process disclosed in EP 1 840 145 comprises forming an oil phase comprising an aliphatic isocyanate monomer, for example tetramethyl-m-xylylene diisocyanate (TMXDI), an aromatic isocyanate prepolymer, for example polymethylene polyphenyl isocyanate (PAPI), an acetylene carbamide monomer, for example tetra-

butoxymethyl acetylene carbamide, an active ingredient, one or more solvents and other components, such as antioxidants and the like. The oil phase is dispersed in an aqueous phase, to form an emulsion. The aqueous phase comprises water, with one or more surfactants, one or more water soluble polymers, such as polyvinylpyrrolidone, one or more gums and the like. Polymerisation of the isocyanate and acetylene carbamide components is induced by heating the dispersion, whereby a polymer shell is formed at the interface of the dispersed organic phase and the aqueous phase.

An improved formulation for the microencapsulation of compounds, such as clomazone has now been found.

In particular, it has been found that clomazone may be encapsulated in microcapsules having a wall formed from amphoteric polymer electrolytes, more particularly by a process of coacervation. In preferred embodiments, the microcapsules are formed from the coacervation of cellulose derivatives, such as sodium carboxymethyl cellulose, natural gums, such as gum arabic, and gelatin. The microcapsules may be further formulated in known manners, for example as a suspension in water, for subsequent application and use.

Accordingly, in a first aspect, the present invention provides a composition comprising microencapsulated clomazone, the clomazone being contained within microcapsules having a microcapsule wall formed by the coacervation of a plurality of amphoteric polymer electrolytes.

In a further aspect, the present invention provides a composition comprising microencapsulated clomazone, the clomazone being contained within microcapsules having a microcapsule wall formed from a cellulose derivative, a natural gum and gelatin.

The composition of the present invention comprises microcapsules having a wall formed from a material that is very low in toxicity and is biodegradable. The composition is highly stable and allows the release rate of the clomazone active ingredient to be accurately controlled. As a result, the potential for the active ingredient to drift from the locus of application is reduced, resulting in the composition having a low environmental impact. Overall, the composition is relatively inexpensive and simple to prepare.

As described in more detail below, the composition of the present invention may be prepared by coacervation techniques.

The composition of the present invention comprises clomazone contained within microcapsules. Clomazone may be present in the composition in an amount of from 0.5 to 25% by weight of the microcapsules, more preferably from 1.0 to 20.0 %, still more preferably from 1.5 to 15% by weight of the mircrocapsules.

The composition of the present invention comprises microcapsules having a wall comprising a cellulose derivative, a natural gum and gelatin.

The cellulose derivative may be any suitable derivative of cellulose. Preferred derivatives are cellulosic gums, in particular carboxyalkyl cellulose. A particularly preferred cellulosic gum is carboxymethyl cellulose. The cellulose derivative is preferably present as a salt, more preferably a metal, in particular a salt of a metal from Group I or Group II of the Periodic Table, with Group I metal salts being particularly preferred. Sodium salts are particularly preferred. An especially preferred cellulosic gum for use in forming the microcapsules is sodium carboxymethyl cellulose.

The cellulose derivatives for use in forming the microcapsules of the composition are known in the art and either available commercially or prepared by techniques known in the art.

The cellulose derivative may be present in the microcapsule wall in an amount of from 1 to 30% by weight, more preferably from 2 to 25%, still more preferably from 2.5 to 20% by weight. An amount in the range of from 2.5 to 17.5% is particularly preferred.

The wall of the micrcapsules further comprises a natural gum. Natural gums may be extracted from plants or prepared by microbial fermentation, as is known in the art. Suitable natural gums are known in the art and are commercially available. The natural gum is most preferably a polyelectrolyte. Preferred gums include gum arabic, gum ghatti, gum tragacanth and karaya gum. A particularly preferred natural gum is gum arabic.

The natural gum may be present in the wall of microcapsules in an amount of from 5 to 75% by weight, more preferably from 7.5 to 70%, still more preferably from 10 to 65% by weight. An amount in the range of from 10 to 60% is particularly preferred.

The wall of the microcapsules of the present invention also further comprises gelatin. Gelatin is well known in the art and is commercially available.

Gelatin may be present in the microcapsule wall in an amount of from 5 to 90% by weight, more preferably from 10 to 90%, still more preferably from 12 to 85% by weight.

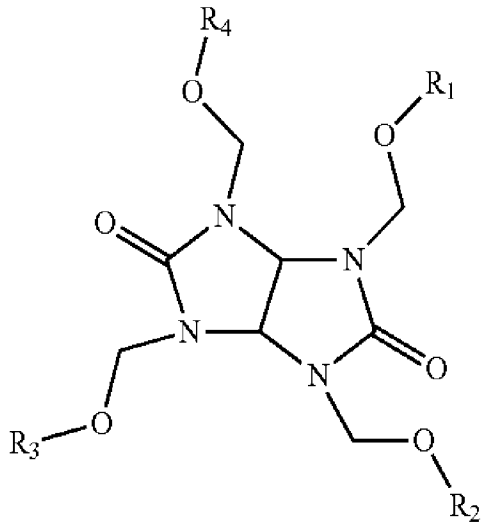
The microcapsules of the composition of the present invention are formed from a cellulose derivative, a natural gum and gelatin, as discussed

hereinbefore. In order to increase the strength of the microcapsules, the material of the microcapsule wall may further comprise a cross-linking agent. A preferred cross-linking agent is a glycoluril resin.

The glycoluril resin may be generated from the condensation reaction of glycoluril and an aldehyde. Suitable aldehydes are known in the art and include, for example, formaldehyde, paraformaldehyde, acetaldehyde, butyraldehyde, paraldehyde, glyoxal, furfuraldehyde, propinonaldehyde, benzaldehyde, and mixtures thereof. Preferred embodiments of the present invention are those that employ a glycoluril resin prepared from formaldehyde, acetaldehyde, and butyraldehyde as the cross-linking agent for the wall material of the microcapsules.

Examples of suitable glycoluril resins suitable for use in the present invention include highly alkylated/alkoxylated, partially alkylated/alkoxylated, or mixed alkylated/alkoxylated glycoluril resins. More specifically, the glycoluril resin may be methylated, n-butylated, or isobutylated.

Alkoxylated glycoluril resins suitable for use in the present invention are known in the art, for example from US 2011/026903, and may be represented by the following formula (I):



wherein R_1, R_2, R_3, and R_4 each independently represents a hydrogen atom or an alkyl group. Preferred compounds of Formula (I) in which R_1, R_2, R_3, and R_4 each independently represents an alkyl group are those in which the alkyl group has from 1 to 12 carbon atoms, more preferably from 1 to 8 carbon atoms, still more preferably from 1 to 6 carbon atoms, most preferably from 1 to 4 carbon atoms. R_1, R_2, R_3, and R_4 may reach represent the same or different alkyl groups. The alkyl groups may be straight chain or branched.

Specific examples of commercially available glycoluril resins include CYMEL® 1170, 1171 and 1172. CYMEL® glycoluril resins are commercially available from CYTEC Industries, Inc.

The substantially fully mixed-alkylated acetylene carbamide derivatives and substantially fully methylolated acetylene carbamide derivatives are a new class of cross-linking agents, the starting material of which is acetylene carbamide, also known as acetylene diurea or glycoluril. Acetylene carbamide is prepared by reacting two moles of urea with one mole of glyoxal.

The precise chemical name for acetylene carbamide is tetrahydroimidazo-(4, 5-d) imidazole 2, 5(1H, 3H)-dione. Acetylene carbamide may be fully methylolated by reacting one mole of acetylene carbamide with four moles of formaldehyde. The resulting product is identified as tetramethylol acetylene carbamide. Tetramethylol acetylene carbamide may then be reacted with a selected amount of methanol so as to partially methylate the fully methylolated acetylene carbamide, which procedure may then be followed by alkylation with a higher aliphatic monohydric alcohol, for example containing from 2 to 4 carbon atoms. The monohydric alcohols may be primary or secondary alcohols. Examples of suitable higher monohydric aliphatic alcohols include ethanol, n-propanol, isopropanol, n-butanol, isobutanol and the like. It may be advantageous to fully methylate the tetramethylol acetylene carbamide and then, by use of a transetherification reaction, incorporate the desired measure of ethanol, propanol or butanol into the acetylene carbamide derivative.

The fully etherified, fully methylolated acetylene carbamide derivatives are not generally considered to be resinous materials since they are, as individual entities, simple pure compounds or mixtures of simple pure compounds. However, they are potentially resin-forming compounds, which react with certain ionic water-dispersible, non-gelled polymeric materials when subjected to heat, more particularly when subjected to heat under acidic conditions.

The concept of the average degree of methylation, or more broadly alkylation, and the concept of the average degree of methylolation will be discussed hereinbelow in order that this concept may be fully understood.

Theoretically, it is possible to methylolate acetylene carbamide fully, that is, to produce tetramethylol acetylene carbamide. However, frequently, analysis of a commercial composition purporting to be tetramethylol acetylene carbamide shows a fractional degree of methylolation, that is an average

degree of methylolation of less that 4.0. It is well recognized that fractional methylolation of a given molecule is not considered possible. As a consequence, when a composition displays on analysis a degree of methylolation of 3.70, 3.80, or 3.90, it has to be recognized that this is an average degree of methylolation of the acetylene carbamide compound and indicates that the aforementioned methylol composition is composed of a mixture of a major amount of tetramethylol acetylene carbamide with minor amounts of trimethylol acetylene carbamide and, perhaps, lesser amounts, including traces, of such derivatives as dimethylol acetylene carbamide and/or monomethylol acetylene carbamide. The same concept of averages is also applicable to the alkylation or etherification of the tetramethylol acetylene carbamide composition. As a consequence, when analysis of a given composition shows that the degree of methylation, for example, is, on average, between about 0.9 and 3.60 and that the higher alkylation has an average degree of ethylation, propylation and/or butylation, between about 2.80 and 0.40, it must be concluded that there is present in such a composition a plurality of the mixed ethers of the tetramethylol acetylene carbamide. For example, the composition may contain monomethyl ether, triethyl ether of tetramethylol acetylene carbamide; dimethyl ether, diethyl ether of tetramethylol acetylene carbamide; or trimethyl ether, monoethyl ether of tetramethylol acetylene carbamide. There may also be traces of the tetramethyl ether of tetramethylol acetylene carbamide present. There may also be present with the varying methyl ethers of tetramethylol acetylene carbamide varying mono, di and tri ethyl ethers, mono, di and tri propyl ethers and mono, di and tri butyl ethers of tetramethylol acetylene carbamide. It is possible to produce a monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether of tetramethylol acetylene carbamide which could be classed as a tetramixed-alkylated derivative. It is generally preferred, however, to make use of only one higher monohydric alcohol containing from 2 to 4 carbon atoms with the methyl alcohol in making a mixed full ether of the tetramethylol acetylene carbamide. The dimixed-alkylated products are

therefore preferred. However, the trimixed-alkylated derivatives as well as the tetramixed-alkylated derivatives may also be employed.

The cross-linking agent may be present in the microcapsule wall in an amount of from 5 to 90% by weight, more preferably from 10 to 90%, still more preferably from 12 to 85% by weight.

The weight ratio of the cellulose derivative to the natural gum in the material of the microcapsule wall is preferably in the range of from 0.075 to 0.75, more preferably from 0.1 to 0.65. The weight ratio of the cellulose derivative to gelatin is preferably from 0.075 to 0.6, still more preferably from 0.08 to 0.5. The weight ratio of the cellulose derivative to the cross-linking agent is preferably from 0.075 to 0.6, still more preferably from 0.08 to 0.5. The weight ratio of the natural gum to the gelatin is preferably in the range of from 0.25 to 3.0, more preferably from 0.3 to 2.0. The weight ratio of the natural gum to the cross-linking agent is preferably in the range of from 0.25 to 3.0, more preferably from 0.3 to 2.0. The weight ratio of the gelatin to the cross-linking agent is preferably in the range of from 0.3 to 3.0, still more preferably from 0.4 to 2.5.

In one embodiment, the wall of the microcapsules comprises the cellulose derivative, natural gum, gelatin and cross linking agent in the weight ratio of 1:4:5:5. In another embodiment, the wall material of the microcapsules comprises the cellulose derivative, natural gum, gelatin and cross linking agent in the weight ratio of 0.4:1.6:2:2.

The microcapsules of the composition contain clomazone as the active ingredient. The proportion of the microcapsules that is clomazone is preferably from 5% to 85%, more preferably from 7.5 to 80%, still more preferably from 9 to 75% by weight.

The compositions of the present invention may include one or more emulsifiers, in particular to facilitate forming an emulsion when the compositions are added to water in a spray tank, prior to application to the locus to be treated. The emulsifiers can be cationic, anionic or nonionic, but are more preferably anionic or nonionic. Examples of particularly suitable anionic surfactants for this purpose are sulfonates such as calcium dodecyl benzenesulfonate. Examples of particularly suitable nonionic surfactants are polyoxyethylated (POE) sorbitan esters such as POE (20) sorbitan trioleate and polyoxyethylated (POE) sorbitol esters such as POE (40) sorbitol hexaoleate. Suitable emulsifiers are known in the art and are commercially available. For example POE (20) sorbitan trioleate is commercially available under the tradename TWEEN 85 marketed by Uniqema. POE (40) sorbitol hexaoleate is commercially available under the tradenames ATLAS G1086 and CIRRASOL G1086 marketed by Uniqema.

The combination of a POE sorbitan ester with a POE sorbitol ester allows the HLB (hydrophilic-lipophilic balance) value of the surfactant to be optimized, so as to obtain the highest quality emulsion (smallest suspended droplets) when the composition is added to water. High quality emulsions typically lead to optimal herbicidal performance. Therefore of particular note for preferred herbicidal performance is a composition of the present invention comprising one or more nonionic surfactants selected from polyoxyethylated (POE) sorbitan esters such as POE (20) sorbitan trioleate and polyoxyethylated (POE) sorbitol esters such as POE (40) sorbitol hexaoleate and mixtures thereof.

The composition of the present invention comprises microcapsules containing clomazone. The clomazone is preferably present in the microcapsules in combination with a liquid carrier, in particular as a solution of clomazone in the liquid carrier. Any suitable liquid carrier may be employed. The liquid carrier of the composition of the present invention preferably

comprises one or more fatty acid esters of an alkanol, more preferably one or more fatty acid esters of C_1 to C_4 alkanols. The fatty acid esters are preferably present in the liquid carrier in an amount of from about 40 to about 99.8% by weight of the liquid carrier.

The fatty acid portions of the fatty acid esters consist of a carboxylate moiety bound to a hydrocarbon chain. Preferred sources for the fatty acids are natural sources, such as seed oil. The fatty acids may be unbranched or branched, but are typically unbranched in natural sources. The hydrocarbon chain can be saturated or unsaturated; preferably the hydrocarbon chain is saturated, that is an alkyl chain, or contains 1 or 2 carbon-carbon double bonds, that is an alkenyl chain. Fatty acid esters formed from fatty acids containing an odd number of carbon atoms, that is an even number of carbon atoms in the hydrocarbon chain, are useful in the compositions of the present invention as well as fatty acid esters formed from fatty acids containing an even number of carbon atoms, that is having an odd number of carbon atoms in the hydrocarbon chain. However, fatty acids obtained from natural sources typically contain an even number of carbon atoms, and therefore esters of fatty acids containing an even number of carbon atoms are preferred for reason of commercial availability and cost. Fatty acid compositions obtained from natural sources, such as seed oils, typically consist of fatty acids having a range of chain lengths and different degrees of unsaturation. Fatty acid ester compositions derived from such fatty acid mixtures are generally useful in the compositions of the present invention without need to first separate the fatty acid esters.

Fatty acids from natural sources contain at least 4 carbon atoms and are limited in general to about 22 carbon atoms. Although esters of lower fatty acids, that is containing as few a 4 carbon atoms, are useful for the present compositions, esters of fatty acids having at least 8, more preferably at least 10, carbon atoms are preferred because of their favorable physical properties,

for example their low volatility. Esters of lower fatty acids can be mixed with esters of higher fatty acids to decrease polarity, water solubility and volatility. As fatty acids obtained from natural sources typically contain 8 to 22 carbon atoms, more typically 10 to 22 carbon atoms, esters of these fatty acids are preferred for reason of commercial availability and cost. The C_{10} to C_{22} fatty acid esters with an even number of carbon atoms are, for example, erucic acid, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. Preferably the one or more fatty esters in the compositions of the present invention comprise at least about 80%, more preferably at least 90%, by weight of esters of fatty acids containing 8 to 22 carbon atoms, preferably 12 to 20 carbon atoms and more preferably 16 to 18 carbon atoms.

Fatty acid compositions obtained from natural sources, for example seed oils, typically consist of fatty acids having a range of chain lengths and different degrees of unsaturation. Fatty acid ester compositions derived from such fatty acid mixtures can be useful in the compositions of the present invention without the need to first separate the fatty acid esters. Suitable fatty acid ester compositions obtained from plants include seed and fruit oils of sunflower, rapeseed, olive, corn, soybean, cotton and linseed. In one preferred embodiment of the composition of the present invention the one or more fatty acid esters comprise fatty acid methyl esters derived from seed oils of sunflower, soybean, cotton or linseed. A particularly preferred embodiment is a composition in which the one or more fatty acid esters comprise fatty acid methyl esters are derived from soybean oil (also known as methylated soybean oil or methyl soyate).

Fatty acid esters of alkanols and methods for their preparation are well known in the art. For example, “biodiesel” typically comprises fatty acid esters of ethanol or more commonly methanol. Two principal routes used to prepare fatty acid alkanol esters are transesterification, starting with another fatty acid ester (often a naturally occurring ester with glycerol), and direct esterification

starting with the fatty acid. A variety of methods are known for these two routes. For example, direct esterification can be accomplished by contacting a fatty acid with an alkanol in the presence of a strong acid catalyst such as sulfuric acid. Transesterification can be accomplished by contacting a starting fatty acid ester with the alcohol in the presence of a strong acid catalyst, such as sulfuric acid, or, more commonly, a strong base, such as sodium hydroxide.

Alkylated seed oils are the transesterification products of seed oils with an alkanol. For example methylated soybean oil, also known as methyl soyate, comprises methyl esters produced by the transesterification of soybean oil with methanol. Methyl soyate thus comprises methyl esters of fatty acids in the approximate molar ratio that the fatty acids occur when esterified with glycerol in soybean seed oil. Alkylated seed oils such as methyl soyate can be distilled to modify the proportion of methyl fatty acid esters.

As noted, the liquid carrier is present together with clomazone within the microcapsules. The ratio of clomazone to the liquid carrier may be from 0.005 to 0.4, more preferably from 0.0075 to 0.3, still more preferably from 0.01 to 0.25.

The composition of the present invention may further comprise one or more stablishers. Suitable stabilizers are known in the art and are commercially available. Lignosufonates are particularly preferred stabilizers for inclusion in the composition of the present invention.

Lignosulfonates have been surprisingly discovered to considerably increase the stability of the microcapsules in mixtures with fatty acid alkanol esters in the compositions of the present invention. The amount of the one or more lignosulfonates in the compositions of the present invention can range from about 0.1 to about 20% by weight of the composition, but for reasons of

cost the amount is preferably no more than about 10%, more preferably no more than about 8%, still more preferably no more than about 6% and most preferably no more than about 5% of the composition by weight. Preferably the one or more lignosulfonates amount to at least about 0.5% of the composition by weight, although lesser amounts down to about 0.1% can be used. More preferably the one or more lignosulfonates amount to at least about 1% of the composition and even more preferably at least about 2% of the composition by weight. The amount of lignosulfonates needed to provide a desired degree of stability depends upon the other components in the composition, and can be determined by simple experimentation.

Lignin, the basic building block of the lignosulfonates is formed in woody plants and is a complex natural polymer with regard to structure and homogeneity. Lignosulfonates are sulfonated plant lignins and are commercially well known co-products of the paper industry. The lignosulfonates of use in the compositions of the present invention may be prepared by a chemical modification of the basic lignin building block using a sulfite pulping process or a kraft pulping (also known as sulfate pulping) process including subsequent sulfonation. These pulping processes are well known in the paper industry. The sulfite pulping process and the kraft pulping process are described in literature published by Lignotech (for example, “Specialty Chemicals for Pesticide Formulations”, October, 1998) and MeadWestvaco Corp (for example, “From the Forests to the Fields”, June, 1998). Crude lignosulfonate preparations typically contain, in addition to sulfonated lignin, other plant derived chemicals such as sugars, sugar acids and resins, as well as inorganic chemicals. Although such crude lignosulfonate preparations can be used for the compositions of the present invention, preferably the crude preparations are first refined to provide higher purity of lignosulfonate. Lignosulfonates within the context of the present disclosure and claims also include lignosulfonates that have been extensively chemically modified. Examples of lignosulfonates that have been extensively

chemically modified are oxylignins in which the lignin has been oxidized in a process reducing the number of sulfonic acid and methoxyl groups and causing rearrangements increasing the number of phenolic and carboxylic acid groups. An example of an oxylignin is VANISPERSE A marketed by Borregaard LignoTech.

Lignosulfonates vary according to cation, degree of sulfonation and average molecular weight. The lignosulfonates for use in the composition of the present invention may contain sodium, calcium, magnesium, zinc, potassium or ammonium cations or mixtures thereof, but preferably contain sodium. The degree of sulfonation is defined as the number of sulfonate groups per 1000 unit molecular weight of lignosulfonate and in commercially available products typically ranges from about 0.5 to about 4.7. The lignosulfonates in the compositions of the present invention preferably contain a degree of sulfonation ranging from about 0.5 to about 3.0. Lignosulfonates containing a degree of sulfonation from about 0.5 to about 3.0 can be prepared by controlled sulfonation in the kraft pulping process. For example, the degree of sulfonation using the kraft pulping process is 2.9 for the commercially available product REAX 88A, 0.8 for REAX 85A and 1.2 for REAX 907. The average molecular weight of commercially available lignosulfonates typically ranges from about 2,000 to about 15,100. The lignosulfonates used in the compositions of the present invention preferably have an average molecular weight above about 2,900.

Examples of commercially available refined lignosulfonate products useful in the compositions of the present invention include, but are not limited to, REAX 88A (sodium salt of a chemically modified low molecular weight kraft lignin polymer solubilized by five sulfonate groups, marketed by MeadWestvaco Corp.), REAX 85A (sodium salt of a chemically modified high molecular weight kraft lignin polymer, marketed by MeadWestvaco Corp.), REAX 907 (sodium salt of a chemically modified high molecular weight kraft

lignin polymer, marketed by MeadWestvaco Corp.), REAX 100M (sodium salt of a chemically modified low molecular weight kraft lignin polymer marketed by MeadWestvaco Corp.) and Kraftspearse DD-5 (sodium salt of a chemically modified high molecular weight kraft lignin polymer, marketed by MeadWestvaco Corp.).

The compositions of the present invention may include as one or more additional formulating ingredients additional surfactants besides lignosulfonates. The properties of these additional surfactants include dispersants and wetting agents. The surfactants can be nonionic or ionic, for example anionic, and can include polymeric moieties such as polyoxyethylation. Suitable surfactants are described in *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, N.J., as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964. Examples of suitable surfactants include polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, polyethoxylated sorbitol fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, N,N-dialkyltaurates, lignin sulfonates, naphthalene sulfonate, formaldehyde condensates, polycarboxylates, glycerol esters, polyoxyethylene/polyoxypropylene block copolymers, and alkylpolyglycosides where the number of glucose units, referred to as degree of polymerization (D.P.), can range from 1 to 3 and the alkyl units can range from C_6 to C_{14} (see *Pure and Applied Chemistry* 72, 1255-1264).

The amount of surfactant present will depend upon the particular surfactants being employed. For example, a lignosulfonate may be present in an amount of from 0.1 to 15% by weight of the microcapsules, preferably from 0.5 to 10 % by weight.

The composition of the present invention may further comprise other components known in the art and included in such compositions. For example, the composition may comprise one or more components to modify the viscosity of the liquid phase. Suitable viscosity modifiers are known in the art and include ethyl cellulose, xanthan gum, polyvinyl alcohol, and polyacrylic acid sodium.

In one exemplary embodiment, the composition of the present invention is prepared from the following components (with parts indicated by weight):

Clomazone: 1 to 10 parts;
Microcapsules having a wall comprising: cellulose derivative: 0.4 to 1 parts; natural gum: 1.6 to 4 parts; gelatin: 2 to 5 parts; and cross-linking agent: 2 to 5 parts;
Emulsifier: 1-4 parts;
Liquid carrier: 40-99 parts;
Stabilizer: 1-3 parts;
Viscosity modifiers: 2-8 parts; and
Water: 140 to 160 parts.

The present invention also provides, in a further aspect, a method to prepare the composition described above. Accordingly, there is provided a method for preparing a microencapsulated clomazone composition, the method comprising:

a) preparing an aqueous solution of a cellulose derivative and a natural gum;

b) adding clomazone and a liquid carrier to the solution prepared in step (a) and agitating to form an emulsion comprising a water-immiscible phase in water;

c) preparing an aqueous solution of gelatin; and

d) combining the solution prepared in step (c) with the emulsion prepared in step (b).

In the method of the present invention, complex coacervation techniques are used to form the microcapsules, thereby encapsulating the clomazone active ingredient.

In step (a) of the method, a solution of the cellulose derivative and the natural gum in water is formed. In step (b), clomazone and the liquid carrier are added to the aqueous solution. In preferred embodiments, the clomazone is dissolved in the liquid carrier. One or more emulsifiers and/or stabilizers may be added to the mixture, as required. The resulting mixture is agitated, as is known in the art, to form a stable emulsion comprising a dispersion of water immiscible droplets in a continuous water phase.

A solution of gelatin in water is formed in step (c). The resulting solution is combined with the aforementioned emulsion, preferably with mixing. The result of this combination is to form the microcapsules having a wall formed from the cellulose derivative, the natural gum and gelatin and containing clomazone. To effect the formation of the microcapsules, the mixtures may be heated when combined. Suitable temperatures will depend upon such factors as the components being used. A typical temperature is in the range of from 25 to 65°C, more preferably from 35 to 55°C. The pH of the gelatin mixture may be adjusted, preferably to provide acidic conditions. The acidic conditions may be obtained by the addition to the mixture of a suitable acid. Weak acids are preferred, for example a carboxylic acid, in particular a C_1 to C_4 carboxylic acid, with acetic acid being a convenient acid. The pH is

preferably adjusted to be below 5.5, more preferably below 5.0, in particular in the range of from 3 to 4.5. The reaction period required to form the microcapsules will depend upon the components and the reaction conditions. A typical reaction period is from 30 to 70 minutes, more preferably from 40 to 60 minutes. The reaction may be allowed to proceed at a reduced temperature, for example at about room temperature.

As noted above, the wall material of the microcapsules preferably comprises a cross-linking agent. Accordingly, in a preferred embodiment, the method of the present invention comprises as a further step:

e) adding to the resulting mixture a cross-linking agent.

The mixture resulting from step (d) is preferably cooled prior to the addition of the cross-linking agent. A temperature in the range of from 0 to 10°C, more preferably from 0 to 5°C is applied. Further, the pH of the resulting mixture is preferably increased, more preferably to be alkaline. A pH in the range of up to 9 may be employed, more preferably from 8 to 10. The pH may be increased by the addition of a suitable alkali. Suitable alkalis are known in the art and include Group I metal hydroxides. Sodium hydroxide is a particularly suitable alkali. Suitable reaction periods for the cross-linked wall material form are from from 30 to 70 minutes, more preferably from 40 to 60 minutes. The reaction may be allowed to proceed at an elevated temperature, for example at about 30 to 50°C, to allow the wall material to form.

Further components to be included in the composition, such as viscosifiers, may be introduced once the composition once the wall forming reactions have been allowed to complete.

In the method of the present invention, the microcapsule wall is formed by a coacervation process, in particular in which water-soluble polymer electrolytes with opposite charge are employed, in known manner. In the

present invention, amphoteric polymer electrolytes are used, in particular gelatin. Gelatin is positively charged when it is below the isoelectric point, achieved by adjusting the pH. This gelatin is mixed with the negative charged aqueous solution of the cellulose derivative and the natural gum. The negatively charged gelatin is allowed to react with the positively charged cellulose derivative and the natural gum. As a result of the complex coacervation, the cellulose derivative, for example sodium carboxymethyl cellulose, the natural gum, for example gum arabic, and gelatin form the wall material of microcapsules.

One embodiment of the method of the present invention may be summarized as comprising the following steps:

a. Preparation of emulsion: Dissolve sodium carboxymethyl cellulose and gum arabic in deionized water; add clomazone , emulsifiers, liquid carrier and, optionally one or more stabilizers; homogenize the emulsion by agitation using an impellor rotating at a speed of from 3000 to 10000 r/min for 5 to 30min to form a stable oil in water emulsion A.

b. Coacervation Process: Dissolve gelatin in deionized water to form solution B.

c. Solution B is well mixed with emulsion A at a temperature of from 35 to 55°C; adjust the pH to 3 to 4.5 by the addition of 10% acetic acid; hold at room temperature for 40 to 60 min to form a mixture C.

d. Crosslink: Mixture C is cooled to a temperature of from 0 to 5°C; adjust the pH to be in the range of from 8 to 10 by the addition of 20% sodium hydroxide solution; add the cross-linking agent; allow the resulting mixture to react for 40 to 60 min; and then slowly warm to 30-50°C.

The microcapsules once prepared may be formulated in any suitable manner. Suitable formulations and formulating techniques for such microcapsules are known in the art. A suspension or slurry of the microcapsules in a suitable diluent, most preferably water, is one preferred embodiment for shipping, storing, and ultimately dispensing the composition to the area to be treated. Conventional spraying apparatus is used for application of these formulations.

The aqueous suspension may have included therein suspending agents, for example, cross-linked acrylic acid interpolymers, as discussed in US 3,426,004, other suspending agents, such as hydroxyethyl cellulose, gums, clays, sub-micron size silica and other inorganic materials; wetting agents and dispersants such as detergents, polyvinyl alcohols, gelatin, methyl cellulose, casein and clays. Further, the formulation may comprise so-called "stickers", that is materials which will cause the capsules to stick onto the foliage of the treated plants and not drop to the ground, such as gelatin, bentonites, gums, polysulfides, polyacrylic acid, and both petroleum and animal oils.

The formulation may be applied directly to the target area. Alternatively, the composition may be further diluted, prior art application. For example, a convenient water dispersion, suspension or slurry for shipping and storage will consist of from about 10 to 30% by weight of microcapsules, more preferably about 25%, of the pesticide-containing microcapsules, which will be diluted with water to about 1% by weight for spraying.

It has been found that the formulations of the present invention exhibit a high level of stability when being shipped and stored.

The compositions of the present invention may be used to control unwanted plant growth at a locus.

Accordingly, in a further aspect, the present invention provides a method of controlling plant growth at a locus, the method comprising applying to the locus a composition as described hereinbefore.

The present invention further provides the use of the compositions described hereinbefore in the control of plant growth.

The compositions may be applied to the area where control of plant growth is desired, prior to or after emergence of the target plants, for exmaple by spraying onto the surface of the soil or onto the foliage of the plants. The user may, if desired, blend the formulation into the upper layer of soil by cultivation.

As noted above, the compositions of the present invention are particularly suitable for the formulation of clomazone. Clomazone may be formulated and/or applied together with other compatible active ingredients, including herbicides, insecticides, fungicides, nematocide, plant growth regulators, safeners, fertilizers, and other agricultural chemicals. Acetochlor, alachlor and metolachlor are preferred herbicides for forming mixtures with clomazone.

In applying the other active compounds with the formulation of this invention, whether formulated alone or with other agricultural chemicals, an effective amount of each active ingredient is employed. The amount constituting an effective amount is variable, depending on the ratio of added ingredients to clomazone and other factors, such as the type of soil, the expected pattern of rainfall or irrigation, the plant species to be controlled, and the crop, if any, to be grown.

Generally, a uniform application of from about 0.01 to about 2.0 kilogram per hectare of clomazone will be employed, more preferably about 0.3 to about 1.5 kilogram per hectare. Generally, the rate of application of clomazone in the field will be about two to four times that in the greenhouse.

The present invention is further described, for illustrative purposes, by way of the following examples.

EXAMPLE 1

This example demonstrates the preparation of certain acetylene carbamide derivatives that may be used in forming the microcapsules of the present invention. Amounts indicated are by weight, unless otherwise stated.

Preparation of acetylene carbamide

Into a suitable reaction vessel equipped with stirrer, thermometer and reflux condenser, there was introduced 765 parts of urea and 875 parts of water. To this slurry, 282 parts of concentrated sulfuric acid was charged and the mixture was heated to 70° C. At 70° C, 605 parts of glyoxal (40% aqueous solution and free from formaldehyde) were added slowly to the clear solution such that the reaction temperature was maintained between 75° - 80° C. After the addition of the glyoxal, the reaction mixture was held at 75° C. for one hour and then cooled. The separated crystalline acetylene carbamide was filtered and washed with water and with a dilute aqueous caustic solution.

The acetylene carbamide obtained after drying had a melting point of 298° - 300° C and the yield was 88% (525 parts).

Preparation of Tetramethylol acetylene carbamide

Into a suitable reaction vessel equipped with a stirrer, thermometer and reflux condenser, there was introduced 688 parts (10 mol) of aqueous formaldehyde (44%), and the pH was adjusted to 8.7 with 22 parts of 0.5 N NaOH solution. To this solution, there was added 284 parts (2 mol) of acetylene carbamide at 40° C. During the resulting reaction, the temperature was allowed to rise up to 55° C. At this stage, most of the acetylene carbamide entered into solution. After about 15 minutes, the pH was adjusted to 8.0 with five parts of 0.5 N NaOH. A clear, pale yellow colored solution was obtained. The clear solution was distilled at 50° C., under reduced pressure, to remove water until the reaction vessel content was about 640 parts. The resulting syrup in the vessel was poured into 800 parts of methanol. The resulting white crystalline precipitate was filtered and dried.

The total yield of the tetramethylol acetylene carbamide was 483 parts (92%) and had a melting point of 132° - 136° C.

Preparation of Dimethoxymethyl Diethoxymethyl acetylene carbamide

Into a suitable reaction vessel, equipped as before, there was charged 320 parts (10 mol) of methanol, 460 parts of ethanol (10 mol), and 20 parts of 70% concentrated nitric acid. To this acidic alcoholic mixture, there was

charged 262 parts (1 mol) of tetramethylol acetylene carbamide and the reaction mixture was heated to 40° C., with stirring. After about 20 minutes, all of the tetramethylol acetylene carbamide had gone into solution. When the reaction mixture became clear, it was cooled to 22° C. and 45 parts of 20% sodium hydroxide solution were added to neutralize the reaction mixture to a pH of 7-8. The neutralized clear solution was heated slowly to 105°C. under reduced pressure to remove substantially all of the alcohol-water mixture. The resultant syrup was filtered hot at 80° C. to remove the inorganic salts and other impurities.

The yield of the syrupy dimethoxymethyl diethoxymethyl acetylene carbamide was 320 parts. The structure of this product was confirmed by nuclear magnetic resonance spectroscopy. The pan solids were 95.0% and the foil solids were 98.5%. The Gardner-Holdt viscosity was Z_3 - Z_4 (at 25° C.). The product was soluble in water as well as in benzene.

Preparation of Methylated Ethylated acetylene carbamide

Into a suitable reaction vessel, equipped as before, there was introduced 142 parts (1 mol) of acetylene carbamide and 300 parts (4.4 mol) of aqueous formaldehyde (44%). The pH was adjusted to 7.5-8.0 with about 6 parts of 0.5 N NaOH solution. The reaction mixture was heated to 80° C. for 15 minutes. The pH of the reaction mixture was adjusted again with 0.5 N NaOH solution to about 7-7.5. The resultant pale yellow colored solution of tetramethylol acetylene carbamide was distilled at 50° C. under reduced pressure until the weight of the syrup in the reaction vessel was between about 305-310 parts. To this syrup, 160 parts (5 mol) of methanol and 6 parts of concentrated nitric acid was added at 50° C. There was a slight exotherm after the addition. The reaction temperature was held at about 55°-60° C. for

30 minutes and later cooled to 22° C. The resulting mixture was neutralized to a pH of 7-8 with a 20% NaOH solution and then slowly heated to 105° C. under reduced pressure to remove substantially all of the alcohol and water. To the resulting syrup, 92 parts (2 mol) of ethanol and 4 parts of nitric acid were added and the charge was heated to about 70° C. The reaction mixture was held at that temperature for 30 minutes. After cooling the reaction mixture to 22° C., it was neutralized to a pH of 7.5 using a 20% NaOH solution. The neutralized solution was heated slowly to 105° C. under reduced pressure, to remove all of the alcohol-water mixture. The resultant syrup was filtered hot at 80° C. to remove inorganic salts and other impurities.

The yield of the syrup was 320 grams. The foil solids were 99.5 % and the product was soluble in water. The nuclear magnetic resonance analysis indicated that the ratio of methoxy to ethoxy groups in the product was 1:0.63, respectively, that is an average degree of methylation of about 2.4 and degree of ethylation 1.6.

The procedure for the preparation of the methylated ethylated acetylene carbamide was repeated in all essential details except that during the second alkylation step, 138 parts (3 mol) of ethanol were used. The final syrupy product was soluble in water. The foil solids were 99%. The nuclear magnetic resonance analysis indicated that the ratio of methoxy to ethoxy groups in the product was 1:0.81, respectively. The product was water-soluble and was also soluble in benzene.

Preparation of Methylated Butylated acetylene carbamide

The process for the preparation of the methylated ethylated acetylene carbamide set forth hereinabove was repeated in all essential details except

that the methylolated acetylene carbamide was first reacted with 192 parts (6 mol) of methanol.

The second alkylation stage was accomplished with n-butanol as follows: To the syrup obtained after the methylation step there was added 74 parts (1 mol) of n-butanol and 1 part of nitric acid. The reaction mixture was heated to 105° C. for one-half hour. The distillate, which appeared to be methanol, was removed using a Dean-Stark trap. The pale yellow colored solution was cooled to 20° C. and neutralized to a pH of 7-7.5 with a 0.5 N NaOH solution. The unreacted butanol and any water in the reaction mixture were removed under reduced pressure at 121° C.

The resultant approximately 100% solids viscous liquid was analyzed by N.M.R. and found to have a methoxy:butoxy ratio of 1:0.32 respectively, that is an average degree of methylation of about 3, and degree of butylation 1.0. The product remained liquid and did not crystallize on storage at ambient temperature. The product was sparingly soluble in water but was soluble in benzene.

EXAMPLE 2

Various examples of the compositions of the present invention were prepared, indicated as Examples A to E below. The components used in the preparation of Examples A to E are summarized in the following table:

		Example				
Step	Component (g)	A	B	C	D	E
a. Preparation of emulsion	Sodium carboxymethyl cellulose	0.55	0.4	1	0.7	0.85
	Gum Arabic	2.2	1.6	4	2.8	3.4
	Deionized water	106	100	120	110	113
	Clomazone	1	3.2	5.5	7.8	10
	Emulsifier	2.5	1	1.95	4	2.25
	Liquid carrier	50	40	80	60	80
	Stabilizer	2.5	1	1.95	4	2.25
b. Complex coacervation	Gelatin	2.75	2	5	3.5	4. 25
	Deionized water	106	100	120	110	113
c. Crosslink	Cross-linking agent	3.5	2	5	2. 75	4.25
	Viscosifying agent	6.5	8	2	5	3.5

The emulsifier used in Examples A to E was POE (20), sorbitan trioleate nonionic surfactant (ex. Uniqema; TWEEN 85™) and POE (40), sorbitol hexaoleate nonionic surfactant (ex. Uniqema; ATLAS G1086™).

The liquid carrier was a C_{16}-C_{18} fatty acid methyl ester (ex. Cognis Corp.; AGNIQUE ME 18SDU™).

The stabilizer used was lignosulfonate (ex. MeadWestvaco Corp.; REAX 88A™)

The cross-linking agent used in was tetrakis(methyoxymethyl) glycoluril (Powderlink 1174™).

The Viscosifying agent used in the examples was xanthan gum.

The compositions of Examples A to E were prepared using the following general method:

a. Preparation of emulsion: Dissolve sodium carboxymethyl cellulose and gum arabic in deionized water; add clomazone , emulsifiers, liquid carrier and the stabilizer; homogenize the emulsion by agitation using an impellor rotating at a speed of from 3000 to 10000 r/min for 5 to 30min to form a stable oil in water emulsion A.

b. Coacervation Process: Dissolve gelatin in deionized water to form solution B.

c. Solution B is well mixed with emulsion A at a temperature of from 35 to 55°C; adjust the pH to 3 to 4.5 by the addition of 10% acetic acid; hold at room temperature for 40 to 60 min to form a mixture C.

d. Crosslink: Mixture C is cooled to a temperature of from 0 to 5°C; adjust the pH to be in the range of from 8 to 10 by the addition of 20% sodium hydroxide solution; add the cross-linking agent; allow the resulting mixture to react for 40 to 60 min; and then slowly warm to 30-50°C.

e. The viscosifier is added to the resulting mixture.

In each of Examples A to E, the resulting composition comprised microcapsules having a stable wall and containing clomazone. The microcapsules exhibited an advantageous rate of release of the clomazone active ingredient when applied to plants at a locus, with little to no drift of the clomazone to neighbouring areas. The clomazone exhibited an activity in controlling plant growth at least as high as the commercially available EC formulations.

CLAIMS

1. A composition comprising microencapsulated clomazone, the clomazone being contained within microcapsules having a microcapsule wall formed by the coacervation of a plurality of amphoteric polymer electrolytes.

2. The composition according to claim 1, wherein the clomazone is contained within microcapsules having a microcapsule wall formed from a cellulose derivative, a natural gum and gelatin.

3. The composition according to either of claims 1 or 2, wherein the cellulose derivative comprises a carboxyalkyl cellulose.

4. The composition according to claim 3, wherein the cellulose derivative comprises carboxymethyl cellulose.

5. The composition according to any preceding claim, wherein the cellulose derivative is present as a salt.

6. The composition according to any preceding claim, wherein the cellulose derivative is present in the microcapsule wall in an amount of from 1 to 30% by weight.

7. The composition according to any preceding claim, wherein the natural gum comprises gum arabic, gum ghatti, gum tragacanth, karaya gum, or a mixture thereof.

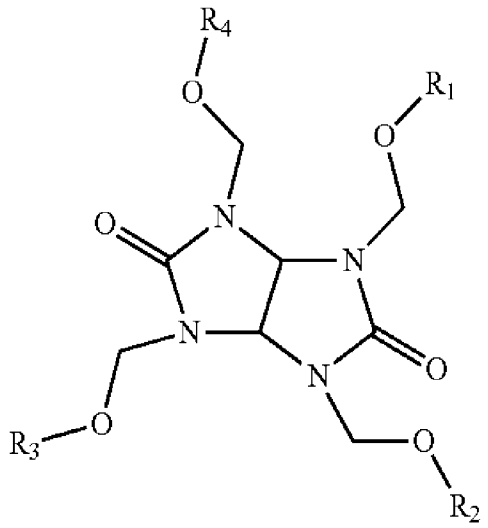
8. The composition according to any preceding claim, wherein the natural gum is present in the microcapsule wall in an amount of from 5 to 75% by weight.

9. The composition according to any preceding claim, wherein gelatin is present in the microcapsule wall in an amount of from 5 to 90% by weight.

10. The composition according to any preceding claim, wherein the microcapsules comprise a cross-linking agent.

11. The composition according to claim 10, wherein the cross-linking agent is a glycoluril resin.

12. The composition according to claim 11, wherein the glycoluril resin as the following general formula (I):



wherein R_1, R_2, R_3, and R_4 each independently represents a hydrogen atom or an alkyl group. Preferred compounds of Formula (I) in which R_1, R_2, R_3, and R_4 each independently represents an alkyl group are those in which the alkyl group has from 1 to 12 carbon atoms, more preferably from 1 to 8 carbon atoms, still more preferably from 1 to 6 carbon atoms, most preferably from 1

to 4 carbon atoms. R_1, R_2, R_3, and R_4 may reach represent the same or different alkyl groups.

13. The composition according to any of claims 10 to 12, wherein the cross-linking agent is present in the microcapsule wall in an amount of from 5 to 90% by weight.

14. The composition according to any of claims 10 to 13, wherein the cellulose derivative, natural gum, gelatin and cross linking agent are present in the microcapsule wall in the weight ratio of from 0.4:1.6:2:2 to 1:4:5:5.

15. The composition according to any preceding claim, wherein the clomazone is present in the microcapsules in combination with a liquid carrier.

16. The composition according to claim 15, wherein the clomazone is dissolved in the liquid carrier.

17. The composition according to either of claims 15 or 16, wherein the liquid carrier is a fatty acid ester of an alkanol.

18. The composition according to any preceding claim, further comprising a stabilizer.

19. The composition according to claim 18, wherein the stabilizer comprises a lignosulfonate.

20. A method for preparing coacervation of preparing a microencapsulated clomazone composition comprising encapsulating clomazone by the coacervation of a plurality of amphoteric polymer electrolytes.

21. The method for preparing a microencapsulated clomazone composition according to claim 20, the method comprising:

a) preparing an aqueous solution of a cellulose derivative and a natural gum;

b) adding clomazone and a liquid carrier to the solution prepared in step (a) and agitating to form an emulsion comprising a water-immiscible phase in water;

c) preparing an aqueous solution of gelatin; and

d) combining the solution prepared in step (c) with the emulsion prepared in step (b).

22. The method according to claim 22, wherein clomazone is dissolved in the liquid carrier.

23. The method according to either of claims 21 or 22, wherein the pH of the gelatin solution in step (c) is adjusted to be below 5.5.

24. The method according to any of claims 21 to 23, wherein the cellulose derivative comprises a carboxyalkyl cellulose.

25. The method according to claim 24, wherein the cellulose derivative comprises carboxymethyl cellulose.

26. The method according to any of claims 21 to 25, wherein the cellulose derivative is present as a salt.

27. The method according to any of claims 21 to 26, wherein the natural gum comprises gum arabic, gum ghatti, gum tragacanth, karaya gum, or a mixture thereof.

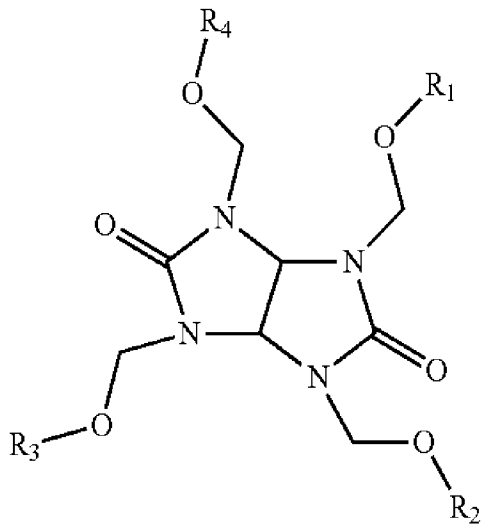
28. The method according to any of claims 21 to 27, further comprising as a further step:

e) adding to the resulting mixture a cross-linking agent.

29. The method according to claim 28, wherein the mixture resulting from step (d) is cooled to a temperature of from 0 to 10°C, prior to the addition of the cross-linking agent.

30. The method according to either of claims 28 or 29, wherein the cross-linking agent is a glycoluril resin.

31. The method according to claim 30, wherein the glycoluril resin as the following general formula (I):



wherein R_1, R_2, R_3, and R_4 each independently represents a hydrogen atom or an alkyl group. Preferred compounds of Formula (I) in which R_1, R_2, R_3, and R_4 each independently represents an alkyl group are those in which the alkyl group has from 1 to 12 carbon atoms, more preferably from 1 to 8 carbon

atoms, still more preferably from 1 to 6 carbon atoms, most preferably from 1 to 4 carbon atoms. R_1, R_2, R_3, and R_4 may reach represent the same or different alkyl groups.

32. A suspension formulation comprising a composition according to any of claims 1 to 20.

33. The use of a composition according to any of claims 1 to 20 or a formulation according to claim 32 in the control of plant growth at a locus.

34. A method for controlling plant growth at a locus comprising applying to the locus a composition according to any of claims 1 to 20 or a formulation according to claim 32.

35. A pesticidal composition substantially as hereinbefore described.

36. A method for preparing a pesticidal composition substantially as hereinbefore described.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/075129

A. CLASSIFICATION OF SUBJECT MATTER

A01N 25/28(2006.01)i; A01N 25/04(2006.01)i; A01N 43/80(2006.01)i; A01P 13/00(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)

A01N 25/-; A01N 43/-; A01P 13/-

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)

CNABS, CNKI, VEN, ISI Web of Knowledge, CA, ROTAM, +capsule+, +encapsulat+, clomazone, cellulose, gum, gelatin, glycoluril, crosslink+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	GB 2498146A (ROTAM AGROCHEM INTERNATIONAL CO. LTD) 03 July 2013 (2013-07-03) claims 1-36	1-36
X	CN 101427675A (GE, YANRUI) 13 May 2009 (2009-05-13) claims 1-6, description, page 4, paragraph [0004]	1-10, 13-29, 32-36
Y	CN 101427675A (GE, YANRUI) 13 May 2009 (2009-05-13) claims 1-6, description, page 4, paragraph [0004]	11-12, 30-31
Y	CN 101235035A (HOU, ZHONGDE) 06 August 2008 (2008-08-06) abstract, description, paragraph [0002]	11-12, 30-31

☐ 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
16 June 2014	**09 July 2014**
Name and mailing address of the ISA/ **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN) 6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China** Facsimile No. **(86-10)62019451**	Authorized officer **FENG,Shuwen** Telephone No. **(86-10)82246763**

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2014/075129

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
GB 2498146A	03 July 2013	无	
CN 101427675A	13 May 2009	CN 101427675B	06 June 2012
CN 101235035A	06 August 2008	CN 101235035B	16 June 2010