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(54) Title: ALGINATE COATING FOR SEED TREATMENT

(57) Abstract: Disclosed are methods of treating seeds comprising (a) applying a coating of an alginate optionally containing one or more crop protection agents and/or one or more nutrients, and (b) crosslinking the alginate with a divalent metal ion.

## ALGINATE COATING FOR SEED TREATMENT

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application Serial No. 61/898,219, filed October 31, 2013, the disclosure  
5 of which is incorporated herein by reference in its entirety.

### FIELD OF THE INVENTION

The present invention relates to the field of agrochemical coatings for seeds. The invention provides a method of seed coating using alginates, optionally  
10 containing insecticidal, nematocidal or fungicidal active ingredients, and/or nutrients.

### BACKGROUND OF THE INVENTION

The global demand of seed treatment has been primarily driven by the growth of the commercial seeds market. Increasing global farming and  
15 reduction in arable land has generated the need for high yield productivity, further boosting the market for seed treatment.

Production of alginate beads/pellets is usually accomplished by dropping a sodium alginate solution including the viable structures into a  $\text{CaCl}_2$  solution, allowing the outside-to-inside growth of beads. However, the complete coating of  
20 larger structures such as plant seeds using this technique is not practical.

The commercially existing alginate seed coating process is either not crosslinked, thereby precluding slow release of the active ingredient (AI), or uses a soaking/dipping approach that is not amenable to seed coating and handling.

### 25 BRIEF SUMMARY OF THE INVENTION

The alginate coating technology described herein enables us to introduce the controlled release function to the pre-existing or newly-applied biological/chemical active ingredients on the seed surface. One aspect of the present invention is directed to a spray-based alginate seed coating process that uses  
30 two separate spray steps to introduce the alginate based seed coating onto the seed surface followed by the cross linking of the coating.

One aspect of the invention is directed to a method of seed treatment comprising (a) applying to seeds a coating of an alginate, optionally containing one or

more crop protection agents selected from the group consisting of insecticides, nematocides and fungicides, and/or one or more nutrients; and (b) crosslinking the alginate with a divalent metal ion. In one embodiment, the seeds are a pretreated seeds. In one embodiment the divalent metal ion is selected from the group consisting of  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$  and  $\text{Zn}^{+2}$ . In one embodiment the crosslinking is effected by applying a divalent metal ion solution. In one embodiment the divalent metal ion solution comprises an aqueous solution of a divalent metal salt. Preferably the divalent metal salt is a calcium salt, selected from the group consisting of calcium chloride, calcium carbonate and calcium sulfate. In one embodiment the divalent metal ion solution is applied by spraying. In one embodiment the application of the alginate coating is also applied via spraying.

Another aspect of the invention is directed to a method of seed treatment including (a) spraying seeds with a solution of a soluble alginate containing one or more crop protection agents selected from the group consisting of insecticides, nematocides and fungicides, and/or one or more nutrients, to form coated seeds; and (b) spraying the coated seeds with an aqueous solution of a calcium salt in order to crosslink the alginate. In one embodiment the seeds are pretreated seeds. In another embodiment, the crop protection agent is an insecticide selected from a group consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb, acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos trichlorfon, endosulfan, ethiprole, fipronil, pyrafluprole and pyriprole, acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid, thiamethoxam, spinosad, spinetoram, abamectin, emamectin benzoate, ivermectin, lepimectin, milbemectin, hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen, pymetrozine, flonicamid, pyrifluquinazon, clofentezine, hexythiazox, etoxazole, diafenthiuron, fenbutatin oxide, propargite, chlorfenapyr, bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium, bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, buprofezin, cyromazine, methoxyfenozide, tebufenozide, halofenozide,

chromafenozide, amitraz, pyridaben, tebufenpyrad, tolfenpyrad, flufenimer, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocy, fluacrypyrim, indoxacarb, metaflumizone, spiroadicofen, spiromesifen, spirotetramat, flubendiamide, (R)-3-Chlor-N1- {2- methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-  
 5 methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-4-1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1- methyl-2- methylsulfonylethyl)phthalamid, chloranthraniliprole, cy- anthraniliprole, azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl, sulfoxaflo, acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cyper-  
 10 methrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate, permethrin, silafluofen, tefluthrin, tralomethrin, and any suitable combinations thereof. In a further embodiment, the insecticide is acetamiprid.

Another aspect of the invention is directed to a coated seed including a plant  
 15 seed core and a controlled release coating that includes crosslinked alginate and a crop protection agent selected from the group consisting of insecticides, nematocides and fungicides, and/or one or more nutrients, and combinations thereof. In one embodiment, the plant seed core is a seed selected from the group consisting of monocotyledons, dicotyledons, gymnosperms and mixtures thereof. In another  
 20 embodiment, the crop protection agent is an insecticide selected from the group consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb, acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton,  
 25 ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos trichlorfon, endosulfan, ethiprole, fipronil, pyrafluprole and pyriprole, acetamiprid, chlothianidin, dinotefuran,  
 30 imidacloprid, nitenpyrathiacloprid, thiamethoxam, spinosad, spinetoram, abamectin, emamectin benzoate, ivermectin, lepimectin, milbemectin, hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen, pymetrozine, flonicamid, pyrifluquinazon, clofentezine, hexythiazox, etoxazole, diafenthiuron, fenbutatin oxide, propargite, chlorfenapyr, bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium,

bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, buprofezin, cyromazine, methoxyfenozide, tebufenozide, halofenozide, chromafenozide, amitraz, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocy, fluacrypyrim, indoxacarb, 5 metaflumizone, spiroadiclofen, spiromesifen, spirotetramat, flubendiamide, (R)-3-Chlor-N1- {2- methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-4-1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1- methyl-2-methylsulfonylethyl)phthalamid, chloranthraniliprole, cy- anthraniliprole, 10 azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl, sulfoxaflor, acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate, permethrin, silafluofen, tefluthrin, tralomethrin, and any suitable combinations 15 thereof. In another embodiment, the crop protecting agent is a neonicotinoid selected from the group consisting of acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid and thiamethoxam.

#### DETAILED DESCRIPTION OF THE INVENTION

This document is not limited to the particular methods, processes, 20 compositions, or methodologies described, as these may vary. The technology used in the description is for the purpose of describing the particular versions or embodiments only, and it is not intended to limit the scope of the present invention which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly 25 understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that 30 the invention is not entitled to antedate such disclosure by virtue of prior invention.

As used in this document, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to a "calcium salt" is a reference to one or more calcium salts and equivalents thereof known to those skilled in the art, and so forth.

As used in this document, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45% to 55%.

As used in this document, the phrase "an effective amount" is meant to be read in light of the subject immediately related to the phrase as to the intended utilities. As such, "an effective amount" to cause crosslinking refers to any such concentration that facilitates formation of crosslinking.

As used in this document, the term "comprises" or "comprising" means includes at least the following but does not exclude others.

10 Sodium alginate is the sodium salt of alginic acid, which is obtained by extraction from various species of deep-sea weed like Phaeophyceae. Sodium alginate is a polysaccharide, as are starch and cellulose. Sodium alginate has been used as both a binder and a disintegrant in a variety of oral and topical pharmaceutical formulations. In agriculture applications, alginate has been  
15 exploited to encapsulate viable structures for different purposes. Naked embryos have been entrapped in calcium alginate to produce synthetic seeds (Patel *et al.*, 2000) or viable cells of microorganisms have been entrapped in calcium alginate to produce alginate pellets or to coat plant seeds for biological seed treatment (Russo *et al.*, 2001; Haverson and Kimbrough, 2002). Production of alginate beads is  
20 usually accomplished by dropping sodium alginate solution including viable structures into a CaCl<sub>2</sub> solution, allowing the outside-to-inside growth of beads. However, the procedure of inclusion of large structures such as plant seeds with this technique is impractical.

Alginate salts have been used for compositions in the treatment of plants for  
25 protection thereof. WO2011US48748, CN103392737 (A), and US2012021911 (A1) describe plant treatment compositions comprising metal alginate salts and at least one amine compound useful in the treatment of plants, particularly food crops. US5,977,023 provides a pesticidal composition containing a water-insoluble alginate, which is prepared by treating a solid composition containing (a) a pesticidally active  
30 ingredient which is a pest-controlling active ingredient or a plant growth-regulating active ingredient and (b) an alginic acid or a water-soluble alginate with an aqueous solution containing a divalent or polyvalent cation which can convert said alginic acid or water-soluble alginate into a water-insoluble alginate.

One aspect of the present invention is directed to a spray-based alginate seed coating process that uses two alternative spray steps to introduce the alginate based seed coating onto the seed surface and the cross linking of the coating, respectively. In one embodiment, the seed coating formulations can be prepared by first milling  
5 pesticide particles and then mixing milled pesticide particles directly into a sodium alginate solution, or adding sodium alginate to the existing SC formulations of the pesticides. This seed coating formulation can be then applied to the seed surface via spray.

In another embodiment, the AIs are in a suitable liquid formulation that may  
10 be sprayed on the seed surface. In at least such embodiment, the liquid formulation must contain other excipients such as surfactants, viscosity adjustors, pH adjustors and any other suitable ingredients. In this embodiment, suitable surfactant may be a nonionic surfactant, cationic, anionic, amphoteric compound. By the way of examples suitable nonionic surfactants may include alkanolamides (such as cocamide  
15 diethanolamide, lauric acid monoisopropanolamide, and ethoxylated myristamide), xyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers (such as alkylaryl polyglycol ethers) and fluorocarbons (such as ethoxylated polyfluorinated alcohol); anionic surfactants including alkyl-, alkylaryl- and arylsulfonates (such as sodium lauryl sarcosinate and such as sodium alkylbenzenesulfonate), alkyl-, alkylaryl- and  
20 arylsulfates, protein hydrolysates, derivatives of polycarboxylic acid (such as ammonium lauryl ether carboxylate), olefin sulfonates (such as sodium alpha olefin sulfonate), sarcosinates (such as ammonium cyclohexyl palmitoyl taurinate), succinates (such as disodium N-octadecyl sulfosuccinamate), phosphorus derivatives (such as phosphoric acid esters and their equivalent salts); cationic surfactants  
25 including alkylbenzyltrimethylammonium chloride; and amphoteric surfactants including betaine. The total concentration of selected agents in the formulation will be dependent on the type of formulation, active ingredients employed and may comprise between about 0.1% and about 50% of the final formulation, preferably between about 0.3% and about 50%.

30 In one aspect of the invention, the seeds that can be treated with the presently described process include but are not limited to genetically modified or non-modified corn, wheat, oat, rye, soybean, cotton, flax, jute, rape, canola, linseed, sesame, safflower, sunflower, clover, beet, sugar beet, sorghum, millet, rice, peanut pea, beans, cucumber, pepper, melon, cabbage, onion, squash, lettuce, asparagus, cabbage,

eggplant, tomato, tobacco, flower seed and trufgrass. In at least a preferred embodiment, the seeds are any one of corn, wheat, oat, rye, soybean and cotton.

Any apparatus capable of coating/spraying seeds can be used to realize this process. One such commercial seed treater is the "Wintersteiger Hege 11 Seed  
5 Treater". After spray application of the pesticide/alginate seed coating, a water solution of  $\text{CaCl}_2$  is then sprayed onto the seed coating surface to introduce the crosslinking of the coating. In additiona, different concentrations of the alginate and  $\text{CaCl}_2$  can be used in the coating process to adjust the release rate of the resultant seed coating. In at least one embodiment, the coating may contain two  
10 or more active ingredients.

In one embodiment, commercially pre-treated seeds can be coated with a layer of alginate coating to introduce the controlled release property to the AIs of the pre-treatment. In this process, only sodium alginate solution (i.e., without the AI mixed) is sprayed onto the seed surface and followed by the cross linking via  
15  $\text{CaCl}_2$  spray. In this way the introduction of a controlled release property to the AI on the pre-treated seeds can be achieved using the crosslinked alginate resulting from the two-step spray process. In an alternative embodiment, the alginate solution may contain one or more Ais which are then applied on to the surface of the pretreated seed, thereby facilitating continous release for all  
20 respective AIs employed on th seed itself.

For the two steps of applying the alginate coating solution and the crosslinking agent  $\text{CaCl}_2$ , the procedures can be altered as well, i.e., first apply the  $\text{CaCl}_2$  material on the seed surface followed by applying of the alginate coating solution.

25 Addition of other functional agents such as nutrients to the alginate solution can also be employed in the alginate coating formulations. Further, the coating thickness and the concentrations of the AI in the formulations can easily be adjusted.

In another embodiment, the controlled release coating may contain additional crop protection agents such as an insecticide, a nematocide, a fungicide, and/or one  
30 or more growth enhancing nutrients, and combinatins thereof. Suitable crop protection agents includes:

Insecticides: A1) the class of carbamates consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb; A2) the class of organophosphates consisting



of acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, 5 oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos and trichlorfon; A3) the class of cyclodiene organochlorine compounds such as endosulfan; A4) the class of fiproles consisting of ethiprole, fipronil, pyrafluprole and pyriprole; A5) the class of neonicotinoids 10 consisting of acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid and thiamethoxam; A6) the class of spinosyns such as spinosad and spinetoram; A7) chloride channel activators from the class of mectins consisting of abamectin, emamectin benzoate, ivermectin, lepimectin and milbemectin; A8) juvenile hormone mimics such as hydroprene, kinoprene, methoprene, fenoxycarb and pyriproxifen; A9) selective homopteran feeding blockers such as pymetrozine, 15 flonicamid and pyrfluquinazon; A10) mite growth inhibitors such as clofentezine, hexythiazox and etoxazole; A11) inhibitors of mitochondrial ATP synthase such as diafenthiuron, fenbutatin oxide and propargite; uncouplers of oxidative phosphorylation such as chlorfenapyr; A12) nicotinic acetylcholine receptor channel 20 blockers such as bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium; A13) inhibitors of the chitin biosynthesis type 0 from the benzoylurea class consisting of bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron and teflubenzuron; A14) inhibitors of the chitin biosynthesis type 1 such as buprofezin; A15) moulting disruptors such as cyromazine; A16) ecdyson receptor 25 agonists such as methoxyfenozide, tebufenozide, halofenozide and chromafenozide; A17) octopamin receptor agonists such as amitraz; A18) mitochondrial complex electron transport inhibitors pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocyl or fluacrypyrim; A19) voltage-dependent sodium channel blockers such as indoxacarb and metaflumizone; 30 A20) inhibitors of the lipid synthesis such as spirodiclofen, spiromesifen and spirotetramat; A21) ryanodine receptor-modulators from the class of diamides consisting of flubendiamide, the phthalamide compounds (R)-3-Chlor-N1- {2-methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-methyl-2-methylsulfonyl)ethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-4-[1,2,2,2 -

tetrafluor-1-(trifluoromethyl)ethyl]phenyl} -N2-(1- methyl-2-  
 methylsulfonylethyl)phthalamid, chloranthraniliprole and cy- anthraniliprole; A22)  
 compounds of unknown or uncertain mode of action such as azadirachtin,  
 amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl, sulfoxaflor; or  
 5 A23) sodium channel modulators from the class of pyrethroids consisting of  
 acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cyper- methrin,  
 alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin,  
 esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate,  
 permethrin, silafluofen, tefluthrin and tralomethrin and any suitable combinations  
 10 thereof.

Fungicides: B1) azoles selected from the group consisting of bitertanol,  
 bromuconazole, cyproconazole, difenoconazole, diniconazole, enilconazole,  
 epoxiconazole, fluquinconazole, fenbuconazole, flusilazole, flutriafol, hexaconazole,  
 imibenconazole, ipconazole, metconazole, myclobutanil, penconazole,  
 15 propiconazole, prothioconazole, simeconazole, triadimefon, triadimenol,  
 tebuconazole, tetraconazole, triticonazole, prochloraz, pefurazoate, imazalil,  
 triflumizole, cyazofamid, benomyl, carbendazim, thia- bendazole, fuberidazole,  
 ethaboxam, etridiazole and hymexazole, azaconazole, diniconazole-M, oxpoconazol,  
 paclobutrazol, uniconazol, 1-(4-chloro-phenyl)-2-([1 ,2,4]triazol-1-y1)-  
 20 cycloheptanol and imazalilsulfphate; B2) strobilurins selected from the group  
 consisting of azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-  
 methyl, methominostrobin, orysastrobin, picoxystrobin, pyraclostrobin,  
 trifloxystrobin, enestroburin, methyl (2-chloro-541-(3-  
 methylbenzyloxyimino)ethyl]benzyl)carbamate, methyl (2-chloro-5-[1-(6-  
 25 methylpyridin-2-ylmethoxyimino)ethyl]benzyl)carbamate and methyl 2-(ortho-(2,5-  
 dimethylphenyloxymethylene)- phenyl)-3-methoxyacrylate, 2-(2-(6-(3-chloro-2-  
 methyl-phenoxy)-5-fluoro-pyrimidin-4-yloxy)-phenyl)-2-methoxyimino-N-methyl-  
 acetamide and 3-methoxy-2-(2-(N-(4-methoxy-phenyl)-  
 cyclopropanecarboximidoylsulfanylmethyl)-phenyl)-acrylic acid methyl ester; B3)  
 30 carboxamides selected from the group consisting of carboxin, benalaxyl, benalaxyl-  
 M, fenhexamid, flutolanil, furametpyr, mepronil, metalaxyl, mefenoxam, ofurace,  
 oxadixyl, oxycarboxin, penthiopyrad, isopyrazam, thifluzamide, tiadinil, 3,4-  
 dichloro-N-(2-cyanophenyl)isothiazole-5-carboxamide, dimethomorph, flumorph,  
 flumetover, fluopicolide (picobenzamid), zoxamide, carpropamid, diclocymet,

mandipropamid, N-(2-(443-(4-chlorophenyl)prop-2-ynyloxy]-3-methoxyphenyl)ethyl)-2-methanesulfonyl-amino-3-methylbutyramide, N-(2-(4-[3-(4-chloro-phenyl)prop-2-ynyloxy]-3-methoxy-phenyl)ethyl)-2-ethanesulfonylamino-3-methylbutyramide, methyl 3-(4-chlorophenyl)-3-(2-  
5 isopropoxycarbonyl-amino-3-methyl-butrylamino)propionate, N-(4'-bromobiphenyl-2-yl)-4-difluoromethyl-1-methylthiazole-6-carboxamide, N-(4'-trifluoromethyl-biphenyl-2-yl)-4-difluoromethyl-2-methylthiazole-5-carboxamide, N-(4'-chloro-3'-fluorobiphenyl-2-yl)-4-difluoromethyl-2-methyl-thiazole-5-carboxamide, N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-3-difluoro-methyl-1-methyl-  
10 pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazole-4-carboxamide, N-(2-cyano-phenyl)-3,4-dichloroisothiazole-5-carboxamide, 2-amino-4-methyl-thiazole-5-carboxanilide, 2-chloro-N-(1,1,3-trimethyl-indan-4-yl)-nicotinamide, N-(2-(1,3-dimethylbutyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-(4'-chloro-3',5-  
15 difluoro-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(4'-chloro-3',5-difluoro-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluoro-biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',5-difluoro-4'-methyl-biphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(3',5-difluoro-4'-methyl-  
20 biphenyl-2-yl)-3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(cis-2-bicyclopropyl-2-yl-phenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(trans-2-bicyclopropyl-2-yl-phenyl)-3-difluoro-methyl-1-methyl-1H-pyrazole-4-carboxamide, fluopyram, N-(3-ethyl-3,5,5-trimethyl-cyclohexyl)-3-formylamino-2-hydroxy-benzamide, oxytetracyclin, silthiofam, N-(6-  
25 methoxy-pyridin-3-yl) cyclopropanecarboxamide, 2-iodo-N-phenyl-benzamide, N-(2-bicyclo-propyl-2-yl-phenyl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-yl-carboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethyl-pyrazol-4-ylcarboxamide,  
30 N-(3',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-

trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-  
 5 fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-  
 10 dimethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-  
 15 methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide, N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-  
 20 carboxamide, N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-S-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3'-chloro-4'-fluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-S-trifluoromethyl-1H-pyrazole-4-  
 25 carboxamide, N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazole-4-carboxamide, N-(3'-chloro-4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-S-difluoromethyl-1H-pyrazole-4-  
 30 carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-3-

trifluoromethyl-1 H-pyrazole-4- carboxamide, N-(3',4'-difluoro-5-fluorobiphenyl-2-y1)-1-methyl-3-trifluoromethyl-1 H- pyrazole-4-carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-y1)-1 - methyl-S-difluoromethyl-1 H-pyrazole-carboxamide, N-(3',4'-difluoro-5- fluorobiphenyl-2-y1)-1 -methyl-3-difluoromethyl-1 H-pyrazole-4-  
 5 carboxamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-y1)-1,3-dimethyl-1 H-pyrazole-4-carboxamide, N-(3'-chloro-4'-fluoro-5-fluorobiphenyl-2-y1)-1-methyl-3- difluoromethyl-1 H-pyrazole-4-carboxamide, N-(4'-fluoro-4-fluorobiphenyl-2-y1)-1 - methyl-3-trifluoromethyl-1 H-pyrazole-4-carboxamide, N-(4'-fluoro- 5- fluorobiphenyl-2-y1)-1-methyl-3-trifluoromethyl-1H-pyrazole-4-carboxamide,N-  
 10 (4'-chloro-5-fluorobiphenyl-2-y1)-1- methyl-3-trifluoromethyl-1 H- pyrazole-4- carboxamide, N-(4'-methyl-5-fluorobiphenyl-2-y1)-1-methyl-3-trifluoromethyl-1 H-pyrazole-4-carboxamide, N-(4'-fluoro-5- fluorobiphenyl-2-y1)-1,3-dimethyl-1 H-pyrazole-4-carboxamide, N-(4'- chloro-5-fluorobiphenyl-2-y1)-1,3-dimethyl-1 H-pyrazole-4-carboxamide, N-(4'-methyl-5-fluorobiphenyl-2-y1)-1,3-dimethyl-1 H-  
 15 pyrazole-4-carboxamide, N-(4'-fluoro-6-fluorobiphenyl-2-y1)-1-methyl-3- trifluoromethyl-1 H- pyrazole-4-carboxamide, N-(4'-chloro-6-fluorobiphenyl-2- y1)-1-methyl-3- trifluoromethyl-1 H-pyrazole-4-carboxamide, N-[2-(1 ,1 ,2,3,3,3- hexafluoropropoxy)-phenyl]-3-difluoromethyl-1-methyl-1 H-pyrazo le-4- carbox amide, N-[4'-(trifluoromethylthio)-biphenyl-2-y1]-3 -difluoromethyl-1-methyl-1 H-  
 20 pyrazole-4-carboxamide and N44'-(trifluoromethylthio)-biphenyl-2-y1]-1-methyl- 3-trifluoromethyl-1-methyl-1H-pyrazole-4-carboxamide; B4) heterocyclic compounds selected from the group consisting of fluazinam, pyrifenoxy, bupirimate, cyprodinil, fenarimol, ferimzone, mepanipyrim, nuarimol, pyrimethanil, triforine, fenpiclonil, fludioxonil, aldimorph, dodemorph, fenpropimorph, tridemorph,  
 25 fenpropidin, iprodione, procymidone, vinclozolin, famoxadone, fenamidone, othilinone, proben- azole, 5-chloro-7-(4-methyl-piperidin-1 -y1)-6-(2,4,6- trifluorophenyl)4,1,2,4]triazolo[1,5-a]pyrimidine, anilazine, diclomezine, pyroquilon, proquinazid, tricyclazole, 2-butoxy-6-iodo-3-propylchromen-4-one, acibenzolar-S-methyl, captafol, captan, dazomet, folpet, fenoxanil, quinoxifen,  
 30 N,N-dimethyl-3-(3-bromo-6-fluoro-2-methylindole-1-sulfonyl)- [1 ,2,4]triazole-1- sulfonamide, 5-ethyl-6-octyl4,1,2,4]triazolo[1 ,5-a]pyrimidin-2,7-diamine, 2,3,5,6- tetrachloro-4-methanesulfonyl-pyridine, 3,4,5-trichloro-pyridine-2,6-di-carbonitrile, N-(1-(5-bromo-3-chloro-pyridin-2-y1)-ethyl)-2,4-dichloro-nicotinamide, N-((5- bromo-3-chloro pyridin-2-y1)-methyl)-2,4-dichloro-nicotinamide, diflumetorim,

nitrapyrin, dodemorphacetate, fluoroimid, blasticidin-S, chinomethionat, debacarb, difenzoquat, difenzoquat-methylsulphat, oxolinic acid and piperalin; B5) carbamates selected from the group consisting of mancozeb, maneb, metam, methasulphocarb, metiram, ferbam, propineb, thiram, zineb, ziram, diethofencarb, iprovalicarb, 5 bentiavalicarb, propamocarb, propamocarb hydrochlorid, 4-fluorophenyl N-(1-(1-(4-cyanophenyl)-ethanesulfonyl)but-2-yl)carbamate, methyl 3-(4-chloro-phenyl)-3-(2-isopropoxycarbonylamino-3-methyl-butyrylamino)propanoate; or B6) other fungicides selected from the group consisting of guanidine, dodine, dodine free base, iminoctadine, guazatine, antibiotics: kasugamycin, streptomycin, polyoxin, 10 validamycin A, nitrophenyl derivatives: binapacryl, dinocap, dinobuton, sulfur-containing heterocyclyl compounds: dithianon, isoprothiolane, organometallic compounds: fentin salts, organophosphorus compounds: edifenphos, iprobenfos, fosetyl, fosetyl-aluminum, phosphorous acid and its salts, pyrazophos, tolclofos-methyl, organochlorine compounds: dichlofluanid, flusulfamide, hexachloro- 15 benzene, phthalide, pencycuron, quintozone, thiophanate-methyl, tolylfluanid, others: cyflufenamid, cymoxanil, dimethirimol, ethirimol, furalaxyl, metrafenone and spiroxamine, guazatine-acetate, iminoc-tadine-triacetate, iminoctadine-tris(albesilate), kasugamycin hydrochloride hydrate, dichlorophen, pentachlorophenol and its salts, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl- 20 benzenesulfonamide, dicloran, nitrothal-isopropyl, tecnazen, biphenyl, bronopol, diphenylamine, mildiomyacin, oxincopper, prohexadione calcium, N-(cyclopropylmethoxyimino-(6-difluoromethoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl- 25 phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluormethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methylformamidine and N'-(5-difluormethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, and any combinations thereof.

Nematicides: Benomyl, cloethocarb, aldoxycarb, tirpate, diamidafos, 30 fenamiphos, cadusafos, dichlofenthion, ethoprophos, fensulfothion, fosthiazate, heterophos, isamidofof, isazofos, phosphocarb, thionazin, imicyafos, mecarphon, acetoprole, benclonthiaz, chloropicrin, dazomet, fluensulfone and suitable combinations thereof.

Plant Growth Regulators: D1) Antiauxins, such as clofibric acid, 2,3,5-tri-iodobenzoic acid; D2) Auxins such as 4-CPA, 2,4-D, 2,4-DB, 2,4-DEP, dichlorprop, fenoprop, IAA, IBA, naphthaleneacetamide,  $\alpha$ -naphthaleneacetic acids, 1-naphthol, naphthoxyacetic acids, potassium naphthenate, sodium naphthenate, 2,4,5-T; D3) 5 cytokinins, such as 2iP, benzyladenine, 4-hydroxyphenethyl alcohol, kinetin, zeatin; D4) defoliants, such as calcium cyanamide, dimethipin, endothal, ethephon, merphos, metoxuron, pentachlorophenol, thidiazuron, tribufos; D5) ethylene inhibitors, such as aviglycine, 1-methylcyclopropene; D6) ethylene releasers, such as ACC, etacelasil, ethephon, glyoxime; D7) gametocides, such as fenridazon, maleic 10 hydrazide; D8) gibberellins, such as gibberellins, gibberellic acid; D9) growth inhibitors, such as abscisic acid, ancymidol, butralin, carbaryl, chlorphonium, chlorpropham, dikegulac, flumetralin, fluoridamid, fosamine, glyphosine, isopyrimol, jasmonic acid, maleic hydrazide, mepiquat, piproctanyl, prohydrojasmon, propham, tiaojiean, 2,3,5-tri-iodobenzoic acid; D10) morphactins, 15 such as chlorfluren, chlorflurenol, dichlorflurenol, flurenol; D11) growth retardants, such as chlormequat, daminozide, flurprimidol, mefluidide, paclobutrazol, tetacyclacis, uniconazole; D12) growth stimulators, such as brassinolide, brassinolide-ethyl, DCPTA, forchlorfenuron, hymexazol, prosuler, triacontanol; D13) unclassified plant growth regulators, such as bachmedesh, benzofluor, 20 buminafos, carvone, choline chloride, ciobutide, clofencet, cyanamide, cyclanilide, cycloheximide, cyprosulfamide, epocholeone, ethychlozate, ethylene, fuphenthiourea, furalane, heptopargil, holosulf, inabenfide, karectazan, lead arsenate, methasulfocarb, prohexadione, pydanon, sintofen, triapenthenol, trinexapac.

In another aspect of the present invention, suitable combination of any one of 25 insecticides, herbicides, fungicides, nematocides and plant growth promoters are provided to expand and provide better coverage in the furrow.

One aspect of the invention is directed to a method of seed treatment comprising (a) applying to seeds a coating of an alginate, optionally containing one or more crop protection agents selected from the group consisting of insecticides, 30 nematocides, stress-reducing agents and fungicides, and/or one or more nutrients for seedling and plant growth; and (b) crosslinking the alginate coating with a divalent metal ion. The alginate is preferably a soluble alginate, such as sodium or potassium alginate. In one embodiment, the seeds are a pretreated seeds. Seeds can be pretreated with fungicides, insecticides, nematocides, and the like. Pretreated seeds

can be commercial products, or can be treated immediately before coating with the alginate. In one embodiment, the insecticide is acetamiprid.

In one embodiment the divalent metal ion is selected from the group consisting of  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$  and  $\text{Zn}^{+2}$ . Preferably the divalent metal ion is  $\text{Ca}^{+2}$ . In one  
5 embodiment the crosslinking is effected by applying a divalent metal ion solution. In one embodiment the divalent metal ion solution comprises an aqueous solution of a divalent metal salt, preferably a calcium salt selected from the group consisting of calcium chloride, calcium carbonate and calcium sulfate. In one embodiment the  
10 divalent metal ion solution is applied by spraying. In one embodiment the application of the alginate coating is also applied via spraying.

Another aspect of the invention is directed to a method of seed treatment comprising (a) spraying seeds with a solution of a soluble alginate containing one or more crop protection agents selected from the group consisting of insecticides, nematocides, stress-reducing agents and fungicides, and/or one or more nutrients, to  
15 form coated seeds; and (b) spraying the coated seeds with an aqueous solution of a calcium salt in order to crosslink the alginate. In one embodiment the seeds are pretreated seeds. Seeds can be pretreated with fungicides, insecticides, nematocides, and the like. Pretreated seeds can be commercial products, or can be treated immediately before coating with the alginate.

20 In at least one aspect, the presently described controlled release seed treatment provides numerically and statistically significant improvement for controlling undesirable pests, insects, fungus and/or nematodes as compared to non-controlled release products of the same active ingredient. In more preferred embodiment, the improvement is particularly significant at later residual dates such as 35, 42, 52, 59, 66,  
25 81 or 88 days after planting the presently described seeds. In at least one embodiment, the control of cotton aphid was statistically significant compared to non-controlled formulation of the same or comparable active ingredient; at least at 50 days after treatment and further remained its statistically significant impact for at least 88 days after plantation of the treated seeds.

30 Another aspect of the invention is directed to a coated seed including a plant seed core and a controlled release coating that includes crosslinked alginate and a crop protection agent selected from the group consisting of insecticides, nematocides and fungicides, and/or one or more nutrients, and combinations thereof. In one embodiment, the plant seed core is a seed selected from the group consisting of



monocotyledons, dicotyledons, and mixtures thereof. In another embodiment, the crop protection agent is an insecticide selected from the group consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb, acephate, azinphos-ethyl, azinphos-
 5 methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl,
 10 quinalphos, terbufos, tetrachlorvinphos, triazophos trichlorfon, endosulfan, ethiprole, fipronil, pyrafluprole and pyriprole, acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid, thiamethoxam, spinosad, spinetoram, abamectin, emamectin benzoate, ivermectin, lepimectin, milbemectin, hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen, pymetrozine, flonicamid, pyrifluquinazon,
 15 clofentezine, hexythiazox, etoxazole, diafenthiuron, fenbutatin oxide, propargite, chlorfenapyr, bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium, bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, buprofezin, cyromazine, methoxyfenozide, tebufenozide, halofenozide, chromafenozide, amitraz, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim,
 20 cyenopyrafen, cyflumetofen, hydramethylnon, acequinocy, fluacrypyrim, indoxacarb, metaflumizone, spirotetramat, spiromesifen, spirotetramat, flubendiamide, (R)-3-Chlor-N1- {2- methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1- methyl-2-
 25 methylsulfonylethyl)phthalamid, chloranthraniliprole, cy- anthraniliprole, azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl, sulfoxaflor, acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvaterate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate,
 30 permethrin, silafluofen, tefluthrin, tralomethrin, and any suitable combinations thereof. In another embodiment, the crop protecting agent is a neonicotinoid selected from the group consisting of acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid and thiamethoxam.

EXAMPLES

**Example 1. Controlled Release Acetamiprid Residual Study**

The residual activity of a controlled release (“CR”) acetamiprid cotton seed treatment (“ST”), a non-controlled release (“NCR”) acetamiprid (“ST”), and Cruiser  
 5 ST cotton (thiamethoxam) was tested against cotton aphid (“CA”) in a microbially active soil/sand mixture.

Table 1. Treatments

<b>Formulation Type</b>	<b>Rates Tested (ppm or g ai/ha)</b>
CR acetamiprid cotton ST	0.3 mg / seed
CR acetamiprid cotton ST	0.5 mg / seed
NCR acetamiprid cotton ST	0.5mg / seed
Blank formulation	0.5mg equivalent
Cruier ST cotton	standard
Untreated check	

In this study, the CA were infested upon cotyledons out to 28 days after  
 10 planting (“DAP”). At 35 DAP and onward, the CA were infested upon the first true leaves. The results show that the seed treatments provided greater than 95% control to CA through 28 DAP, and statistically improved control with CR acetamiprid compared to NCR acetamiprid at evaluation dates between 35 DAP and 88 DAP.

Table 2. % control of cottonaphid upto 88 days after planting.

		35DAP	42DAP	49DAP	52DAP	59DAP	66DAP	81DAP	88DAP
Treatment	RATE	% Control	% Control	% Control	% Control	% Control	% Control	% Control	% Control
CR acetamiprid	0.3mg ai/seed	93	73	67	76	6	82	41	32
CR acetamiprid	0.5mg ai/seed	100	80	77	98	92	91	72	77
NCR acetamiprid	0.5mg ai/seed	88	95	66	85	85	83	51	36
Blank	0.5mg ai equiv.	dropped	dropped	dropped	dropped	dropped	dropped	dropped	dropped
Cruiser ST	ST	98	81	68	84	79	70	49	22
UTC	—	2c	3b	3b	2c	6c	5c	1c	2c

This study showed that 0.5 mg of the CR seed treatment provided numerical and statistical improved control at later residual dates, 49 DAP – 88 DAP, compared to the NCR and the standard Cruiser ST. No activity was observed with the blank formulation.

Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the invention should not be limited to the description and the preferred versions contained within this specification.

## CLAIMS

What is claimed is:

1. A method of seed treatment comprising:
  - (a) applying to seeds a coating of an alginate, optionally containing one or  
5 more crop protection agents selected from the group consisting of insecticides,  
nematocides and fungicides, and/or one or more nutrients; and
  - (b) crosslinking the alginate with a divalent metal ion.
2. The method of claim 1, wherein said insecticide is acetamiprid.  
10
3. The method of claim 1, wherein said divalent metal ion is selected from the  
group consisting of  $\text{Ca}^{+2}$ ,  $\text{Ba}^{+2}$  and  $\text{Zn}^{+2}$ .
4. The method of claim 1, wherein said crosslinking is effected by applying a  
15 divalent metal ion solution.
5. The method of claim 4, wherein said divalent metal ion solution comprises an  
aqueous solution of a divalent metal salt.
- 20 6. The method of claim 5, wherein said divalent metal salt is a calcium salt.
7. The method of claim 6, wherein said calcium salt is selected from the group  
consisting of calcium chloride, calcium carbonate and calcium sulfate.
- 25 8. The method of claim 4, wherein said divalent metal ion solution is applied by  
spraying.
9. The method of claim 1, wherein the application of the alginate coating is via  
spraying.  
30
10. A method of seed treatment comprising:
  - (a) spraying seeds with a solution of a soluble alginate containing one or more  
crop protection agents selected from the group consisting of insecticides,

nematocides and fungicides, and/or one or more nutrients, to form coated seeds; and

(b) spraying said coated seeds with an aqueous solution of a calcium salt in order to crosslink the alginate.

5

11. The method of claim 10, wherein said seeds are pretreated seeds.

12. The method of claim 1, wherein said seeds are pretreated seeds.

10 13. The method of claim 1, wherein the insecticide is selected from the group consisting of aldicarb, alanycarb, benfuracarb, carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb, acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, 15 ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos trichlorfon, endosulfan, ethiprole, fipronil, pyrafluprole and pyriprole, acetamiprid, chlothianidin, dinotefuran, 20 imidacloprid, nitenpyrathiacloprid, thiamethoxam, spinosad, spinetoram, abamectin, emamectin benzoate, ivermectin, lepimectin, milbemectin, hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen, pymetrozine, flonicamid, pyrifluquinazon, clofentezine, hexythiazox, etoxazole, diafenthiuron, fenbutatin oxide, propargite, chlorfenapyr, bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium, 25 bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, buprofezin, cyromazine, methoxyfenozide, tebufenozide, halofenozide, chromafenozide, amitraz, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocy, fluacrypyrim, indoxacarb, metaflumizone, spiroidiclofen, spiromesifen, spirotetramat, flubendiamide, (R)-3- 30 Chlor-N1- {2- methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-4-1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1- methyl-2-methylsulfonylethyl)phthalamid, chloranthraniliprole, cy- anthraniliprole, azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl,

sulfoxaflor, acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate, permethrin, silafluofen, tefluthrin, tralomethrin, and any suitable combinations  
5 thereof.

14. The method of claim 13, wherein the insecticide is acetamiprid.

15. A coated seed comprising a plant seed core and a controlled release coating  
10 comprising crosslinked alginate and a crop protection agent selected from the group consisting of insecticides, nematocides and fungicides, and/or one or more nutrients, and combinations thereof.

16. The coated seed of claim 15, wherein the plant seed core is a seed selected  
15 from the group consisting of monocotyledons, dicotyledons, gymnosperms or mixtures thereof.

17. The coated seed of claim 15, wherein the crop protection agent is an  
insecticide selected from the group consisting of aldicarb, alanycarb, benfuracarb,  
20 carbaryl, carbofuran, carbosulfan, methiocarb, methomyl, oxamyl, pirimicarb, propoxur and thiodicarb, acephate, azinphos-ethyl, azinphos-methyl, chlorfenvinphos, chlorpyrifos, chlorpyrifos-methyl, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidaphos, methidathion, mevinphos, monocrotophos, oxymethoate,  
25 oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, pirimiphos-methyl, quinalphos, terbufos, tetrachlorvinphos, triazophos trichlorfon, endosulfan, ethiprole, fipronil, pyrafluprole and pyriprole, acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid, thiamethoxam, spinosad, spinetoram, abamectin, emamectin benzoate, ivermectin,  
30 lepimectin, milbemectin, hydroprene, kinoprene, methoprene, fenoxycarb, pyriproxyfen, pymetrozine, flonicamid, pyrifluquinazon, clofentezine, hexythiazox, etoxazole, diafenthiuron, fenbutatin oxide, propargite, chlorfenapyr, bensultap, cartap hydrochloride, thiocyclam and thiosultap sodium, bistrifluron, diflubenzuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, buprofezin,

cyromazine, methoxyfenozide, tebufenozide, halofenozide, chromafenozide, amitraz, pyridaben, tebufenpyrad, tolfenpyrad, flufenimer, cyenopyrafen, cyflumetofen, hydramethylnon, acequinocy, fluacrypyrim, indoxacarb, metaflumizone, spiroticlofen, spiromesifen, spirotetramat, flubendiamide, (R)-3-Chlor-N1- {2-  
5 methyl-4-[1,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1-methyl-2-methylsulfonylethyl)phthalamid and (S)-3-Chlor-N1- {2-methyl-441,2,2,2 - tetrafluor-1-(trifluormethyl)ethyl]phenyl} -N2-(1- methyl-2-methylsulfonylethyl)phthalamid, chloranthraniliprole, cy- anthraniliprole, azadirachtin, amidoflumet, bifenazate, fluensulfone, piperonyl butoxide, pyridalyl,  
10 sulfoxaflor, acrinathrin, allethrin, bifenthrin, cyfluthrin, lambda-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, tau-fluvalinate, permethrin, silafluofen, tefluthrin, tralomethrin, and any suitable combinations thereof.

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18. The seed of claim 15, wherein the crop protecting agent is a neonicotinoid selected from the group consisting of acetamiprid, chlothianidin, dinotefuran, imidacloprid, nitenpyrathiacloprid and thiamethoxam.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/62862

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> <b>IPC(8) - A01C 1/06 (2014.01)</b> <b>CPC - A01C 1/06</b> According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC - A01C 1/06 (2014.01); CPC - A01C 1/06; USPC - 47/57.6, 504/100 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 47/57.6, 504/100 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Google Patents (US, EP, WIPO); Dialog Proquest (NPL); Patbase (CN, DE, EP, FR, GB, JP, KR, US, WIPO); Search terms: alginate, alginic acid, extract phaeophyceae, insecticid*, nematocid*, fungicid*, seed, plant, kernel, cover, coat, coating, protect, layer, crosslink, metal, ion, divalent, calcium, ca, valen*, polyvalen*, multivalen*, acetamiprid		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/0220454 A1 (CHEN et al.) 30 August 2012 (30.08.2012); entire document, especially para [0002], [0006], [0013], [0017], [0021], [0022], [0024], [0025], [0028], [0030], [0036], [0042]	1, 3, 9, 12, 13, 15-17
Y	[0045], [0062].	2, 4-8, 10, 11, 14, 18
Y	WO 2011/103594 A1 (EDWARDS et al.) 25 August 2011 (25.08.2011); entire document, especially p 2, ln 1-4, 6-15, 29-p 3, ln 6; p 4, ln 25-27; p 16, ln 18-20; p 18, ln 1-3; p 42, ln 19-24	4-8, 10, 11
Y	US 2010/0234219 A1 (LAHM et al.) 16 September 2010 (16.09.2010); entire document, especially para [0026], [0254], [0284].	2, 14, 18
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>		
* 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 05 January 2015 (05.01.2015)		Date of mailing of the international search report <b>28 JAN 2015</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774