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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 September 2010 (10.09.2010)

PCT

(10) International Publication Number
WO 2010/100638 A2

(51) International Patent Classification:
A01N 25/28 (2006.01) *A01N 57/16* (2006.01)
A01N 47/40 (2006.01) *A01P 7/04* (2006.01)
A01N 51/00 (2006.01)

(21) International Application Number:
PCT/IL2010/000154

(22) International Filing Date:
24 February 2010 (24.02.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/202,484 4 March 2009 (04.03.2009) US

(71) Applicant *(for all designated States except US)*: **CELSIUS PROPERTY B.V. AMSTERDAM (NL)** [CH/CH]; Schaffhausen Branch, 5 Spitalstrasse, CH-8200 Schaffhausen (CH).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **COOPER, Guy** [IL/CH]; 11 Kilchbergsteig, CH-8038 Zurich (CH). **CASTAGNA, Renato** [IT/CH]; Hinder Neuchilch, CH-4-8213 Neunkirch (CH). **BENETTI, Ernesto** [BR/BR]; Rua Espirito Santo N° 1570 ap. N° 1201, Londrina -PR (BR).

(74) Agents: **PYERNIK RUTMAN** et al.; Beit Etzion, 91 Herzl St., P.O.Box 10012, 84106 Beer-Sheva (IL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2010/100638 A2

(54) **Title**: SEED TREATMENT AND PESTICIDAL COMPOSITION

(57) **Abstract**: The invention relates to a method of protecting one or both of a seed and a plant grown from the seed against pest infestation, by treating the seed with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos. Also disclosed are a composition and kit for treating a seed and a seed comprising said combination of compounds.

SEED TREATMENT AND PESTICIDAL COMPOSITION

FIELD OF THE INVENTION

The invention relates to a method of protecting a seed and/or a plant grown from the seed against pest infestation.

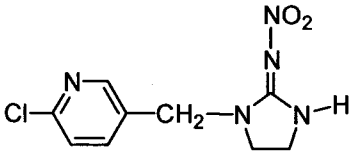
BACKGROUND OF THE INVENTION

The damage to crop plants as a result of pest infestation occurs mostly as early as when the seed is infested during storage, after the seed is introduced into the soil, and during and immediately after germination of the plants. Therefore, protecting the seed and the germinating plant by the use of suitable compositions is of particularly great importance.

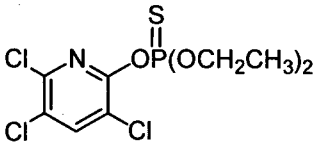
Chloronicotinyl insecticide compounds (Neonicotinoids) act as agonists on the insect nicotinic acetylcholine receptor (nAChR). They represent the most effective chemical class for the control of sucking insect pest such as aphids, whiteflies, leaf- and planthoppers, thrips, some micro lepidoptera and a number of coleopteran pests. Chloronicotinyl insecticide compounds are widely used for seed treatment in cotton, corn, cereals, sugar beet, oilseed rape and other crops (Alfred Albert et al., Mini-review Applied aspects of neonicotinoid uses in crop protection (Pest Management Science, 64, 1099-1105, 2008).
A representative compound of this group is imidacloprid.

The pesticide imidacloprid is described in EP 192060 and US 4,742,060 (Example 11). The compound (chemically named: 1-[

(6-Chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine} is represented by the following formula :



The pesticide chlorpyrifos is described in US 3,244,586. The compound [chemically named O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate] is represented by the following formula:



Chlorpyrifos is a non-systemic insecticide with contact, stomach, and respiratory action.
Chlorpyrifos use for seed treatment is very limited and confined to minor crops and/or few pests as compared to Chloronicotinyl insecticide compounds. Chlorpyrifos is not used for seed treatment in several important crops like oil seed rape, Sugar beet, Cereals etc.

CN 1299596 discloses a composition comprising imidacloprid and chlorpyrifos. The composition, which is especially provided in the form of a sprayable emulsion, in which the two compounds are present at concentrations of 0.1-5% and 10-40% by weight, respectively, in combination with a suitable vehicle, is reported to be effective particularly against above-ground pests by means of foliar application.

US Patent No. 6,660,690 describes seed treatment method using a combination of insecticides.

It will be highly advantageous to have a new method and composition for seed treatment effective against a broad spectrum of pests.

Further, it will be highly advantageous to have an effective seed treatment method and composition broadening and/or improving the effect of chloronicotinyl insecticide compounds.

SUMMARY OF THE INVENTION

The invention relates to a method of protecting one or both of a seed and a plant grown from the seed against pest infestation, by treating the seed with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

The invention further relates to a composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

The invention additionally related to a seed coating composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid,

clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and(b) chlorpyrifos.

The invention further relates to use of (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

Moreover, the invention relates to a kit comprising (a) at least one container including a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; (b) at least one container including chlorpyrifos; and (c) instructions for applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

Further, the invention relates to a kit comprising (a) at least one container including (i) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (ii) chlorpyrifos; and (b) instructions for applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

Moreover, the invention relates to a seed comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

Additionally, the invention relates to a seed coated with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

BRIEF DESCRIPTION TO FIGURES

Fig. 1 is a photograph illustrating the visible differences between the plants grown from the treated seeds and the control (Example 3-4). T1 refers to control (Example 4)and T6 refers to treated seeds (Example 3).

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that the combination of a chloronicotinyl insecticide compound (e.g. imidacloprid) and chlorpyrifos is useful for controlling soil dwelling pests. Such a combination is advantageous since it is capable of significantly expanding the efficacy spectrum of a chloronicotinyl insecticide compound (e.g. imidacloprid) and/or reducing the required application rates.
Further, it has been found that the combination is capable of significantly improving the efficacy of imidacloprid against pests not satisfactorly controlled by imidacloprid.
It has been further found that the combination is capable of improving the level of control achieved on pest by either of the two compounds alone.

The present invention is accordingly directed to a method of protecting one or both of a seed and a plant grown from the

seed against pest infestation, by treating the seed with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

When the chloronicotinyl insecticide compounds and chlorpyrifos are mentioned in the present invention, it is intended to include also salts, solvates, and tautomeric forms of the above-mentioned compounds.

As used herein, the terms "***treating the seeds***" and "***seed treatment***" or the like refer preferably to the application of the active compounds directly to the seeds themselves prior to planting, and/or in their immediate vicinity during planting. Most preferably the active compounds are applied directly to the seeds themselves. These terms comprise all suitable seed treatment techniques known in the art, such as seed dressing, seed dusting, seed coating, seed imbibition (e.g. seed soaking), seed foaming (e.g. covering in foam), and seed pelleting.

The seed treatment application of the active compounds may be carried out, e.g. by spraying, foaming, dusting or otherwise covering the seeds before sowing of the seeds and/or before emergence of the plants.

As used herein the term ***"seed"*** is to be broadly interpreted to include anything that can be sown and can potentially be set in place (soil) to grow a crop.
The term ***"seed"*** embraces seeds and plant propagules of all kinds including but not limited to true seeds, seed pieces,

grains, suckers, corms, bulbs, fruit, tubers, cuttings, cut shoots and similar forms, and preferably means a true seeds.

The use of the terms "***a***" and "***an***" and "***the***" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

The chloronicotinyl insecticide compound and the chlorpyrifos may be applied simultaneously or sequentially. The application of the chloronicotinyl insecticide compound and the chlorpyrifos may be in any desired order.

The term "***administered sequentially***" means the successive administration of a dosage form including a first compound of the invention (i.e. one of a chloronicotinyl insecticide compound and chlorpyrifos), and then administration of a dosage form of a second compound, which is different than the first compound. When administered sequentially the chloronicotinyl insecticide compound and the chlorpyrifos are included in separate compositions. If the chloronicotinyl insecticide compound and the chlorpyrifos are administered sequentially, the order of administering thereof may be interchangeable.

The term "***administered simultaneously***" or "***administered concomitantly***" means administering the compounds substantially concurrently. These terms encompasses not only administering at least two compounds according to the

invention in a single formulation but also the administration of each compound (i.e a chloronicotinyl insecticide compound and chlorpyrifos) in its own separate formulation. Where separate formulations are used, the compounds can be administered at essentially the same time, i.e., concurrently.

The combination may include any combination of the above (a) chloronicotinyl insecticide compound; and (b) chlorpyrifos, i.e., of individual compounds and of any sub-group combination. For example, if a number of different chloronicotinyl insecticide compounds (in combination with chlorpyrifos) are disclosed and discussed, each and every combination of the chloronicotinyl insecticide compound and chlorpyrifos are specifically contemplated. Thus, if a combination of (a) chloronicotinyl insecticide compounds e.g. A, B, C, or mixtures thereof; and (b) chlorpyrifos (D) is disclosed, then even if each is not individually recited, each compound is individually and collectively contemplated. Thus, each of the combinations A-D, B-D, C-D, are specifically contemplated and should be considered disclosed from disclosure of (a) A, B, C, or mixtures thereof; and (b) D. Likewise, any subset or combination of these is also specifically contemplated and disclosed. Thus, for example, the sub-group of (a) A, B, or mixtures thereof; and (b) D are specifically contemplated and should be considered disclosed from disclosure of a combination of (a) A, B, C, or mixtures thereof; and (b) D.

The weight ratio of the chloronicotinyl insecticide compound and the chlorpyrifos may be from 100:1 to 1:10, specifically

from 50:1 to 1:10, more specifically from 50:1 to 1:5. The weight ratio of the chloronicotinyl insecticide compound and the chlorpyrifos may be from 10:1 to 1:10. In a specific embodiment the weight ratio of the chloronicotinyl insecticide compound and the chlorpyrifos may be from 10:1 to 1:5, even more specifically the weight ratio may be from 5:1 to 1:5.

According to certain embodiments the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 3.5:1 to 1:2.5, specifically from 3.3:1 to 1:2.5. According to this embodiment, the chloronicotinyl insecticide compound is preferably imidacloprid.
According to certain embodiments the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 3:1 to 1:2. According to this embodiment, the chloronicotinyl insecticide compound is preferably imidacloprid.

According to a specific embodiment the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from about 2.5:1 to about 1:1. According to this embodiment, the chloronicotinyl insecticide compound is preferably imidacloprid.

The combination of the chloronicotinyl insecticide compound and chlorpyrifos may be used for treating the seeds of various crops, and more specifically the following species of plants: cereals (e.g. wheat, barley, oats, rye, triticale, millet, sorghum) oil seeds (e.g. oil seed rape, sunflower, mustard etc.), Legumes (e.g. soybean, field beans etc.), rice, corn, cotton, root and tuber crops (e.g.

potatoes etc.) as well as vegetables (e.g. leafy, stem, fruiting, brassicas and bulb). The mixture of the chloronicotinyl insecticide compound and chlorpyrifos may be effectively employed for controlling many pests and especially a variety of soil dwelling pests, including but not limited to corn stalk borer (*Elasmopalpus lignosellus*), grubs and beetles (e.g. *Phyllophaga* sp. and *Diloboderus sp.*), corn rootworm (*Diabrotica sp.*), maggots - including corn seed maggot (e.g. *Delia platura sp.*), cutworm (*Agrotis sp.*), wireworm (Agriotes sp.), or any combination of the above.

Additional non-limiting examples of soil dwelling pests include coleoptera (e.g. *Melontha Melontha*), dipterae (e.g. *Tipula oleracea*), ensiferae (e.g. *Grillotalpa grillotalpa*), or any combination of the above.

The mixture of the chloronicotinyl insecticide compound and chlorpyrifos may also exhibit a pesticidal effect on above-ground pests like aphids, leafhoppers, bugs, beetles (e.g. *Phyllotreta sp.*) and others.
According to certain embodiments the seeds are selected from cereals, oil seeds, Legumes, rice, corn, cotton, root and tuber crops, and vegetables.

According to certain embodiments the pest is selected from corn stalk borer, grubs and beetles, corn rootworm, maggots, cutworm, wireworm, and any combination thereof.

Acording to a specific embodiment said pest is corn stalk borer (*Elasmopalpus lignosellus*). According to a specific

embodiment the combination is for treating seeds of soybean and/or corn.

Acording to a specific embodiment said pest is cutworm (e.g. Agrotis segetum). Acording to a specific embodiment the combination is for treating seeds of crops selected from sugar beet and maize.

The term ***"soil dwelling pest"***, as used herein, refers to pests that cause damage to plants or crops while staying in the soil. The damage can be to the seeds, roots, hypocotyl or to other parts of the plant which are under the soil surface or just in the soil surface.

According to certain embodiments the seed treatment is to control a pest, and especially a soil dwelling pest. Such a seed treatment thus involves a pesticidal effect or a pesticidal activity providing protection against damage done by the pest to a seed and/or a plant grown from the seed.

As used herein, the terms ***"pesticidal effect"*** and ***"pesticidal activity"*** mean any direct or indirect action on the target pest that results in reduction of feeding damage on one or more of the treated seeds, fruits, roots, shoots and/or foliage of plants grown from treated seeds as compared to untreated seeds or to plants grown from untreated seeds. Such direct or indirect actions include for example killing the pest, repelling the pest from the plant seeds, fruits, roots, shoots and/or foliage, inhibiting the feeding of the pest on, or the laying of its eggs on, the plant seeds, fruits, roots, shoots and/or foliage, and inhibiting or preventing reproduction of the pest. The

pesticidal effect may be at any pest cycle stage (e.g. adults, larvae, eggs, etc.).

The combination of the chloronicotinyl insecticide compound and chlorpyrifos is applied to the seeds in a pesticidally effective amount, namely, in an amount sufficient for providing protection to the seed and/or parts of the plant that grows from the seed. Protection is achieved wherever there is a statistically significant reduction in the damage caused by the pest in comparison to untreated plants. The rates of application of the chloronicotinyl insecticide compound and chlorpyrifos may be in the ranges between 1 and 3500 g a.i./100kg seed for each compound, in a specific embodiment in the ranges between 1 and 2500g a.i./100kg seed, in a more specific embodiment in the ranges between 1 and 1500g a.i./100kg seed, in a more specific embodiment in the ranges between 10g and 1000g a.i./100 kg seed for each compound, and even more specifically from 35g to 700g chloronicotinyl insecticide compound per 100 kg of seed and 35g to 700 g chlorpyrifos per 100 kg of seed. The exact quantities and the specific weight ratio of the two active ingredients depend, among others, on the crop to be treated and the pest to be controlled. In general, for the rates of application noted above, the weight ratio chloronicotinyl insecticide compound:chlorpyrifos may be suitably adjusted for example in the ranges between 10:1 and 1:10, or 10:1 and 1:5, or 5:1 and 1:5 and more specifically from 3.3:1 to 1:2.5, in some embodiments 3:1 to 1:2, specifically from 3:1 to 1:1.8, more specifically from 2.5:1 to 1:1.5 and in certain embodiments from about 2.5:1 to about 1:1, inclusive, more specifically about 1:1.

In some embodiments the weight ratio chloronicotinyl insecticide compound:chlorpyrifos may be 100:1 and below, 50:1 and below, 10:1 and below, 8:1 and below, 5:1 and below, 3.5 and below, 3.3 and below, 3 and below, 2.5 and below.

In some embodiments the weight ratio chloronicotinyl insecticide compound:chlorpyrifos may be 1:20 an above, 1:10 and above, 1:8 and above, 1:5 and above, 1:2.5 and above, 1:2 and above, 1:1.8 and above, 1:1.5 and above, 1:1.3 and above, 1:1 and above.

The weight ratio of chloronicotinyl insecticide compound:chlorpyrifos may be an intermediate range selected from the above indicated values.

In a specific embodiment the weight ratio chloronicotinyl insecticide compound:chlorpyrifos may be in the range (a) 1:1.8 and above; and (b) a value selected from 10:1 and below, 8:1 and below, 5:1 and below, 3.5 and below, 3.3 and below, 3 and below, 2.5 and below.

As used herein the term "about" means +/- 20% of the indicated value.

The application rates may vary depending on the crops and type of pest.

For example, corn seeds may be effectively treated for the control of the pest *Elasmopalpus lignosellus*, using about 180-250 g imidacloprid/100 kg seed together with about 90-125 g chlorpyrifos /100 kg seed. As to the treatment of soybean seeds, it has been found that about 50-100 g imidacloprid/100 kg seeds, together with about 30-150 g

chlorpyrifos /100 kg seeds, more specifically about 50-120 g chlorpyrifos/ 100 kg seeds provide satisfactory control of the pest *Elasmopalpus lignosellus*, known as a highly destructive pest.

Maize seeds may be effectively treated for the control of the pest *Agrotis Segetum (cutworm)*, using for example about 55 - 180 g imidacloprid/100,000 seeds (about 180-600 g imidacloprid/100 kg seed) together with about 15 - 110 g chlorpyrifos/100,000 seeds (about 50-350 g chlorpyrifos/100 kg seed).

Sugar Beet seeds may be effectively treated for the control of the pest *Agriotis Segetum (Cutworm)*, using for example about 20 - 90 g imidacloprid/100,000 seeds (about 600-2700g imidacloprid/100 kg seed) together with about 20-100 chlorpyrifos/100,000 seeds (about 600-3000 g chlorpyrifos/100 kg seed).

Sugar Beet seeds may be effectively treated for the control of the pest *Agriotis Segetum (Cutworm)*, using for example about 20-90 thiametoxam/100,000 seeds (about 600-2700g thiametoxam/100 kg seed) together with about 20-100 chlorpyrifos/100,000 seeds (about 600-3000 g chlorpyrifos/100 kg seed).

The rates of application of the chloronicotinyl insecticide compound and chlorpyrifos may be in the range 1 to 1500 g/Ha for each compound.

Preferably the range is 20 to 180 g/Ha for the chloronicotinyl insecticide compound. Preferably the range is 1 to 250 g/Ha for Chlorpyrifos.

As used herein the terms ***"Ha"*** or ***"ha"*** refers to hectare.

In certain embodiments the combination of compounds may be synergistic. A synergistic effect of a combination of compounds is present when the activity of the active compound combinations exceeds the total of the activities of the active compounds when applied individually. The expected activity for a given combination of active compounds can be calculated by the Colby's formula (S. R. Colby, Weeds 15 (1967), 20-22) and compared to the observed efficacies. If the observed response of the combination is greater than the expected (or predicted) response then the combination is said to be synergistic.

In certain embodiments the combination of compounds of the present invention may exhibit an improved germination rate as compared to untreated control and/or individual compounds. Thus, the combination of compounds of the present invention may have higher germination rate as compared to untreated control and/or individual compounds.

In general, an effective seed treatment involves uniformly coating the seed with the pesticide. To this end, the pesticide may be suitably formulated, e.g., as a wettable powder, a sticky dust, a suspension or suspension concentrate (flowable concentrate), a soluble powder, an emulsion, or as a solute in solution. The pesticide formulation may be optionally diluted with water in a mixing tank prior to application. Then, in case of small volume of seeds, a prescribed amount of the formulation is mixed with the seeds in a rotating container, affording a uniform distribution of the pesticides onto the seeds. Continuous

flow treaters, useful for the treatment of large volumes of seeds and being adapted for the application of different types of formulations are also available. Briefly, the treaters have quantitative inlet compartments for controlling the amounts of the seeds and pesticides to be mixed, and a revolving drum mixer where the pesticide formulation and the seed come together to achieve the uniform coating of the pesticide formulation onto the seeds. The pesticide formulation can be applied to seeds by any standard seed treatment methodology, including but not limited to mixing in a container (e.g., a bottle or bag), mechanical application, tumbling, spraying, and immersion.

According to an embodiment of the invention chlorpyrifos is in a form of first particles.

According to a preferred embodiment the first particles comprising chlorpyrifos and a first carrier material.

According to a preferred embodiment of the invention, the chlorpyrifos is in a form of first particles, said particles comprising chlorpyrifos enclosed in a first carrier material.

As used herein the terms ***"chlorpyrifos is enclosed in a first carrier material"***, ***"active ingredient is enclosed in a carrier material"*** and similar terms, denotes encapsulating, coating, embedding, entrapping, dissolving, dispersing or any other manner of incorporating the active ingredient (active compound) in a carrier material.

According to a preferred embodiment chlorpyrifos is microencapsulated in the first carrier material.

According to a preferred embodiment the first carrier material is a polymer.

According to this embodiment the shell of the microcapsules described bellow is made of the first carrier material (e.g. a polymer).

As used herein the term ***"microencapsulated"***, or ***"microcapsules"*** refers to particles having a core-shell structure, i.e. particles having a shell component and a core component, whereby the core component (core material) is encapsulated by the shell component (shell material). The core material comprises the active ingredient. As used herein, the term ***"microcapsules"*** refers to a single core microcapsules or multiple core microcapsules. Preferably this term refers to single core microcapsules. The core material of the microcapsules is surrounded by a shell material.

As used herein the terms ***"core"***, ***"core component"*** or ***"core material"*** may be used interchangeably. These terms refer to the inside part of the microcapsules comprising the active ingredient, which is surrounded by the shell of the microcapsules. The core material comprises the active ingredient and optionally excipients such as a liquid excipient (e.g. a water-immiscible liquid), a solid or semi-solid excipient. The liquid excipient may be used to dissolve or disperse the active ingredient. Thus, the active

ingredient may be for example dissolved or suspended in the liquid excipient of the core material.

As used herein the terms ***"shell", "shell component" or "shell material"*** may be used interchangeably. These terms refer to the coating, a membrane or wall that surrounds the core material of the microcapsules in which the active ingredient is located.

Thus the active ingredient may be enclosed in a first carrier material (e.g. a polymer) and further optionally enclosed in other carrier material.

The active ingredient may be optionally enclosed in other carrier materials for example the excipients constituting the core of the microcapsules and/or diluents surrounding the shell of the microcapsules. The term "*other carrier material*" means a carrier material or diluent different than the first carrier material.

The shell of the microcapsules typically comprises a polymer or a mixture of polymers.

The case of a plurality of cores embedded or dispersed in a shell material, is also referred herein to matrix structure particles.

The first carrier material is preferably a polymer such as polyurea, polyamides, epoxy resins, polyurethanes, polyester, polycarbonate, polysulfonamide, styrene polymer, and mixtures thereof.

The shell of the microcapsules may be a polycondensate. The polycondensate may be prepared from reactive components which are well known in the art.

The shell of the microcapsules preferably comprises a water insoluble polymer. The water insoluble polymer is preferably selected from polyurea, polyamides, epoxy resins, polyurethanes, polyester, polycarbonate, polysulfonamide, styrene polymer, and mixtures thereof.
According to a preferred embodiment of the invention the polymer is polyurea.

The water insoluble polymer may have a solubility in water of 1 mg/liter and below, 0.5 mg/liter and below, 0.1 mg/liter and below, 0.01 mg/liter and below, 0.001 mg/liter and below, 0.0001 mg/liter and below, at room temperature. By the term "room temperature" is meant 20 - 25^{0}C. The water insoluble polymer may have a solubility above zero and up to the values indicated above.

The concentration of the shell based on the total weight of the microcapsules may be from about 0.5% to about 70% w/w, for example from about 1% to 70% w/w, from about 1% to about 50% w/w, specifically from about 1% to about 30% w/w, preferably from about 1% to about 20% w/w, more preferably from about 5 to about 20% w/w, more preferably from about 8% to about 18% w/w, even more preferably from about 10% to about 15% w/w.

According to certain embodiments, the concentration of the shell based on the total weight of the microcapsules is from

about 2% to about 70% w/w, for example from about 5% to 50% w/w, specifically from about 5% to about 30% w/w.

As used herein by the term about is meant ± 20% of the indicated value.

Microcapsulating procedure for use in the preparation of the microcapsules includes for example, an interfacial polymerization process. An interfacial polymerization process is preferable for preparing the microcapsules owing to a wide selection range for microcapsule shell materials.

For example, the polycondensate shell may be prepared by reacting a first reactive component selected from a polyisocyanate, a polyacid chloride, a polychloroformate and a polysulfonyl chloride with a complementary second reactive component selected from a polyamine and polyol to form the appropriate polycondensate shell.

It is appreciated that there are other complementary reactive components useful in an interfacial condensation process, which react to form polycondenstes.
It is further appreciated that mixtures of first reactive components and mixtures of second reactive components may be used.

Polyurethane microcapsule shells can be prepared, for example, by interfacial polymerization of polyvalent isocyanate compounds and polyhydric alcohol compounds; polyurea microcapsule shells by interfacial polymerization of polyvalent isocyanate compounds and polyvalent amine compounds; polyamide microcapsule shells by interfacial

polymerization of polyvalent acid chloride compounds and polyvalent amine compounds; polyester microcapsule shells by interfacial polymerization of polyvalent acid chloride compounds and polyhydric alcohol compounds, etc.

According to certain embodiments of the present invention the particles are matrix particles.

As used herein the term ***"matrix"*** is defined as a surrounding carrier material in which an active ingredient is entrapped, embedded, dissolved, dispersed or otherwise distributed. Particles of the present invention may comprise a matrix that includes one or more carrier materials (e.g. polymers) in which an active ingredient is entrapped, embedded, dissolved, dispersed, or otherwise distributed. The particles may also include one or more excipients or additives, such as surfactants.

The distribution of the active ingredient in the matrix may be at a molecular level or the distribution may be as fine particles comprising a plurality of molecules of the active ingredient. The distribution may be substantially homogeneous throughout the matrix material or the distribution may exhibit a concentration gradient through a cross-section of the matrix material.

The concentration of the active ingredient in the matrix may be from about 0.1% to about 99%, more specifically from about 0.1% to about 90%w/w.

The matrix particles can be produced by any process that results in a matrix-structured particles including but not limited to solvent evaporation, coacervation, emulsion polymerization, and spray drying.

For example, according to solvent evaporation method, matrix particles may be prepared for example by dissolving at least one active ingredient and a polymer in a water immiscible liquid to form a hydrophobic solution; mixing the hydrophobic solution and an aqueous medium at a shear rate and for a time period sufficient to produce an emulsion having droplets of the hydrophobic solution dispersed in the aqueous medium; and evaporating the organic solvent from the emulsion to produce a plurality of particles.

The release of the active ingredient from the particles may depend on the polymer, size of the particle, the loading of the active ingredient, etc.

According to certain embodiments of the invention the first carrier material may be a water immiscible liquid. In such a case the particles may be in the form of liquid droplets comprising chlorpyrifos.

According to certain embodiments of the invention the first particles are a solid particulate matter of chlorpyrifos.

According to a preferred embodiment of the invention chlorpyrifos is microencapsulated in a polymer (i.e the shell of the microcapsules is made of a polymer).

According to another embodiment of the invention the chloronicotinyl insecticide compound is in the form of second particles.

According to an embodiment of the invention the second particles comprising a chloronicotinyl insecticide compound and a second carrier material.

According to an embodiment of the invention the second particles comprising the chloronicotinyl insecticide compound enclosed in a second carrier material.

As used herein the term ***"chloronicotinyl insecticide compound enclosed in a second carrier material"*** has a similar meaning as *"chlorpyrifos enclosed in a first carrier material"* defined above.

The second carrier material may be for example a polymer (such as a hydrophilic polymer, or a hydrogel), a polysaccharide, a surfactant, a water immiscible liquid, and mixtures thereof.

According to certain embodiments the second particles may be in the form of a liquid droplet.

According to a preferred embodiment the second particle is a solid particulate matter of the chloronicotinyl insecticide compound.

As used herein the term ***"solid particulate matter of chloronicotinyl insecticide compound"*** denotes solid particles made wholly or substantially wholly of the

chloronicotinyl insecticide compound (it is appreciated that minute negligible amount of impurities may be included in the particles). This term refers to a solid particulate matter free form of the chloronicotinyl insecticide compound and denotes that the chloronicotinyl insecticide compound is present in its *"naked"* form meaning that it is not present in the particles in a manner intimately encapsulated, embedded, entrapped, encased, dissolved or dispersed in a carrier material (e.g. a polymer). This term denotes that the solid particulate matter of the chloronicotinyl insecticide compound is present in a composition in direct contact with the ambient surrounding (e.g. composition diluent).

The solid particulate matter of the compounds of the invention may be provided in a form such as a suspension or suspension concentrate, a slurry, a paste, or a foam.

As used herein the term ***"solid particulate matter of chlorpyrifos"*** has a similar meaning as described above with respect to the chloronicotinyl insecticide compound.

The particles of the present invention preferably adheres to the surface of a seed. Without being limited by theory, it is thought that the particle becomes trapped in crevices on the seed. Adhesion of the particle to the seed can be enhanced or achieved by the use of conventional "sticking agents" ("stickers" or "tackifiers") or other compounds that can be used for applying various coatings to seeds, referred herein also as "binding agents". Examples of such sticking agents are hydrophilic polymers or surfactants.

When referring to the particle's size, as used herein the term ***"particles"*** in connection with particle's dimensions will refer collectively to the first and second particles in any structure of the particles e.g. microcapsules, matrix-structure particles, solid particulate matter of the active ingredient, liquid droplets, etc.

The size of the particles (in diameter) is preferably in the micrometer range (i.e. the particles are preferably in the form of microparticles).

A particle size distribution of d_x is defined as a distribution where x percent by volume of the particles are equal or smaller than the size indicated, as determined by laser diffraction.

Accordingly, as used herein the term ***"d90"*** denotes that 90% of the particles have the stated diameter or less (measured by volume). Thus, for examples, for particles stated to have d90=100 micrometer (micron), this means that 90% of the particles have a diameter of 100 micrometer or less.

Preferably the size of the particles is characterized by d90=250 micrometer.

The size of the particles may be characterized by d90=100 micrometer, specifically d90=50 micrometer, more specifically, d90=25 micrometer, still more specifically d90=15 micrometer, or d90=12 micrometer, even more specifically d90=10 micrometer.

The size of the particles (d90) may be an intermediated between the above-mentioned values, e.g. d90 in the range 10 - 250 micrometer.

It is appreciated that the size of the particles will depend on the specific formulation used and its mode of application (i.e. whether applied directly to the seed or its locus), for example, granules or other formulation forms which are applied to the soil may be characterized at times by higher dimensions for example d90=1000 micrometer, or even higher dimensions. Thus in certain embodiments d90 may be in the in the range 10 - 1000 micrometer.

According to a preferred embodiment, the chlorpyrifos is microencapsulated in a polymer and the chloronicotinyl insecticide compound is in a form of solid particulate matter.

According to a preferred embodiment of the invention, the imidacloprid is in the form of a solid particulate matter, and clorpyrifos is enclosed in a first carrier material, preferably in a polymeric material, more preferably chlorpyrifos is microencapsulated in a polymer.

According to certain embodiments of the invention the chloronicotinyl insecticide compound is selected from imidacloprid, thiamethoxam, clothianidin, and mixtures thereof. According to a specific embodiment of the invention the chloronicotinyl insecticide compound is selected from imidacloprid, thiamethoxam, and mixtures thereof.

According to a preferred embodiment of the invention the chloronicotinyl insecticide compound is imidacloprid.

According to another preferred embodiment of the invention the chloronicotinyl insecticide compound is thiamethoxam.

According to a specific embodiment of the invention the chloronicotinyl insecticide compound is Clothianidin.

According to certain embodiments, the chloronicotinyl insecticide compound and chlorpyrifos are provided in a composition further comprising an agriculturally acceptable carrier. The agriculturally acceptable carrier may be as defined hereinafter.

In order to coat the seeds with effective amounts of the chloronicotinyl insecticide compound and chlorpyrifos, the active ingredients are used in the form of composition(s) which comprise solid, semi-solid or liquid carriers and additives for promoting the desired mode of application, as described in more detail below. It should be noted that the active compounds may be formulated either separately, each compound in a distinct formulation, or together, combined in a mixed formulation. The compounds are preferably applied to the seeds essentially simultaneously (if two separate formulations are used, then these formulations may be pre-mixed shortly before the seeds are coated, in order to assure a uniform coating onto the seeds)). It is also possible to apply the two or more separate formulations in succession, with a short time interval between the application of the formulations. A non-limiting list of

operative formulations includes (the commonly used two-letter code is also given):
capsule suspension for seed treatment (CF);
suspension or flowable concentrate for seed treatment (FS);
solution for seed treatment (LS);
Water dispersible powder for slurry seed treatment (WS);
gel for seed treatment (GF); and
a mixed formulation of CF and FS (ZC).

The combination of the chloronicotinyl insecticide compound and chlorpyrifos is capable of effectively exerting its pesticidal activity for protecting a plant against e.g. soil dwelling pests for example when the two active ingredients are applied to the seeds by means of different delivery forms, such that the chloronicotinyl insecticide compound can become available to the seeds essentially immediately, while chlorpyrifos may be provided in a delivery form capable of modifying its release. Suitable formulations satisfying the properties noted above are now described in detail.

Regarding the chloronicotinyl insecticide compound, an especially suitable delivery form meeting the demand noted above for the immediate availability of the compound is a FS formulation, in which small (preferably in the micrometer range) chloronicotinyl insecticide compound particles in a solid particulate form (in a "free" form of the compound) are homogeneously suspended in water in the presence of one or more additives selected from the group consisting of wetting agents (e.g. surfactants), dispersants, antimicrobial agents, antifreeze agents, thickeners, stabilizers and possibly other conventional additives. The

preparation of the chloronicotinyl insecticide compound (e.g. imidacloprid) FS formulation involves uniformly blending the additives noted above (e.g., the dispersants) in water, to form a homogeneous dispersion, and adding the chloronicotinyl insecticide compound under shearing. A subsequent milling, e.g., in a pearl-mill, to obtain a population of chloronicotinyl insecticide compound particles with d90 of for example equal or less than 10 ?m may then follow, if needed. Finally, a stabilizer may be added to the dispersion under shearing. The concentration of chloronicotinyl insecticide compound in the resultant suspension preferably varies in the range of 30 and 70 % by weight. Imidacloprid formulations that are suitable for use according to the method of the present invention are commercially available (e.g. Seedoprid 600 FS, Makhteshim Chemical Works LTD., in which the concentration of Imidacloprid is approximately 600 g/liter, with a density of about 1.25 g/ml).

Regarding chlorpyrifos, the delivery form that may be applied for the seed treatment according to the invention is preferably a CF formulation. Techniques for preparing capsules incorporating an active ingredient are known in the art. For example, according to the interfacial polycondensation method, the following procedure may be used: an organic phase is provided, which contains the active ingredient in a liquid form, namely, either in a molten state or as a solute, together with a first, oil-soluble monomer (e.g., isocyanate). A dispersant (surfactant)-containing aqueous phase is also provided. The two phases are then mixed to form an oil-in-water emulsion.

Then a second monomer, which is water soluble, is added to the emulsion (e.g., one or more amine monomers), whereby a polymeric shell is formed (e.g. made of polyurea), encapsulating the active material (e.g. as a liquid core). Suitable chlorpyrifos capsule suspension formulations are described, for example, in US 5,925,464 and US 5,549,903. According to a specific embodiment clorpyrifos capsules are prepared as described in US 5,549,903. Chlorpyrifos capsule suspension formulations that are suitable for use according to the method of the present invention are also commercially available (e.g. Pyristar, Pyristar 250 CF, Makhteshim Chemical Works LTD., in which the concentration of chlorpyrifos is approximately 250 g/liter, with a density of about 1.1 g/ml).

The invention further provides a composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

Preferably the composition is for use in protecting one or both of a seed and a plant grown from the seed against pest infestation.

Preferably the composition further comprises an agriculturally acceptable carrier.

As used herein the term ***"agriculturally acceptable carrier"*** covers all excipients, e.g., inert diluents, dispersants, surfactants, tackifiers, binders, etc. that are ordinarily used in pesticide formulation technology. A suitable carrier

may be for example a solid, semi-solid or liquid carrier depending on the desired formulation, and are well known in the art. In a specific embodiment preferred carriers include polar liquid carriers preferably an aqueous carrier e.g. water.

In general, the compositions may comprise from 0.001 to 99% by weight, more specifically from about 0.01 to 95% by weight of the active compounds.

The active compound concentrations in the ready-to-use products may be varied within the range from about 0.01 to 80% by weight, and more specifically from about 0.1 to 60% by weight.

The specific features of the composition (e.g. weight ratios, active ingredient (a.i.) form, particles' structure composition, etc.) may be as described herein with respect to the method aspect.

According to a preferred embodiment the composition is in the form of an aqueous suspension.

According to a preferred embodiment the composition is in the form of an aqueous suspension comprising a solid particulate matter of a chloronicotinyl insecticide compound, and microcapsules of chlorpyrifos.

According to certain embodiments the chloronicotinyl insecticide compound is selected from imidacloprid, thiamethoxam, clothianidin, and mixtures thereof. According to a preferred embodiment of the invention the

chloronicotinyl insecticide compound is imidacloprid. According to another preferred embodiment of the invention the chloronicotinyl insecticide compound is thiamethoxam. According to a specific embodiment of the invention the chloronicotinyl insecticide compound is clothianidin.

According to a preferred embodiment of the present invention the composition comprises a chloronicotinyl insecticide compound (preferably imidacloprid or thiamethoxam) and chlorpyrifos in the mixing ratio described above (preferably from 3.5:1 to 1:2.5, specifically 3.3:1 to 1:2.5, in some embodiments 3:1 to 1:2, specifically 3:1 to 1:1.8 and in certain embodiments from about 2.5:1 to about 1:1, respectively), together with a liquid carrier, preferably an aqueous carrier. The concentrations of the chloronicotinyl insecticide compound (e.g. imidacloprid) and chlorpyrifos in the composition of the invention are preferably in the ranges between 50 g/liter and 300 g/liter and between 30 g/liter and 220 g/liter, respectively (according to a specific embodiment in the ranges between 50 g/liter and 300 g/liter and between 30 g/liter and 150 g/liter, respectively). More specifically, as an alternative for the separate formulations set forth above, a mixed formulation, in which chloronicotinyl insecticide compound (e.g. imidacloprid) and chlorpyrifos are provided as FS and CF formulations, respectively, stabilized together in a liquid carrier (an acceptable two letter code for such type of formulation is ZC) is particularly suitable for application in the seed treatment according to the invention.

According to a preferred embodiment of the present invention the composition is in the form of an aqueous suspension

comprising a solid particulate matter of chloronicotinyl insecticide compound, and microcapsules of chlorpyrifos. The composition may optionally include a thickening agent, specifically polysaccharide gum such as xanthan gum. The composition may optionally include a binding agent as described in the invention. The aqueous suspension may be loaded with solid particulate matter of chloronicotinyl insecticide compound and microcapsules of chlorpyrifos according to the concentrations indicated in the invention.

According to certain embodiments the chloronicotinyl insecticide compound is suspended, dispersed, emulsified or dissolved in the composition.

According to certain embodiments chlorpyrifos is suspended, dispersed, or emulsified in the composition. According to a specific embodiment clorpyrifos is in the form of a capsule (more particularly microcapsule) suspended in the composition.

The chloronicotinyl insecticide compound may be present in the composition in the form of for example, a solid particulate matter, soluble powder, wettable powder, a granule, liquid droplets, a solute, etc.

Clorpyrifos may be present in the composition in the form of for example capsules (specifically microcapsules), powder (e.g. wettable powder), granules, liquid droplets, solid particulate matter of chlorpyrifos, etc.

According to certain embodiments of the invention the compositions may be for example emulsions (ES) (e.g. oil-in-

water emulsions (EW), microemulsions (ME)), solution or granules (e.g., water dispersible granule (WG)). Such compositions may be for example applied to the locus of the seed (namely to the soil and not directly applied to the seed), if desired.

The active compound combinations may be used in the form of premix compositions or the compounds may be applied to the seed to be treated simultaneously or in succession, if desired together with composition auxiliaries such as carriers, surfactants or other adjuvants, typically employed in formulation technology.

The formulations may be prepared in a known manner, for example by extending the active compound with auxiliaries suitable for the formulation of agrochemicals, for example carriers (e.g., liquid, semi-solid, or solid carriers), and if desired surfactants, binders, antifoaming agents, preservatives, anti-freezing agents, for the treatment of seeds may also be added (See generally e.g. Alan Knowlas, New Developments in Crop Protection Product Formulations, AgrowReports, May 2005).
The composition may be prepared by introducing into a suitable vessel the desired quantities of a suspension of solid particulate matter of chloronicotinyl insecticide compound and a capsule suspension of chlopyrifos (which are either commercially available, or can be made by the methods described above), and mixing the same for a sufficient time, while optionally gradually adding, either continuously or in a portion-wise manner, e.g. the thickening agent, which is most suitably provided as an aqueous solution in which the thickener is present at a preferable concentration of about

1 to 5% (w/v). Optionally, additional additives such as a binding agent may be added. The mixing operation is conveniently carried out at room temperature and may last between 10 minutes to several hours (the longer times apply for commercial scale production), affording a stable suspension containing chloronicotinyl insecticide compound solid particulate matter form together with chlorpyrifos capsules.

The composition may further comprise a binding agent as described in the invention.

Moreover, the invention relates to a seed coating composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

The seed coating composition may further comprise a binding agent.

According to certain embodiments the binding agent is selected from polyvinylpyrrlodone, polyvinyl alcohol, polyvinyl acetate, copolymers of polyvinyl alcohol, copolymers of polyvinyl acetate, acrylic polymers, acrylic copolymers, acrylamide polymers, acrylamide copolymers, celluloses, polysaccharides, proteins, fats, oils, and mixtures thereof. The celluloses are preferably cellulose ethers such as methylcellulose, hydroxypropylmethylcellulose, hydroxypropylcellulose, carboxymethylcellulose. Non-limiting examples of polysaccharades include alginates, chitosans, starch,

modified starch, and dextrins. The proteins may be for example gelatin, zein, shellac, and gum arabics.

The binding agent serves as a sticking agent to adhere the active ingredient to the seed surface.

In certain embodiments the weight ratio of the binding agent to the chloronicotinyl insecticide compound and chlorpyrifos (i.e. total weight of the active ingredients) is in the range 1:1000 to 1:1, more specifically 1:400 to 1:2, more specifically 1:200 to 1:4, even more specifically 1:100 to 1:4. According to certain embodiments the weight ratio of the binding agent to the chloronicotinyl insecticide compound and chlorpyrifos may be 1:1 and below, 1:4 and below, 1:5 and below, or 1:10 and below. According to certain embodiments the weight ratio of the binding agent to the chloronicotinyl insecticide compound and chlorpyrifos may be 1:1000 and above, 1:400 and above, 1:200 and above, 1:100 and above, 1:50 and above. The weight ratio may be any intermediate between the above mentioned values.

In certain embodiments the weight ratio of the binding agent to the total solid content in the composition is as indicated above with respect to the weight ratio of the binding agent to the chloronicotinyl insecticide compound and chlorpyrifos (i.e. total weight of the active ingredients). The term "solid content" refers to the solid matter in the compositions including the active ingredients and excipients, present in the composition in a solid form.

Optionally, a plasticizer may be used in the coating formulation. Plasticizers are typically used to make the

film that is formed by the coating layer more flexible, to improve adhesion and spreadability, and to improve the speed of processing. Improved film flexibility is important to minimize chipping, breakage or flaking during storage, handling or sowing processes. Many various plasticizers may be used, however, useful plasticizers include for example polyethylene glycol, glycerol, butylbenzylphthalate, and glycol benzoates.

the weight ratio of the chloronicotinyl insecticide compound and the chlorpyrifos may be as described in the present invention. In a specific embodiment the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 10:1 to 1:10.

The invention further provides use of (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

Preferably the use is for protecting one or both of a seed and a plant grown from the seed against pest infestation.

The invention additionally provides a kit comprising (a) at least one container including a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; (b) at least one container including chlorpyrifos; and (c) instructions for

applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

The term *"locus of the seed"* means the immediate vicinity of the seed e.g the surrounding area in the soil (in which the seed is sown).

The kit is preferably for use in protecting one or both of a seed and a plant grown from the seed against pest infestation.

The chloronicotinyl insecticide compound and the chlorpyrifos may be applied simultaneously or sequentially.

Moreover, the invention provides a kit comprising (a) at least one container including (i) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (ii) chlorpyrifos; and (b) instructions for applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

The instructions may be in the form of printed matter, for example either as inserts or labels.

Moreover, the invention relates to a seed comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

As used herein by the term ***"a seed comprising"*** is meant that the seed is coated with and/or includes the combination of compounds as defined above.

As used herein the term ***"seed is coated with and/or includes"*** denotes that the active compounds may be present on the surface of the seed and/or may be absorbed into the inside part of the seed as result of penetration, after application of the compounds to the seed. This term also encompasses a seed coated with and/or including a composition comprising the combination of compounds or a mixture of compositions each comprising different active ingredient.

The term ***"coating"*** denotes any process that endows the outer surfaces of the seeds partially or completely with a layer or layers of non-plant material.
The active ingredient may be included in the seed as a result of imbibition. The term ***"imbibition"*** refers to any process that results in penetration of the active ingredient into the germinable parts of the seed and/or its natural sheath, shell, hull, husk, and/or integument.

Additionally, the invention provides a seed coated with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

Coating may be applied to the seeds using conventional coating techniques and machines, such as fluidized bed techniques, the roller mill method, rotostatic seed

treaters, and drum coaters. Other methods such as the spouted beds technique may also be useful. The seeds may be pre-sized before coating. Such procedures are known in the art. Seed coating methods and apparatus for their application are disclosed in, for example, U.S. Pat. Nos. 6,261,371, 5,918,413, 5,891,246, 5,554,445, 5,107,787, 5,080,925, 4,759,945 and US Application Publication No. 2008/0092256, incorporated herein by reference in their entirety.

According to another aspect of the invention there is provided a method of protecting one or both of a seed and a plant grown from the seed against pest infestation, by treating the seed with chlorpyrifos, wherein said seed is selected from sugar beet, oil seed rape, cereals, and potatoes.
Chlorpyrifos may be used alone or in combination with chloronicotinyl insecticide compounds against one or more pests as described in the invention. In a specific embodiment chlorpyrifos may be used to treat corn stalk borer (Elasmopalpus lignosellus).

It is appreciated that the chloronicotinyl insecticide compounds and the chlorpyrifos, described in the invention in a particular aspect may be characterized by the various features, e.g. compositions, particles' structures, weight ratios, rates of applications etc., described in the present invention in the other aspects.

It is appreciated that one or more features, aspects, or embodiments of the present invention can be combined with

one or more other features, aspects or embodiments of the present invention.

It is recognized that all embodiments of the invention, including those specifically described for different aspects of the invention, can be combined with any other embodiments of the invention as appropriate.

EXAMPLES

Materials

Chlorpyrifos 250 CS: (Pyristar 250 CF, Pyristar, Makhteshim Chemical Works LTD., Israel, with a concentration of about 250 g A.I./liter and density of about 1.1 g/ml). A capsule suspension of chlorpyrifos (microencapsulated chlorpyrifos) is available under the tradename Pyristar 250 CF or Pyristar.

Imidacloprid 600 SC: (Seedoprid 600 FS, Makhteshim Chemical Works LTD., Israel, with a concentration of about 600 g A.I./liter and density of about 1.25 g/ml). A formulation prepared (laboratory scale), essentially equivalent to commercial product Seedoprid 600 FS (Makhteshim Chemical Works LTD.) was provided by Makhteshim Chemical Works LTD, will be referred herein below as Seedoprid 600 FS.

Chinook (Bayer Crop Sciences): a commercially available product, contains 100g Imidacloprid + 100 g Beta-cyfluthrin per liter.

Standak (BASF), a commercially available product, contains 250g Fipronil/liter.

Cruiser 70WS (Syngenta): a commercially available product, containing Thiamethoxam as active ingredient (a.i) 700 g a.i./Kg.

Cruiser 600FS (Syngenta) a commercially available product containing 600 grams a.i Thiamethoxam per liter.

Poncho 600FS (Bayer Crop Sciences): a commercially available product, including Clothianidin as active ingredient, 600 grams a.i per liter.

Poncho Beta (Bayer Crop Sciences): a commercially available product, including Clothianidin + beta-Cyfluthrin as active ingredients, containing 400 gram/liter of Clothianidin and 53.3 gram/liter of beta-Cyfluthrin.

Cruiser Force (Syngenta): a commercially available tank mix product, includes thiamethoxam + Tefluthrin as active ingredients. Cruiser contains 600 grams a.i thiamthoxam per liter and Force ST contains 200 grams a.i. Tefluthrin per liter.

Example 1

Mixed formulation (ZC) of imidacloprid and chlorpyrifos

A suspension concentrate of imidacloprid particles (Imidacloprid 600SC- 216 kg) and capsule suspension of chlorpyrifos (Chlorpyrifos 250 CS, 461 kg) were charged into a reactor and were mixed for two hours at room temperature, during which period an aqueous solution of xanthan gum was added portion-wise. The composition is described in Table 1.

Table 1

Raw Materials	Quantity for 1000 liter
Chlorpyrifos 250 CS	461 kg
Imidacloprid 600 SC	216 kg
xanthan gum 2% w/v solution	40 kg
Soft water	Up to 1000 liter

Chlorpyrifos 250 CS: (Pyristar 250 CF, Pyristar, Makhteshim Chemical Works LTD., Israel, with a concentration of about 250 g A.I./liter and density of about 1.1 g/ml).
Imidacloprid 600 SC: (Seedoprid 600 FS, Makhteshim Chemical Works LTD., Israel, with a concentration of about 600 g A.I./liter and density of about 1.25 g/ml).

The resulting white-creamy suspension comprises imidacloprid and chlorpyrifos each in a concentration of 105 g/l.

Example 2

Mixed formulation (ZC) of imidacloprid and chlorpyrifos

The procedure of Example 1 was repeated, using the quantities of the starting material described in table 2:

Table 2

Materials	Quantity for 1000 liter
Chlorpyrifos 250 CS	461 kg
Imidacloprid 600 SC	432 kg
Xanthan gum 2% w/v solution	22.5 kg
Soft water	Up to 1000 liter

The resulting white-creamy suspension comprises imidacloprid and chlorpyrifos in concentrations of 210 g/l and 105 g/l, respectively.

Example 3 (of the invention) and 4-5 (comparative)

Activity against *Elasmopalpus lignosellus* in corn

In the experiment described in this example, imidacloprid was used in the form of a commercially available concentrated suspension which was already mentioned above (Seedoprid, with a concentration of about 600 g A.I./liter and density of about 1.25 g/ml). Chlorpyrifos was used in the form of a commercially available capsule suspension mentioned above (Pyristar, with a concentration of about 250 g A.I./liter and density of about 1.1 g/ml). The corn seeds to be treated were of cultivar PL 6882.

The two commercially available pesticide formulations were added in suitable quantities into a transparent plastic bag, such that the ratio of application was 210 g imidacloprid to 100 kg corn seed and 105 g chlorpyrifos to 100 kg corn seed. The corn seeds to be treated were introduced and sealed in the bag, and agitated to allow a good adherence of the formulations onto the seeds.

Treated seeds were planted in a soil mix Dystrophic Red Dark Latosoil sandy, consisting of 62% of sand, 30% of clay and 8% of mire and having an organic content of 8 g/ liter. In order to test the efficacy of the treatment regimen indicated above, a set consisting of five pots was used, with six treated corn seeds sown in each pot. A corresponding set was used for the control. Thus, the treatment and the control were each based on five replications.

The volume of the soil in each pot was 1.5 liter. The pots were overhead irrigated for 24 hours and 12 hours prior to sowing. After sowing, the pots were irrigated from below (lower part), adding from about 30 mL to 50 mL daily to the plate supporting the pot, according to plant evapotranspiration, keeping the soil surface dry. After full germination, pots were trimmed, leaving only three plants per pot. Plants were submitted to artificial infestation with recently ecloded larva, with three larva per plant after sowing.

Plants were evaluated 30 days after the infestation. To this end, the plants were removed from the pots and the larva attack on the plants stem basis was counted.
Table 3 below presents the pesticidal combination tested and the rate of application as noted above, and the mean result of damaged plants, calculated for the five pots planted with treated seeds, and the corresponding control set:

Table 3

Example	Active ingredient(s)	Rate of application in terms of volume of commercially available formulations used mL /100 kg seeds	Rate of application in terms of g a.i./100 kg seeds	Mean number of damaged plants / pot	%E[2]
3	Imidacloprid + clorpyrifos	350 ml Seedoprid + 420 ml Pyristar	210 + 105	0.0 c	100

4 control	no active ingredient			3.0 a[1]	
5 comparative	Imidacloprid	350 ml Seedoprid	210	2.0 b	33.33

[1] Means followed by the same letter in the column do not differ statistically at the 5% of probability according to the scott Knott test.
[2] Efficiency calculated by the abbot formula (Abbot W.S., A method for computing the effectiveness of insecticide, Journal of Economic Entomology, 18, p. 265-267, 1925).

Figure 1 is a photograph illustrating the visible differences between the plants grown from the treated seeds and the control, shown in the right and left sides of the photograph, respectively (designated T1 (control) and T6 (treated)).

Example 6-12 (of the invention) and 13-16 (comparative)

Activity against *Elasmopalpus lignosellus* in soybean

The combination of imidacloprid and chlorpyrifos was tested according to the methodolgy described in the previos set of examples. However, for the treatment of soybean seeds, the rate of application that was tested was 60-90 g imidacloprid to 100 kg seed and 30-120 g of Chlorpyrifos to 100 kg seed. Other parameters (the method of coating the seeds with the commercially available formulations, the composition of the soil, number of replication for the treatment regimen and the control experiments, number of plants in each pot, and evaluation were as described in the previous examples). Soybean cultivar used in this experiment was Valiosa.

The table below summarizes the pesticidal (insecticidal) combination tested and the rate of application as noted above, and the mean result of damaged plants, calculated for the five pots planted with treated seeds and the corresponding control set:

Table 4

Example	Active ingredient(s)	Rate of application in terms of volume of commercially available formulations used mL /100 kg seeds	Rate of application in terms of g a.i./100 kg seeds	Mean number of damaged plants / pot	%E[2]
6	Imidacloprid + chlorpyrifos	100 ml Seedoprid + 480 ml Pyristar	60 + 120	0.0 c[1]	100
7	Imidacloprid + chlorpyrifos	100 ml Seedoprid + 360 ml Pyristar	60 + 90	1.2 b	60
8	Imidacloprid + chlorpyrifos	100 ml Seedoprid + 240 ml Pyristar	60 (*) + 60 (*)	0.4 c	86.7
9	Imidacloprid + chlorpyrifos	100 ml Seedoprid + 120 ml Pyristar	60 + 30	1.6 b	46.7
10	Imidacloprid + chlorpyrifos	150 ml Seedoprid + 480 ml Pyristar	90 + 120	0.0 c	100
11	Imidacloprid + chlorpyrifos	150 ml Seedoprid + 360 ml Pyristar	90 + 90	0.4 c	86.7

12	Imidacloprid + chlorpyrifos	150 ml Seedoprid + 240 ml Pyristar	90 + 60	1.2 b	60
13 control	no active ingredient			3.0 a	
14 comparative	Imidacloprid	150 ml Seedoprid	90	2.8 a	6.7
15 comparative	Imidacloprid	100 ml Seedoprid	60	2.8 a	6.7
16 comparative	Fipronil	200 ml Standak	50	0.4 c	86.7

[1] Means followed by the same letter in the column do not differ statistically at the 5% of probability according to the scott Knott test.
[2] Efficiency calculated by the abbot formula.
* Equivalent dose rate per hectare (ha): approximately 30g/ha Imidacloprid and 30g/ha Chlorpyrifos.

The results show significant increase in activity of imidacloprid against *Elasmopalpus lignosellus* in soybean, by addition of chlorpirifos.

Example 17 (of the invention) and 18-20 (comparative)

Activity against *Agrotis Segetum* (Cutworm) in Maize

Imidacloprid suspension concentrate and Chlorpyrifos capsule suspension were used in the forms mentioned in the preceding examples.

Trial data:
Experiments were conducted in greenhouse. Cultivar: Rosalie, Thousand seed weight: 298 g (before seed treatment). Fungicide treatment included 400g/l Thiram (tradename: Proseed, Syngenta) and 25 g/l Fludioxonil and 10 g/l

Metalaxyl-M (tradename: Maxim XL, Syngenta) as base treatment. Insecticide seed treatments were carried out using a rotary disc coater. Plots consisted of: Plastic boxes (lxwxh=46x31x15cm); soil medium included: 60% sandy clay with 10% silt, 30% hydrosubstrate granules, 10% plotting compost; soil depth in boxes was 10 cm; No. of seeds per plot was 24; sowing depth was 4 cm; Cutworm larval stage: L4 - L5; No. of replicates (n): 4. Experiments were conducted using randomized block design.

The trial replicates were not exposed to cutworm at the same time. Plants of replicates 3 and 4 were exposed to cutworms 10 days prior to the assessment and plants of replicates 1 and 2 were exposed to cutworms seven days prior to the assessment. This was done in order to determine phytotoxicity effects due to the seed treatments prior to larval infestation.

Three leaves were unfolded 13 days after sowing and seven or ten days after cutworm exposure.

Assessment:
Plant loss was evaluated according to the number of cut seedling or completely consumed non-viable seedling.

Results are shown in Table 5.

Table 5

Example	**Active ingredient**	**Rate of application in terms of g a.i. per 100,000 seeds or g a.i. per 100 kg seeds**		**Number plants loss (% of plants loss)**
		g a.i. per 100,000 seeds	**Approxim-ate g a.i. rate per 100 kg seeds (based on seeds weight[1])**	
17	Imdacloprid + Chlorpyrifos	80* + 25*	264 + 82.5	4.8 a (20%)
18 Control	No active ingredient			9.5 b (40%)
19 Comparative	Imdacloprid	80	264	7.0 ab (29%)
20 Comparative	Chlorpyrifos	25	82.5	8.8 b (37%)

Means in the same column followed by different letters are significantly different at the 5% of probability.
*Equivalent dose rate per hectare (ha): approximately 56g/ha Imidacloprid and 17.5g/ha Chlorpyrifos.
[1] Calculated Based on 1000 seeds weight..

The combination of compounds of the present invention did not show phytotoxic effects. The results show an improvement using the combined treatment as compared to the single treatments.

Example 21 (of the invention) and 22-25 (comparative)

Activity against Agrotis Segetum in Sugar Beet (Imidacloprid + Chlorpyrifos)

Imidacloprid and chlorpyrifos were used in the forms described in the preceding examples. The seeds were treated by SESvanderHave (Tienen, Belgium). All seeds were first treated with a fungicide TMTD (active agent thiram) and Tachigaren (active agent hymexazol) layer and then with an Insecticide layer.

Experiments were conducted in greenhouse, using random design. Number of replicates was 4. Material plots was open, plastic boxes (l x w x h = 36 x 26 x 12 cm). To each experimental plot a pipe was placed vertically in the centre. Hydro-pellets were added at the bottom of each plot. Soil medium was sandy loam soil. The soil had a humidity of 10%. Soil depth in boxes was 6 cm. Number of seeds per plot was 12. Soil depth was 3-4 cm. Irrigation was conducted at the day of sawing (after sawing) (400 ml), 2 days after sawing (350 ml), 5 days after sawing (400 ml), and 14 days after sawing (400 ml).

Cutworm were released into the plots one day after sowing and four days after sowing. Two specimens were introduced each time. Number of cutworms per plot was 4. Cutworm larval stage was 4th and 5th larval stage (L4 and L5).

The results in table 6 below refer to three weeks after sowing when the plants were on average 18 days exposed to cutworm activity. Results are presented as No. of plant loss (% plants loss).

Table 6

Example	Active ingredient	Rate of application in terms of g a.i. per 100,000 seeds or g a.i. per 100 kg seeds		plants loss Number (% plants loss)
		g a.i. per 100,000 seeds	Approxi-mate g a.i. rate per 100 kg seeds (based on seeds weight**)	
21	Imidacloprid + Chlorpyrifos	30* + 50*	900 + 1500	3.5 ab (29%)
22 Control	No active ingredient			10.8 d (90%)
23 Comparative	Imidacloprid	30	900	11.3 d (94%)
24 Comparative	Chlorpyrifos	50	1500	4.5 abc (38%)
25 Comparative (Standard)	Thiamethoxam[1]	60		5.5 abc (46%)
	Clothianidin[2]	60		7.3 bcd (61%)
	Clothianidin + beta Cyfluthrin[3]	60 + 8		2.5 a (21%)
	Thiamethoxam+ Tefluthrin[4]	60+ 8		3.8 ab (32%)

Means in the same column followed by different letters are significantly different at the 5% of probability.
1. Cruiser 70WS (Syngenta); 2. Poncho 600FS (Bayer CropScience); 3. Poncho Beta (Bayer CropScience); 4. Cruiser Force (Syngenta).
*Equivalent dose rate per hectare (ha): approximately 36 g/ha Imidacloprid and 60g/ha Chlorpyrifos.
**Calculated based on 1000 seeds weight.

The combination of compounds of the present invention did not show phytotoxic effects. The results show a better control of Agrotis Segetum in Sugar Beet, when using the combination of compounds of the invention especially as compared to imidacloprid.

Example 26 (of the invention) and 27-29 (comparative)
Activity against Agrotis Segetum in Sugar Beet (Thiamethoxam + Chlorpyrifos)

Experiments were conducted as described in the preceding experiments (Examples 21-25).

Table 7

Example	**Active ingredient**	**Rate of application in terms of g a.i. per 100,000 seeds or g a.i. per 100 kg seeds**		**Plants loss Numbers (%Plant loss)**
		g a.i. per 100,000 seeds	**Approximate g a.i. rate per 100 kg seeds (based on seeds weight**)**	
26	Thiamethoxam + Chlorpyrifos	60* + 75*	1800 + 2250	4 a (33%)
27 Control	No active ingredient			10.8 c (90%)
28 Comparative (standard)	Thiamethoxam	60	1800	5.5 ab (46%)

29 Comparative	Chlorpyrifos	75	2250	6.8 bc (57%)

Means in the same column followed by different letters are significantly different at the 5% of probability.
*Equivalent dose rate per hectare (ha): approximately 72 g/ha Thiamethoxam and 90 g/ha Chlorpyrifos.
**Calculated based on 1000 seeds weight.

The results show that combination of Thiamethoxam and chlorpyrifos is more effective than either of the two individual compounds.
The plants did not show phytotoxicity symptoms.

Conclusions:
The results in the above examples show that the spectrum of effective control of the combination compounds is broader than the spectrum of individual compounds.
Thus, the combination can broaden the spectrum of pests a seed can be protected against, beyond what is already known for each individual component in seed treatment.
The combination was found to be effective in major pests which are very poorly controlled by imidacloprid alone (table 3, 4 and 6).
The combination was shown to improve the level of control achieved on pest by either of the two compounds alone (Table 5). The combination was shown to improve the level of control achieved on pest by either of the two compounds alone even for pests on which the control of each individual compound is medium to good (Table 7).
The combination of compounds were found to be at least as effective as the tested standards.
The combinations of compounds were safe to the tested plants.

While this invention has been shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that many alternatives, modifications and variations may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference.

Claims

1) A method of protecting one or both of a seed and a plant grown from the seed against pest infestation, by treating the seed with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

2) The method of claim 1 wherein said chloronicotinyl insecticide compound and said chlorpyrifos are applied simultaneously or sequentially.

3) The method of any one of the preceding claims wherein the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 10:1 to 1:10.

4) The method of any one of the preceding claims wherein the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 3.5:1 to 1:2.5.

5) The method of any one of the preceding claims wherein the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 3:1 to 1:2.

6) The method of any one of the preceding claims, wherein said chlorpyrifos is in a form of first particles, said particles comprising chlorpyrifos enclosed in a first carrier material.

7) The method of claim 6 wherein said chlorpyrifos is microencapsulated in said first carrier material.

8) The method of claim 6 or 7, wherein said first carrier material is a polymer.

9) The method of claim 1 wherein said chloronicotinyl insecticide compound is in the form of second particles.

10) The method of claim 9 wherein said second particles comprising said chloronicotinyl insecticide compound enclosed in a second carrier material.

11) The method of claim 9 wherein said second particle is a solid particulate matter of said chloronicotinyl insecticide compound.

12) The method of any one of the preceding claims wherein said chlorpyrifos is microencapsulated in a polymer and said chloronicotinyl insecticide compound is in a form of solid particulate matter.

13) The method according to any one of the preceding claims wherein said chloronicotinyl insecticide compound is selected from imidacloprid, thiamethoxam, clothianidin, and mixtures thereof.

14) The method according to any one of the preceding claims wherein said chloronicotinyl insecticide compound is imidacloprid.

15) The method of claim 1 wherein said seeds are selected from cereals, oil seeds, Legumes, rice, corn, cotton, root and tuber crops, and vegetables.

16) The method of claim 1 wherein said pest is selected from corn stalk borer, grubs and beetles, corn rootworm, maggots, cutworm, wireworm, and any combination thereof.

17) A composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

18) The composition of claim 17 for use in protecting one or both of a seed and a plant grown from the seed against pest infestation.

19) The composition of claim 17 or 18 wherein the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 10:1 to 1:10.

20) The composition of any one of claims 17-19, wherein said chlorpyrifos is in a form of first particles, said particles comprising chlorpyrifos enclosed in a first carrier material.

21) The composition of claim 20 wherein said chlorpyrifos is microencapsulated in said first carrier material.

22) The composition of claim 20 or 21, wherein said first carrier material is a polymer.

23) The composition of any one of claims 17-22 wherein said chloronicotinyl insecticide compound is in the form of second particles.

24) The composition of claim 23 wherein said second particles comprising said chloronicotinyl insecticide compound enclosed in a second carrier material.

25) The composition of claim 23 wherein said second particle is a solid particulate matter of said chloronicotinyl insecticide compound.

26) The composition according to any one of claims 17-25 wherein said composition further comprises an agriculturally acceptable carrier.

27) The composition according to any one of claims 17-26 in the form of an aqueous suspension comprising a solid particulate matter of a chloronicotinyl insecticide compound, and microcapsules of chlorpyrifos.

28) The composition according to any one of claims 17-27, wherein said chloronicotinyl insecticide compound is selected from imidacloprid, thiamethoxam, clothianidin, and mixtures thereof.

29) The composition according to any one of claims 17-28, further comprising a binding agent.

30) The composition according to claim 29 wherein said binding agent is selected from polyvinylpyrrlodone, polyvinyl alcohol, polyvinyl acetate, copolymers of

polyvinyl alcohol, copolymers of polyvinyl acetate, acrylic polymers, acrylic copolymers, acrylamide polymers, acrylamide copolymers, celluloses, polysaccharides, proteins, fats, oils, and mixtures thereof.

31) A seed coating composition comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

32) The seed coating composition according to claim 31, further comprising a binding agent.

33) The seed coating composition according to claim 32 wherein said binding agent is selected from polyvinylpyrrlodone, polyvinyl alcohol, polyvinyl acetate, copolymers of polyvinyl alcohol, copolymers of polyvinyl acetate, acrylic polymers, acrylic copolymers, acrylamide polymers, acrylamide copolymers, celluloses, polysaccharides, proteins, fats, oils, and mixtures thereof.

34) The seed coating composition of claim 31 wherein the weight ratio of said chloronicotinyl insecticide compound and said chlorpyrifos is from 10:1 to 1:10.

35) Use of (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos, for treating a seed.

36) A kit comprising (a) at least one container including a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; (b) at least one container including chlorpyrifos; and (c) instructions for applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

37) The kit of claim 36 for use in protecting one or both of a seed and a plant grown from the seed against pest infestation.

38) The kit of claim 36 wherein said chloronicotinyl insecticide compound and said chlorpyrifos are applied simultaneously or sequentially.

39) A kit comprising (a) at least one container including (i) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (ii)chlorpyrifos; and (b) instructions for applying said chloronicotinyl insecticide compound and said chlorpyrifos onto one or both of a seed and locus thereof.

40) A seed comprising (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid, clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

41) A seed coated with (a) a chloronicotinyl insecticide compound selected from imidacloprid, thiacloprid,

clothianidin, thiamethoxam, acetamiprid, nytenpyram, dinotefuran, and mixtures thereof; and (b) chlorpyrifos.

Figure 1