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EP 0295117 A1 **US 6121193 A**
US 20120053221 A1 **US 20100016155 A1**
US 20020098221 A1

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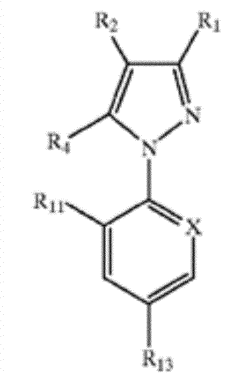
INT CL **A01N**
Other: **EPODOC, WPI.**

(54) Title of the Invention: **Agrochemical composition and method of use thereof**
Abstract Title: **Agrochemical composition with polyether adhesion promoter**

(57) An agrochemical composition comprises: A) 1-arylpyrazole(s) of Formula (I)



Formula (I)

wherein R_1 is halogen, CN, or methyl; R_2 is $S(O)_nR_3$, 4,5-dicyanoimidazol-2-yl, or haloalkyl; R_3 and R_7 are alkyl or haloalkyl; R_4 is hydrogen, halogen, NR_5R_6, $S(O)_mR_7$, $C(O)R_7$, $C(O)OR_7$, alkyl, haloalkyl, OR_8, or $-N=C(R_9)(R_{10})$; R_5 and R_6 are hydrogen, alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$, $S(O)_rCF_3$, or together form a divalent alkylene radical optionally interrupted by 1-2 divalent heteroatoms; R_8 is alkyl, haloalkyl, or hydrogen; R_9 is alkyl or hydrogen; R_{10} is optionally substituted phenyl or heteroaryl; R_{11} and R_{12} are hydrogen, halogen, CN, or NO_2; R_{13} is halogen, haloalkyl, haloalkoxy, $S(O)_qCF_3$ or SF_5; m, n, q, and r are 0-2; X is trivalent nitrogen or C-R_{12}; with the proviso that when R_1 is methyl, either (i) R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3, and X is nitrogen or (ii) R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is C-Cl; and B) polyether adhesion promoter(s) comprising (a) at least 16 polyoxyethylene and/or polyoxypropylene units or (b) a chain of ethylene oxide units and a hydrophobic portion, wherein the ratio of ethylene oxide units to the length of the hydrophobic portion is at least 0.5.

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AGROCHEMICAL COMPOSITION AND METHOD OF USE THEREOF

The present invention relates to an agrochemical composition, in particular to a composition comprising a pesticidally active pyrazole derivative, more particularly to the aforesaid composition further comprising an adhesion promoter. The present invention also relates to the use of the aforementioned composition, in particular in the treatment of seeds.

Numerous technologies are currently used to treat seeds with the purpose of enhancing crop performance. These treatments include inter alia the coating, pelleting and/or film overcoating of seeds. A range of agrochemical compositions in the form of, for example, dusts, liquids and slurries have long been used to control soil-borne and seed-borne diseases, as well as pests in seeds.

Recent developments in seed treatment technology have focused on the use of techniques to deliver pesticides to seeds. One of the common techniques is coating seeds with agrochemical formulations. In particular, it is common for crop producers to apply agrochemically active ingredients to seeds, especially for the protection of the seeds against diseases and pests, and/or for the enhancement of yields of the eventual crops. These agrochemically active ingredients can be applied the ground before sowing the seeds or may be applied directly onto the seeds before they are sown. The agrochemically active ingredients applied to seeds can protect sprouts and seedlings against diseases and pests in the post-germination and seedling stages, for example. However, in regions with soil of high humidity and/or during the rainy season, there is the problem of leaching of the agrochemically active ingredients from the seeds, leading to a significant decrease in the amount of the active ingredients remaining on the seeds, which in turn lowers the efficacy of the agrochemically active ingredients on seeds. Further, even small amounts of agrochemically active

ingredients leached from pre-treated seeds in this way and present in the run-off rain water can cause problems of environmental pollution.

To tackle the above problems, agrochemical compositions containing 1-arylpyrazoles and a high-molar-mass hyper-branched polymer were disclosed in US 6,121,193. The aim of these compositions is to improve the adhesion properties of the active ingredients onto the seeds. In particular, US 6,121,193 discloses an agrochemical composition comprising from 0.5 to 50% by weight of at least one 1-arylpyrazole of a given formula and an effective amount of a high-molar-mass hyperbranched polymer. The hyperbranched polymer is preferably in the form of an aqueous suspension. Hyperbranched polymers disclosed in US 6,121,193 are polyethyleneamines, polyamidoamides, polyethyleneimines, polyethers and copolymers derived therefrom. US 6,121,193 particularly prefers polyethyleneimine hyperbranched polymers, with this being the only hyperbranched polymer specifically described and exemplified.

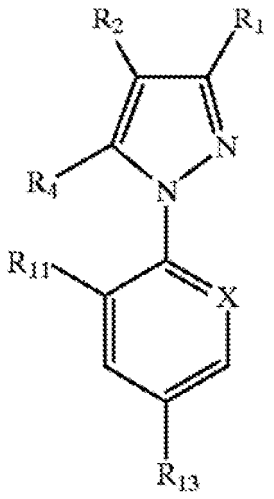
However, while the adhesion properties of the 1-arylpyrazole compositions of US 6,121,193 may be improved, the viscosity of such compositions is greatly increased. This increase in viscosity makes the application process more difficult and time-consuming. Further, the coating formed on the seeds is also uneven.

Accordingly, there is a need for an improved agrochemical formulation for the treatment of seeds. It would be advantageous if the formulation had a viscosity such that application of the formulation to seeds was made easier and quicker and the resultant coating on the seeds could be more even. It would be particularly advantageous if these properties could be obtained while maintaining the adhesion of the formulation to the seeds and without reducing the efficacy of the active ingredients.

It has now been found that a particularly advantageous formulation of 1-arylpyrazoles for the treatment of seeds may be formed by combining the pyrazole derivatives with a polyether having at least 16 polyoxyethylene moieties therein.

According to a first aspect of the present invention there is provided an agrochemical composition comprising:

A) at least one agrochemical active ingredient of 1-arylpyrazoles of formula (I)



(I)

in which:

R_1 represents a halogen atom or CN or a methyl group ;

R_2 represents $S(O)_n R_3$ or 4,5-dicyanoimidazol-2-yl or haloalkyl;

R_3 represents alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or $NR_5 R_6$, $S(O)_m R_7$, $C(O)R_7$ or $C(O)OR_7$, alkyl, haloalkyl or OR_8 or $–N=C(R_9)(R_{10})$ radical;

R_5 and R_6 independently represent a hydrogen atom or alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$ or $S(O)_r CF_3$ radical or R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen, nitrogen or sulphur;

R_7 represents alkyl or haloalkyl;

R_8 represents alkyl or haloalkyl or a hydrogen atom;

R_9 represents alkyl or a hydrogen atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or more halogen atoms or groups such as OH, –O-alkyl, –S-alkyl, CN or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen

atom or CN or NO_2 ;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $S(O)_q$ CF_3 or SF_5 group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a C–R_{12} radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is C–Cl; and

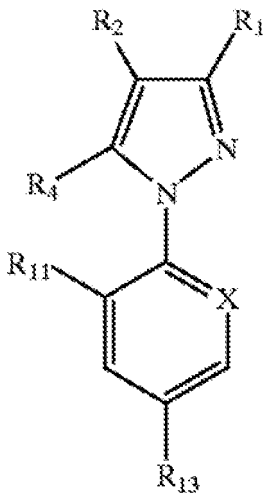
B) one or more adhesion promoters comprising a polyether the said polyether containing at least 16 polyoxyethylene moieties.

It has been found that polyethers having at least 16 polyoxyethylene moieties provide advantageous adhesion of the 1-arylpyrazole formulation to seeds being treated, without resulting in a significant increase in the viscosity of the formulation and without reducing the efficacy of the active ingredient.

It has further been found that a formulation of 1-arylpyrazoles having an advantageous adhesion to the seeds, without being unacceptably viscous is provided by employing a polyether having a chain of ethylene oxide (EO) units and a hydrophobic portion, in which the ratio of the number of ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is in a particular ratio. More particularly, the adhesion of the 1-arylpyrazoles to seeds is increased when the ratio of the number of ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is above 0.5, more preferably in the range of from 0.5 to 3.0.

Accordingly, in a further aspect, the present invention provides an agrochemical composition comprising:

A) at least one agrochemical active ingredient of 1-arylpyrazoles of formula (I)



(I)

in which:

R_1 represents a halogen atom or CN or a methyl group ;

R_2 represents $S(O)_n$ R_3 or 4,5-dicyanoimidazol-2-yl or haloalkyl;

R_3 represents alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or NR_5 R_6, $S(O)_m$ R_7, $C(O)R_7$ or $C(O)OR_7$, alkyl, haloalkyl or OR_8 or –N=C(R_9)(R_{10}) radical;

R_5 and R_6 independently represent a hydrogen atom or alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$ or $S(O)_r$ CF_3 radical or R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen, nitrogen or sulphur;

R_7 represents alkyl or haloalkyl;

R_8 represents alkyl or haloalkyl or a hydrogen atom;

R_9 represents alkyl or a hydrogen atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or more halogen atoms or groups such as OH, –O-alkyl, –S-alkyl, CN or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom or CN or NO_2 ;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $S(O)_q$ CF_3 or SF_5 group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a C–R_{12} radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is C–Cl; and

B) one or more adhesion promoters comprising a polyether having a chain of ethylene oxide (EO) units and a hydrophobic portion, in which the ratio of the number of ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5.

In a further aspect, the present invention provides a method of treating seeds comprising applying to the seeds a composition as hereinbefore defined.

In a still further aspect of the present invention, there is provided a method of controlling soil-borne pests at a locus comprising applying a composition as hereinbefore defined to seeds and sowing the seeds at the locus.

Still further, there is provided a method of protecting emerging seedlings of a crop against one or more insect organisms in the soil environment, the method comprising applying to the seeds of the crop a composition as hereinbefore defined.

It has been found that compositions of the present invention exhibit an excellent adhesion to the seeds being treated, in particular providing adhesion of the active 1-arylpyrazole to the seeds. Use of the compositions in the treatment of seeds results in the active ingredient remaining adhered to the seeds after the seeds have been sown, in particular in soils of high water content or humidity and/or during heavy rain, such as in the rainy season. As a result, the active ingredient remains effective in protecting the seeds in such conditions. Further,

the high adhesion of the compositions to the treated seeds significantly reduces the leaching of the active component from the seeds, in turn reducing potentially harmful effects to surrounding areas or the environment.

Treatment of seeds with a composition of the present invention results in improved growth of the eventual plants, including an earlier germination of the seeds and an increase in the weight of sprouts and roots of the growing plants.

The composition of the present invention is particularly useful in the treatment and protection of the seeds of rice, corn, cotton, dry bean, soybean and wheat.

Still further, the present invention provides a seed treated with a composition as hereinbefore described. The seeds of this aspect of the invention reduce the exposure of operators and users of the seed product to the active ingredient, in turn increasing the safety of the materials.

In yet further aspect, the present invention provides the use as an adhesion promoter of a polyether having a chain of ether-linked units comprising at least 16 ethylene oxide (EO) moieties.

Still further, the present invention provides the use as an adhesion promoter of a polyether comprising a hydrophobic portion in combination with the chain of ethylene oxide (EO) units, in which the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5.

As described in more detail hereinafter, the agrochemical composition of the present invention may contain optionally one or more agriculturally acceptable solid or liquid carriers and/ or one or more agriculturally acceptable surfactants, depending upon the manner in which the composition is formulated.

As noted above, the composition of the present invention comprises, as an active pesticidal ingredient, a 1-arypyrazole of the above given formula (I). In the formula (I) recited above, alkyl and alkoxy moieties preferably have from 1 to 6 carbon atoms, still more preferably from 1 to 4 carbon atoms. The divalent alkylene radical generally comprise a 5-, 6- or 7-membered ring, including the heteroatom, if present.

Preferred compounds of formula (I) are those in which R_1 represents –CN.

R_4 is a group of formula NR_5R_6 in many preferred compounds, in particular in which R_5 and R_6 are both hydrogen.

Preferred compounds are also those in which R_{11} is a halogen atom, in particular chlorine.

Similarly, preferred compounds are those in which X is a group –C-R_{12}, in which R_{12} is a halogen atom, in particular chlorine.

R_{13} is trifluoromethyl in many preferred compounds.

Many preferred compounds are those comprising a 2,6-dichloro-α,α,α-trifluoro-p-tolyl group.

Examples of preferred 1-arylpyrazoles of formula (I) of the present invention include:

- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (fipronil);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[2-methylallylamino]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (flufiprole);
- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(ethyl)sulfinyl]pyrazole-3-carbonitrile (ethiprole);

- 1-[5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-(methylsulfinyl)pyrazol-3-yl]ethanone (acetoprole);
- O-[1-(4-chlorophenyl)pyrazol-4-yl O-ethyl S-propyl phosphorothioate] (pyraclofos);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[fluoromethylthio]-5-[(pyrazinylmethyl)amino]pyrazole-3-carbonitrile (pyrafluprole);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[difluoromethylthio]-5-[(2-pyridylmethyl)amino]pyrazole-3-carbonitrile (pyriprole);
- 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (pyrolan); and
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[4-hydroxy-3-methoxybenzylideneamino]-4-[trifluoromethylthiopyrazole]-3-carbonitrile (vaniliprole).

The most preferred compound of formula (I) for use in the composition of the present invention is 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(trifluoromethyl)sulfinyl]-pyrazole-3-carbonitrile (fipronil).

Compounds of formula (I) can be prepared according to methods known in the art or methods analogous thereto, for example one of the methods described in WO 87/3781, WO 93/6089, WO 94/21606 or EP 295117. Many compounds of formula (I) are commercially available.

In the agrochemical composition of the present invention used in seed treatment, the compound of formula (I) may be present in any suitable amount to provide a composition effective in protecting the seeds being treated. Preferably, the composition of formula (I) is present in the composition in an amount of from 0.5 to 50% by weight, more preferably from 0.75 to 30%, still more preferably from 1 to 20% by weight.

The composition of the present invention further comprises an adhesion promoter, which is a compound that enhances or increases the adhesion of the

active ingredient to the seeds being treated. The adhesion promoters are selected from polymers or copolymers of polyethers.

The polymers or copolymers of polyethers used as adhesion promoters may be branched, in particular hyperbranched. The term hyperbranching is a reference to the polymer molecules having a high degree of branching. Hyperbranching of the polyether molecules may be obtained in known manner, for example by crosslinking or grafting of groups such as hydroxyl, anionic or lipophilic groups. Preferably, the polymers or copolymers of polyethers used as adhesion promoters contain substantially no hyperbranching.

In the first aspect of the invention, the polyether molecule comprises a chain of ether-linked units comprising at least 16 ethylene oxide (EO) moieties, more preferably at least 20 ethylene oxide (EO) moieties, still more preferably at least 25 ethylene oxide (EO) moieties. Suitable polyether compounds are those having from 16 to 50 ethylene oxide (EO) moieties, more preferably from 18 to 45 EO moieties. In some embodiments of the invention, the polyether comprises 20 to 40 EO moieties, more preferably still from 20 to 35, especially from 25 to 35 EO moieties.

Preferred polyethers are polyethers having at least 16 polyoxyethylene moieties. Examples of such preferred polyethers include fatty alcohol polyethylene glycol, reaction products of fatty acids with ethylene oxide, tristyryl polyether, tributylphenol polyether, polyoxyethylene tristyrylphenol, polyoxyethylene-polyoxypropylene block copolymers, and octoxynol.

In a second aspect of the invention, the polyether molecule present as an adhesion promoter comprises a hydrophobic portion in combination with a chain of ethylene oxide (EO) units, in which the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5, more preferably at least 1.0, still more preferably at least 1.5. Preferred polyethers are

those having the aforementioned ratio in the range of from 0.5 to 3.0. Preferably, the aforementioned ratio is in the range of from 0.7 to 2.5, still more preferably in the range of from 1.0 to 2.0.

In this respect, the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is a reference to the ratio of the number of carbon atoms in the units. For example a C_{16}-C_{18} fatty alcohol polyglycol ether having 25 ethylene oxide units has a ratio of ethylene oxide (EO) units to hydrophobic portion of the molecule of 25/16 to 25/18, which is 1.56 to 1.39.

The polyether molecule comprises a hydrophobic portion. In this context, the "hydrophobic portion" refers to the hydrocarbon chain bonded to the ethylene oxide chain. Such hydrocarbon chains can be saturated or unsaturated, optionally substituted with alkyl groups. The length of the hydrophobic portion of the polyether molecule is based on the total number of carbon atoms of the hydrocarbon chain. For example, an iso-tridecyl alcohol polyglycol ether with 10 ethylene oxide units has a ratio of 10/13, that is 0.77. Furthermore, polyethers of use in the present invention include polyethers endcapped with an alkyl group. An example is C_{12}-C_{18} fatty alcohol ethoxylate butyl ether with 10 EO units, which has a ratio of EO units to hydrophobic portion of 10/ (12+4) to 10/ (18+4), which is 0.63 to 0.46.

Preferred polyethers are those in which the hydrophobic portion includes a fatty alcohol. Examples of such polyethers include polyethers of fatty alcohols, for example polyethers of oleyl alcohol and stearyl alcohol. Other examples of suitable polyethers are those derived from fatty acids, for example lauric acid, myristic acid and coconut fatty acid. Polyethers derived from block copolymers, such as polyoxyethylene-polyoxypropylene block copolymers may also be used.

In a particularly preferred embodiment, the composition of the present invention comprises as an adhesion promoter a polyether having a chain of ether-

linked units comprising at least 16 ethylene oxide (EO) moieties, the molecule further comprising a hydrophobic portion in combination with the chain of ethylene oxide (EO), in which the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5, more preferably from 0.5 to 3.0.

In the composition of the present invention, the ratio by weight of the adhesion promoter to the weight of the agrochemical active ingredient may be in any suitable range to provide the required adhesion of the active ingredient to the seeds to be treated, without resulting in the composition having an excessive viscosity. Preferably, the ratio is in the range of from 0.005 to 5, more preferably from 0.0075 to 3, still more preferably from 0.01 to 2.

The agrochemical composition of the present invention may contain optionally one or more auxiliaries. The auxiliaries employed depend upon such factors as the type of formulation and/or the way in which the formulation is to be applied by the end user. Suitable auxiliaries include all customary formulation adjuvant or components, such as solvents, surfactants, stabilizers, anti-foaming agents, anti-freezing agents, preservatives, antioxidants, colorants, thickeners and inert fillers. Such auxiliaries are known in the art and are commercially available.

The composition may contain one or more solvents. The solvent may be organic or inorganic. Suitable solvents may be selected from the customary solvents which thoroughly dissolve the agrochemical active ingredients employed. Such solvents are known in the art and are commercially available. Examples of suitable solvents include water, aromatic solvents (for example, xylene, such as Solvesso™ solvent products), mineral oils, animal oils, vegetable oils, alcohols (for example, methanol, butanol, pentanol, benzyl alcohol), ketones (for example, cyclohexanone, γ-butyrolactone), pyrrolidones (for example, N-Methyl-2-pyrrolidone (NMP), N-Octyl-2-pyrrolidone (NOP)), acetates (for example, glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters.

The composition according to the present invention may further contain one or more surfactants. The number, type and amount of surfactant present will depend upon the nature of the formulation and the manner in which the composition is to be used. Suitable surfactants are known in the art and include, but are not limited to, alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid and dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulphates, alkylsulfonates, arylsulfonates, fatty alcohol sulphates, fatty acids and sulfated fatty alcohol glycol ethers, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose and ethylene oxide /propylene oxide block copolymers.

The agrochemical composition of the present invention may further contain one or more polymeric stabilizers. Suitable polymeric stabilizers that may be used in the present invention include, but are not limited to, polypropylene, polyisobutylene, polyisoprene, copolymers of monoolefins and diolefins, polyacrylates, polystyrene, polyvinyl acetate, polyurethanes or polyamides. Suitable stabilizers are known in the art and are commercially available.

The composition may further comprise an anti-foaming agent. Suitable anti-foam agents include all substances which can normally be used for this purpose in agrochemical compositions. Suitable anti-foaming agents are known in the art and are commercially available. Particularly preferred anti-foaming agents are mixtures of polydimethylsiloxanes and perfluroalkylphosphonic acids, such as the organic silicone anti-foam agents available from GE or Compton.

Further, the composition may optionally comprise one or more antioxidants. Suitable antioxidants are all substances which can normally be used for this purpose in agrochemical compositions, which are known in the art. Preference is given, for example, to butylated hydroxytoluene (BHT).

A binder may also be included in the composition. The binder component is preferably composed of an adhesive polymer that may be natural or synthetic, and is without phytotoxic effect on the seed to be coated. The binder may be selected from vinyl acetates, polyvinyl alcohols, methylcelluloses, polyvinyl pyrrolidone, and the like. Again, suitable binders are known in the art.

Depending upon the type of formulation, the composition may further contain one or more inert fillers. Such inert fillers are known in the art and available commercially. They include, for example, natural ground minerals, such as kaolins, aluminas, talc, chalk, quartz, attapulgite, montmorillonite, and diatomaceous earth, or synthetic ground minerals, such as highly dispersed silicic acid, aluminum oxide, silicates, and calcium phosphates and calcium hydrogen phosphates. Suitable inert fillers for granules include, for example, crushed and fractionated natural minerals, such as calcite, marble, pumice, sepiolite, and dolomite, or synthetic granules of inorganic and organic ground materials, as well as granules of organic material, such as sawdust, coconut husks, corn cobs, and tobacco stalks.

The composition according to the present invention may further contain one or more thickeners. Suitable thickeners include all substances which can normally be used for this purpose in agrochemical compositions. For example, suitable thickeners include xanthan gum, polyvinyl alcohol, cellulose and its derivatives, clay hydrated silicates, magnesium aluminum silicates or a mixture thereof. Again, such thickeners are known in the art and available commercially.

The above compounds are listed as examples and are not intended to be an exhaustive list of compounds that can be used in the composition of the present invention.

The composition according to the present invention can be provided in any suitable formulation, including solid or liquid forms. Solid formulations include dustable powders, wettable powders and water dispersible granules. Liquid formulations include dilute aqueous suspensions, suspension concentrates, pastes, gels or aqueous dispersions.

Preferably, the compositions are formulated as aqueous suspensions and suspension concentrates (SC), which are particularly advantageous because of their ease of use during their application to the seeds.

The compositions may be used to treat a wide range of seeds. Seeds that are applicable for treatment with the agrochemical composition according to the present invention include corn (sweet and field), soybean, wheat, barley, oats, rice, cotton, sunflower, alfalfa, sorghum, rapeseed, sugarbeet, Brassica spp., tomato, bean, carrot, tobacco and flower seed, for example, pansy, impatiens, petunia and geranium. The most preferred seeds for treatment include rice, corn, cotton, dry bean, soybean and wheat.

The composition of the present invention may be used to provide protection against a wide range of pests. Specific target pest organisms include insects of the following order:

- Plant parasitic nematodes, for example, *Meloidogyne incognita*, *Heterodera glycines Ichinohe* (Soybean Cyst Nematode);
- Coleoptera, for example, grubworm, *Elateridae*, weevil, *Sitophilus zeamais*, *Tenebrio molitor*, *Paederus*, *Cerambycidae* (Longhorned Beetle), *Oryzophagus oryzae, Diabrotica speciosa, Phyllophaga cubana , Sternechus subsignatus, Diloboderus abderus* etc.;

- Lepidoptera, for example, *Agrotis ipsilon* (black cutworm), *Spodoptera exigua Hiibner* (beet armyworm), *Chilo suppressalis*, *Pyrausta nubilalis Hübner* , *Pieridae*, *Grapholitha molesta Busck*, *Tortricidae* (leaf roller moth), *Carposina nipponensis*, *Hellula undalis Fabricius* (Cabbage webworm), etc.;
- Gastropoda, for example, snail, *Agriolimax agrestis* (Linnaeus), etc.;
- Orthoptera, for example, *Gryllotalpa* (mole cricket), locust, *Blattella germanica* (german cockroach), *nauphoeta cinerea* (Lobster Roach) etc.;
- Plant parasitic mites, for example, *Tetranychus urticae Koch* (Two-spotted spider mite), *Tetranychus cinnabarinus* (red spider mite), purple rust mite, *Rhizoglyphus echinopus* (Bulb mite), etc.;
- Thysanoptera, for example, *Thrips palmi Karny*, *Thrips flavidulus*, *Thrips hawaiiensis, Frankliniella schultzei*;
- Diptera, for example, *Culex*, mosquito, *Chironomidae*, *Musca domestica* (house fly), etc.;
- Hymenoptera, for example, ants, *Vespidae, Athalia*, etc.;
- Blattaria, for example, Japanese termite, *Reticulitermes bitumulus*, etc.

In addition to treatment with the composition of the present invention, the seed may be treated with one or more other pesticides, for example one or more fungicidally active agents, fertilizers and/or biocontrol agents.

Suitable pesticides for use in the composition of the present invention include those listed herein and those listed in The Pesticide Manual, 9th Ed., Editor, Charles Worthing, published by the British Crop Protection Council and hereby incorporated by reference.

A fungicide may be applied to the seed prior to the coating layer of the composition described herein. The application of a fungicide as a dust, slurry or the like is a well known practice in the art. Suitable examples of fungicides include Captan (N-(trichloromethylthio)-cyclohex-4-ene-1,2-dicarboximide), Thiram (tetramethylthioperoxydicarbonic diamide), Metalaxyl, Fludioxonil (4-(2,2-difluoro-1,3-benzodioxol-4-yl)-1*H*-pyrrole-3-carbonitrile), and Oxadixyl (*N*-(2,6-

dimethylphenyl)-2-methoxy-*N*-(2-oxo-3-oxazolidinyl)acetamide). One skilled in the art will be aware of other beneficial fungicides suitable for combating harmful pathogens which are not only a problem for a particular locus where the coated seed is to be grown but also suitable for the protection of seeds in storage before planting.

The amount of fungicide composition to be added will vary according to such factors as the activity of the fungicidally active ingredient, but in general may range from about 0.001 to about 10% by weight of the seed and preferably from about 0.01 to 2.0%. However, for a particular situation the amount may be greater or less.

Suitable biocontrol agents for use with the composition of the present invention are bacteria of the genera Rhizobium, Bacillus, Pseudomonas, and Serratia, fungi of the genera Trichoderma, Glomus, and Gliocladium and mycorrhizal fungi.

The composition of the present invention is applied to the seeds most preferably to form a coating on the seeds. Conventional means of coating may be used for carrying out the coating. Various coating machines are known and available to one skilled in the art. Three well-known techniques include the use of drum coaters, fluidized bed techniques and spouted beds. The seeds to be treated may be pre-sized prior to coating. After coating, the seeds are preferably dried and then, optionally, sized by transferring to a sizing machine. Suitable sizing machines, which are known in the art, are the common machines for seed sizing in the industry.

The amount of the composition to be applied will vary depending on the size of the seed to be coated. The insecticidally active ingredient of the coating must not inhibit germination of the seed and should be efficacious at least during that time in the life cycle of the target insect which causes injury to the crop. One

skilled in the art will appreciate that this time will vary depending on the target insect, among other factors. In general the coating will be efficacious for approximately 0 to 120 days after sowing. The coating of the present invention will contain an amount of insecticide that is insecticidally effective. An insecticidally effective amount used herein means that amount of insecticide that will kill insect pests in the larvae or pupae stage of growth or will consistently reduce or retard the amount of damage produced to the seeds or plants by insect pests.

Seeds treated with the composition of the present invention have the following advantages: They pose less risk with respect to operators handling the seeds and reduced exposure, in particular to dust. The pesticides can be applied in a uniform way and loss of pesticides during transportation and handling is significantly reduced or prevented. Phytotoxicity to the seeds and developing seedlings and therefore there is little or no adverse effect on germination, seedling emergence and seedling development. Additionally, placement of pesticides, particularly insecticides, closer to the insect soil feeding zone is possible with compositions of the present invention, which in turn may improve insect control. Unlike the adhesion agents generally used in seed treatments, seeds treated with the present invention show improved adhesion of the active ingredients to the seeds, in particular in soils of higher humidity and/or during the rainy season.

Specific embodiments of the present invention are described hereinafter by way of example only.

Determination of Adhesion

The adhesion of the composition to seeds treated with the composition may be determined by the following procedure. The spraying of water simulates the situation of a soil with a high humidity or of a rainy season.

Soak 1kg of seeds in water for 48 hours and thereafter drain. Take 100g of these seeds.

Dilute the composition being tested with water to obtain a treatment solution containing 25mg of the agrochemical active ingredient.

Apply the resulting treatment solution to the 100g of drained seeds by mixing the seeds with the treatment solution.

Spray the treated seeds with water according to the following steps:

Drain the treated seeds for 2 hours. Place 40g of the treated seeds in a measuring cylinder with 250ml of water. Close the cylinder with a stopper and rotate the cylinder about the horizontal axis five times. Rotating the cylinder means turning the cylinder through 180° downward, and then 180° upward in the opposite direction. Dry the seeds at 30°C for 15 hours. The amount of the agrochemical active ingredient adhered to the seeds is determined by HPLC chromatography.

The adhesion level after spraying equals the weight of the agrochemical active ingredient determined by the chromatography divided by the total weight of the active ingredient present in the treatment solution. The adhesion level after spraying is expressed in weight percentage.

Example 1: Aqueous suspension with 25% formula (I) compound

An aqueous suspension composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (Fipronil)	25%
C_{16}-C_{18} fatty alcohol polyoxyethylene ether (25EO)	0.5%
Alkyl polysaccharide	1%
Hydroxyethyl cellulose	0.6%
1,2-Benzisothiazolin-3-one	0.3%
Red pigment	2%
Propylene glycol	5%
Silicon oil as anti-foaming agent	0.2%
Water	Balance to 100%

The particle size of the formula (I) compound in the aqueous suspension was lowered to approximately 3mm by processing in a sand mill.

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on rice seeds is 80%. By comparison, the adhesion level obtained with the same composition but prepared without the fatty alcohol polyoxyethylene ether was 30%.

Example 2: Aqueous suspension with 20% formula (I) compound

An aqueous suspension composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (Flufiprole)	20%
Tristyryl polyoxyethylene ether (20EO)	0.1%
Alkyl polysaccharide	1%
Hydroxyethyl cellulose	0.6%
1,2-Benzisothiazolin-3-one	0.3%
Red pigment	2%
Propylene glycol	5%
Silicon oil as anti-foaming agent	0.2%
Water	Balance to 100%

The particle size of the formula (I) compound in the aqueous suspension was lowered to approximately 3mm by processing in a sand mill.

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on corn seeds is 90%. By comparison, the adhesion level obtained with the same composition but prepared without the tristyryl polyoxyethylene ether was 50%.

Example 3: Aqueous suspension with 5% formula (I) compound

An aqueous suspension composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (fipronil)	5%
Tributylphenol ethoxylate (25EO)	1%
Alkyl polysaccharide	1%
Hydroxyethyl cellulose	0.6%
1,2-Benzisothiazolin-3-one	0.3%
Red pigment	2%
Propylene glycol	5%
Silicon oil as anti-foaming agent	0.2%
Water	Balance to 100%

The particle size of the formula (I) compound in the aqueous suspension was lowered to approximately 3mm by processing in a sand mill.

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on cotton seeds is 90%. By comparison, the adhesion level obtained with the same composition but prepared without the polyether was 40%.

Example 4: Aqueous suspension with 50% formula (I) compound

An aqueous suspension composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (Pyriprole)	50%
Oleyl alcohol polyglycol ether (20EO)	2%
Alkyl polysaccharide	1%
Hydroxyethyl cellulose	0.6%
1,2-Benzisothiazolin-3-one	0.3%
Red pigment	2%
Propylene glycol	5%
Silicon oil as anti-foaming agent	0.2%
Water	Balance to 100%

The particle size of the formula (I) compound in the aqueous suspension was lowered to approximately 3mm by processing in a sand mill.

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on dry bean seeds is 88%. By comparison, the adhesion level obtained with the same composition but prepared without the polyether was 35%.

Example 5: Aqueous suspension with 0.5% formula (I) compound

An aqueous suspension composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (fipronil)	0.5%
Polyoxyethylene (15EO)-polyoxypropylene (20PO) block copolymer	2.5%
Alkyl polysaccharide	1%
Hydroxyethyl cellulose	0.6%
1,2-Benzisothiazolin-3-one	0.3%
Red pigment	2%
Propylene glycol	5%
Silicon oil as anti-foaming agent	0.2%
Water	Balance to 100%

The particle size of the formula (I) compound in the aqueous suspension was lowered to approximately 3mm by processing in a sand mill.

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on soybean seeds is 95%. By comparison, the adhesion level obtained with the same composition but prepared without the polyether was 45%.

Example 6: Paste with 30% formula (I) compound

A paste composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (fipronil)	30%
Octylphenol polyoxyethylene ether (20-25EO)	4.0%
Sodium ligninsulfonate	10.0%
Water	Balance to 100%

The composition has a homogeneous appearance and a good flowability after storage at room temperature or 54°C for 15 days.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on wheat seeds is 98%. By comparison, the adhesion level obtained with the same composition but prepared without the octylphenol polyoxyethylene ether was 40%.

Example 7: Water dispersible granule with 40% formula (I) compound

A water dispersible granule composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (fipronil)	40%
C_{12}-C_{14} fatty alcohol polyoxyethylene ether (20EO)	5%
Sodium lauryl benzenesulfonate	3%
Sucrose	Balance to 100%

With the water dispersible granule, an aqueous suspension of required concentration is obtained through dilution of the water dispersible granule with an appropriate amount of water.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on soybean seeds is 93%. By comparison, the adhesion level obtained with the same composition but prepared without the fatty alcohol polyoxyethylene ether was 50%.

Example 8: Wettable powder with 10% formula (I) compound

A wettable powder composition was prepared having the following composition (expressed in weight %).

Formula (I) compound (fipronil)	10%
C_{12}-C_{14} fatty alcohol polyoxyethylene ether (20EO)	1.5%
Sodium lauryl benzenesulfonate	3%
Sucrose	Balance to 100%

With the above wettable powder, an aqueous suspension of required concentration is obtained through dilution of the wettable powder with an appropriate amount of water.

The adhesion of the composition to treated seeds was tested using the above testing method. The adhesion level after spraying the above aqueous suspension on wheat seeds is 96%. By comparison, the adhesion level obtained with the same composition but prepared without the fatty alcohol polyoxyethylene ether was 55%.

As can be seen the use of the polyether resulted in each case in a significant and advantageous increase in the adhesion of the active ingredient to the treated seeds.

Testing Examples

The efficacy of the compositions prepared in Examples 1 to 8 was tested as follows:

Seed treatment with insecticidal seed coating agent

Compositions of the Examples 1 to 8 are sprayed onto 1kg of seeds in the amount of 5% by weight of the seed until all the compositions are utilized. The seeds are dried in a rotating pan at approximately 20 r.p.m. with an air flow of approximately 32 c.f.m and a temperature of 50°C. In order to prevent germination of seed, the temperature may be periodically adjusted to maintain the seed temperature at or less than 35°C.

Testing Example 1

Result of germination and field emergence rate of rice seeds.

Germination of the seeds treated with the abovementioned agrochemical compositions is tested under the testing rules of the Association of Official Seed Analysts (AOSA). Sprouts and roots are separated after 7 to 10 days of germination. Dry weight of sprouts and roots are recorded to assess the growth of the seedlings. For the field emergence rate test, rice seeds are sown in trays, either in peat-rich compost or in soil from the Camargue, with two rows per treatment. Each treatment is repeated for four replicates. In all examples, each tray is placed in water (to simulate rice-paddy conditions) after germination of the

seeds. Emergence counts are taken every other day commencing from the first day of germination until the 21st day after emergence. The percentage of emergence at all locations is illustrated in Table 1.

This table shows that the abovementioned agrochemical compositions do not adversely affect seedling emergence.

The treatments are described as follows:

Treatments 1-8: Rice seeds are treated with Examples 1 to 8 according to the seed treatment method described in the testing example;

Treatment 9: Untreated seeds.

Table 1

Treatment	Germination percentage (%)	Sprout (mg)	Root (mg)	Emergence percentage (%)
1	99	12.2	13.3	92
2	98	10.2	12.5	93
3	99	11.4	10.4	93
4	99	12.4	12.4	94
5	98	13.2	11.5	95
6	99	12.6	12.5	91
7	99	11.8	11.3	92
8	98	11.4	10.2	93
9	98	12.3	10.3	91

The information in the above Table 1 shows that the agrochemical compositions of the present invention do not adversely affect the germination and seedling emergence of rice when compared to the untreated seeds.

Efficacy test against *Sitophilus oryzae* (rice weevil)

Treated and untreated rice seeds are placed on a petri dish with 9cm depth, and allowed to stand in a room at an ambient temperature of 25°C. In the second and the third month after treatment, five male and female adult *Sitophilus oryzaes* (rice weevils) (ten in total) are introduced into the petri dish, with five replicates. The number of dead *Sitophilus oryzaes* (rice weevils) and the number of eggs laid on rice seeds are examined two days later. The mortality is computed by the following formula and the average values of the results are shown in Table 2.

Mortality = [Number of dead *Sitophilus oryzaes* (rice weevils) / 50 *Sitophilus oryzaes* (rice weevils)] × 100%

Table 2

Treatment	At the second month after treatment		At the third month after treatment	
	Mortality (%)	Number of eggs laid	Mortality (%)	Number of eggs laid
1	95	1	90	2
2	95	1	90	2
3	94	2	91	2
4	93	2	92	2
5	95	1	91	2
6	94	2	90	3
7	96	1	90	3
8	97	1	91	3
9	0	50	0	100

The information in the above Table 2 shows that the agrochemical composition of the present invention controls *Sitophilus oryzae* (rice weevil) well when compared to untreated seeds.

Testing Example 2

Result of germination and field emergence rate of wheat seeds

Germination and field emergence rate of wheat seeds are tested as described in Testing Example 1. The results are set out in Table 3.

The treatments are described as follows:

Treatments 1-8: Wheat seeds are treated with Examples 1 to 8 according to the seed treatment method described in the testing example;

Treatment 9: Untreated seeds

Table 3

Treatment	Germination percentage (%)	Sprout (mg)	Root (mg)	Emergence percentage (%)
1	99	11.2	11.3	94
2	98	10.2	11.5	95
3	99	10.4	9.4	96
4	99	10.4	10.4	94
5	98	10.2	9.5	95
6	99	10.6	10.5	94
7	99	10.8	10.3	96
8	98	10.4	9.2	95
9	99	10.3	10.3	94

The information in the above Table 3 shows that the agrochemical compositions of the present invention do not adversely affect the germination and seedling emergence of wheat when compared to untreated seeds.

Efficacy test against *Elateridae*

Efficacy against *Elateridae* on wheat seeds is tested as described in Testing Example 1 and the mortality is computed. The results are set out in Table 4.

Table 4

Treatment	Mortality at the second month after treatment (%)	Mortality at the third month after treatment (%)
1	100	90
2	100	90
3	100	91
4	100	92
5	100	91
6	100	90
7	100	90
8	100	91
9	0	0

The information in the above Table 4 shows that the agrochemical compositions of this invention control *Elateridae* well when compared to untreated seeds.

Testing Example 3

Result of germination and field emergence rate of soybean seeds

Germination and the field emergence rate of soybean seeds are tested as described in Testing Example 1. The results are set out in Table 5.

The treatments are described as follows:

Treatments 1-8: Soybean seeds are treated with Examples 1 to 8 according to the seed treatment method described in the testing example;

Treatment 9: Untreated seeds

Table 5

Treatment	Germination percentage (%)	Sprout (mg)	Root (mg)	Emergence percentage (%)
1	99	8.2	10.3	95
2	98	9.2	10.5	95
3	99	9.4	9.4	96
4	99	8.4	10.4	94
5	98	9.2	10.5	95
6	99	9.6	10.5	96
7	99	8.8	10.3	97
8	98	9.4	10.2	96
9	99	8.3	10.3	95

The information in the above Table 5 shows that the agrochemical compositions of the present invention do not adversely affect the germination and seedling emergence of soybean when compared to untreated seeds.

Efficacy test against soybean cyst nematode

Efficacy against cyst nematode on soybean seeds is tested as described in Testing Example 1 and the mortality is computed. The results are set out in Table 6 below.

Table 6

Treatment	Mortality at the second month after treatment (%)	Mortality at the third month after treatment (%)
1	98	93
2	98	93
3	98	90
4	98	91
5	97	93
6	97	95
7	96	90
8	95	93
9	0	0

The information in the above Table 6 shows that the agrochemical compositions of the present invention control soybean cyst nematode well when compared to untreated seeds.

Testing Example 4

Result of germination and field emergence rate of cotton seeds

Germination and the field emergence rate of cotton seeds are tested as described in Testing Example 1. The results are set out in Table 7.

The treatments are described as follows:

Treatments 1-8: Cotton seeds are treated with Examples 1 to 8 according to the seed treatment method described in the testing example;

Treatment 9: Untreated seeds

Table 7

Treatment	Germination percentage (%)	Sprout (mg)	Root (mg)	Emergence percentage (%)
1	99	6.2	7.3	96
2	98	7.2	7.5	96
3	99	6.4	6.4	96
4	99	6.4	7.4	95
5	98	6.2	6.5	95
6	99	6.6	7.5	96
7	99	6.8	6.3	96
8	98	7.4	6.2	95
9	99	6.3	6.3	95

The information in the above Table 7 shows that the agrochemical compositions of the present invention do not adversely affect the germination and seedling emergence of cotton when compared to untreated seeds.

Efficacy test against *Agrotis ipsilon* (black cutworm)

Efficacy against *Agrotis ipsilon* (black cutworm) on cotton seeds is tested as described in Testing Example 1 and the mortality is determined. The results are set out in Table 8.

Table 8

Treatment	At the second month after treatment		At the third month after treatment	
	Morality (%)	Number of eggs laid	Mortality (%)	Number of eggs laid
1	95	1	90	2
2	95	1	90	2
3	94	2	91	2
4	93	2	92	2
5	95	1	91	2
6	94	2	90	3
7	96	1	90	3
8	97	1	91	3
9	0	50	0	50

The information in the above Table 8 shows that the agrochemical compositions of the present invention control *Agrotis ipsilon* (black cutworm) well when compared to untreated seeds.

Testing Example 5

Result of germination and field emergence rate of corn seeds

Germination and the field emergence rate of corn seeds are tested as described in Testing Example 1. The results are set out in Table 9.

The treatments are described as follows:

Treatments 1-8: Corn seeds are treated with Examples 1 to 8 according to the seed treatment method described in the testing example;

Treatment 9: Untreated seeds

Table 9

Treatment	Germination percentage (%)	Sprout (mg)	Root (mg)	Emergence percentage (%)
1	99	10.2	12.3	96
2	98	9.2	115	95
3	99	10.4	11.4	96
4	99	9.4	10.4	94
5	98	10.2	10.5	95
6	99	10.6	11.5	96
7	99	10.8	11.3	96
8	99	10.4	10.2	96
9	99	10.3	10.3	95

The information in the above Table 9 shows that the agrochemical compositions of the present invention do not adversely affect the germination and seedling emergence of corn when compared to untreated seeds.

Efficacy test against grubworm

Efficacy against grubworm on corn seeds is tested as described in Testing Example 1 and the mortality is computed. The results are shown in Table 10.

Table 10

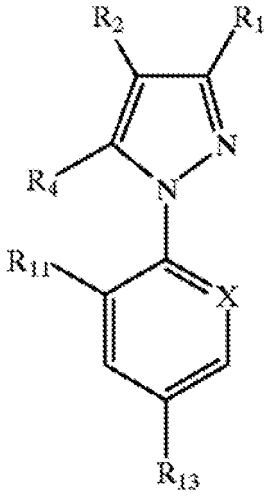
Treatment	Mortality at the second month after treatment (%)	Mortality at the third month after treatment (%)
1	95	92
2	95	92
3	95	90
4	96	91
5	96	93
6	97	94
7	94	91
8	95	93
9	0	0

The information in the above Table 10 shows that the agrochemical compositions of the present invention control grubworm well when compared to untreated seeds.

CLAIMS

1. An agrochemical composition comprising:

A) at least one agrochemical active ingredient of 1-arylpyrazoles of formula (I)



(I)

in which:

R_1 represents a halogen atom or CN or a methyl group ;

R_2 represents $S(O)_n R_3$ or 4,5-dicyanoimidazol-2-yl or haloalkyl;

R_3 represents alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or $NR_5 R_6$, $S(O)_m R_7$, $C(O)R_7$ or $C(O)OR_7$, alkyl, haloalkyl or OR_8 or $–N=C(R_9)(R_{10})$ radical;

R_5 and R_6 independently represent a hydrogen atom or alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$ or $S(O)_r CF_3$ radical or R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen, nitrogen or sulphur;

R_7 represents alkyl or haloalkyl;

R_8 represents alkyl or haloalkyl or a hydrogen atom;

R_9 represents alkyl or a hydrogen atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or

more halogen atoms or groups such as OH, –O-alkyl, –S-alkyl, CN or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom or CN or NO_2 ;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $S(O)_q$ CF_3 or SF_5 group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a C–R_{12} radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is C–Cl; and

B) one or more adhesion promoters comprising a polyether having a chain of ethylene oxide (EO) units and a hydrophobic portion, in which the ratio of the number of ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5.

2. The composition according to claim 1, in which R_1 represents –CN.

3. The composition according to either of claims 1 or 2, wherein R_4 is a group of formula NR_5R_6.

4. The composition according to claim 3, wherein one or both of R_5 and R_6 is hydrogen.

5. The composition according to any preceding claim, wherein R_{11} is a halogen.

6. The composition according to claim 5, wherein the halogen is chlorine.

7. The composition according to any preceding claim, wherein X is a group -C-R_{12} in which R_{12} is halogen.

8. The composition according to claim 7, wherein the halogen is chlorine.

9. The composition according to any preceding claim, wherein R_{13} is trifluormethyl.

10. The composition according to any preceding claim, wherein the compound of formula I comprises a 2,6-dichloro-α,α,α-trifluoro-p-tolyl group.

11. The composition according to any preceding claim, wherein the compound of formula I is selected from:

- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (fipronil);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[2-methylallylamino]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (flufiprole);
- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(ethyl)sulfinyl]pyrazole-3-carbonitrile (ethiprole);
- 1-[5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-(methylsulfinyl)pyrazol-3-yl]ethanone (acetoprole);
- O-[1-(4-chlorophenyl)pyrazol-4-yl O-ethyl S-propyl phosphorothioate] (pyraclofos);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[fluoromethylthio]-5-[(pyrazinylmethyl)amino]pyrazole-3-carbonitrile (pyrafluprole);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[difluoromethylthio]-5-[(2-pyridylmethyl)amino]pyrazole-3-carbonitrile (pyriprole);
- 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (pyrolan); and

1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[4-hydroxy-3-methoxybenzylideneamino]-4-[trifluoromethylthiopyrazole]-3-carbonitrile (vaniliprole).

12. The composition according to any preceding claim, wherein the composition of formula (I) is present in the composition in an amount of from 0.5 to 50% by weight.

13. The composition according to any preceding claim, wherein the adhesion promoter comprises substantially no hyperbranching.

14. The composition according to any preceding claim, wherein the polyether molecule comprises a chain of ether-linked units comprising at least 16 ethylene oxide (EO) moieties.

15. The composition according to claim 14, wherein the polyether molecule comprises a chain of ether-linked units comprising at least 20 ethylene oxide (EO) moieties.

16. The composition according to any preceding claim, wherein the adhesion promoter is selected from polyethers of a fatty alcohol, polyethers derived from fatty acids, and polyethers derived from block copolymers.

17. The composition according to claim 16, wherein the adhesion promoter is selected from a polyether of oleyl alcohol, stearyl alcohol, lauric acid, myristic acid and coconut fatty acid, or a polyether derived from a polyoxyethylene-polyoxypropylene block copolymer.

18. The composition according to any preceding claim, wherein the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is from 0.5 to 3.0.

19. The composition according to claim 18, wherein the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is from 0.75 to 2.0.

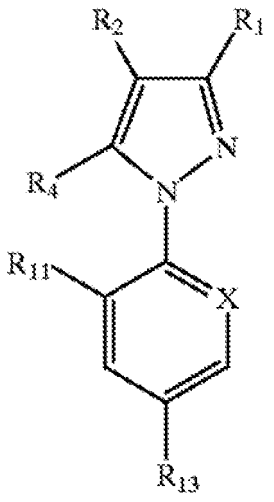
20. The composition according to any preceding claim, wherein the ratio by weight of the adhesion promoter to the weight of the compound of formula I is in the range of from 0.005 to 5.

21. The composition according to any preceding claim, further comprising one or more solvents, surfactants, stabilizers, anti-foaming agents, anti-freezing agents, preservatives, antioxidants, colorants, thickeners, binders or inert fillers.

22. The composition according to any preceding claim, when formulated as an aqueous suspension or a suspension concentrate (SC).

23. An agrochemical composition comprising:

A) at least one agrochemical active ingredient of 1-arylpyrazoles of formula (I)



(I)

in which:

R_1 represents a halogen atom or CN or a methyl group ;

R_2 represents $S(O)_n R_3$ or 4,5-dicyanoimidazol-2-yl or haloalkyl;

R_3 represents alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom or $NR_5 R_6$, $S(O)_m R_7$, $C(O)R_7$ or $C(O)OR_7$, alkyl, haloalkyl or OR_8 or $–N=C(R_9)(R_{10})$ radical;

R_5 and R_6 independently represent a hydrogen atom or alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$ or $S(O)_r CF_3$ radical or R_5 and R_6 can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen, nitrogen or sulphur;

R_7 represents alkyl or haloalkyl;

R_8 represents alkyl or haloalkyl or a hydrogen atom;

R_9 represents alkyl or a hydrogen atom;

R_{10} represents a phenyl or heteroaryl group optionally substituted by one or more halogen atoms or groups such as OH, –O-alkyl, –S-alkyl, CN or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom or CN or NO_2 ;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $S(O)_q CF_3$ or SF_5 group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a $C–R_{12}$ radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is C–Cl; and

B) one or more adhesion promoters comprising a polyether the said polyether containing at least 16 polyoxyethylene and/or polyoxypropylene moieties.

24. The composition according to claim 23, in which R_1 represents –CN.

25. The composition according to either of claims 23 or 24, wherein R_4 is a group of formula NR_5R_6.

26. The composition according to claim 25, wherein one or both of R_5 and R_6 is hydrogen.

27. The composition according to any of claims 23 to 26, wherein R_{11} is a halogen.

28. The composition according to claim 27, wherein the halogen is chlorine.

29. The composition according to any of claims 23 to 28, wherein X is a group -C-R_{12} in which R_{12} is halogen.

30. The composition according to claim 29, wherein the halogen is chlorine.

31. The composition according to any of claims 23 to 30, wherein R_{13} is trifluormethyl.

32. The composition according to any of claims 23 to 31, wherein the compound of formula I comprises a 2,6-dichloro-α,α,α-trifluoro-p-tolyl group.

33. The composition according to any of claims 23 to 32, wherein the compound of formula I is selected from:

- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (fipronil);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[2-methylallylamino]-4-[(trifluoromethyl)sulfinyl]pyrazole-3-carbonitrile (flufiprole);
- 5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[(ethyl)sulfinyl]pyrazole-3-carbonitrile (ethiprole);
- 1-[5-amino-1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-(methylsulfinyl)pyrazol-3-yl]ethanone (acetoprole);
- O-[1-(4-chlorophenyl)pyrazol-4-yl O-ethyl S-propyl phosphorothioate] (pyraclofos);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[fluoromethylthio]-5-[(pyrazinylmethyl)amino]pyrazole-3-carbonitrile (pyrafluprole);
- 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-4-[difluoromethylthio]-5-[(2-pyridylmethyl)amino]pyrazole-3-carbonitrile (pyriprole);

- 3-methyl-1-phenylpyrazol-5-yl dimethylcarbamate (pyrolan); and 1-[2,6-dichloro-α,α,α-trifluoro-p-tolyl]-5-[4-hydroxy-3-methoxybenzylideneamino]-4-[trifluoromethylthiopyrazole]-3-carbonitrile (vaniliprole).

34. The composition according to any of claims 23 to 33, wherein the composition of formula (I) is present in the composition in an amount of from 0.5 to 50% by weight.

35. The composition according to any of claims 23 to 34, wherein the adhesion promoter comprises substantially no hyperbranching.

36. The composition according to any of claims 23 to 35, wherein the polyether molecule comprises a chain of ether-linked units comprising at least 20 ethylene oxide (EO) moieties.

37. The composition according to claim 36, wherein the polyether molecule comprises a chain of ether-linked units comprising at least 25 ethylene oxide (EO) moieties.

38. The composition according to any of claims 23 to 37, wherein the adhesion promoter is selected from polyethers of a fatty alcohol, polyethers derived from fatty acids, and polyethers derived from block copolymers.

39. The composition according to claim 38, wherein the adhesion promoter is selected from a polyether of oleyl alcohol, stearyl alcohol, lauric acid, myristic acid and coconut fatty acid, or a polyether derived from a polyoxyethylene-polyoxypropylene block copolymer.

40. The composition according to any of claims 23 to 39, wherein the polyether molecule comprises a hydrophobic portion in combination with a chain of ethylene oxide (EO) units, in which the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5.

41. The composition according to claim 40, wherein the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is from 0.5 to 3.0.

42. The composition according to any of claims 23 to 41, wherein the ratio by weight of the adhesion promoter to the weight of the compound of formula I is in the range of from 0.005 to 5.

43. The composition according to any of claims 23 to 42, further comprising one or more solvents, surfactants, stabilizers, anti-foaming agents, anti-freezing agents, preservatives, antioxidants, colorants, thickeners, binders or inert fillers.

44. The composition according to any of claims 23 to 43, when formulated as an aqueous suspension or a suspension concentrate (SC).

45. A method of treating seeds comprising applying to the seeds a composition as claimed in any preceding claim.

46. A method of controlling soil-borne pests at a locus comprising applying a composition as claim in any of claims 1 to 44 to seeds and sowing the seeds at the locus.

47. A method of protecting emerging seedlings of a crop against one or more insect organisms in the soil environment, the method comprising applying to the seeds of the crop a composition as claimed in any of claims 1 to 44.

48. The method according to any of claims 45 to 47, wherein the seeds are of rice, corn, cotton, dry bean, soybean or wheat.

49. A seed treated with a composition as claimed in any of claims 1 to 44.

50. Use as an adhesion promoter of a polyether having a chain of ether-linked units comprising at least 16 ethylene oxide (EO) moieties.

51. Use as an adhesion promoter of a polyether comprising a hydrophobic portion in combination with the chain of ethylene oxide (EO) units, in which the ratio of the ethylene oxide (EO) units to the length of the hydrophobic portion of the polyether molecule is at least 0.5.

52. The use according to either of claims 50 or 51, wherein the said polyether is used as an adhesion promoter for a 1-arylpyrazole.

53. An agrochemical composition substantially as hereinbefore described.

54. A method of treating seeds substantially as hereinbefore described.

Application No:	GB1518882.4	**Examiner:**	Dr Albert Mthupha
Claims searched:	1-54	**Date of search:**	21 April 2016

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-52.	US2010/0016155 A1 (TARANTA et al), see particularly para. [0001]-[0005], [0076], Example 1 and claim 11.
X	1-52.	US6121193 A (SEGAUD et al), see particularly column 3, lines 8-10, column 5, lines 8-60, Examples 1, 6, 7 & 9, and claim 1.
X	1-52.	EP0295117 A1 (MAY & BAKER), see particularly Composition Example 2 and claim 1.
X	1-52.	US2002/0098221 A1 (TARANTA et al), see particularly para. [0049], Example 15 and claim 1.
X	1-52.	US2012/0053221 A1 (ISHAQUE et al), see para. [0349], Examples 8, 12, 16, 17 & 19-23 and claim 25.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

A01N

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI.

International Classification:

Subclass	Subgroup	Valid From
A01N	0025/24	01/01/2006
A01N	0043/48	01/01/2006