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(54) Title: PESTICIDAL COMBINATIONS

(57) Abstract: The present invention relates to pesticidal combinations comprising thiodicarb and a benzoylurea selected from the group triflumuron, diflubenuron, lufenuron, and novaluron, that show good pesticidal activities.

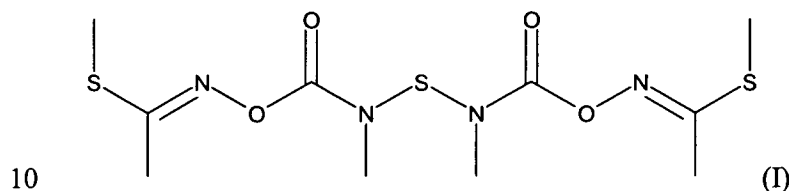
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Pesticidal combinations

The present invention relates to novel insecticidal combinations comprising one or more carbamate and one or more benzoylurea that show surprisingly good insecticidal, acaricidal and nematocidal activities.

- 5 The present invention further relates to the use of these combinations for the treatment of plant propagation material, and to a method for protecting plant propagation material and/or shoots and foliage of a plant grown from plant propagation material from damage by a pest or a fungus. Treated plant propagation material is also provided.

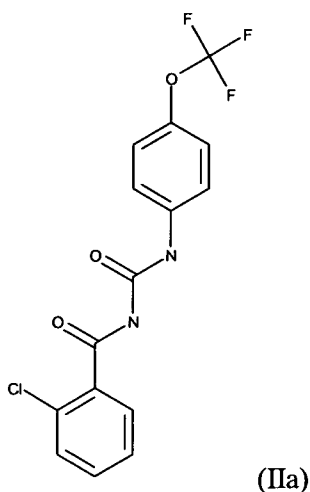
It is known that carbamates like thiodicarb of the formula (I)



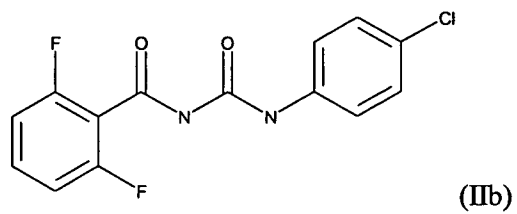
have insecticidal, acaricidal and nematocidal activity.

It is further known that certain benzoylureas like:

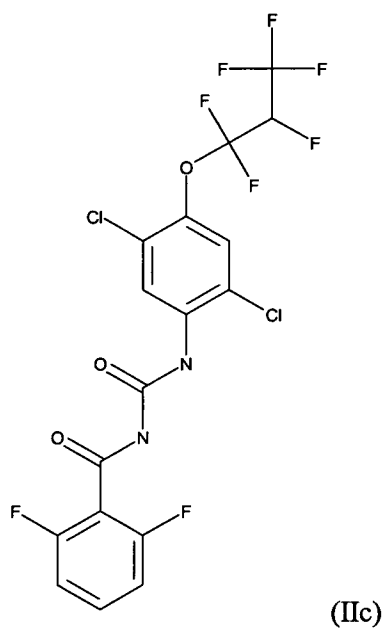
triflumuron of the formula (IIa)



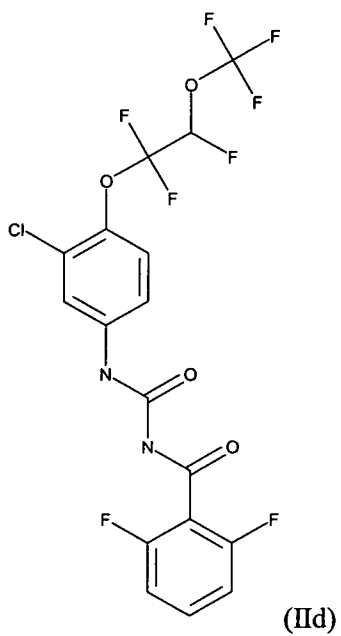
- 15 diflubenzuron of the formula (IIb)



lufenuron of the formula (IIc)



and novaluron of the formula (IId)



have insecticidal, and acaricidal activity.

The activity of the compounds of formula I and those of the formulae (IIa) to (IId) is in general good. However, especially at low application rates and on certain pests they do not always satisfy the needs of agricultural practice, and economically efficient and ecologically safe pest control is still being sought.

- 5 Further demands on insecticidal compounds include the reduction of the dosage rate; a substantial broadening of the spectrum of pests that can be controlled, including resistant pests and fungi; increased safety in use; reduced phytotoxicity and thus better tolerance by plants; the control of pests in their different development stages; better behavior during production of the insecticidal or/and fungicidal compounds, for example during grinding or mixing, during their storage or
10 during their use; a very advantageous biocidal spectrum, even at low rates of concentration, while being well tolerated by warm-blooded organisms, fish and plants; and achievement of an additional effect, e.g. an algicidal, anthelmintic, avicidal, bactericidal, molluscicidal, nematocidal, plant-activating, rodenticidal or virucidal action.

- Further specific demands on insecticidal and fungicidal compounds to be used on plant
15 propagation material include negligible phytotoxicity when applied to the plant propagation material, compatibility with soil conditions (e.g. concerning binding of the compound to the soil), systemic activity in the plant, no negative impact on germination, and efficacy during appropriate pest life cycle.

- The objectives of the invention are to meet one or more of the demands mentioned above, such as
20 the reduction of the dosage rate, a broadening of the spectrum of pests that can be controlled, including resistant pests and fungi, and in particular the specific demands for the applicability on plant propagation material.

Thiodicarb of formula (I) forms group (A).

- Whereas, triflumuron of the formula (IIa), diflubenzuron of the formula (IIb), lufenuron of the
25 formula (IIc), and novaluron of the formula (IIId) altogether form group (B)

The compounds of formulae (I) and (IIa) to (IIId) are described in compendia such as The Pesticide Manual, 14th edition, C. D. S. Thomlin (Ed.), British Crop Protection Council, Surrey, UK, 2006.

- Surprisingly it was found that combinations of active agents comprising thiodicarb and one or
30 more compounds selected from group (B) display synergistic activities.

The synergistic action of the combination of thiodicarb and a compound of group (B) according to the invention extends the range of action of the thiodicarb and of the compound (B) primarily by reducing the dosage rate and by broadening of the spectrum of pests that can be controlled. Thus, the combination of a thiodicarb and a compound of group (B) according to the invention still achieves a high degree of pest control even in cases where the individual compounds of the combination according to the invention do not show sufficient activity at the low application rates employed.

In addition to the synergistic effect described above, the combinations according to the invention may show further surprising advantages including increased safety in use; reduced phytotoxicity and thus better tolerance by plants; the control of pests in their different development stages; better behavior during production of the insecticidal or/and fungicidal compounds, for example during grinding or mixing, during their storage or during their use; a very advantageous biocidal spectrum, even at low rates of concentration, while being well tolerated by warm-blooded organisms, fish and plants; and achievement of an additional effect, e.g. an algicidal, anthelmintic, avicidal, bactericidal, molluscicidal, nematocidal, plant-activating, rodenticidal or virucidal action.

It was further surprisingly found that the combinations according to the invention are particularly suited for the protection of seed and/or shoots and foliage of a plant grown from the seed from damage by pests or fungi. Thus, the combinations according to the invention show negligible phytotoxicity when applied to the plant propagation material, compatibility with soil conditions (e.g. concerning binding of the compound to the soil), systemic activity in the plant, no negative impact on germination, and efficacy during appropriate pest life cycle.

Throughout this document the expression "combination" stands for the various combinations of components A) and B), for example in a single "ready-mix" form, in a combined spray mixture composed from separate formulations of the single active ingredient components, such as a "tank-mix".

Preferred time ranges of seed treatment applications are from X to Y hours/days/weeks.

The order of applying the components A) and B) is in general not essential for working the present invention.

The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young

plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

The combinations according to the invention can be applied for combating pests in agriculture,
5 forestry, in the protection of storage and materials, and in hygiene applications.

Preferred are combinations comprising thiodicarb and one compound of group (B).

Further preferred are combinations comprising thiodicarb and two compounds selected from group (B).

Embodiments of the present invention include:

10 Embodiment 1: A combination containing thiodicarb and a compound selected from group (B).

Embodiment 2: A combination containing thiodicarb and triflumuron.

Embodiment 3: A combination containing thiodicarb and diflubenzuron.

Embodiment 4: A combination containing thiodicarb and lufenuron.

Embodiment 5: A combination containing thiodicarb and novaluron.

15 Where a compound (A) or a compound (B) can be present in tautomeric form, such a compound is understood hereinabove and hereinbelow also to include, where applicable, corresponding tautomeric forms, even when these are not specifically mentioned in each case.

Compounds (A) or compounds (B) having at least one basic centre are capable of forming, for example, acid addition salts, e.g. with strong inorganic acids, such as mineral acids, e.g.
20 perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted substituted, e.g. halo-substituted, C1-C4 alkanecarboxylic acids, e.g. acetic acid, saturated or unsaturated dicarboxylic acids, e.g. oxalic, malonic, succinic, maleic, fumaric and phthalic acid, hydroxycarboxylic acids, e.g. ascorbic, lactic, malic, tartaric and citric acid, or benzoic acid, or with organic sulfonic acids, such as
25 unsubstituted or substituted, e.g. halo-substituted, C1-C4alkane- or aryl-sulfonic acids, e.g. methane- or p-toluene-sulfonic acid. Compounds (A) or compounds (B) having at least one acid group are capable of forming, for example, salts with bases, e.g. metal salts, such as alkali metal or alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower

- alkylamine, e.g. ethyl-, diethyl-, triethyl- or dimethyl-propyl-amine, or a mono-, di- or tri-hydroxy-lower alkylamine, e.g. mono-, di- or tri-ethanolamine. In addition, corresponding internal salts may optionally be formed. In the context of the invention, preference is given to agrochemically advantageous salts. In view of the close relationship between the compounds (A) or the
- 5 compounds (B) in free form and in the form of their salts, hereinabove and herein below any reference to the free compounds (A) or free compounds (B) or to their salts should be understood as including also the corresponding salts or the free compounds (A) or free compounds (B), respectively, where appropriate and expedient. The equivalent also applies to tautomers of compounds (A) or compounds (B) and to their salts.
- 10 The weight ratios of the active agents of the combination as well as the application rate depend on the kind and occurrence of the pests and fungi. Optimal weight ratios and application rates can be determined by test series for each use. In general, the weight ratio of component A) to component B) is between 1000:1 and 1:100, preferred between 625:1 and 1:100, more preferred between 125:1 and 1:50, and most preferred between 25:1 and 1:5.
- 15 The active ingredient combination according to the invention [in the preferred case, where only at least one compound (B) is included in the combination] comprises the compound (A) and the compound (B) preferably in a mixing ratio of from 100:1 to 1:6000, especially from 50:1 to 1:50, more especially in a ratio of from 20:1 to 1:20, even more especially from 10:1 to 1:10, very especially from 5:1 and 1:5, special preference being given to a ratio of from 2:1 to 1:2, and a ratio
- 20 of from 4:1 to 2:1 being likewise preferred, above all in a ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. Those mixing ratios are understood to include, on the one hand, ratios by weight and also, on other hand,
- 25 molar ratios.

According to the invention all plants and plant parts can be treated. By plants is meant all plants and plant populations such as desirable and undesirable wild plants or cultigens (including naturally occurring cultigens). Cultigens can be plants obtained by conventional propagation and optimisation methods or by bioengineering and genetic engineering methods or by combinations

30 of these methods, including transgenic plants and including plant varieties protectable or not protectable by plant varieties protective rights. By plant parts is meant all above ground and below ground parts and organs of plants such as shoot, leaf, blossom and root, whereby for example leaves, needles, stems, branches, blossoms, fruiting bodies, fruits and seed as well as

roots, corms and rhizomes are listed. Crops and vegetative and generative propagating material, for example cuttings, corms, rhizomes, runners and seeds also belong to plant parts.

The especially advantageous action of the agents of the invention are emphasised in respect of the application for cereals, for example, wheat, oats, barley, spelt, triticale, and rye, but also maize, 5 millet, rice, sugar cane, soy, sunflower, potatoes, cotton, rape, canola, tobacco, sugar beet, fodder beet, asparagus, hops as well as fruit plants (including rosaceous fruit, for example apples and pears, stone-fruits, for example peaches, nectarines, cherries, plums and apricots, citrus fruit, for example, oranges, grapefruit, limes, lemons, kumquats, mandarins and satsumas, nuts, for example pistachios, almonds, walnuts and pecan nuts, tropical fruits, for example, mango, papaya, 10 pineapple, dates and bananas, and grapes) and vegetables (including leaf vegetables, for example endives, lambs lettuce, fennel, globe and loose-leaf salad, chard, spinach and chicory, brassicas, for example, cauliflower, broccoli, Chinese cabbage, kale (winter kale or curly kale), kohlrabi, brussel sprouts, red cabbage, white cabbage and savoy, fruiting vegetables, for example, aubergines, cucumbers, paprika, marrow, tomatoes, courgettes and sweetcorn, root vegetables, for 15 example celeriac, turnip, carrots, swedes, radishes, horse radish, beetroot, salsify, celery, pulses, for example, peas and beans, and bulb vegetables, for example leeks and onions).

Preferred plants to work the invention on are:

Cotton, soybean, corn, potatoes, tomatoes, and leafy vegetables.

Particularly preferred plants to work the invention on are:

20 Cotton, soybean, corn, potatoe.

Very particularly preferred plants to work the invention on are:

Cotton, soybean, corn.

Non-limiting examples for pests are chewing insects, e.g. coleoptera and Lepidoptera as well as homoptera and dipteran seafminers.

25 The active compound combinations, having good plant compatibility and favourable homeotherm toxicity, are suitable for controlling animal pests, in particular insects, arachnids and nematodes, encountered in agriculture, in forests, in the protection of stored products and materials and in the hygiene sector. They are preferably used as crop protection compositions for foliar and soil treatment.

They are effective against normally sensitive and resistant species and against all or individual stages of development. The above mentioned pests include:

From the order of the Isopoda, for example, *Oniscus asellus*, *Armadillidium vulgare*, *Porcellio scaber*. From the order of the Diplopoda, for example, *Blaniulus guttulatus*. From the order of the
 5 Chilopoda, for example, *Geophilus carpophagus*, *Scutigera* spp. From the order of the Symphyla, for example, *Scutigera* spp. From the order of the Thysanura, for example, *Lepisma saccharina*. From the order of the Collembola, for example, *Onychiurus armatus*. From the order of the Orthoptera, for example, *Acheta domesticus*, *Gryllotalpa* spp., *Locusta migratoria migratorioides*, *Melanoplus* spp., *Schistocerca gregaria*. From the order of the Blattaria, for
 10 example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*. From the order of the Dermaptera, for example, *Forficula auricularia*. From the order of the Isoptera, for example, *Reticulitermes* spp. From the order of the Phthiraptera, for example, *Pediculus humanus corporis*, *Haematopinus* spp., *Linognathus* spp., *Trichodectes* spp., *Damalinia* spp. From the order of the Thysanoptera, for example, *Hercinothrips femoralis*, *Thrips tabaci*, *Thrips palmi*,
 15 *Frankliniella occidentalis*. From the order of the Heteroptera, for example, *Eurygaster* spp., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus*, *Triatoma* spp. From the order of the Homoptera, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Aphis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Phylloxera vastatrix*, *Pemphigus* spp., *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*,
 20 *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp., *Psylla* spp. From the order of the Lepidoptera, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella xylostella*,
 25 *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spp., *Euxoa* spp., *Feltia* spp., *Earias insulana*, *Heliothis* spp., *Mamestra brassicae*, *Panolis flammea*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Tineola bisselliella*, *Tinea pellionella*, *Hofmannophila pseudospretella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura*
 30 *fumiferana*, *Clysia ambiguella*, *Homona magnanima*, *Tortrix viridana*, *Cnaphalocerus* spp., *Oulema oryzae*. From the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anthonomus* spp., *Sitophilus*
 35 spp., *Otiorrhynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lyctus* spp., *Meligethes aeneus*,

- Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis, Costelytra zealandica, Lissorhoptrus oryzophilus. From the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis, Vespa spp. From the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphora erythrocephala, Lucilia spp., Chrysomya spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae, Tipula paludosa, Hylemyia spp., Liriomyza spp. From the order of the Siphonaptera, for example, Xenopsylla cheopis, Ceratophyllus spp. From the order of the Arachnida, for example, Scorpio maurus, Latrodectus mactans, Acarus siro, Argas spp., Ornithodoros spp., Dermanyssus gallinae, Eriophyes ribis, Phyllocoptruta oleivora, Boophilus spp., Rhipicephalus spp., Amblyomma spp., Hyalomma spp., Ixodes spp., Psoroptes spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp., Tetranychus spp., Hemitarsonemus spp., Brevipalpus spp.
- 15 The plant-parasitic nematodes include, for example, Pratylenchus spp., Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Globodera spp., Meloidogyne spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp., Trichodorus spp., Bursaphelenchus spp.

Preferred pests to work the invention on are:

- 20 Spodoptera spp, Heliothis spp, Helicoverpa spp, Trichoplusia ni, Pseudoplusia includens, Rachiplusia spp, Anticarsia gemmatilis, Premnotypes vorax and Earias spp.

Particularly preferred pests to work the invention on are:

Spodoptera spp, Heliothis spp, Anticarsia gemmatilis, Premnotypes vorax

Very particular preferred pests to work the invention on are:

- 25 Spodoptera spp, Heliothis spp, Anticarsia gemmatilis

Most preferred pests are:

Spodoptera frugiperda, Spodoptera littoralis, Heliothis armigera, Anticarsia gemmatilis

The treatment of plants and plant parts with the active compound combination is according to the invention carried out directly or by action on their environment, habitat or storage area by means

of the normal treatment methods, e.g., by dipping, spraying, evaporation, misting, scattering, coating, and with propagation material, especially seeds, also by single or multiple coating.

The combinations of the invention are particularly suitable for the treatment of seeds. A large part of the damage caused by pests and pathogens on cultigens occurs by infestation of the seed during storage and after sowing the seed in the ground as well as during and immediately after germination of the plants. This phase is especially critical since the roots and shoots of the growing plant are particularly sensitive and even a small amount of damage can lead to withering of the whole plant. There is therefore considerable interest in protecting the seed and the germinating plant by the use of suitable agents.

The control of pests and pathogens by treatment of the seeds of plants has been known for a considerable time and is the object of continuous improvement. However, there are a number of problems in the treatment of seed that cannot always be satisfactorily solved. Therefore it is worthwhile to develop methods for the protection of seeds and germinating plants which makes the additional application of plant protection agents after seeding or after germination of the plants superfluous. It is further worthwhile to optimize the amount of the applied active material such that the seed and the germinating plants are protected against infestation by pests as best as possible without the plants themselves being damaged by the active compound applied. In particular, methods for the treatment seed should also take into account the intrinsic insecticidal and fungicidal properties of transgenic plants in order to achieve optimal protection of the seed and germinating plants with a minimal expenditure of plant protection agents.

The present invention relates therefore especially to a method for the protection of seed and germinating plants from infestation with pests and pathogens in that the seed is treated with a combination of the invention.

The invention comprises a procedure in which the seed the treated at the same time with a compound of Group A and a compound selected from group B. It further comprises a method in which the seed is treated with compound of Group A and a compound selected from group B separately.

The invention also comprises a seed, which has been treated with a compound of Group A and a compound selected from group B at the same time. The invention also comprises a seed, which has been treated with a compound of Group A and a compound selected from group B separately. For the latter seed, the active ingredients can be applied in separate layers. These layers can optionally be separated by an additional layer that may or may not contain an active ingredient.

In addition the invention relates also to the use of the combination of the invention for the treatment seed for protection of the seed and the germinating plants from pests. Furthermore the invention relates to seed which was treated with an agent of the invention for protection from pests.

- 5 One of the advantages of the invention is because of the special systemic properties of the agents of the invention treatment with these agents protects not only the seed itself from pests but also the plants emerging after sprouting. In this way the direct treatment of the culture at the time of sowing or shortly thereafter can be omitted.

- 10 A further advantage is the synergistic increase in insecticidal and/or fungicidal activity of the agents of the invention in comparison to the respective individual active compounds, which extends beyond the sum of the activity of both individually applied active compounds. In this way an optimization of the amount of active compound applied is made possible.

- 15 It is also be regarded as advantageous that the combinations of the invention can also be used in particular with transgenic seeds whereby the plants emerging from this seed are capable of the expression of a protein directed against pests and pathogens. By treatment of such seed with the agents of the invention certain pests and pathogens can already be controlled by expression of the, for example, insecticidal protein, and it is additionally surprising that a synergistic activity supplementation occurs with the agents of the invention, which improves still further the effectiveness of the protection from pest and pathogen infestation.

- 20 The agents of the invention are suitable for the protection of seed of plant varieties of all types as already described which are used in agriculture, in greenhouses, in forestry, in garden construction or in vineyards. In particular, this concerns seed of maize, peanut, canola, rape, poppy, olive, coconut, cacao, soy cotton, beet, (e.g. sugar beet and feed beet), rice, millet, wheat, barley, oats, rye, sunflower, sugar cane or tobacco. The agents of the invention are also suitable for the treatment of the seed of fruit plants and vegetables as previously described. Particular importance is attached to the treatment of the seed of maize, soy, cotton, wheat and canola or rape. Thus, for example, the combinations of the invention including the active compounds thiodicarb and triflumuron are particularly suitable for the treatment of maize seed.

- 30 As already described, the treatment of transgenic seed with an agent of the invention is of particular importance. This concerns the seeds of plants which generally contain at least one heterologous gene that controls the expression of a polypeptide with special insecticidal properties. The heterologous gene in transgenic seed can originate from microorganisms such as *Bacillus*, *Rhizobium*, *Pseudomonas*, *Serratia*, *Trichoderma*, *Clavibacter*, *Glomus* or *Gliocladium*. The

present invention is particularly suitable for the treatment of transgenic seed that contains at least one heterologous gene that originates from *Bacillus* sp. and whose gene product exhibits activity against the European corn borer and/or western corn rootworm. Particularly preferred is a heterologous gene that originates from *Bacillus thuringiensis*.

- 5 Within the context of the present invention the agent of the invention is applied to the seed alone or in a suitable formulation. Preferably the seed is handled in a state in which it is so stable, that no damage occurs during treatment. In general treatment of the seed can be carried out at any time between harvest and sowing. Normally seed is used that was separated from the plant and has been freed of spadix, husks, stalks, pods, wool or fruit flesh. Use of seed that was harvested, purified,
10 and dried to moisture content of below 15 % w/w. Alternatively, seed treated with water after drying and then dried again can also be used.

- In general care must be taken during the treatment of the seed that the amount of the agent of the invention and/or further additive applied to the seed is so chosen that the germination of the seed is not impaired and the emerging plant is not damaged. This is to be noted above all with active
15 compounds which can show phytotoxic effects when applied in certain amounts.

- The agents of the invention can be applied directly, that is without containing additional components and without being diluted. It is normally preferred to apply the agent to the seed in the form of a suitable formulation. Suitable formulations and methods for seed treatment are known to the person skilled in the art and are described, for example, in the following documents: US
20 4,272,417 A, US 4,245,432 A, US 4,808,430 A, US 5,876,739 A, US 2003/0176428 A1, WO 2002/080675 A1, WO 2002/028186 A2.

Compositions, which are especially useful for seed treatment, are e.g.:

- A Soluble concentrates (SL, LS)
- D Emulsions (EW, EO, ES)
- 25 E Suspensions (SC, OD, FS)
- F Water-dispersible granules and water-soluble granules (WG, SG)
- G Water-dispersible powders and water-soluble powders (WP, SP, WS)
- H Gel-Formulations (GF)
- I Dustable powders (DP, DS)

Conventional seed treatment formulations include for example flowable concentrates FS, solutions LS, powders for dry treatment DS, water dispersible powders for slurry treatment WS, water-soluble powders SS and emulsion ES and EC and gel formulation GF. These formulations can be applied to the seed diluted or undiluted. Application to the seeds is carried out before sowing,
5 either directly on the seeds or after having pregerminated the latter. Preferred are FS formulations.

In the treatment of seed, the application rates of the inventive combination are generally from 0.1 to 10 kg per 100 kg of seed. The separate or joint application of the compounds I and II or of the combinations of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence
10 of the plants.

The invention also relates to the propagation products of plants, and especially the seed comprising, that is, coated with and/or containing, a combination as defined above or a composition containing the combination of two or more active ingredients or a combination of two or more compositions each providing one of the active ingredients. The seed comprises the
15 inventive combinations in an amount of from 0.1 g to 10 kg per 100 kg of seed.

The composition comprising a combination of pesticides 45 can be applied "neat", that is, without any diluting or additional components present. However, the composition is typically applied to the seeds in the form of a pesticide formulation. This formulation may contain one or more other desirable components including but not limited to 50 liquid diluents, binders to serve as a matrix for the pesticide, fillers for protecting the seeds during stress conditions, and plasticizers to improve flexibility, adhesion and/or spreadability of the coating. In addition, for oily pesticide formulations containing little or no filler, it may be desirable to add 55 to the formulation drying agents such as calcium carbonate, kaolin or bentonite clay, perlite, diatomaceous earth or any other adsorbent material. Use of such components in seed treatments is known in the art. See, e.g.,
20 U.S. Pat. No. 5,876,739. The skilled artisan can readily select desirable 60 components to use in the pesticide formulation depending on the seed type to be treated and the particular pesticide that is selected. In addition, readily available commercial formulations of known pesticides may be used, as demonstrated in the examples below.

The seeds may also be treated with one or more of the following ingredients: other pesticides,
30 including compounds which act only below the ground; fungicides, such as captan, thiram, metalxyl, fludioxonil, oxadixyl, and isomers of each of those materials, and the like; herbicides, including compounds selected from carbamates, thiocarbamates, acetamides, triazines, dinitroanilines, glycerol ethers, pyridazinones, uracils, phenoxy, ureas, and benzoic acids; herbicidal safeners such as benzoxazine, benzhydryl derivatives, N,N-diallyl dichloroacetamide,

various dihaloacyl, oxazolidinyl and thiazolidinyl compounds, ethanone, naphthalic anhydride compounds, and oxime derivatives; fertilizers; and biocontrol agents such as naturally-occurring or recombinant bacteria and fungi from the genera *Rhizobium*, *Bacillus*, *Pseudomonas*, *Serratia*, *Trichoderma*, *Glomus*, *Gliocladium* and mycorrhizal fungi. These ingredients may be added as a
5 separate layer on the seed or alternatively may be added as part of the pesticide composition.

Preferably, the amount of the novel composition or other ingredients used in the seed treatment should not inhibit generation of the seed, or cause phytotoxic damage to the seed.

The composition of the present invention can be in the form of a suspension; emulsion; slurry of particles in an aqueous medium (e.g., water); wettable powder; wettable granules (dry flowable);
10 and dry granules. If formulated as a suspension or slurry, the concentration of the active ingredient in the formulation is preferably about 0.5% to about 99% by weight (w/w), preferably 5-40%.

As mentioned above, other conventional inactive or inert ingredients can be incorporated into the formulation. Such inert ingredients include but are not limited to: conventional sticking agents, dispersing agents such as mefhylcellulose (Methocel A15LV or Methocel A15C, for example,
15 serve as combined dispersant/sticking agents for use in seed treatments), polyvinyl alcohol (e.g., Elvanol 51-05), lecithin (e.g., Yelkinol P), polymeric dispersants (e.g., polyvinylpyrrolidone/vinyl acetate PVP/VA S-630), thickeners (e.g., clay thickeners such as Van Gel B to improve viscosity and reduce settling of particle suspensions), emulsion stabilizers, surfactants, antifreeze compounds (e.g., urea), dyes, colorants, and the like. Further inert ingredients useful in the present
20 invention can be found in McCutcheon's, vol. 1, "Emulsifiers and Detergents" MC Publishing Company, Glen Rock, N.J., U.S.A., 1996. Additional inert ingredients useful in the present invention can be found in McCutcheon's, vol.2, "FunctionalMaterials," MC Publishing Company, Glen Rock, N.J., U.S.A., 1996.

The pesticides, compositions of pesticide combinations, and formulations of the present invention
25 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. Any conventional active or inert material can be used for contacting seeds with pesticides according to the present invention, such as conventional film-coating materials including but not limited to water-based film coating materials such as Sepiret (Seppic, Inc.,
30 Fairfield, N.J.) and Opacoat (Berwind Pharm. Services, Westpoint, Pa.).

Seed coating: The subject combination of pesticides can be applied to a seed as a component of a seed coating. Seed coating methods and compositions that are known in the art are useful when they are modified by the addition of one of the embodiments of the combination of pesticides of

the present invention. Such coating methods and apparatus for their application are disclosed in, for example, U.S. Pat. Nos. 5,918,413, 5,891,246, 5,554,445, 5,389,399, 5,107,787, 5,080,925, 4,759,945 and 4,465,017. Seed coating compositions are disclosed, for example, in U.S. Pat. Nos. 5,939,356, 5,882,713, 5,876,739, 5,849,320, 5,834,447, 5,791,084, 5,661,103, 5,622,003, 5,580,544, 5,328,942, 5,300,127, 4,735,015, 4,634,587, 4,383,391, 4,372,080, 4,339,456, 4,272,417 and 4,245,432, among others. Useful seed coatings contain one or more binders and at least one of the subject combinations of pesticides.

Useful seed coatings contain one or more binders and at least one of the subject combinations of pesticides.

- 10 Binders that are useful in the present invention preferably comprise 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 polyvinyl acetates; polyvinyl acetate copolymers; polyvinyl alcohols; polyvinyl alcohol copolymers; celluloses, including ethylcelluloses, methylcelluloses, hydroxymethylcelluloses, hydroxypropyl-celluloses and carboxymethylcellulose; polyvinylpyrrolidones; polysaccharides, including starch, modified starch, dextrans, maltodextrins, alginate and chitosans; fats; oils; proteins, including gelatin and zeins; gum arabics; shellacs; vinylidene chloride and vinylidene chloride copolymers; calcium lignosulfonates; acrylic copolymers; polyvinylacrylates; polyethylene oxide; acrylamide polymers and copolymers; polyhydroxyethyl acrylate, methylacrylamide monomers; and polychloroprene.
- 15
- 20 It is preferred that the binder be selected so that it can serve as a matrix for the subject combination of pesticides. While the binders disclosed above may all be useful as a matrix, the specific binder will depend upon the properties of the combination of pesticides. The term "matrix", as used herein, means a continuous solid phase of one or more binder compounds throughout which is distributed as a discontinuous phase one or more of the subject combinations
- 25 of pesticides. Optionally, a filler and/or other components can also be present in the matrix. The term matrix is to be understood to include what may be viewed as a matrix system, a reservoir system or a microencapsulated system. In general, a matrix system consists of a combination of pesticides of the present invention and filler uniformly dispersed within a polymer, while a reservoir system consists of a separate phase comprising the subject combination of pesticides,
- 30 that is physically dispersed within a surrounding, rate-limiting, polymeric phase. Microencapsulation includes the coating of small particles or droplets of liquid, but also to dispersions in a solid matrix.

The amount of binder in the coating can vary, but will be in the range of about 0.01 to about 25% of the weight of the seed, more preferably from about 0.05 to about 15%, and even more preferably from about 0.1% to about 10%.

As mentioned above, the matrix can optionally include a filler. The filler can be an absorbent or an inert filler, such as are known in the art, and may include woodflours, clays, activated carbon, sugars, diatomaceous earth, cereal flours, fine-grain inorganic solids, calcium carbonate, and the like. Clays and inorganic solids which may be used include calcium bentonite, kaolin, china clay, talc, perlite, mica, vermiculite, silicas, quartz powder, montmorillonite and mixtures thereof. Sugars which may be useful include dextrin and maltodextrin. Cereal flours include wheat flour, oat flour and barley flour.

The filler is selected so that it will provide a proper microclimate for the seed, for example the filler is used to increase the loading rate of the active ingredients and to adjust the control-release of the active ingredients. The filler can aid in the production or process of coating the seed. The amount of filler can vary, but generally the weight of the filler components will be in the range of about 0.05 to about 75% of the seed weight, more preferably about 0.1 to about 50%, and even more preferably about 0.5% to 15%.

The pesticides that are useful in the coating are those combinations of pesticides that are described herein. The amount of pesticide that is included in the coating will vary depending upon the type of seed and the type of active ingredients, but the coating will contain an amount of the combination of pesticides that is pesticidally effective. When insects are the target pest, that amount will be an amount of the combination of insecticides that is insecticidally effective. As used herein, an insecticidally effective amount means that amount of insecticide that will kill insect pests in the larvae or pupal state of growth, or will consistently reduce or retard the amount of damage produced by insect pests. In general, the amount of pesticide in the coating will range from about 0.005 to about 50% of the weight of the seed. A more preferred range for the pesticide is from about 0.01 to about 40%; more preferred is from about 0.05 to about 20%.

The exact amount of the combination of pesticides that is included in the coating is easily determined by one of skill in the art and will vary depending upon the size of the seed to be coated. The pesticides of the coating must not inhibit germination of the seed and should be efficacious in protecting the seed and/or the plant during that time in the target insect's life cycle in which it causes injury to the seed or plant. In general, the coating will be efficacious for approximately 0 to 120 days after sowing.

The coating is particularly effective in accommodating high pesticidal loads, as can be required to treat typically refractory pests, such as corn root worm, while at the same time preventing unacceptable phytotoxicity due to the increased pesticidal load.

Optionally, a plasticizer can 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 plasticizers may be used. However, useful plasticizers include polyethylene glycol, glycerol, butylbenzylphthalate, glycol benzoates and related compounds. The range of plasticizer in the coating layer will be in the range of from about 0.1 to about 20% by weight.

When the combination of pesticides used in the coating is an oily type formulation and little or no filler is present, it may be useful to hasten the drying process by drying the formulation. This optional step may be accomplished by means well known in the art and can include the addition of calcium carbonate, kaolin or bentonite clay, perlite, diatomaceous earth, or any absorbent material that is added preferably concurrently with the pesticidal coating layer to absorb the oil or excess moisture. The amount of calcium carbonate or related compounds necessary to effectively provide a dry coating will be in the range of about 0.5 to about 10% of the weight of the seed.

The coatings formed with the combination of pesticides are capable of effecting a slow rate of release of the pesticide by diffusion or movement through the matrix to the surrounding medium.

The coating can be applied to almost any crop seed that is described herein, including cereals, vegetables, ornamentals and fruits.

In addition to the coating layer, the seed may be treated with one or more of the following ingredients: other pesticides including fungicides and herbicides; herbicidal safeners; fertilizers and/or biocontrol agents. These ingredients may be added as a separate layer or alternatively may be added in the pesticidal coating layer.

The pesticide formulation 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 spouted beds may also be useful. The seeds may be presized before coating. After coating, the seeds are typically dried and then transferred to a sizing machine for sizing. Such procedures are known in the art.

The pesticide-treated seeds may also be enveloped with a film overcoating to protect the pesticide coating. Such overcoatings are known in the art and may be applied using conventional fluidized bed and drum film coating techniques.

In another embodiment of the present invention, a pesticide can be introduced onto or into a seed
5 by use of solid matrix priming. For example, a quantity of the pesticide can be mixed with a solid matrix material and then the seed can be placed into contact with the solid matrix material for a period to allow the pesticide to be introduced to the seed. The seed can then optionally be separated from the solid matrix material and stored or used, or the mixture of solid matrix material plus seed can be stored or planted directly. Solid matrix materials which are useful in the
10 present invention include polyacrylamide, starch, clay, silica, alumina, soil, sand, polyurea, polyacrylate, or any other material capable of absorbing or adsorbing the pesticide for a time and releasing that pesticide into or onto the seed. It is useful to make sure that the pesticide and the solid matrix material are compatible with each other. For example, the solid matrix material should be chosen so that it can release the pesticide at a reasonable rate, for example over a
15 period of minutes, hours, or days.

The present invention further embodies inhibition as another method of treating seed with the pesticide. For example, plant seed can be combined for a period of time with a solution comprising from about 1% by weight to about 75% by weight of the pesticide in a solvent such as water. Preferably the concentration of the solution is from about 5% by weight to about 50% by
20 weight, more preferably from about 10% by weight to about 25% by weight. During the period that the seed is combined with the solution, the seed takes up (imbibes) a portion of the pesticide. Optionally, the mixture of plant seed and solution can be agitated, for example by shaking, rolling, tumbling, or other means. After inhibition, the seed can be separated from the solution and optionally dried, for example by patting or air drying.

In yet another embodiment, a powdered pesticide can be mixed directly with seed. Optionally, a sticking agent can be used to adhere the powder to the seed surface. For example, a quantity of seed can be mixed with a sticking agent and optionally agitated to encourage uniform coating of the seed with the sticking agent. The seed coated with the sticking agent can then be mixed with the powdered pesticide. The mixture can be agitated, for example by tumbling, to encourage
30 contact of the sticking agent with the powdered pesticide, thereby causing the powdered pesticide to stick to the seed.

The present invention also provides a seed that has been treated by the method described above. The treated seeds of the present invention can be used for the propagation of plants in the same manner as conventional treated seed. The treated seeds can be stored, handled, sowed and tilled in

the same manner as any other pesticide treated seed. Appropriate safety measures should be taken to limit contact of the treated seed with humans, food or feed materials, water and birds and wild or domestic animals.

Colby Formula

- 5 The good insecticidal action of the active compound combinations according to the invention can be seen from the examples which follow. While the individual active compounds exhibit weaknesses with regard to the action, the combinations demonstrate an action which exceeds the simple summation of action.

Formula for the calculation of the kill rate of a combination of two active compounds

- 10 The expected activity for a given combination of two active compounds can be calculated (cf. COLBY, S.R.; "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", Weeds 15, pages 20-22, 1967):

if

15 X = the kill rate, expressed in % of the untreated control, when employing active compound A at an application rate of m ppm, or a concentration of m g/ha

Y = the kill rate, expressed in % of the untreated control, when employing active compound B at an application rate of n ppm, or a concentration of n g/ha

20 E = the kill rate, expressed in % of the untreated control, when employing active compounds A and B at application rates of m and n ppm, or concentrations of m and n g/ha

then
$$E = X + Y - \frac{X \times Y}{100}$$

- 25 If the actual insecticidal kill rate is higher than the calculated one, the kill rates of the combination are superadditive, i.e. a synergistic effect is present. In this case, the kill rate that is actually observed has to be higher than the value, calculated using the formula above, for the expected kill rate (E).

Example A**Plutella xylostella -Test**

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycoether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- Cabbage leaves (*Brassica oleracea*) are treated by being sprayed with the preparation of the active compound in the desired concentration and are infested with larvae of the diamond back moth
10 (*Plutella xylostella*) as long as the leaves are still moist.

After the specified period of time, the mortality in % is determined. 100 % means that all the caterpillars have been killed; 0 % means that none of the caterpillars have been killed.

According to the present application in this test e.g. the following combination shows a synergistic effect in comparison to the single compounds:

- 15 Table A, Page 1

Plant damaging insects

Plutella xylostella - Test

<u>Active Ingredient</u>	<u>Concentration</u> <u>in ppm</u>	<u>Mortality</u> <u>in % after 6 days</u>
Triflumuron	0,8	0
Thiodicarb	4	0
Triflumuron + Thiodicarb (1 : 5) according to the invention	0,8 + 4	obs.* cal.** 65 0

* obs. = observed insecticidal efficacy

** cal. = efficacy calculated with Colby-formula

Example B**Spodoptera frugiperda - Test**

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycoether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) are treated by being sprayed with the preparation of the active compound in the desired concentration and are infested with larvae of the fall army worm

- 10 (*Spodoptera frugiperda*) as long as the leaves are still moist.

After the specified period of time, the mortality in % is determined. 100 % means that all the caterpillars have been killed; 0 % means that none of the caterpillars have been killed.

According to the present application in this test e.g. the following combination shows a synergistic effect in comparison to the single compounds:

- 15 Table B, Page 1

Plant damaging insects

Spodoptera frugiperda - Test

<u>Active Ingredient</u>	<u>Concentration</u> <u>in ppm</u>	<u>Mortality</u> <u>in % after 6 days</u>
Triflumuron	0,032	15
Thiodicarb	0,16	50
Triflumuron + Thiodicarb (1 : 5) according to the invention	0,032 + 0,16	obs.* cal.** 100 57,5

* obs. = observed insecticidal efficacy

** cal. = efficacy calculated with Colby-formula

Patent claims:

1. Combination of active agents comprising thiodicarb one or more compound selected from group (B), which contains triflumuron, diflubenzuron, lufenuron, and novaluron.
5
2. Combination according to claim 1, wherein the group (B) consists of triflumuron.
3. Combination according to claim 1, wherein the group (B) consists of diflubenzuron.
- 10 4. Combination according to claim 1, wherein the group (B) consists of lufenuron.
5. Combination according to claim 1, wherein the group (B) consists of novaluron.
- 15 6. Combination according to any of claims 1-5, wherein the weight ratio of thiodicarb to the component selected from group (B) is between 1000:1 and 1:100, more preferably between 125:1 and 1:50.
7. Use of a combination according to any of claims 1 to 6 for the treatment of seed.
- 20 8. Use according to claim 7 for the treatment of transgenic seed.
9. Method for protecting a seed and/or shoots and foliage of a plant grown from the seed from damage by a pest or a fungus, the method comprising treating an unsown seed with a combination according to any of claims 1 to 6.

10. Method according to claim 9, wherein the seed is treated with thiodicarb at the same time that it is treated with component(s) selected from group (B).
11. Method according to claim 9, wherein the seed is treated with component A) at a different
5 time than it is treated with the component(s) selected from group (B).
12. A seed that has been treated with a combination according to any of claims 1 to 6.
13. A seed according to claim 12, wherein the seed is selected from the group consisting of corn,
10 soybean, cotton, rice, sorghum, sugar beet, wheat, barley, rye, sunflower, tomato, sugarcane, tobacco, rape and oats.
14. A seed according to claim 12, wherein the seed is a transgenic seed.
- 15 15. A seed according to any of claims 12 to 14, wherein the seed has been treated with component A) at the same time that it has been treated with component(s) B).
16. A seed according to any of claims 12 to 14, wherein the seed has been treated with component A) at a different time than it has been treated with component(s) B).
- 20
17. Method according to claim 9, wherein the plant is treated with thiodicarb at the same time that it is treated with component(s) selected from group (B).
18. Method according to claim 9, wherein the plant is treated with component A) at a different
25 time than it is treated with the component(s) selected from group (B).

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/006118

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N47/24

ADD. A01N47/34

A01P5/00

A01P7/04

A01P7/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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

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

EPO-Internal, CHEM ABS Data, WPI Data, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 33 38 669 A1 (CELAMERCK GMBH & CO KG [DE]) 6 December 1984 (1984-12-06) the whole document	
A	WO 2005/058039 A (BAYER CROPSCIENCE AG [DE]; ANDERSCH WOLFRAM [DE]; HUNGENBERG HEIKE [DE]) 30 June 2005 (2005-06-30) the whole document	
A	WO 95/33380 A (CIBA GEIGY AG [CH]; SKILLMAN STEPHEN WILSON [CH]; BUHOLZER FRANZ [CH]) 14 December 1995 (1995-12-14) the whole document	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

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

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

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

& document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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