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Description

TECHNICAL FIELD

[0001] The present invention relates to a co-crystal consisting of a diamide-based insecticidal-active ingredient, selected from cyantraniliprole, chlorantraniliprole and cyclaniliprole, and a neonicotinoid-based insecticidal-active ingredient, acetamiprid, a method for producing the same, and an agrochemical composition containing the same.

[0002] The present invention claims priority on the basis of Japanese Patent Application No. 2013-235073 filed in Japan on November 13, 2013.

BACKGROUND OF THE INVENTION

[0003] Active compounds contained in agrochemicals such as insecticides, acaricides, fungicides, or herbicides, or in agents for controlling wood-destroying organisms such as termites are required to appropriately control elution thereof in order to maintain effects thereof or to reduce phytotoxicity in plants or toxicity in humans and animals.

[0004] There have been attempts to formulate active compounds having low water solubility so as to increase elution thereof. In contrast, there have been attempts to formulate active compounds having high water solubility so as to reduce the elution rate thereof.

[0005] Neonicotinoid-based compounds belong to a compound group which exhibits an insecticidal effect as a nicotinic acetylcholine receptor agonist or antagonist. Many compounds included therein have high water solubility. Therefore, reducing the phytotoxicity caused by application at a high concentration and maintaining effects over a long period of time by reducing the elution rate or the hoarding amount have been considered. As a method for adjusting the elution rate, a compound in which the neonicotinoid-based compound is included in a multimolecular host compound has been proposed (Patent Document 2). In addition, there is a case in which a change in elution properties is caused by formation of a co-crystal. For example, Patent Document 1 discloses a co-crystal composed of imidacloprid, which is an insecticide, and oxalic acid.

DOCUMENTS OF RELATED ART

Patent Documents

[0006]

Patent Document 1: WO 2010/118833
Patent Document 2: WO 2006/006596

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007] An object of the present invention is to provide an insecticidal composition or the like which exhibits excellent insecticidal effects over a long period of time by adequately controlling the water solubility of an insecticidal-active compound, and in which there is no concern of phytotoxicity on useful plants.

MEANS TO SOLVE THE PROBLEMS

[0008] The present inventors have conducted extensive studies in order to solve the above-described problems, and as a result, they have found that a neonicotinoid-based insecticidal-active ingredient, acetamiprid, and a diamide-based insecticidal-active ingredient, selected from cyantraniliprole, chlorantraniliprole and cyclaniliprole, form a co-crystal, and the use of the co-crystal is effective for reducing elution of the neonicotinoid-based insecticidal ingredient having high water solubility, as a result of which the present invention has been completed.

[0009] The present invention relates to the following.

(1) A co-crystal consisting of a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, wherein
the diamide-based insecticidal-active ingredient is cyantraniliprole, chlorantraniliprole, or cyclaniliprole, and
the neonicotinoid-based insecticidal-active ingredient is acetamiprid.

(2) The co-crystal according to (1), wherein the molar ratio of the diamide-based insecticidal-active ingredient to the

neonicotinoid-based insecticidal-active ingredient is 0.3 to 3.

(3) A method for producing the co-crystal of any one of (1 or (2), including: suspending the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient in a solvent to obtain a suspension, and heating and stirring the suspension.

(4) The method for producing the co-crystal according to (3), wherein the heating temperature is higher than or equal to 40°C but lower than or equal to the boiling point of the solvent.

(5) The method for producing the co-crystal according to (4), wherein the heating temperature is higher than or equal to 60°C but lower than or equal to the boiling point of the solvent.

(6) The method for producing the co-crystal according to any one of (3) to (5), wherein the solvent is water.

(7) An agrochemical composition containing the co-crystal of any one of (1) to (2).

(8) The agrochemical composition according to (7), wherein the agrochemical composition is an insecticide.

(9) A seed treatment agent containing the co-crystal of any one of (1) to (2).

(10) The seed treatment agent according to (9), wherein the seed treatment agent is an aquatic suspended concentrate composition.

(11) A method for treating a seed, including: coating a seed with the agrochemical composition containing the co-crystal of any one of (1) to (2).

EFFECTS OF THE INVENTION

[0010] The water solubility of the neonicotinoid-based insecticidal-active ingredient in the co-crystal according to the present invention is lower than the water solubility of the neonicotinoid-based insecticidal-active ingredient itself. An agrochemical composition such as an insecticidal composition containing the co-crystal according to the present invention realizes elution of a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient into water at an adequate rate, and thereby excellent insecticidal effects are maintained over a long period of time and there is no concern of phytotoxicity on useful plants.

BRIEF DESCRIPTION OF DRAWINGS

[0011]

FIG. 1 is a view showing a result obtained by conducting differential scanning calorimetry (DSC measurement) of a co-crystal consisting of acetamiprid and cyantraniliprole.

FIG. 2 is a view showing a result obtained by conducting DSC measurement of a mixture composed of acetamiprid and cyantraniliprole.

FIG. 3 is a view showing X-ray diffraction of the co-crystal consisting of acetamiprid and cyantraniliprole.

FIG. 4 is a view showing X-ray diffraction of acetamiprid.

FIG. 5 is a view showing X-ray diffraction of cyantraniliprole.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0012] A co-crystal according to the present invention consists of a diamide-based insecticidal-active ingredient, acetamiprid, and a neonicotinoid-based insecticidal-active ingredient, selected from cyantraniliprole, chlorantraniliprole and cyclaniliprole.

[0013] Among the diamide-based insecticidal-active ingredients cyantraniliprole is more preferable.

[0014] It is considered that the co-crystal according to the present invention is formed by stabilizing a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient through molecular interaction, such as hydrogen bonding, π-orbital stacking, or van der Waals force.

[0015] In the co-crystal according to the present invention, the molar ratio of the diamide-based insecticidal-active ingredient to the neonicotinoid-based insecticidal-active ingredient (the diamide-based insecticidal-active ingredient / the neonicotinoid-based insecticidal-active ingredient) is preferably within a range of 0.3 to 3.0, more preferably 0.5 to 2.0, still more preferably 0.8 to 1.25, and particularly preferably 0.9 to 1.1.

[0016] The formation of the co-crystal according to the present invention can be confirmed through thermal analysis (TG/DTA), differential scanning calorimetry (DSC), infrared absorption spectrum (IR), X-ray diffraction pattern, ^{13}C-CP/MAS-solid NMR spectrum, or the like. In addition, the components of the co-crystal can be confirmed through thermal analysis, differential scanning calorimetry (DSC), ^{1}H-NMR spectrum, ^{13}C-NMR spectrum, ^{29}Si-NMR spectrum, gel filtration chromatography (GPC), high performance liquid chromatography (HPLC), elemental analysis, or the like.

[0017] Examples of the method for producing the co-crystal according to the present invention include:

(i) a method including: mixing a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, and an auxiliary ingredient as necessary; and subjecting the mixture to a mechanochemical solid phase reaction;
(ii) a method including: suspending a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, and an auxiliary ingredient as necessary, in a solvent to obtain a suspension; and heating and stirring the suspension;
(iii) a method including: dissolving a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, and an auxiliary ingredient as necessary, in a solvent, and then, depositing a co-crystal; and
(iv) a method including: mixing a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, and an auxiliary ingredient as necessary; and heating to melt the mixture.

[0018] Among these, the method (ii) or (iii) is preferable.

[0019] Examples of the auxiliary ingredient to be used as necessary in the method for producing the co-crystal according to the present invention include a surfactant, an extending agent, an effect-reinforcing assistant, an antioxidant, an ultraviolet absorber, and a stabilizing agent.

[0020] The mechanochemical solid phase reaction in the method (i) is preferably performed by dry pulverization.

[0021] Although the solvent available in the method (ii) is not particularly limited, it is preferable that the solvent be a liquid medium in which at least one of the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient can be dissolved at a solubility of greater than or equal to 100 ppm. Examples of the solvent include: water; monohydric alcohols such as methanol, ethanol, propanol, isopropanol, and butanol; glycols such as ethylene glycol, diethylene glycol, propylene glycol, and glycerin; and ketone such as acetone, methylethyl ketone, and methylisobutyl ketone. The solvent may be used alone or in combination of two or more thereof. Among these, water is preferably used as the solvent.

[0022] After the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient are suspended in the solvent, the resultant may be stirred for a certain time or may be allowed to stand without being stirred. After the resultant is suspended, the resultant is heated and stirred for a certain time. The time for stirring or heating the resultant is not particularly limited, but a preferable range thereof is greater than or equal to 30 minutes but less than or equal to 1 day. The time depends on the intended use of the co-crystal, and any time may be set as long as at least a part of the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient, preferably 10% by mass to 100% by mass thereof, more preferably 50% by mass to 100% by mass thereof, and particularly preferably 90% by mass to 100% by mass thereof, form the co-crystal. The time can be determined by the above-described method for confirming the formation of the co-crystal, or measuring changes in solid particle size in the suspension over time. The heating temperature is preferably greater than or equal to 40°C but lower than or equal to the boiling point of the solvent, and more preferably greater than or equal to 60°C but lower than or equal to the boiling point of the solvent.

[0023] It is preferable that the above-mentioned step of heating and stirring the suspension be conducted in the presence of a surfactant. Although the following may be used as a surfactant, it is preferable that at least one selected from the group consisting of non-ionic surfactants such as polyoxyethylene glycol tristyrylphenyl ether, lignin sulfonate, and dialkylsulfo succinate be used.

[0024] The solvent available in the method (iii) is not particularly limited, provided that the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient can be entirely dissolved therein. Specific examples of the solvent include acetone, acetonitrile, methanol, ethanol, ethyl acetate, dichloromethane, chloroform, tetrahydrofuran, n-hexane, cyclohexane, benzene, toluene, and xylene. The solvent may be used alone or in combination of two or more thereof. Among these, acetone is preferable.

[0025] The deposition of the co-crystal may be performed by mixing the resultant with a poor solvent, or cooling the resultant. Although the following procedure is strictly different from the recrystallization procedure, the co-crystal can be obtained by solely distilling away the solvent.

[0026] In the method (iv), any heating temperature may be set, provided that the heating temperature is a temperature or higher at which at least the mixture of the diamide-based insecticidal-active ingredient and the neonicotinoid-based insecticidal-active ingredient is melted, and a temperature at which neither the diamide-based insecticidal-active ingredient nor the neonicotinoid-based insecticidal-active ingredient is decomposed. The temperature is not necessarily no less than melting temperatures independently shown by each of the above-described ingredients, and the temperature may be lower than the melting temperatures depending on the property of the above-described mixture. The heating temperature is preferably higher than or equal to 85°C, more preferably higher than or equal to 90°C, and even more preferably higher than or equal to 100°C.

[0027] The thus produced co-crystal can be used to produce an agrochemical composition according to the present invention, such as an insecticidal composition, in a form of being produced as it is or through further purifying the co-crystal, depending on the intended use.

[0028] The agrochemical composition according to the present invention, particularly the insecticidal composition, contains the co-crystal as an active ingredient thereof.

[0029] The co-crystal, as an active ingredient, may be contained alone or in combination of two or more thereof. The agrochemical composition according to the present invention may contain other agrochemical-active ingredients in addition to the co-crystal, and may contain an auxiliary ingredient, depending on the intended use and the dosage form.

[0030] Examples of other agrochemical-active ingredients which may be contained in the agrochemical composition according to the present invention include insecticides, acaricides, nematicides, fungicides, herbicides, plant growth regulators, resistance-inducing agents, pest repellents, and anti-viral agents, and more specific examples thereof include the following compounds.

Insecticide:

[0031]

(1) Organic (thio)phosphate bases: acephate, azamethiphos, azinphos-methyl, azinphos-ethyl, buromophos-ethyl, bromfenvinphos, BRP, chlorpyrifos, chlorpyrifos-methyl, chlorfenvinphos, cadusafos, carbophenothion, chloroethoxyfos, chlormephos, coumaphos, cyanofenphos, cyanophos, dichlorvos, dicrotophos, dimethoate, disulfoton, demeton-S-methyl, dimethylvinphos, demeton-S-methylsulfone, dialifos, diazinon, dichlofenthion, dioxabenzophos, disulfoton, ethion, ethoprophos, etrimfos, EPN, fenamiphos, fenitrothion, fenthion, fensulfothion, fonofos, formothion, phosmethylan, heptenophos, isazophos, iodofenphos, isofenphos, isoxathion, malathion, mevinphos, methamidophos, methidathion, monocrotophos, mecarbam, methacrifos, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phosalone, phosmet, phosphamidon, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, profenofos, prothiofos, fosthiazate, phosphocarb, propaphos, propethamphos, prothoate, pyridaphenthion, pyraclofos, quinalphos, sulprophos, sulfotepp, tetrachlorvinphos, terbufos, triazophos, trichlorfon, tebupirimfos, temephos, thiometon, vamidothion, and imicyafos;
(2) Carbamate bases: alanycarb, aldicarb, bendiocarb, benfuracarb, carbaryl, carbofuran, carbosulfan, phenothiocarb, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, thiodicarb, ethiofencarb, fenobucarb, MIPC, MPMC, MTMC, furathiocarb, XMC, aldoxicarb, allyxycarb, aminocarb, bufencarb, butacarb, butocarboxim, butoxycarboxim, cloethocarb, dimetilan, formetanate, metam-sodium, metolcarb, promecarb, thiophanox, trimethacarb, and xylylcarb;
(3) Pyrethroid bases: allethrin, bifenthrin, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, cyphenothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, ethofenprox, fenpropathrin, fenvalerate, imiprothrin, permethrin, prallethrin, pyrethrin, pyrethrin I, pyrethrin II, resmethrin, silafluofen, fluvalinate, tefluthrin, tetramethrin, tralomethrin, transfluthrin, profluthrin, dimefluthrin, acrinathrin, cycloprothrin, halfenprox, flucythrinate, bioallethrin, bioethanomethrin, biopermethrin, bioresmethrin, transpernethrin, empenthrin, fenfluthrin, fenpirithrin, flubrocythrinate, flufenprox, flumethrin, metofluthrin, phenothrin, protrifenbute, pyresmethrin, terallethrin, meperflutherin, and tetramethylfluthrin;
(4) Growth-regulating substances:

  (a) Chitin synthesis inhibitors: chlorfluazuron, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron, bistrifluron, noviflumuron, buprofezin, fluazuron, and penfluron;
  (b) Ecdysone agonists: halofenozide, methoxyfenozide, tebufenozide, chromafenozide, and azadirachtin;
  (c) Juvenile hormone analogs: pyriproxyfen, methoprene, epofenonane, hydroplane, kinoprene, triprene, diofenolan, and fenoxycarb; and
  (d) Lipid biosynthesis inhibitors: spirodiclofen, spiromesifen, and spirotetramat;

(5) Nicotine receptor agonist/antagonist compounds: nicotine, bensultap, cartap, thiocyclam, thiosultap, and nereistoxin;
(6) GABA antagonist compounds: acetoprole, ethiprole, fipronil, vaniliprole, pyrafluprole, and pyriprole;
(7) Macrocyclic lactone insecticides: abamectin, emamectin benzoate, milbemectin, lepimectin, spinosad, ivermectin, selamectin, doramectin, eprinomectin, moxidectin, milbemycin oxime, and spinetoram;
(8) METI I compounds: fenazaquin, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim, fenpyroximate, and pyrimidifen;
(9) METI II and III compounds: acequinocyl, fluacrypyrim, hydramethylnon, and cyenopyrafen;
(10) Uncoupler compounds: chlorfenapyr, binapacryl, dinobuton, dinocap, and DNOC;
(11) Oxidative phosphorylation inhibitor compounds: cyhexatin, diafenthiuron, fenbutatin-oxide, propargite, azocyclotin, and tetradifon;
(12) Molting-disrupting compounds: cyromazine;
(13) Mixed function oxidase inhibitor compounds: piperonyl butoxide;
(14) Sodium channel blocker compounds: indoxacarb and metaflumizone;

(15) Microbial agrochemicals: a BT agent, an insect pathogenic virus agent, an insect pathogenic filamentous fungus agent, and a nematode pathogenic filamentous fungus agent; the genus and species Bacillus, silkworm fungus, blackworm fungus, the genus and species Paecilomyces, thuringiensin, and the genus and species Verticillium;
(16) Latrophilin receptor agonist: emodepside;
(17) Octopamine-related agonist: amitraz;
(20) Feeding inhibitors: pymetrozine, flonicamid, and chlordimeform;
(21) Mite growth inhibitors: clofentezine, etoxazole, and hexythiazox;
(22) Other compounds: benclothiaz, bifenazate, pyridalyl, sulfur, cyflumetofen, amidoflumet, 1,3-dichloropropene, DCIP, metaldehyde, pyrifluquinazon, benzoximate, bromopropylate, chinomethionate, chloropicrin, dicyclanil, fenoxacrim, fentrifanil, flubenzimine, gossyplure, japonilure, metoxadiazon, oil, potassium oleate, sulfluramid, tetrasul, triarathene; afidopyropen, pyflubumide, flometoquin, fluensulfone, tralopyril, diflovidazin, methylneodecanamide, and triazamate;
(23) Anthelmintics

(a) Benzimidazole bases: fenbendazole, albendazole, triclabendazole, and oxybendazole;
(b) Salicylanilide bases: closantel and oxyclozanide
(c) Substituted phenol base: nitroxinil;
(d) Pyrimidine base: pyrantel;
(e) Imidazothiazole base: levamisole;
(f) Tetrahydropyrimidine: praziquantel; and
(g) Other anthelmintics: cyclodiene, ryania, clorsulon, metronidazole, and demiditraz.

Fungicides:

[0032]

(1) Benzimidazole bases: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl, chlorofenazole, and debacarb;
(2) Dicarboximide bases: chlozolinate, iprodione, procymidone, and vinclozolin;
(3) DMI-fungicide bases: imazalil, oxpoconazole, pefurazoate, prochloraz, triflumizole, triforine, pyrifenox, fenarimol, nuarimol, azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, etaconazole, and furconazole-cis; diclobutrazol, diniconazole-M, dodemorph acetate, fluconazole, imazalil-sulfate, naftifine, uniconazole P, viniconazole, and voriconazole;
(4) Phenyl amide bases: benalaxyl, benalaxyl-M, clozylacon, furalaxyl, metalaxyl, metalaxyl-M, oxadixyl, and ofurace;
(5) Amine bases: aldimorph, dodemorph, fenpropimorph, tridemorph, fenpropidin, piperalin, and spiroxamine;
(6) Phosphorothiorate bases: EDDP, iprobenfos, and pyrazophos;
(7) Dithiolane base: isoprothiolane;
(8) Carboxamide: benodanil, boscalid, carboxin, fenfuran, flutolanil, furametpyr, mepronil, oxycarboxin, penthiopyrad, thifluzamide, bixafen, isopyrazam, penflufen, fluxapyroxad, sedaxane, and fluopyram;
(9) Hydroxy-(2-amino)pyrimidine bases: bupirimate, dimethirimol, and ethirimol;
(10) AP fungicide (anilinopyrimidine) bases: cyprodinil, mepanipyrim, pyrimethanil, and andoprim;
(11) N-phenyl carbamate base: diethofencarb;
(12) QoI-fungicide (Qo inhibitor) bases: azoxystrobin, picoxystrobin, pyraclostrobin, kresoxim-methyl, trifluoxystrobin, dimoxystrobin, metominostrobin, orysastrobin, famoxadone, fluoxastrobin, fenamidone, and metominofen; ametoctradin, pyrametostrobin, pyraoxystrobin, pyribencarb; coumethoxystrobin, coumoxystrobin, enestroburin, phenoxystrobin, and triclopyricarb;
(13) PP fungicide (phenylpyrrole) bases: fenpiclonil and fludioxonil;
(14) Quinoline base: quinoxyfen;
(15) AH fungicide (aromatic hydrocarbon) bases: biphenyl, chloroneb, dicloran, quintozene, tecnazene, and chlorothalonil;
(16) MBI-R bases: fthalide, pyroquilon, and tricyclazole;
(17) MBI-D bases: carpropamid, diclocymet, and fenoxanil;
(18) SBI agent: fenhexamid;
(19) Phenyl urea: pencycuron;
(20) QiI-fungicides (Qi inhibitors): cyazofamid, amisulbrom, and frumecyclox;
(21) Benzamide bases: zoxamide and zarilamide;

(22) Enopyranuron bases: blasticidin and mildiomycin;
(23) Hexopyranosyl bases: kasugamycin and kasugamycin hydrochloride;
(24) Glucopyranosyl bases: streptomycin and validamycin;
(25) Cyanoacetamide: cymoxanil;
(26) Carbamates: iodocarb, propamocarb, prothiocarb, and polycarbamate;
(27) Uncoupling agents: binapacryl, dinocap, ferimzone, fluazinam, and meptyldinocap;
(28) Organic tin compounds: triphenyltin acetate, triphenyltin chloride, and triphenyltin hydroxide;
(29) Phosphate esters: phosphorous acid, tolclofos methyl, fosetyl, and adifenphos;
(30) Phthalamic acid base: techlofthalam;
(31) Benzotriazine base: triazoxide;
(32) Benzene sulfonamide base: flusulfamide;
(33) Pyridazinone: diclomezine;
(34) CAA fungicide (carboxylic acid amide) bases: dimethomorph, flumorph, benthiavalicarb-isopropyl, iprovalicarb, mandipropamid, and valifenalate;
(35) Tetracycline: oxytetracycline;
(36) Thiocarbamate base: methasulfocarb;
(37) Resistance-inducing agents: acibenzolar-S-methyl, probenazole, thiazinyl, and isotianil;
(38) Other compounds: etridiazole, polyoxin, polyoxorim, oxolinic acid, hydroxy isoxazole, octhilinone, silthiofam, diflumetrim, ethaboxam, cyflufenamid, proquinazid, metrafenone, fluopicolide, Bordeaux mixtures, copper naphthalate, copper oxide, oxycopper chloride, copper sulfate, mancopper, copper (II) bis(8-quinolinolato), copper (II) hydroxide, organocopper, sulfur, calcium polysulfide, ferbam, manzeb, manebu, metiram, propineb, thiuram, zineb, ziram, captan, captafol, folpet, dichlofluanid, tolylfluanid, dodine, guazatine, iminoctadine, iminoctadine acetate, iminoctadine alkylbenzenesulfonate, anilazine, dithianon, dazomet, chinomethionate, cyprofuram, and fluoroimide; isofetamido, tolprocarb, fenpyrazamine, pyriofenone, and tebufloquin; fluoro folpet, propamidine; benthiazole, bethoxazin, capsaicin, cufraneb, mancozeb, dichlorophene, diphenylamine, flumetover, fluoroimide, flutianil, fosetyl-aluminum, fosetyl-calcium, fosetyl-sodium, irumamycin, methyl isothiocyanate (MITC), natamycin, nitrothal-isopropyl, propamocarb-fosetylate, pyrimorph, pyrrolnitrin, tolnifanide, and trichlamide;

<Plant Growth Regulators>

[0033] Abscisic acid, indolebutyric acid, uniconazole, ethchlozate, ethephone, cloxyfonac, chlormequat, chlorella extract, calcium peroxide, cyanamide, dichlorprop, gibberellin, daminozide, decyl alcohol, trinexapac-ethyl, mepiquat chloride, paclobutrazol, paraffin wax, pyraflufen ethyl, flurprimidol, prohydrojasmon, prohexadione calcium salt, benzylaminopurine, pendimethalin, forchlorfenuron, maleic hydrazide potassium, 1-naphthylacetamide, 4-CPA, MCPB, choline, butralin, 1-methylcyclopropene, aviglycine hydrochloride, and cyprosulfamide.

[0034] The dosage form of the agrochemical composition according to the present invention is not particularly limited, and examples thereof include powder, wettable powder, water-dispersible granule, suspension, and tablet, and suspension concentrate is particularly preferable for a seed-coating agent.

[0035] Examples of the auxiliary ingredient available in the agrochemical composition according to the present invention include a surfactant, an extending agent, an effect-reinforcing assistant, an antioxidant, an ultraviolet absorber, and a stabilizing agent.

[0036] The surfactant available in the present invention may be selected depending on the dosage form and the intended use, and specific examples thereof include: nonionic surfactants such as alkyl phenyl ethers to which polyoxyethylene is added, alkyl ethers to which polyoxyethylene is added, higher fatty acid ester to which polyoxyethylene is added, sorbitan higher fatty acid ester to which polyoxyethylene is added, and polyoxyethylene glycol tristyryl phenyl ether; formaldehyde condensates such as sulfuric acid ester salts of alkyl phenyl ether to which polyoxyethylene is added, alkyl benzene sulfonates, sulfuric acid ester salts of higher alcohols, alkyl naphthalene sulfonates, polycarboxylates, lignin sulfonates, and alkyl naphthalene sulfonate; and isobutylene maleic anhydride copolymer.

[0037] The extending agent available in the present invention may be selected depending on the dosage form and the intended use, and examples thereof include: solvents, such as, water, glycerin, ethylene glycol, propylene glycol, dimethyl sulfoxide, dimethylacetamide, N-methylpyrrolidone, γ-butyrolactone, alcohols, aliphatic hydrocarbons, and aromatic hydrocarbons; thickeners, stabilizers, and binders, such as, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, polyethylene glycol, carboxymethyl cellulose, hydroxypropyl cellulose, gum arabic, xanthan gum, gelatin, casein, pectin, and sodium alginate; solid carriers, such as, talc, clay, bentonite, kaolinite clay, montmorillonite, pyrophyllite, acid clay, diatomaceous earth, vermiculite, apatite, gypsum, mica, silica sand, calcium carbonate, and mineral powder such as pumice powder; white carbon (amorphous silica), and synthetic products such as titanium dioxide; crystalline cellulose, starch, plant-derived powders such as wood flour, cork, and coffee beans; polymer compounds such as polyvinyl chloride and petroleum resin; and water soluble components, such as, ammonium sulfate, ammonium nitrate, ammonium chloride, potassium phosphate, potassium chloride, urea, and sugar.

[0038] The method for producing the agrochemical composition according to the present invention is not particularly limited. Examples thereof include a method in which a co-crystal according to the present invention is formulated in a form of being produced as it is, or after being mixed with an auxiliary ingredient as necessary; a method in which a co-crystal according to the present invention is formulated after being isolated and then mixed with an auxiliary ingredient; and a method in which a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient that form a co-crystal are mixed with an auxiliary ingredient, the mixture is heated to form a co-crystal, an auxiliary ingredient is further added to the co-crystal, as necessary, and then the mixture is formulated.

[0039] Examples of the intended use of the agrochemical composition according to the present invention include agricultural and horticultural use, and home gardening use. It is preferable that the agrochemical use be insecticidal use, and specific examples of the insecticidal use include agricultural and horticultural use, home gardening use, and use in controlling sanitary insect pests, wood insect pests, termites, and ectoparasites or endoparasites on animals.

[0040] An application method of the agrochemical composition according to the present invention is not particularly limited, provided that the used dosage form can be applied to the application method. Specific examples thereof include foliage application; treatments onto propagating materials such as seeds, seed potatoes, and bulbs, by conducting spraying, dust coating, scattering, dipping, or the like; trunk injection; treatments onto soil or cultivation carriers by conducting surface scattering, mixing, irrigating, planting hole treatment, or the like; and application onto water surfaces of paddy fields.

[0041] The agrochemical composition according to the present invention is preferably used as a seed treatment agent. The seed treatment agent is preferably an aquatic suspended concentrate composition. The aquatic suspended concentrate composition may be preferably obtained in accordance with the method (ii) by suspending a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, and an auxiliary ingredient, as necessary, in water to obtain a suspension, and then heating and stirring the suspension.

[0042] Examples of the method for treating seeds include a method in which seeds are coated with the agrochemical composition (seed treatment agent) according to the present invention. Specific examples thereof include a method in which the agrochemical composition according to the present invention is dissolved or dispersed in a sticker solution (a solution obtained by dissolving in water a water-soluble polymer such as PVA (polyvinyl alcohol) or CMC (carboxymethyl cellulose) to improve the adherability when seeds are treated, with a dye or another substance that serves as a mark of agent treatment), the obtained solution or dispersion is mixed with seeds of crops, and then drying the mixture to obtain seeds on which the agent uniformly adheres. In the case where the obtained seeds are sowed in the soil, the agent absorbed through the seed itself or the root sprouted from the seed is entirely spread over the plant, and the crops are protected from noxious insects.

EXAMPLES

[0043] Hereinafter, the present invention will be described in more detail with reference to the examples. However, the present invention is not limited thereto.

Example 1

[0044] 4.7 parts by mass of acetamiprid (manufactured by Nippon Soda Co., Ltd), 10 parts by mass of cyantraniliprole (manufactured by Du Pont Kabushiki Kaisha) (molar ratio of cyantraniliprole to acetamiprid = approximately 1), and 7.91 parts by mass of acetone were put into an eggplant-shaped flask, and then stirred. The mixture was left for 1 day at room temperature. Then, acetone was distilled away by an evaporator at 50°C to obtain a solid product.

[0045] The solid product was subjected to DSC measurement (measurement device: DSC 220 manufactured by Seiko Instruments Inc., the same measurement device was used in the following). The result is shown in FIG. 1. A melting point (approximately 178°C) was found which was different from the melting points of acetamiprid and cyantraniliprole (FIG. 1). The melting point of acetamiprid is approximately 98°C and the melting point of cyantraniliprole is 217°C. The longitudinal axis (left) of the DSC curve represents calories and the horizontal axis represents temperature.

[0046] Powder X-ray diffraction (XRD) of the solid product, acetamiprid, and cyantraniliprole was measured, and the results thereof are shown in FIGS. 3 to 5. The longitudinal axis represents intensity and the horizontal axis represents a diffraction angle. It can be seen that the solid product had a crystal structure different from those of acetamiprid and cyantraniliprole.

[0047] Accordingly, it is considered that the solid product generated in Example 1 was a co-crystal in which acetamiprid and cyantraniliprole were contained at a molar ratio of approximately 1:1.

Comparative Example 1

[0048] 4.7 parts by mass of acetamiprid and 10 parts by mass of cyantraniliprole were dry-mixed to obtain a mixture. The mixture was subjected to DSC measurement, and the results thereof are shown in FIG. 2. The mixture composed of acetamiprid and cyantraniliprole started to melt at approximately 94°C and exhibited behavior different from that of the co-crystal.

Example 2

[0049] 10 parts by mass of acetamiprid, 21 parts by mass of cyantraniliprole, 1.0 part by mass of sodium dialkylsulfosuccinate, 4 parts by mass of polyoxyethylene glycol tristyryl phenyl ether, 0.8 parts by mass of sodium lignin sulfonate, 0.55 parts by mass of a preservative and antifoamer, and 62.7 parts by mass of water were mixed, the mixture was heated at 60°C for 30 minutes while stirring the mixture, and then the resultant was cooled to room temperature. Then, the resultant was subjected to wet-pulverization to obtain a concentrate suspension composition A (aquatic suspended concentrate composition). The obtained concentrate suspension composition A was partially filtrated, and washed with water to obtain a crystal. The obtained crystal was subjected to DSC and XRD measurement to confirm that the spectrum of the obtained crystal was the same as that of the co-crystal obtained in Example 1.

Example 3

[0050] The concentrate suspension composition A obtained in Example 2 was diluted 4000 times with water to obtain a treatment agent (active ingredient amount in terms of acetamiprid: 25ppm, active ingredient amount in terms of cyantraniliprole: 50 ppm).

[0051] The upper leaves of cucumbers were cut while remaining the first true leaves thereof, and the sufficient amount of the treating agent was sprayed thereon using a shoulder sprayer. The 5000-fold dilution of Rabiden 3S was used as a spreading agent. After the predetermined number of days had elapsed, three cotton aphid adults were released in each pot. The number of cotton aphid larvae was counted five days after releasing the cotton aphid adults. Each agent was sprayed on 6 pots, the pots were divided in two groups each composed of 3 pots, and the groups were exchanged at every time of releasing the insects to realize releasing the insects with a short cycle. The results are shown in Table 1.

Comparative Example 2 - Comparative Example 4

[0052] Each test was conducted in the same way as that of Example 3, except that MOSPILAN (registered trademark) SP agent diluted with water (acetamiprid active ingredient amount: 25 ppm), VERIMARK (registered trademark) SC agent diluted with water (cyantraniliprole active ingredient amount: 50 ppm), or a tank mixture agent composed of MOSPILAN (registered trademark) and VERIMARK (registered trademark) (acetamiprid active ingredient amount: 25 ppm, cyantraniliprole active ingredient amount: 50 ppm) was used as a treatment agent. The results are shown in Table 1.

TABLE 1

	Treatment agent	Control rate % 5 days after releasing insects					
		Insect-release 3 days after spraying	Insect-release 6 days after spraying	Insect-release 11 days after spraying	Insect-release 14 days after spaying	Insect-release 19 days after spraying	Insect-release 24 days after spraying
Example 3	Concentrate suspension composition A	100	100	100	100	97.3	90.1
Comparative Example 2	MOSPILAN SP	65.9	26.5	22.5	0	0	0
Comparative Example 3	VERIMARK SC	100	98.3	92.1	93.3	88.4	38.9

(continued)

	Treatment agent	Control rate % 5 days after releasing insects					
		Insect-release 3 days after spraying	Insect-release 6 days after spraying	Insect-release 11 days after spraying	Insect-release 14 days after spaying	Insect-release 19 days after spraying	Insect-release 24 days after spraying
Comparative Example 4	Tank mixture of MOSPILAN SP and SC (Amorphous)	100	100	90.1	89.5	66.2	56.2
Control rate (%) = 100 - (Number of adult insects on treated area / Number of adult insects on untreated area) × 100							

[0053] As is apparent from Table 1, the residual efficacy of the concentrate suspension composition A containing the co-crystal composed of acetamiprid and cyantraniliprole was superior to those of the single agents MOSPILAN and VERIMARK, and the tank mixture agent in which no co-crystal was formed, the active ingredient concentrations of which are the same as that of the concentrate suspension composition A, and the superiority in efficacy exhibited by forming co-crystal was confirmed.

Example 4

[0054] 1 kg of rapeseeds and 40 g of the concentrate suspension composition A prepared in Example 2 were put in a plastic bag (transparent bag formed of polyethylene film), mixed to make the concentrate suspension composition A uniformly adhere to the surface of the seeds, and then the resultant was dried to obtain seeds in which 3.9 ga.i/kg seed of acetamiprid and 8.2 ga.i/kg seed of cyantraniliprole uniformly adhered to the surface of the seeds. Sieved red clay was put on a 9 cm poly pot (pot made of polyvinyl chloride) and 4 rapeseeds were seeded therein. After all the seeds had sprouted, only 3 seedlings remained. After the predetermined number of days had elapsed, three green peach aphid adults were released in each pot. In the case where leaves of the seedlings increased, approximately 1.5 leaves from the top of the seedlings remained and the lower leaves were cut to make investigation and administration easy, and the pots in which the insects were released were covered with drain nets so as to prevent escape of the insects and natural enemies attack. The number of green peach aphid larvae was counted 5 to 6 days after releasing the insects. The results are shown in Table 2.

Comparative Example 5 - Comparative Example 7

[0055] Each test was conducted in the same way as that of Example 4, except that MOSPILAN (registered trademark) SP, VERIMARK (registered trademark) SC, or a tank mixture of MOSPILAN (registered trademark) and VERIMARK (registered trademark) was used instead of the concentrate suspension composition A, and that rapeseeds in which the adhesion amount of acetamiprid was 4.0 ga.i/Kg seed, that of cyantraniliprole was 8.0 ga.i/Kg seed, or the respective adhesion amounts of acetamiprid and cyantraniliprole were independently 3.9 ga.i/Kg seed and 8.0 ga.i/Kg seed, were used. The results are shown in Table 2.

TABLE 2

	Treatment agent	Control rate % 5-6 days after releasing insects			
		Insect-release 8 days after seeding	Insect-release 13 days after seeding	Insect-release 22 days after seeding	Insect-release 35 days after seeding
Example 4	Concentrate suspension composition A	100	90.3	95.9	86.4
Comparative Example 5	MOSPILAN SP	100	95.7	71.4	57.8
Comparative Example 6	VERIMARK SC	54.4	22.6	44.9	68.7

(continued)

	Treatment agent	Control rate % 5-6 days after releasing insects			
		Insect-release 8 days after seeding	Insect-release 13 days after seeding	Insect-release 22 days after seeding	Insect-release 35 days after seeding
Comparative Example 7	Tank mixture of MOSPILAN SP and VERIMARK SC (Amorphous)	100	89.2	67.3	57.1
Control rate (%) = 100 - (Number of adult insects on treated area / Number of adult insects on untreated area) × 100					

[0056] As is apparent from Table 2, in the case where the seeds treated with the concentrate suspension composition A containing the co-crystal were used, high efficacy on green peach aphids was confirmed even when the insects were released 35 days after seeding, the efficacy being superior to that of MOSPILAN SP, VERIMARK SC, or the tank mixture of MOSPILAN SP and VERIMARK SC (amorphous).

Example 5

[0057] 1 kg of corn seeds and 7 g of the concentrate suspension composition A prepared in Example 2 were put in a plastic bag, mixed to make the concentrate suspension composition A uniformly adhere to the surface of the seeds, and then the resultant was dried to obtain seeds in which 0.6 ga.i/kg seed of acetamiprid and 1.4 ga.i/kg seed of cyantraniliprole uniformly adhered to the surface of the seeds.

[0058] In the same manner, 1 kg of corn seeds and 21 g of the concentrate suspension composition A prepared in Example 2 were put in a plastic bag, mixed to make the concentrate suspension composition A uniformly adhere to the surface of the seeds, and then the resultant was dried to obtain seeds in which 1.9 ga.i/kg seed of acetamiprid and 4.0 ga.i/kg seed of cyantraniliprole uniformly adhered to the surface of the seeds.

[0059] A cotton wool pad and a filter paper were put in a cherry cup (cup made of transparent resin) having an opening of 90 mm, and 20 ml of tap water was poured therein. 5 corn seeds were seeded therein, a lid was put on the cup, and then the cup was left still in a temperature-controlled room (at 25°C). After the predetermined number of days had elapsed, the number of sprouted seeds was counted, and the average germinating rate (%) was calculated. The lengths of the sprout and root of seeds sprouted 5 days after seeding were measured, and the average thereof was calculated. The results are shown Table 3.

Comparative Example 8

[0060] The test was conducted in a similar manner to that of Example 5, except that 1 kg of corn seeds was treated with MOSPILAN (registered trademark) SP in an amount of 0.7 ga.i/kg seed or 2.1 ga.i/kg seed instead of the concentrate suspension composition A, and seeds having an adhesion amount of 0.6 ga.i/kg seed or 1.9 ga.i/kg seed were used. The results are shown in Table 3.

TABLE 3

	Tretment agent	Adhesion amount ga.i/kg seed	Average germinating rate (%)			Sprout length (mm)	Root length (mm)
			After 2 days	After 3 days	After 4 days		
Example 4	Concentrate suspension composition A	0.6+1.4 (Acetamine + Cyantraniliprole)	73.3	100	100	23.5	69.9
		1.9+4.0 (Acetamiprid + Cyantraniliprole)	73.3	93.3	93.3	20.8	55.5
Comparative Example 8	MOSPILAN SP	0.6	40.0	93.3	93.3	17.4	43.9
		1.9	0.0	46.7	60.0	4.0	15.9

(continued)

	Tretment agent	Adhesion amount ga.i/kg seed	Average germinating rate (%)			Sprout length (mm)	Root length (mm)
			After 2 days	After 3 days	After 4 days		
Control	Untreated		60.0	93.3	93.3	19.3	63.0

[0061] As is apparent from Table 3, no effects were confirmed on germination and early growth of the seeds on which the co-crystal was adhered (the seeds treated with the concentrate suspension composition A), and it was confirmed that the germinating rate, the sprout length, and the root length thereof were the same as those of untreated seeds. In contrast, a decrease in the germinating rate and poor growth of the seeds treated with MOSPILAN SP was confirmed. Thus, it is clear that early chemical damage can be reduced by forming a co-crystal.

INDUSTRIAL APPLICABILITY

[0062] A co-crystal is provided that exhibits excellent insecticidal effects over a long period of time while reducing chemical damage on useful plants. The method for industrially producing the co-crystal is also provided.

Claims

1. A co-crystal consisting of a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient, wherein
the diamide-based insecticidal-active ingredient is cyantraniliprole, chlorantraniliprole, or cyclaniliprole, and
the neonicotinoid-based insecticidal-active ingredient is acetamiprid.

2. The co-crystal according to Claim 1, wherein a molar ratio of the diamide-based insecticidal-active ingredient to the neonicotinoid-based insecticidal-active ingredient is 0.3 to 3.

3. A method for producing a co-crystal of Claim 1 or 2, comprising: suspending a diamide-based insecticidal-active ingredient and a neonicotinoid-based insecticidal-active ingredient in a solvent to obtain a suspension; and heating and stirring the suspension.

4. The method for producing a co-crystal according to Claim 3, wherein a heating temperature is higher than or equal to 40°C but lower than or equal to a boiling point of the solvent.

5. The method for producing a co-crystal according to Claim 4, wherein the heating temperature is higher than or equal to 60°C but lower than or equal to the boiling point of the solvent.

6. The method for producing a co-crystal according to any one of Claims 3 to 5, wherein the solvent is water.

7. An agrochemical composition comprising a co-crystal of Claim 1 or 2.

8. The agrochemical composition according to Claim 7, wherein the agrochemical composition is an insecticide.

9. A seed treatment agent comprising a co-crystal of Claim 1 or 2.

10. The seed treatment agent according to Claim 9, wherein the seed treatment agent is an aquatic suspended concentrate composition.

11. A method for treating a seed, comprising: coating a seed with an agrochemical composition comprising a co-crystal of Claim 1 or 2.

Patentansprüche

1. Co-Kristall, bestehend aus einem Insektizid-Wirkstoff auf Diamidbasis und einem Insektizid-Wirkstoff auf Neonicotinoidbasis, wobei
der Insektizid-Wirkstoff auf Diamidbasis Cyantraniliprol, Chlorantraniliprol oder Cyclaniliprol ist und
der Insektizid-Wirkstoff auf Neonicotinoidbasis Acetamiprid ist.

2. Co-Kristall nach Anspruch 1, wobei das Molverhältnis des Insektizid-Wirkstoffs auf Diamidbasis zum Insektizid-Wirkstoff auf Neonicotinoidbasis 0,3 bis 3 beträgt.

3. Verfahren zur Herstellung eines Co-Kristalls nach Anspruch 1 oder 2, das Folgendes umfasst: das Suspendieren eines Insektizid-Wirkstoffs auf Diamidbasis und eines Insektizid-Wirkstoffs auf Neonicotinoidbasis in einem Lösungsmittel, um eine Suspension zu erhalten; und das Erhitzen und Rühren der Suspension.

4. Verfahren zur Herstellung eines Co-Kristalls nach Anspruch 3, wobei die Erhitzungstemperatur 40 °C oder mehr beträgt, aber niedriger als oder gleich dem Siedepunkt des Lösungsmittels ist.

5. Verfahren zur Herstellung eines Co-Kristalls nach Anspruch 4, wobei die Erhitzungstemperatur 60 °C oder mehr beträgt, aber niedriger als oder gleich dem Siedepunkt des Lösungsmittels ist.

6. Verfahren zur Herstellung eines Co-Kristalls nach einem der Ansprüche 3 bis 5, wobei das Lösungsmittel Wasser ist.

7. Agrochemische Zusammensetzung, umfassend einen Co-Kristall nach Anspruch 1 oder 2.

8. Agrochemische Zusammensetzung nach Anspruch 7, wobei die agrochemische Zusammensetzung ein Insektizid ist.

9. Saatgutbehandlungsmittel, umfassend einen Co-Kristall nach Anspruch 1 oder 2.

10. Saatgutbehandlungsmittel nach Anspruch 9, wobei das Saatgutbehandlungsmittel eine wässrig-suspendierte Konzentratzusammensetzung ist.

11. Verfahren zur Behandlung von Saatgut, das Folgendes umfasst: das Beschichten von Saatgut mit einer agrochemischen Zusammensetzung, die einen Co-Kristall nach Anspruch 1 oder 2 umfasst.

Revendications

1. Co-cristal constitué d'un agent actif insecticide à base de diamide et d'un agent actif insecticide à base de néonicotinoïde, dans lequel
l'agent actif insecticide à base de diamide est le cyantraniliprole, le chlorantraniliprole, ou le cyclaniliprole, et
l'agent actif insecticide à base de néonicotinoïde est l'acétamiprid.

2. Co-cristal selon la revendication 1, dans lequel le rapport molaire de l'agent actif insecticide à base de diamide à l'agent actif insecticide à base de néonicotinoïde est de 0,3 à 3.

3. Procédé pour produire un co-cristal selon la revendication 1 ou 2, comprenant : la mise en suspension d'un agent actif insecticide à base de diamide et d'un agent actif insecticide à base de néonicotinoïde dans un solvant pour que soit obtenue une suspension ; et le chauffage et l'agitation de la suspension.

4. Procédé pour produire un co-cristal selon la revendication 3, dans lequel la température de chauffage est supérieure ou égale à 40°C mais inférieure ou égale au point d'ébullition du solvant.

5. Procédé pour produire un co-cristal selon la revendication 4, dans lequel la température de chauffage est supérieure ou égale à 60°C mais inférieure ou égale au point d'ébullition du solvant.

6. Procédé pour produire un co-cristal selon l'une quelconque des revendications 3 à 5, dans lequel le solvant est l'eau.

7. Composition agrochimique comprenant un co-cristal selon la revendication 1 ou 2.

8. Composition agrochimique selon la revendication 7, laquelle composition agrochimique est un insecticide.

9. Agent de traitement des semences comprenant un co-cristal selon la revendication 1 ou 2.

10. Agent de traitement des semences selon la revendication 9, lequel agent de traitement des semences est une composition concentrée en suspension aqueuse.

11. Procédé pour traiter une semence comprenant : l’enrobage de la semence avec une composition agrochimique comprenant un co-cristal selon la revendication 1 ou 2.

FIG. 1

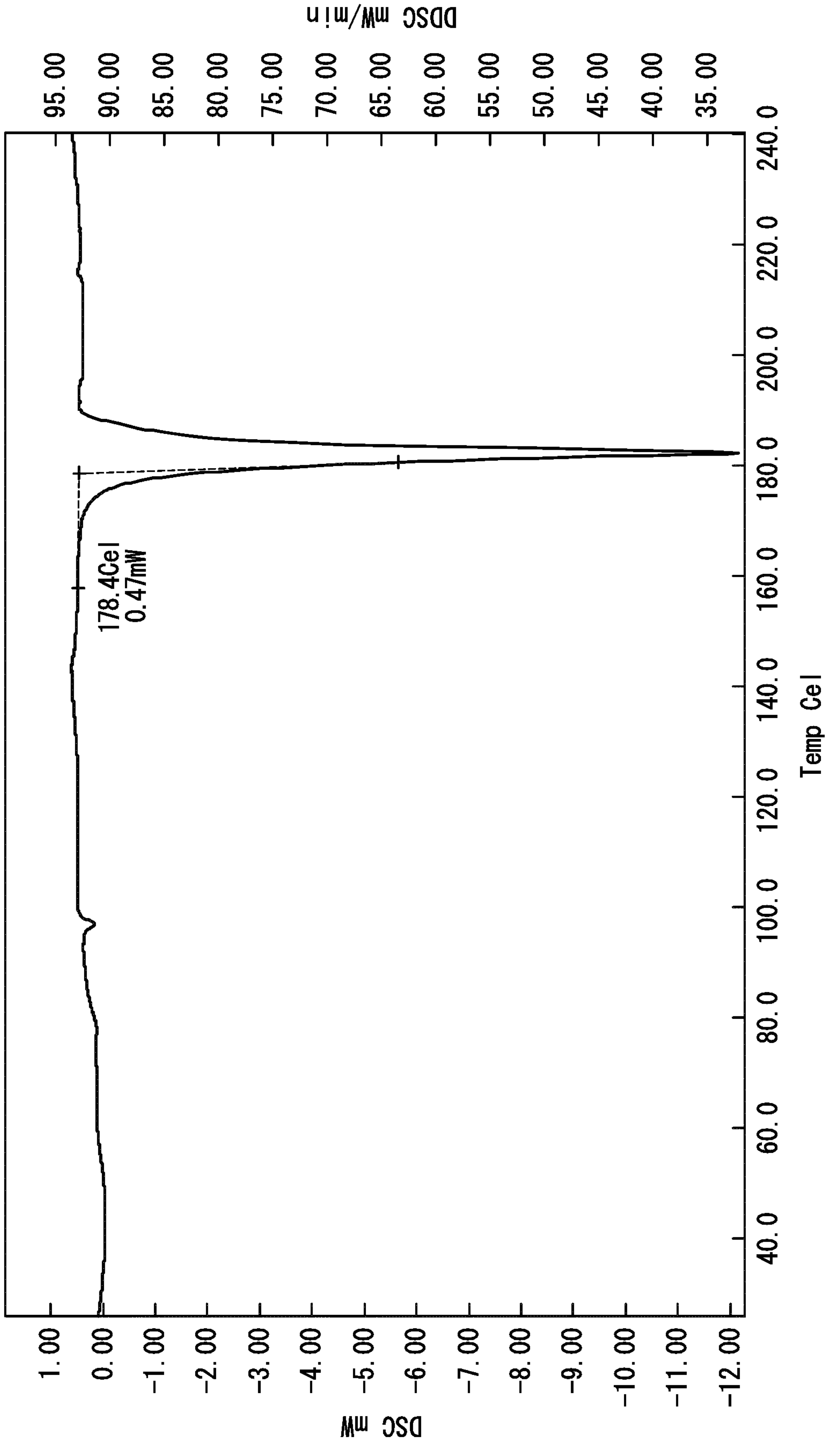
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FIG. 2

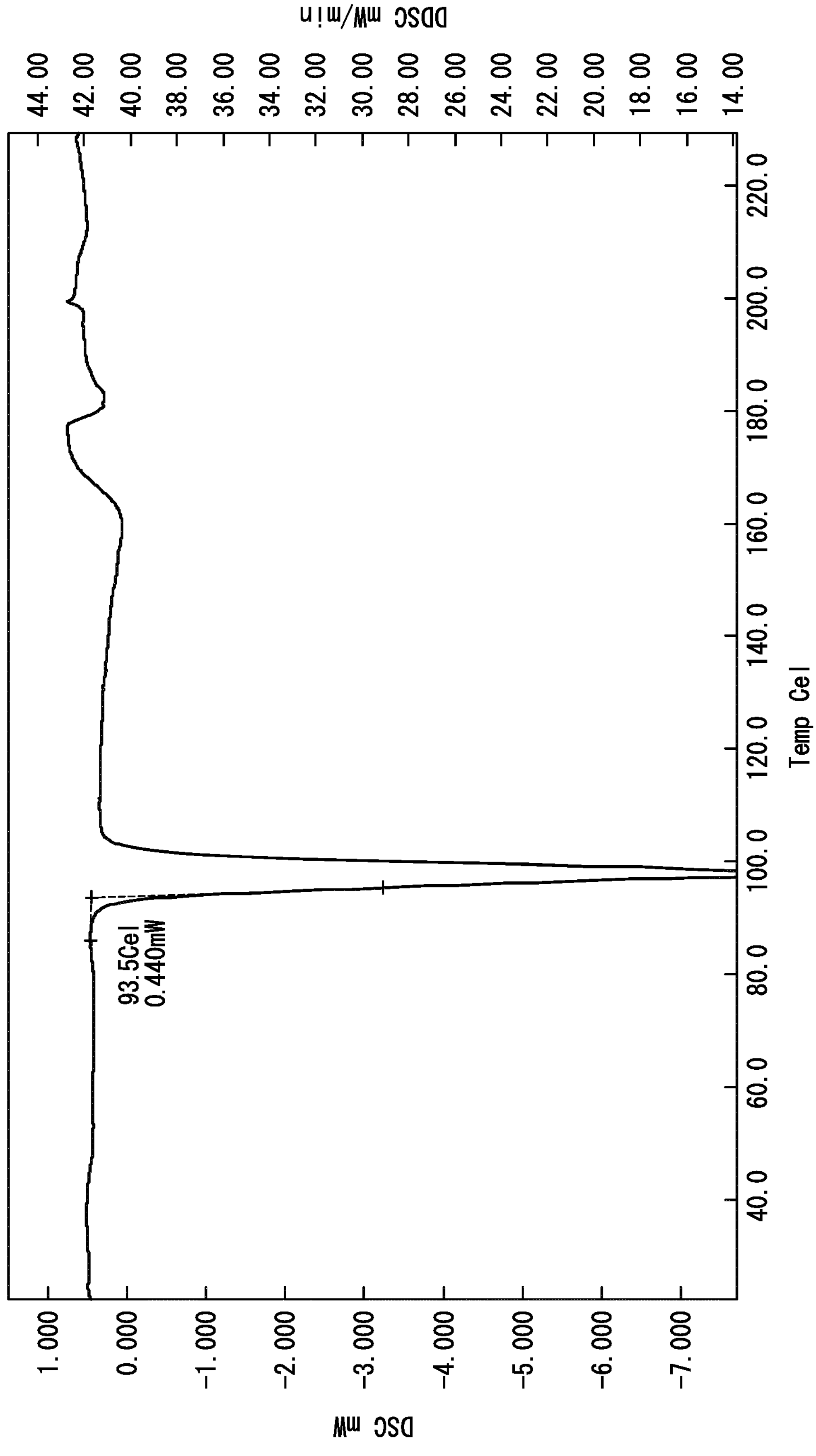
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FIG. 3

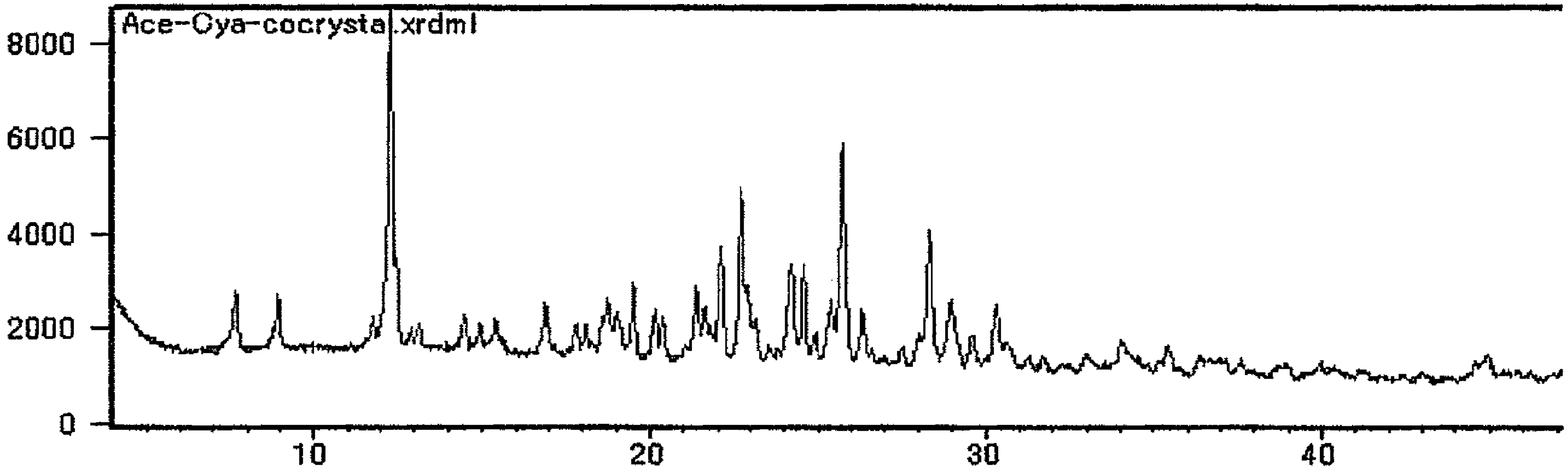


FIG. 4

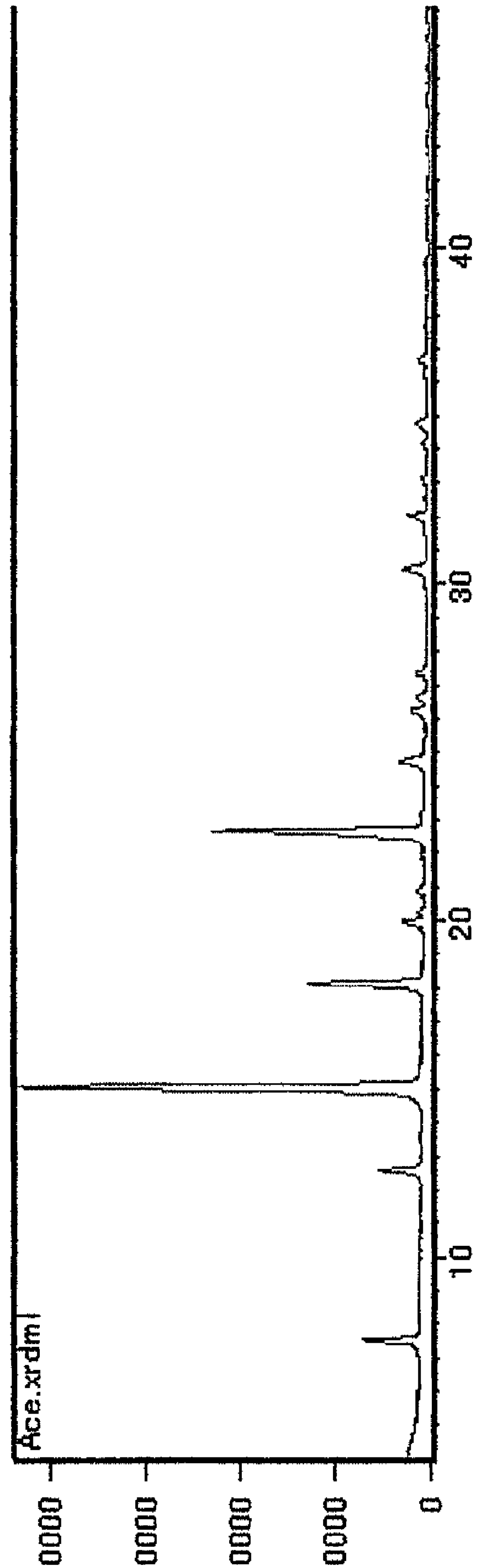
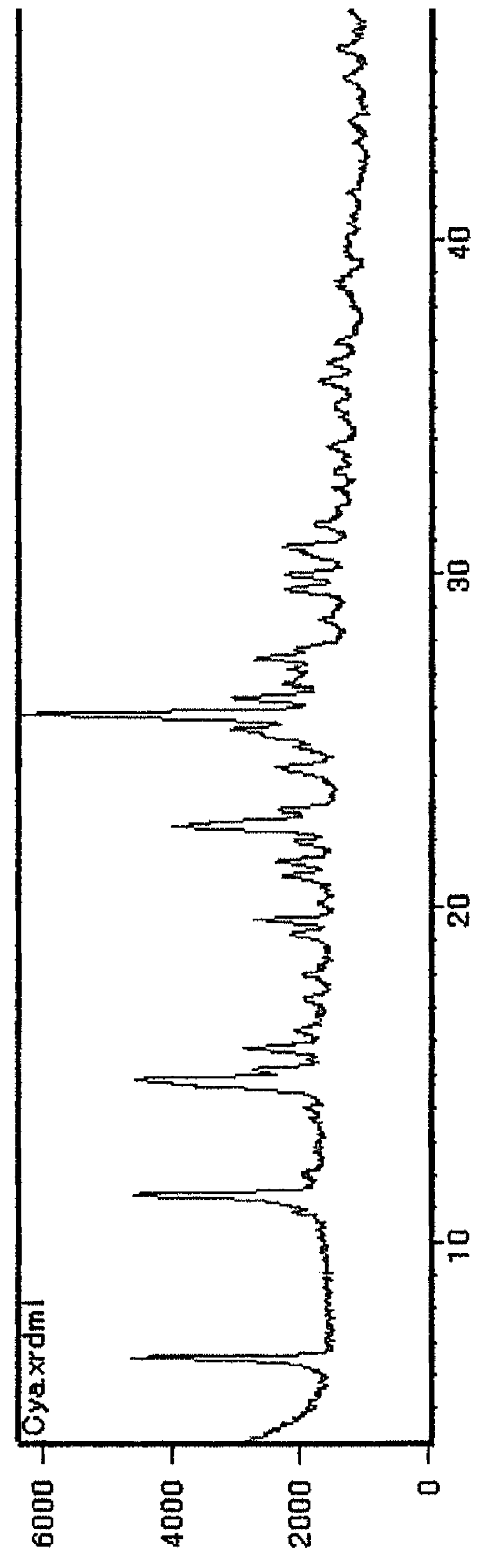


FIG. 5



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