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- (54) Benævnelse: **Æteriserede lactatestere, fremgangsmåde til fremstilling af disse og deres anvendelse til forbedring af virkningen af plantebeskyttelsesmidler**
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**EP-A1- 1 702 941**  
**WO-A2-2007/028538**  
**DE-A1-102007 018 983**  
**JP-A- 6 122 655**  
**DATABASE CAPLUS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SAITO, YUTAKA ET AL: "Preparation of 1a-(acyloxymethoxycarbonyl)mitomycin C as prodrugs", XP002666948, gefunden im STN Database accession no. 1989:614326 & JP 1 113391 A (KYOWA HAKKO KOGYO CO., LTD., JAPAN) 2. Mai 1989 (1989-05-02)**



## Description

**[0001]** The invention relates to new etherified lactate esters, processes for their production, and their use for improving the activity of active agrochemical ingredients in and on plants.

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**[0002]** WO-A-1991/14366 describes lactate and lactate derivatives as active ingredients that regulate the growth of grapes. The substances are here directly prepared in water in a specified dose without further additions and used as foliar spray solution at an early growth stage of the grapes. The use of lactate derivatives for improving the activity of plant-protecting agents at the plant level is, however, neither disclosed nor suggested in this document.

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**[0003]** WO-A-2000/18227 describes alkyl lactates in high concentrations as suspending agents for insoluble active agrochemical ingredients in non-aqueous suspension concentrates. The use of alkyl lactates for improving the activity at the plant level is neither disclosed nor suggested in this document. WO-A-2000/18227 also does not disclose any etherified lactate esters.

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**[0004]** WO-A-2003/075657 describes lactate esters in high concentrations as crystallisation inhibitors and solvents for insoluble active agrochemical ingredients - in particular, azole fungicides. The use of lactate esters for improving the activity at the plant level is also neither disclosed nor suggested in this document. WO-A-2003/075657 also does not disclose any etherified lactate esters.

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**[0005]** WO-A-1996/22020 describes the use of aliphatic esters in penetration enhancers. However, WO-A-1996/22020 does not disclose any etherified lactate esters.

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**[0006]** WO-A-2007/028538 describes lactate esters with a free hydroxy function for improving the effectiveness of plant-protecting agents. However, WO-A-2007/028538 does not disclose any etherified lactate esters.

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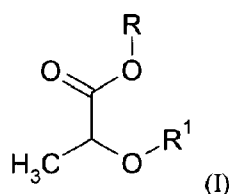
**[0007]** EP-B-1 702 941 describes a process for producing poly(ether ester)polyols, in which, in a first step, one or more monocarboxylic or polycarboxylic acid esters containing hydroxy groups are converted with alkylene oxides with ring opening in the presence of DMC catalysts

(double metal cyanide complex catalysis) into the respective monocarboxylic or polycarboxylic acid esters with one or more attached polyether chains, wherein the alkylene oxide is added, where appropriate, in the presence of a diol or polyol, and, in a second step, the products produced in step a) are subsequently transesterified into OH-functional poly(ether ester)s ([0015]). Suitable as starting components for the production of monocarboxylic or polycarboxylic acid esters with attached polyether chains are lactic acid esters, among others ([0016]). Specific lactic acid esters are not mentioned. The etherified lactate esters according to the invention are also not disclosed. The details of the process are described in ([0017]) - ([0029]). The poly(ether ester)polyols produced in this way are used according to EP-B-1 702 941 as starting substances for the production of polyurethane materials. JP 6122655A discloses the use of lactate esters as detergents.

**[0008]** Not described to date has been a use of lactate esters etherified on the hydroxy group (lactate ester alkoxyates) as improvers of the activity of active agrochemical ingredients in plant-protecting agents. In this case, "plant-protecting agents" are understood to mean the mode of application of the active agrochemical ingredients - for example, the spray liquid.

**[0009]** It has now, surprisingly, been found that the activity of plant-protecting agents at the plant level is significantly improved by certain etherified lactate esters. Accordingly, the etherified lactate esters according to the invention enhance, as wetters, both the retention of the spray liquid of the plant-protecting agents containing the active agrochemical ingredients on the plant - particularly, on the leaves (improved retention) - and the penetration of the active agrochemical ingredients contained in the plant-protecting agents into the plant (improved penetration). This improvement of the properties is already achieved at concentrations of etherified lactate esters that correspond to those of typical wetters or penetration enhancers.

**[0010]** The subject matter of the invention is etherified lactate esters of the formula (I)



where

R

is 2-ethylhexyl or lauryl,

R<sup>1</sup>

is an alkoxylated alkyl radical of the formula  $-(\text{AO})_m\text{-R}'$ , wherein

AO

stands for an ethylene oxide radical, a propylene oxide radical, a butylene oxide radical, or mixtures of ethylene oxide and propylene oxide radicals, and

m

stands for numbers from 2 to 15,

R'

is hydrogen or is a branched or unbranched, saturated, partly saturated, or unsaturated C<sub>1</sub>-C<sub>10</sub> alkyl radical.

**[0011]** In this respect, the ethylene oxide radical, the propylene oxide radical, and the butylene oxide radical are also simply called EO, PO, and BO, respectively, below.

**[0012]** The essential structural chemical element that distinguishes the etherified lactate esters according to the invention from the lactate esters of the prior art is thus the fact that the etherified lactate esters according to the invention are alkoxylated.

**[0013]** Preferred are the following compounds, in which R is 2-ethylhexyl or lauryl (C<sub>12</sub>) and R<sup>1</sup> is an alkoxylated alkyl radical of the formula  $-(\text{AO})_m\text{-R}'$ , where R' is hydrogen or methyl, where m stands for numbers from 2 to 15, and AO has the definition given above.

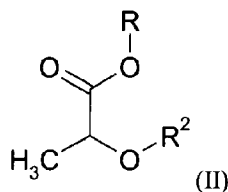
**[0014]** Especially preferred are the following compounds:

Etherified lauryl lactate, i.e., R is lauryl (C<sub>12</sub> alkyl), R<sup>1</sup> is  $-(\text{AO})_m\text{-R}'$ , where R' is hydrogen, and  $-(\text{AO})_m$  is selected from the group consisting of the following alkoxyate radicals:  $-(\text{EO})_5\text{-(PO)}_2$ ,  $-(\text{EO})_5\text{-(PO)}_5$ ,  $-(\text{EO})_8\text{-(PO)}_2$ ,  $-(\text{EO})_8\text{-(PO)}_5$ .

**[0015]** Etherified 2-ethylhexyl lactate, i.e., R is 2-ethylhexyl  $(-\text{CH}_2\text{-CH}(\text{C}_2\text{H}_5)\text{-(CH}_2)_3\text{-CH}_3)$ , R<sup>1</sup> is  $-(\text{AO})_m\text{-R}'$ , where R' is hydrogen, and  $-(\text{AO})_m$  is selected from the group consisting of the following alkoxyate radicals:  $-(\text{EO})_2\text{-(PO)}_2$ ,  $-(\text{EO})_2\text{-(PO)}_5$ ,  $-(\text{EO})_2\text{-(PO)}_{10}$ ,  $-(\text{EO})_2$ ,  $-(\text{EO})_5$ ,  $-(\text{EO})_{10}$ ,  $-(\text{EO})_{15}$ .

**[0016]** The etherified lactate esters according to the invention described here include all enantiomers in this case. The etherified lactate esters according to the invention are preferably present in the (S) form, but the (R) form can also easily be used.

- 5 **[0017]** The etherified lactate esters according to the invention may be produced in accordance with the process described in EP-B-1 702 941. To this end, the lactate esters of the formula (II), in which R has the definition given above and in which R<sup>2</sup> is R', where R' has the definition given above,



- 10 are produced with alkylene oxides (EO, PO, BO, or mixtures thereof) in the presence of DMC catalysts (double metal cyanide complex catalysis). The process conditions, the process sequence, and the catalyst are, in principle, known from EP-B-1 702 941. In this respect, reference is made to EP-B-1 702 941 - in particular, ([0015]) - ([0029]).

- 15 **[0018]** The lactate esters of the formula (II) used as precursor are commercially available. The process may, in this case, be carried out as follows:  
 DMC catalysts suitable for the process according to the invention are, in principle, known from the prior art (see, for example, US-A 3 404 109, US-A 3829505, US-A 3941849, and US-A 5158922). DMC catalysts described in, for example, US-A 5470813, EP-A 700949,  
 20 EP-A 743093, EP-A 761708, WO 97/40086, WO 98/16310, WO 00/47649, and WO 01/80994 have a very high activity in the polymerisation of alkylene oxides and allow for the production of polyethers under optimal conditions with very small catalyst concentrations (100 ppm or less), so that a separation of the catalyst from the finished product is generally no longer required. A typical example are the highly active DMC  
 25 catalysts described in EP-A 700949, which also contain, in addition to a double metal cyanide compound (e.g., zinc hexacyanocobaltate(III)) and an organic complex ligand (e.g., tert-butanol), a polyether with a number average molecular weight of more than 500 g/mol.

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**[0019]** The lactate esters of the formula (II) used according to the invention as starter components can be placed into the reactor or be continuously supplied to the reactor together

with the alkylene oxides during the reaction. In the latter procedure, a small quantity of an addition product of lactate esters of the formula (II) and alkylene oxide, which may also be the product to be produced, is generally placed into the reactor. It is also possible to remove reaction product from the reactor continuously, wherein the DMC catalyst must also be

5 continuously added, in addition to the alkylene oxide and the starter component. The process variants for producing alkylene oxide addition products by DMC catalysis while continuously adding the starter components are, for example, described in WO 97/29146 and WO 98/03571.

10 **[0020]** The DMC-catalysed reaction of the lactate esters of the formula (II) with the alkylene oxides generally takes place at temperatures of 20 to 200 °C - preferably, of 40 to 180 °C, and, particularly preferably, at temperatures of 50 to 150 °C. The reaction can be carried out at total (absolute) pressures of 0.0001 to 20 bar. The polyaddition can be carried out in substance or in an inert organic solvent, such as toluene and/or THF. The quantity of

15 solvent is usually 10 to 30 wt%, based upon the quantity of the etherified lactate ester to be produced.

**[0021]** The catalyst concentration is selected such that good control of the polyaddition reaction is possible under the given reaction conditions. The catalyst concentration is

20 generally 0.0005 wt% to 1 wt% - preferably, 0.001 wt% to 0.1 wt%, and, particularly preferably, 0.001 to 0.03 wt% - based upon the quantity of the etherified lactate ester to be produced. Small quantities (1 - 500 ppm, based upon the starter quantity) of organic or inorganic acids can be added, as described in WO 99/14258, to the lactate esters of the formula (II) used according to the invention as starter components.

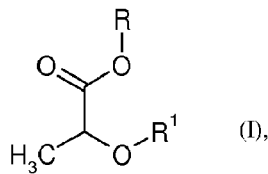
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**[0022]** Anti-aging agents, such as antioxidants, may be added, where appropriate, to the etherified lactate esters produced in this way.

**[0023]** The process for producing the etherified lactate esters according to the invention is

30 also the subject matter of the process.

**[0024]** The subject matter of the invention is also the use of etherified lactate esters of the formula (I) according to the invention



R stands for unbranched or branched, saturated or unsaturated C1-C20 alkyl, and R<sup>1</sup> is an alkoxyated alkyl radical of the formula  $(-AO)_m-R'$ , wherein AO stands for an ethylene oxide radical, a propylene oxide radical, a butylene oxide radical, or mixtures of ethylene oxide and propylene oxide radicals or mixtures of ethylene oxide and butylene oxide radicals, and m stands for numbers from 2 to 30, R' is hydrogen or is a branched or unbranched, saturated, partly saturated, or unsaturated C1-C20 alkyl radical, for improving the activity of active agrochemical ingredients in and on plants. Particularly preferred in this case is the improvement of the penetration of active agrochemical ingredients into plants and the improvement of the retention of active agrochemical ingredients on plants - in particular, on leaves.

**[0025]** The subject matter of the invention is also the use of the etherified lactate esters according to the invention as surfactant, as wetter and sticker as well as emulsifier.

**[0026]** Surprisingly, it was found that many of the etherified lactate esters according to the invention show an excellent foaming behaviour, i.e., foam only slightly - particularly, in aqueous systems. The subject matter of the invention is thus also the use of the etherified lactate esters according to the invention for preventing or reducing foam formation in agrochemical formulations, because, when using other penetration enhancers, this often leads to intensified foam formation and thus the necessity of additionally using de-foaming agents.

**[0027]** The compounds of the formula (I) are used individually or in the form of mixtures. Where etherified lactate esters are mentioned in the description or in the claims, individual compounds according to the invention or mixtures of several compounds according to the invention are explicitly meant.

**[0028]** The etherified lactate esters used according to the invention may, where appropriate, be present as mixtures of different possible isomeric forms - in particular, of stereoisomers - such as E- and Z-, threo- and erythro-, as well as optical isomers. Preferably used are L-lactate derivatives of the formula (I).

**[0029]** The quantity of one or more compounds of the formula (I) in the use according to the invention in plant-protecting agents may vary according to active ingredient and formulation type within wide limits. The compounds of the formula (I) can be used in all common agrochemical formulations - preferably, in liquid ones. The subject matter of the present invention is also the use of etherified lactate esters of the formula (I) for improving the activity at the plant level as a tank-mix additive, i.e., that the etherified lactate esters are only added directly prior to applying a spray liquid produced from a concentrated formulation. However, the compounds may, in principle, also be used in solid formulations.

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**[0030]** The use according to the invention of etherified lactate esters of the formula (I) takes place, for example, in ready-to-apply plant-protecting agents (spray liquids), in which the content of one or more etherified lactate esters of the formula (I) is

- 0.01 to 3 wt%,
- more preferably, 0.01 to 1 wt%,
- very preferably, 0.02 to 0.5 wt%, and
- especially preferably, 0.03 to 0.3 wt%.

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**[0031]** If a plant-protecting agent contains several etherified lactate esters, the indication of quantity should be understood as the total content of all etherified lactate esters.

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**[0032]** The definitions of radicals, value ranges, or explanations given above, either in general or in preferred ranges, may also be arbitrarily combined with each other, i.e., the respective ranges with the preferred ranges.

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**[0033]** Since the mode of action of the etherified lactate esters as penetration enhancers is, in principle, independent of the type of active agrochemical ingredient used, their use in plant-protecting agents containing at least one active ingredient, the biological effectiveness of which can be increased by increased penetration into a crop plant or harmful plant, comes into consideration.

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**[0034]** Since the mode of action of the etherified lactate esters as retention enhancers is also, in principle, independent of the type of the active agrochemical ingredient used, their use

in plant-protecting agents containing at least one active ingredient, the biological effectiveness of which can be increased by improved retention on the crop plant or harmful plant, comes into consideration.

- 5 **[0035]** Preferably mentioned are fungicides, bactericides, insecticides, acaricides, nematocides, herbicides, plant growth regulators, plant nutrients, and repellents.

**[0036]** Mentioned as examples of fungicides are the following:

1. (1) Ergosterol biosynthesis inhibitors, such as aldimorph, azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazole, difenoconazole, diniconazole, diniconazole-M, dodemorph, dodemorph acetate, epoxiconazole, etaconazole, fenarimol, fenbuconazole, fenhexamid, fenpropidin, fenpropimorph, fluquinconazole, flurprimidol, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imazalil, imazalil sulphate, imibenconazole, ipconazole, metconazole, myclobutanil, naftifin, nuarimol, oxpoconazole, paclobutrazole, pefurazoate, penconazole, piperalin, prochloraz, propiconazole, prothioconazole, pyributicarb, pyrifenoxy, quinconazole, simeconazole, spiroxamine, tebuconazole, terbinafine, tetraconazole, triadimefon, triadimenol, tridemorph, triflumizole, triforine, triticonazole, uniconazole, uniconazole-p, viniconazole, voriconazole, 1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol, methyl-1-(2,2-dimethyl-2,3-dihydro-1H-inden-1-yl)-1H-imidazole-5-carboxylate, N'-{5-(difluoromethyl)-2-methyl-4-[3-(trimethylsilyl)propoxy]phenyl}-N-ethyl-N-methylimidoforamamide, N-ethyl-N-methyl-N'-{2-methyl-5-(trifluoromethyl)-4-[3-(trimethylsilyl)propoxy]phenyl}imidoforamamide, and O-[1-(4-methoxyphenoxy)-3,3-dimethylbutane-2-yl]-1H-imidazole-1-carbothioate.
2. (2) Respiration inhibitors (respiratory chain inhibitors), such as bixafen, boscalid, carboxin, diflumetorim, fenfuram, fluopyram, flutolanil, fluxapyroxad, furametpyr, furnecycloz, isopyrazam mixture of syn-epimeric racemate 1RS,4SR,9RS and of anti-empimeric racemate 1RS,4SR,9SR, isopyrazam (anti-epimeric racemate), isopyrazam (anti-epimeric enantiomer 1R,4S,9S), isopyrazam (anti-epimeric enantiomer 1S,4R,9R), isopyrazam (syn-epimeric racemate 1RS,4SR,9RS), isopyrazam (syn-epimeric enantiomer 1R,4S,9R), isopyrazam (syn-epimeric enantiomer 1S,4R,9S), mepronil, oxycarboxin, penflufen, penthiopyrad, sedaxane, thifluzamide, 1-methyl-N-[2-(1,1,2,2-tetrafluoroethoxy)phenyl]-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide, 3-(difluoromethyl)-1-methyl-N-[2-(1,1,2,2-tetrafluoroethoxy)phenyl]-1H-pyrazole-4-

- carboxamide, 3-(difluoromethyl)-N-[4-fluoro-2-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-1-methyl-1H-pyrazole-4-carboxamide, N-[1-(2,4-dichlorophenyl)-1-methoxypropane-2-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, 5,8-difluoro-N-[2-(2-fluoro-4-[[4-(trifluoromethyl)pyridine-2-yl]oxy}phenyl)ethyl]quinazoline-4-amine, N-
- 5 [9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalene-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, N-[(1S,4R)-9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalene-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, and N-[(1R,4S)-9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalene-5-yl]-3-
- 10 (difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide.
3. (3) Respiration inhibitors (respiratory chain inhibitors) acting on complex III of the respiratory chain, such as ametoctradin, amisulbrom, azoxystrobin, cyazofamid, coumethoxystrobin, coumoxystrobin, dimoxystrobin, enestroburin, famoxadone, fenamidone, fenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin,
- 15 oryastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, pyribencarb, triclopyricarb, trifloxystrobin, (2E)-2-(2-[[6-(3-chloro-2-methylphenoxy)-5-fluoropyrimidine-4-yl]oxy]phenyl)-2-(methoxyimino)-N-methylethanamide, (2E)-2-(methoxyimino)-N-methyl-2-(2-[[{(1E)-1-[3-(trifluoromethyl)phenyl]ethylidene}amino]oxy]methyl]phenyl)ethanamide, (2E)-2-
- 20 (methoxyimino)-N-methyl-2-{2-[(E)-{(1-[3-(trifluoromethyl)phenyl]ethoxy)imino)methyl]phenyl}ethanamide, (2E)-2-{2-[[{(1E)-1-(3-[[{(E)-1-fluoro-2-phenylethenyl]oxy}phenyl)ethylidene]amino}oxy]methyl]phenyl]-2-(methoxyimino)-N-methylethanamide, (2E)-2-{2-[[{(2E,3E)-4-(2,6-dichlorophenyl)but-3-en-2-ylidene]amino}oxy]methyl]phenyl}-2-(methoxyimino)-N-
- 25 methylethanamide, 2-chloro-N-(1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl)pyridine-3-carboxamide, 5-methoxy-2-methyl-4-(2-[[{(1E)-1-[3-(trifluoromethyl)phenyl]ethylidene}amino]oxy]methyl]phenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one, methyl-(2E)-2-{2-[[cyclopropyl[(4-methoxyphenyl)imino]methyl]sulphonyl]methyl]phenyl}-3-methoxyprop-2-enoate, N-
- 30 (3-ethyl-3,5,5-trimethylcyclohexyl)-3-(formylamino)-2-hydroxybenzamide, 2-{2-[(2,5-dimethylphenoxy)methyl]phenyl}-2-methoxy-N-methylacetamide, and (2R)-2-{2-[(2,5-dimethylphenoxy)methyl]phenyl}-2-methoxy-N-methylacetamide.
4. (4) Mitosis and cell division inhibitors, such as benomyl, carbendazim, chlorfenazole, diethofencarb, ethaboxam, fluopicolide, fuberidazole, pencycuron, thiabendazole,

thiophanate-methyl, thiophanate, zoaxamide, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)[1,2,4]triazolo[1,5-a]pyrimidine, and 3-chloro-5-(6-chloropyridine-3-yl)-6-methyl-4-(2,4,6-trifluorophenyl)pyridazine.

5. (5) Compounds with multi-site activity, such as Bordeaux mixture, captafol, captan, chlorothalonil, copper preparations like copper hydroxide, copper naphthenate, copper oxide, copper oxychloride, copper sulphate, dichlofluanid, dithianon, dodine, dodine free base, ferbam, fluorofolpet, folpet, guazatine, guazatine acetate, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, mancopper, mancozeb, maneb, metiram, zinc metiram, oxine-copper, propamidine, propineb, sulphur and sulphur preparations like calcium polysulphide, thiram, tolylfluanid, zineb, and ziram.
6. (6) Resistance inductors, such as acibenzolar-S-methyl, isotianil, probenazole, and tiadinil.
7. (7) Amino acid and protein biosynthesis inhibitors, such as andoprim, blasticidin-S, cyprodinil, kasugamycin, kasugamycin hydrochloride hydrate, mepanipyrim, pyrimethanil, and 3-(5-fluoro-3,3,4,4-tetramethyl-3,4-dihydroisoquinoline-1-yl)quinoline.
8. (8) ATP production inhibitors, such as fentin acetate, fentin chloride, fentin hydroxide, and silthiofam.
9. (9) Cell wall synthesis inhibitors, such as benthiavalicarb, dimethomorph, flumorph, iprovalicarb, mandipropamid, polyoxins, polyoxorim, validamycin A, and valifenalate.
10. (10) Lipid and membrane synthesis inhibitors, such as biphenyl, chloroneb, dicloran, edifenphos, etridiazole, iodocarb, iprobenfos, isoprothiolane, propamocarb, propamocarb hydrochloride, prothiocarb, pyrazophos, quintozone, tecnazene, and tolclofos methyl.
11. (11) Melanin biosynthesis inhibitors, such as carpropamid, diclocymet, fenoxanil, phthalide, pyroquilon, tricyclazole, and 2,2,2-trifluoroethyl {3-methyl-1-[(4-methylbenzoyl)amino]butane-2-yl}carbamate.
12. (12) Nucleic acid synthesis inhibitors, such as benalaxyl, benalaxyl-M (kiralaxyl), bupirimate, clozylacon, dimethirimol, ethirimol, furalaxyl, hymexazole, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl, and oxolinic acid.
13. (13) Signal transduction inhibitors, such as chlozolate, fencpiclonil, fludioxonil, iprodione, procymidone, quinoxifen, and vinclozolin.
14. (14) Decouplers, such as binapacryl, dinocap, ferimzone, fluazinam, and meptyldinocap.

15. (15) Other compounds, such as benthiazole, bethoxazin, capsimycin, carvone, chinomethionat, pyriofenone (chlazafenone), cufraneb, cyflufenamid, cymoxanil, cyprosulphamide, dazomet, debacarb, dichlorophen, diclomezine, difenzoquat, difenzoquat methyl sulphate, diphenylamine, ecomate, fenpyrazamine, flumetover, fluoromide, flusulphamide, flutianil, fosetyl aluminium, fosetyl calcium, fosetyl sodium, hexachlorobenzene, irumamycin, methasulphocarb, methyl isothiocyanate, metrafenone, mildiomyacin, natamycin, nickel dimethyl dithiocarbamate, nitrothal isopropyl, octhilinone, oxamocarb, oxyfenthiin, pentachlorophenol and its salts, phenothrin, phosphoric acid and its salts, propamocarb fosetilate, propanosine sodium, proquinazid, pyrimorph, (2E)-3-(4-tert-butylphenyl)-3-(2-chloropyridine-4-yl)-1-(morpholin-4-yl)prop-2-en-1-one, (2Z)-3-(4-tert-butylphenyl)-3-(2-chloropyridine-4-yl)-1-(morpholin-4-yl)prop-2-en-1-one, pyrrolnitrin, tebufloquin, tecloftalam, tolnifanid, triazoxide, trichlamide, zarilamide, (3S,6S,7R,8R)-8-benzyl-3-[[{3-[(isobutyryloxy)methoxy]-4-methoxypyridine-2-yl}carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl 2-methylpropanoate, 1-(4-{4-[(5R)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazole-3-yl]-1,3-thiazol-2-yl}piperidine-1-yl)-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]ethanone, 1-(4-{4-[(5S)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazole-3-yl]-1,3-thiazol-2-yl}piperidine-1-yl)-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]ethanone, 1-(4-{4-[5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazole-3-yl]-1,3-thiazol-2-yl}piperidine-1-yl)-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]ethanone, 1-(4-methoxyphenoxy)-3,3-dimethylbutane-2-yl-1H-imidazole-1-carboxylate, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, 2,3-dibutyl-6-chlorothieno[2,3-d]pyrimidine-4(3H)-one, 2,6-dimethyl-1H,5H-[1,4]dithiino[2,3-c:5,6-c']dipyrrole-1,3,5,7(2H,6H)-tetrone, 2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]-1-(4-{4-[(5R)-5-phenyl-4,5-dihydro-1,2-oxazole-3-yl]-1,3-thiazole-2-yl}piperidine-1-yl)ethanone, 2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]-1-(4-{4-[(5S)-5-phenyl-4,5-dihydro-1,2-oxazole-3-yl]-1,3-thiazole-2-yl}piperidine-1-yl)ethanone, 2-[5-methyl-3-(trifluoromethyl)-1H-pyrazole-1-yl]-1-{4-[4-(5-phenyl-4,5-dihydro-1,2-oxazole-3-yl)-1,3-thiazole-2-yl]piperidine-1-yl}ethanone, 2-butoxy-6-iodo-3-propyl-4H-chromen-4-one, 2-chloro-5-[2-chloro-1-(2,6-difluoro-4-methoxyphenyl)-4-methyl-1H-imidazole-5-yl]pyridine, 2-phenylphenol and its salts, 3-(4,4,5-trifluoro-3,3-dimethyl-3,4-dihydroisoquinolin-1-yl)quinoline, 3,4,5-trichloropyridine-2,6-dicarbonitrile, 3-[5-(4-chlorophenyl)-2,3-dimethyl-1,2-oxazolidin-3-yl]pyridine, 3-chloro-5-(4-chlorophenyl)-4-(2,6-

- difluorophenyl)-6-methylpyridazine, 4-(4-chlorophenyl)-5-(2,6-difluorophenyl)-3,6-  
 dimethylpyridazine, 5-amino-1,3,4-thiadiazole-2-thiol, 5-chloro-N'-phenyl-N'-(prop-2-  
 yn-1-yl)thiophene-2-sulphonohydrazide, 5-fluoro-2-[(4-fluorobenzyl)oxy]pyrimidine-  
 4-amine, 5-fluoro-2-[(4-methylbenzyl)oxy]pyrimidine-4-amine, 5-methyl-6-  
 5 octyl[1,2,4]triazolo[1,5-a]pyrimidine-7-amine, ethyl-(2Z)-3-amino-2-cyano-3-  
 phenylprop-2-enoate, N'-(4-{[3-(4-chlorobenzyl)-1,2,4-thiadiazole-5-yl]oxy}-2,5-  
 dimethylphenyl)-N-ethyl-N-methylimidoforamide, N-(4-chlorobenzyl)-3-[3-  
 methoxy-4-(prop-2-yn-1-yloxy)phenyl]propanamide, N-[(4-  
 chlorophenyl)(cyano)methyl]-3-[3-methoxy-4-(prop-2-yn-1-  
 10 yloxy)phenyl]propanamide, N-[(5-bromo-3-chloropyridine-2-yl)methyl]-2,4-  
 dichloropyridine-3-carboxamide, N-[1-(5-bromo-3-chloropyridine-2-yl)ethyl]-2,4-  
 dichloropyridine-3-carboxamide, N-[1-(5-bromo-3-chloropyridine-2-yl)ethyl]-2-fluoro-  
 4-iodopyridine-3-carboxamide, N-[(E)-[(cyclopropylmethoxy)imino][6-  
 (difluoromethoxy)-2,3-difluorophenyl]methyl]-2-phenylacetamide, N-[(Z)-  
 15 [(cyclopropylmethoxy)-imino][6-(difluoromethoxy)-2,3-difluorophenyl]methyl]-2-  
 phenylacetamide, N'-{4-[(3-tert-butyl-4-cyano-1,2-thiazole-5-yl)oxy]-2-chloro-5-  
 methylphenyl}-N-ethyl-N-methylimidoforamide, N-methyl-2-(1-{[5-methyl-3-  
 (trifluoromethyl)-1H-pyrazole-1-yl]acetyl}piperidine-4-yl)-N-(1,2,3,4-  
 tetrahydronaphthalen-1-yl)-1,3-thiazole-4-carboxamide, N-methyl-2-(1-{[5-methyl-3-  
 20 (trifluoromethyl)-1H-pyrazole-1-yl]acetyl}-piperidine-4-yl)-N-[(1R)-1,2,3,4-  
 tetrahydronaphthalen-1-yl]-1,3-thiazole-4-carboxamide, N-methyl-2-(1-{[5-methyl-3-  
 (trifluoromethyl)-1H-pyrazole-1-yl]acetyl}piperidine-4-yl)-N-[(1S)-1,2,3,4-  
 tetrahydronaphthalen-1-yl]-1,3-thiazole-4-carboxamide, pentyl-{6-[[[(1-methyl-1H-  
 tetrazole-5-yl)(phenyl)methylidene]amino]oxy)methyl]pyridine-2-yl}carbamate,  
 25 phenazine-1-carboxylic acid, quinolin-8-ol, quinolin-8-olsulphate(2:1), and tert-butyl  
 {6-[[[(1-methyl-1H-tetrazole-5-yl)(phenyl)methylene]amino]oxy)methyl]pyridine-2-  
 yl}carbamate.
16. (16) Other compounds, such as 1-methyl-3-(trifluoromethyl)-N-[2'-  
 (trifluoromethyl)biphenyl-2-yl]-1H-pyrazole-4-carboxamide, N-(4'-chlorobiphenyl-2-yl)-3-  
 30 (difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, N-(2',4'-dichlorobiphenyl-2-yl)-3-  
 (difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, 3-(difluoromethyl)-1-methyl-N-  
 [4'-(trifluoromethyl)biphenyl-2-yl]-1H-pyrazole-4-carboxamide, N-(2',5'-difluorobiphenyl-  
 2-yl)-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-carboxamide, 3-(difluoromethyl)-1-  
 methyl-N-[4'-(prop-1-yn-1-yl)biphenyl-2-yl]-1H-pyrazole-4-carboxamide, 5-fluoro-1,3-

dimethyl-N-[4'-(prop-1-yn-1-yl)biphenyl-2-yl]-1H-pyrazole-4-carboxamide, 2-chloro-N-  
 [4'-(prop-1-yn-1-yl)biphenyl-2-yl]pyridine-3-carboxamide, 3-(difluoromethyl)-N-[4'-(3,3-  
 dimethylbut-1-yn-1-yl)biphenyl-2-yl]-1-methyl-1H-pyrazole-4-carboxamide, N-[4'-(3,3-  
 dimethylbut-1-yn-1-yl)biphenyl-2-yl]-5-fluoro-1,3-dimethyl-1H-pyrazole-4-carboxamide,  
 5 3-(difluoromethyl)-N-(4'-ethynylbiphenyl-2-yl)-1-methyl-1H-pyrazole-4-carboxamide, N-  
 (4'-ethynylbiphenyl-2-yl)-5-fluoro-1,3-dimethyl-1H-pyrazole-4-carboxamide, 2-chloro-N-  
 (4'-ethynylbiphenyl-2-yl)pyridine-3-carboxamide, 2-chloro-N-[4'-(3,3-dimethylbut-1-yn-1-  
 yl)biphenyl-2-yl]pyridine-3-carboxamide, 4-(difluoromethyl)-2-methyl-N-[4'-  
 (trifluoromethyl)biphenyl-2-yl]-1,3-thiazole-5-carboxamide, 5-fluoro-N-[4'-(3-hydroxy-3-  
 10 methylbut-1-yn-1-yl)biphenyl-2-yl]-1,3-dimethyl-1H-pyrazole-4-carboxamide, 2-chloro-  
 N-[4'-(3-hydroxy-3-methylbut-1-yn-1-yl)biphenyl-2-yl]pyridine-3-carboxamide, 3-  
 (difluoromethyl)-N-[4'-(3-methoxy-3-methylbut-1-yn-1-yl)biphenyl-2-yl]-1-methyl-1H-  
 pyrazole-4-carboxamide, 5-fluoro-N-[4'-(3-methoxy-3-methylbut-1-yn-1-yl)biphenyl-2-  
 yl]-1,3-dimethyl-1H-pyrazole-4-carboxamide, 2-chloro-N-[4'-(3-methoxy-3-methylbut-1-  
 15 yn-1-yl)biphenyl-2-yl]pyridine-3-carboxamide, (5-bromo-2-methoxy-4-methylpyridine-3-  
 yl)(2,3,4-trimethoxy-6-methylphenyl)methanone, N-[2-(4-[[3-(4-chlorophenyl)prop-2-  
 yn-1-yl]oxy]-3-methoxyphenyl)ethyl]-N2-(methylsulphonyl)valinamide, 4-oxo-4-[(2-  
 phenylethyl)amino]butyric acid, and but-3-yn-1-yl {6-[[[(Z)-(1-methyl-1H-tetrazole-5-  
 yl)(phenyl)methylene]amino]oxy)methyl]pyridine-2-yl}carbamate.

20

**[0037]** All mentioned mixing partners of classes (1) through (16) can, if they are able to do so based upon their functional groups, form salts, where appropriate, with suitable bases or acids.

25

**[0038]** Mentioned as examples of bactericides are the following:

Bronopol, dichlorophen, nitrapyrin, nickel dimethyl dithiocarbamate, kasugamycin, oclothilone, furan carboxylic acid, oxytetracycline, probenazole, streptomycin, tecloftalam, copper sulphate, and other copper preparations.

30

**[0039]** Mentioned as examples of insecticides, acaricides, and nematocides are:

The active ingredients mentioned here by their common names are known and described in, for example, the pesticide manual ("The Pesticide Manual" 14th ed., British Crop

Protection Council 2006) or can be searched for on the Internet (e.g., <http://www.alanwood.net/pesticides>).

- (1) Acetylcholinesterase (AChE) inhibitors, such as carbamates, e.g., alanycarb, aldicarb, bendiocarb, benfuracarb, butocarboxim, 5 butoxycarboxim, carbaryl, carbofuran, carbosulphan, ethiofencarb, fenobucarb, formetanate, furathiocarb, isoprocarb, methiocarb, methomyl, metolcarb, oxamyl, pirimicarb, propoxur, thiodicarb, thiofanox, triazamate, trimethacarb, XMC, and xylylcarb; or
- organophosphates, e.g., acephate, azamethiphos, azinphos-ethyl, azinphos-methyl, 10 cadusafos, chlorethoxyfos, chlorfenvinphos, chlormephos, chlorpyrifos, chlorpyrifos-methyl, coumaphos, cyanophos, demeton-S-methyl, diazinon, dichlorvos/DDVP, dicrotophos, dimethoate, dimethylvinphos, disulphoton, EPN, ethion, ethoprophos, famphur, fenamiphos, fenitrothion, fenthion, fosthiazate, heptenophos, imicyafos, isofenphos, isopropyl O-(methoxyaminothio-phosphoryl) salicylate, isoxathion, malathion, 15 mecarbam, methamidophos, methidathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phenthoate, phorate, phosalone, phosmet, phosphamidon, phoxim, pirimiphos-methyl, profenofos, propetamphos, prothiofos, pyraclofos, pyridaphenthion, quinalphos, sulphotep, tebupirimfos, temephos, terbufos, tetrachlorvinphos, thiometon, triazophos, trichlorfon, and vamidothion.
- 20 (2) GABA-gated chloride channel antagonists, such as cyclodiene organochlorines, e.g., chlordane and endosulphan; or phenylpyrazole (fiprole), e.g., ethiprole and fipronil.
- (3) Sodium channel modulators / voltage-dependent sodium channel blockers, such as pyrethroids, e.g., acrinathrin, allethrin, d-cis-trans allethrin, d-trans allethrin, bifenthrin, 25 bioallethrin, bioallethrin S-cyclopentenyl isomer, bioresmethrin, cycloprothrin, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, gamma-cyhalothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, theta-cypermethrin, zeta-cypermethrin, cyphenothrin [(1R)-trans-isomers], deltamethrin, empenthrin [(EZ)-(1R)-isomers], esfenvalerate, etofenprox, fenpropathrin, fenvalerate, flucythrinate, flumethrin, tau-fluvalinate, halfenprox, 30 imiprothrin, kadethrin, permethrin, phenothrin [(1R)-trans-isomer], prallethrin, pyrethrins (pyrethrum), resmethrin, silafluofen, tefluthrin, tetramethrin, tetramethrin [(1R)- isomers], tralomethrin and transfluthrin; or DDT; or methoxychlor.
- (4) Nicotinergic acetylcholine receptor (nAChR) agonists, such as

neonicotinoids, e.g., acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, and thiamethoxam; or nicotine.

- 5 (5) Nicotinerpic acetylcholine receptor (nAChR) allosteric activators, such as spinosyns, e.g., spinetoram and spinosad.
- (6) Chloride channel activators, such as avermectins/milbemycins, e.g., abamectin, emamectin benzoate, lepimectin, and milbemectin.
- 10 (7) Juvenile hormone imitators, such as juvenile hormone analogues, e.g., hydroprene, kinoprene, and methoprene; or fenoxycarb; or pyriproxyfen.
- (8) Active ingredients with unknown or non-specific mode of action, such as alkyl halides, e.g., methyl bromide and other alkyl halides; or chloropicrin; or sulphuryl fluoride; or borax; or tartar emetic.
- 15 (9) Selective antifeedants, e.g., pymetrozine; or flonicamid.
- (10) Mite growth inhibitors, e.g., clofentezine, hexythiazox, and diflovidazin; or etoxazole.
- (11) Microbial disruptors of the insect gut membrane, such as *Bacillus thuringiensis* subspecies *israelensis*, *Bacillus sphaericus*, *Bacillus thuringiensis* subspecies *aizawai*,  
 20 *Bacillus thuringiensis* subspecies *kurstaki*, *Bacillus thuringiensis* subspecies *tenebrionis*, and BT plant proteins: Cry1Ab, Cry1Ac, Cry1Fa, Cry2Ab, mCry3A, Cry3Ab, Cry3Bb, Cry34/35Ab1.
- (12) Oxidative phosphorylation inhibitors, ATP disruptors, such as diafenthiuron; or organotin compounds, e.g., azocyclotin, cyhexatin, and fenbutatin oxide; or  
 25 propargite; or tetradifon.
- (13) Oxidative phosphorylation decouplers acting by interrupting the H proton gradient, such as chlorfenapyr, DNOC, and sulphuramid.
- (14) Nicotinerpic acetylcholine receptor antagonists, such as bensultap, cartap hydrochloride, thiocyclam, and thiosultap sodium.
- 30 (15) Chitin biosynthesis inhibitors, type 0, such as bistrifluron, chlorfluazuron, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron, teflubenzuron, and triflumuron.
- (16) Chitin biosynthesis inhibitors, type 1, such as buprofezin.
- (17) Moulting disruptors, dipteran, such as cyromazine.

- (18) Ecdysone receptor agonists, such as chromafenozide, halofenozide, methoxyfenozide, and tebufenozide.
- (19) Octoparninergic agonists, such as amitraz.
- (20) Complex III electron transport inhibitors, such as hydramethylnon; or acequinocyl; or  
5 fluacrypyrim.
- (21) Complex I electron transport inhibitors - for example, METI acaricides, e.g., fenazaquin, fenpyroximate, pyrimidifen, pyridaben, tebufenpyrad, and tolfenpyrad; or rotenone (Derris).
- 10 (22) Voltage-dependent sodium channel blockers, e.g., indoxacarb; or metaflumizone.
- (23) Inhibitors of acetyl-CoA carboxylase, such as tetrone and tetramic acid derivatives, e.g., spirodiclofen, spiromesifen, and spirotetramat.
- (24) Complex IV electron transport inhibitors, such as  
15 phosphines, e.g., aluminium phosphide, calcium phosphide, phosphine, and zinc phosphide; or cyanide.
- (25) Complex II electron transport inhibitors, e.g., cyenopyrafen.
- (28) Ryanodine receptor effectors, such as  
20 diamides, e.g., chlorantraniliprole and flubendiamide.

**[0040]** Further active ingredients with unknown mode of action, such as amidoflumet, azadirachtin, benclothiaz, benzoximate, bifenazate, bromopropylate, chinomethionat, cryolite, cyantraniliprole (cyazypyr), cyflumetofen, dicofol, diflovidazin, fluensulphone, flufenerim,  
25 flufiprole, fluopyram, fufenozide, imidaclothiz, iprodione, pyridalyl, pyrifluquinazon, and iodomethane; and also products based upon *Bacillus firmus* (I-1582, BioNeem, Votivo), as well as the following known active compounds:

3-bromo-N-{2-bromo-4-chloro-6-[(1-cyclopropylethyl)carbamoyle]phenyl}-1-(3-chloropyridine-2-yl)-1H-pyrazole-5-carboxamide (known from WO2005/077934), 4-[[[(6-bromopyrid-3-yl)methyl](2-fluoroethyl)amino]furan-2(5H)-one (known from WO2007/115644), 4-[[[(6-fluoropyrid-3-yl)methyl](2,2-difluoroethyl)amino]furan-2(5H)-one (known from  
30 WO2007/115644), 4-[[[(2-chloro-1,3-thiazole-5-yl)methyl](2-fluoroethyl)amino]furan-2(5H)-one (known from WO2007/115644), 4-[[[(6-chloropyrid-3-yl)methyl](2-fluoroethyl)amino]furan-2(5H)-one (known from WO2007/115644), 4-[[[(6-chloropyrid-3-

yl)methyl](2,2-difluoroethyl)amino}furan-2(5H)-one (known from WO2007/115644), 4-[[[(6-chloro-5-fluoropyrid-3-yl)methyl](methyl)amino}furan-2(5H)-one (known from WO2007/115643), 4-[[[(5,6-dichloropyrid-3-yl)methyl](2-fluoroethyl)amino}furan-2(5H)-one (known from WO2007/115646), 4-[[[(6-chloro-5-fluoropyrid-3-yl)methyl](cyclopropyl)amino}furan-2(5H)-one (known from WO2007/115643), 4-[[[(6-chloropyrid-3-yl)methyl](cyclopropyl)amino}furan-2(5H)-one (known from EP-A-0 539 588), 4-[[[(6-chloropyrid-3-yl)methyl](methyl)amino}furan-2(5H)-one (known from EP-A-0539588), [[1-(6-chloropyridine-3-yl)ethyl](methyl)oxido- $\lambda^4$ -sulphanylidene]cyanamide (known from WO2007/149134), and its diastereomers [[(1R)-1-(6-chloropyridine-3-yl)ethyl](methyl)oxido- $\lambda^4$ -sulphanylidene]cyanamide (A), and [[(1S)-1-(6-chloropyridine-3-yl)ethyl](methyl)oxido- $\lambda^4$ -sulphanylidene]cyanamide (B) (also known from WO2007/149134) as well as sulphoxaflor (also known from WO2007/149134), and its diastereomers [(R)-methyl(oxido){(1R)-1-[6-(trifluoromethyl)pyridin-3-yl]ethyl}- $\lambda^4$ -sulphanylidene]cyanamide (A1), and [(S)-methyl(oxido){(1S)-1-[6-(trifluoromethyl)pyridine-3-yl]ethyl}- $\lambda^4$ -sulphanylidene]cyanamide (A2), called diastereomer group A (known from WO 2010/074747, WO 2010/074751), [(R)-methyl(oxido){(1S)-1-[6-(trifluoromethyl)pyridin-3-yl]ethyl}- $\lambda^4$ -sulphanylidene]cyanamide (B1), and [(S)-methyl(oxido){(1R)-1-[6-(trifluoromethyl)pyridine-3-yl]ethyl}- $\lambda^4$ -sulphanylidene]cyanamide (B2), called diastereomer group B (also known from WO 2010/074747, WO 2010/074751), and 11-(4-chloro-2,6-dimethylphenyl)-12-hydroxy-1,4-dioxo-9-azadispiro[4.2.4.2]tetradec-11-en-10-one (known from WO2006/089633), 3-(4'-fluoro-2,4-dimethylbiphenyl-3-yl)-4-hydroxy-8-oxa-1-azaspiro[4.5]dec-3-en-2-one (known from WO2008/067911), 1-{2-fluoro-4-methyl-5-[(2,2,2-trifluoroethyl)sulphinyl]phenyl}-3-(trifluoromethyl)-1H-1,2,4-triazole-5-amine (known from WO2006/043635), [(3S,4aR,12R,12aS,12bS)-3-[(cyclopropylcarbonyl)oxy]-6,12-dihydroxy-4,12b-dimethyl-11-oxo-9-(pyridine-3-yl)-1,3,4,4a,5,6,6a,12,12a,12b-decahydro-2H,11H-benzo[f]pyrano[4,3-b]chromen-4-yl]methylcyclopropanecarboxylate (known from WO2008/066153), 2-cyano-3-(difluoromethoxy)-N,N-dimethylbenzenesulphonamide (known from WO2006/056433), 2-cyano-3-(difluoromethoxy)-N-methylbenzenesulphonamide (known from WO2006/100288), 2-cyano-3-(difluoromethoxy)-N-ethylbenzenesulphonamide (known from WO2005/035486), 4-(difluoromethoxy)-N-ethyl-N-methyl-1,2-benzothiazol-3-amine-1,1-dioxide (known from WO2007/057407), N-[1-(2,3-dimethylphenyl)-2-(3,5-dimethylphenyl)ethyl]-4,5-dihydro-1,3-thiazole-2-amine (known from WO2008/104503), {1'-[(2E)-3-(4-chlorophenyl)prop-2-en-1-yl]-5-fluorospiro[indole-3,4'-piperidin]-1(2H)-yl}(2-chloropyridine-4-yl)methanone (known

from WO2003/106457), 3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1,8-  
 diazaspiro[4.5]dec-3-en-2-one (known from WO2009/049851), 3-(2,5-dimethylphenyl)-8-  
 methoxy-2-oxo-1,8-diazaspiro[4.5]dec-3-en-4-yl ethyl carbonate (known from  
 WO2009/049851), 4-(but-2-yn-1-yloxy)-6-(3,5-dimethylpiperidin-1-yl)-5-fluoropyrimidine  
 5 (known from WO2004/099160), (2,2,3,3,4,4,5,5-octafluoropentyl)(3,3,3-  
 trifluoropropyl)malononitrile (known from WO2005/063094), (2,2,3,3,4,4,5,5-  
 octafluoropentyl)(3,3,4,4,4-pentafluorobutyl)malononitrile (known from WO2005/063094),  
 8-[2-(cyclopropylmethoxy)-4-(trifluoromethyl)phenoxy]-3-[6-(trifluoromethyl)pyridazine-3-  
 yl]-3-azabicyclo[3.2.1]octane (known from WO2007/040280), 2-ethyl-7-methoxy-3-methyl-  
 10 6-[(2,2,3,3-tetrafluoro-2,3-dihydro-1,4-benzodioxin-6-yl)oxy]quinoline-4-yl methyl carbonate  
 (known from JP2008/110953), 2-ethyl-7-methoxy-3-methyl-6-[(2,2,3,3-tetrafluoro-2,3-  
 dihydro-1,4-benzodioxin-6-yl)oxy]quinoline-4-yl acetate (known from JP2008/110953),  
 PF1364 (CAS reg. no. 1204776-60-2) (known from JP2010/018586), 5-[5-(3,5-  
 dichlorophenyl)-5-(trifluoromethyl)-4,5-dihydro-1,2-oxazole-3-yl]-2-(1H-1,2,4-triazole-1-  
 15 yl)benzonitrile (known from WO2007/075459), 5-[5-(2-chloropyridine-4-yl)-5-  
 (trifluoromethyl)-4,5-dihydro-1,2-oxazole-3-yl]-2-(1H-1,2,4-triazole-1-yl)benzonitrile (known  
 from WO2007/075459), 4-[5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4,5-dihydro-1,2-  
 oxazole-3-yl]-2-methyl-N-{2-oxo-2-[(2,2,2-trifluoroethyl)amino]ethyl}benzamide (known  
 from WO2005/085216), 4-[[[(6-chloropyridine-3-yl)methyl](cyclopropyl)amino]-1,3-oxazole-  
 20 2(5H)-one, 4-[[[(6-chloropyridine-3-yl)methyl](2,2-difluoroethyl)amino]-1,3-oxazole-2(5H)-  
 one, 4-[[[(6-chloropyridine-3-yl)methyl](ethyl)amino]-1,3-oxazole-2(5H)-one, 4-[[[(6-  
 chloropyridine-3-yl)methyl](methyl)amino]-1,3-oxazole-2(5H)-one (all known from  
 WO2010/005692), NNI-0711 (known from WO2002/096882), 1-acetyl-N-[4-(1,1,1,3,3,3-  
 hexafluoro-2-methoxypropane-2-yl)-3-isobutylphenyl]-N-isobutyryl-3,5-dimethyl-1H-  
 25 pyrazole-4-carboxamide (known from WO2002/096882), methyl-2-[2-({[3-bromo-1-(3-  
 chloropyridine-2-yl)-1H-pyrazole-5-yl]carbonyl}amino)-5-chloro-3-methylbenzoyl]-2-  
 methylhydrazinecarboxylate (known from WO2005/085216), methyl-2-[2-({[3-bromo-1-(3-  
 chloropyridine-2-yl)-1H-pyrazole-5-yl]carbonyl}amino)-5-cyano-3-methylbenzoyl]-2-  
 ethylhydrazinecarboxylate (known from WO2005/085216), methyl-2-[2-({[3-bromo-1-(3-  
 30 chloropyridine-2-yl)-1H-pyrazole-5-yl]carbonyl}amino)-5-cyano-3-methylbenzoyl]-2-  
 methylhydrazinecarboxylate (known from WO2005/085216), methyl-2-[3,5-dibromo-2-({[3-  
 bromo-1-(3-chloropyridine-2-yl)-1H-pyrazole-5-yl]carbonyl}amino)benzoyl]-1,2-  
 diethylhydrazinecarboxylate (known from WO2005/085216), methyl-2-[3,5-dibromo-2-({[3-  
 bromo-1-(3-chloropyridine-2-yl)-1H-pyrazole-5-yl]carbonyl}amino)benzoyl]-2-

ethylhydrazinecarboxylate (known from WO2005/085216), (5RS,7RS;5RS,7SR)-1-(6-chloro-3-pyridylmethyl)-1,2,3,5,6,7-hexahydro-7-methyl-8-nitro-5-propoxyimidazo[1,2-a]pyridine (known from WO2007/101369), 2-{6-[2-(5-fluoropyridine-3-yl)-1,3-thiazole-5-yl]pyridine-2-yl}pyrimidine (known from WO2010/006713), 2-{6-[2-(pyridine-3-yl)-1,3-thiazole-5-yl]pyridine-2-yl}pyrimidine (known from WO2010/006713), 1-(3-chloropyridine-2-yl)-N-[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]-3-[[5-(trifluoromethyl)-1H-tetrazole-1-yl]methyl]-1H-pyrazole-5-carboxamide (known from WO2010/069502), 1-(3-chloropyridine-2-yl)-N-[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]-3-[[5-(trifluoromethyl)-2H-tetrazole-2-yl]methyl]-1H-pyrazole-5-carboxamide (known from WO2010/069502), N-[2-(tert-butylcarbamoyl)-4-cyano-6-methylphenyl]-1-(3-chloropyridine-2-yl)-3-[[5-(trifluoromethyl)-1H-tetrazole-1-yl]methyl]-1H-pyrazole-5-carboxamide (known from WO2010/069502), N-[2-(tert-butylcarbamoyl)-4-cyano-6-methylphenyl]-1-(3-chloropyridine-2-yl)-3-[[5-(trifluoromethyl)-2H-tetrazole-2-yl]methyl]-1H-pyrazole-5-carboxamide (known from WO2010/069502), and (1E)-N-[(6-chloropyridine-3-yl)methyl]-N'-cyano-N-(2,2-difluoroethyl)ethanimidamide (known from WO2008/009360).

**[0041]** Mentioned as examples of herbicides are the following:

As combination partners for the compounds according to the invention in mixture formulations or in the tank-mix, known active ingredients, for example, can be used, based upon inhibition of, for example, acetolactate synthase, acetyl-CoA carboxylase, cellulose synthase, enolpyruvylshikimate-3-phosphate synthase, glutamine synthetase, p-hydroxyphenylpyruvate dioxygenase, phytoendesaturase, photosystem I, photosystem II, protoporphyrinogen oxidase, as described in, for example, Weed Research 26 (1986), 441-445, or "The Pesticide Manual", 15th edition, The British Crop Protection Council and the Royal Soc. of Chemistry, 2006, and literature cited there. To be mentioned as known herbicides or plant growth regulators which can be combined with the compounds according to the invention are, for example, the following active ingredients (the compounds are designated by the common name according to the International Organisation for Standardisation (ISO), or by the chemical name, or by the code number) and always encompass all modes of application, such as acids, salts, esters, and isomers, such as stereoisomers and optical isomers. In this case, one, and, in part, also several modes of application are mentioned by way of example: acetochlor, acibenzolar, acibenzolar-S-methyl, acifluorfen, acifluorfen-sodium, aclonifen, alachlor, allidochlor, alloxydim, alloxydim-sodium, ametryne, amicarbazone, amidochlor,

amidosulphuron, aminocyclopyrachlor, aminocyclopyrachlor-potassium,  
 aminocyclopyrachlor-methyl, aminopyralid, amitrole, ammonium sulphamate, ancymidol,  
 anilofos, asulam, atrazine, aviglycine, azafenidin, azimsulphuron, aziprotryne,  
 beflubutamid, benazolin, benazolin-ethyl, bencarbazon, benfluralin, benfuresate,  
 5 bensulide, bensulphuron, bensulphuron-methyl, bentazone, benzfendizone,  
 benzobicyclon, benzofenap, benzofluor, benzoylprop, benzyladenine, bicyclopyrone,  
 bifenox, bilanafos, bilanafos-sodium, bispyribac, bispyribac-sodium, bromacil,  
 bromobutide, bromofenoxim, bromoxynil, bromuron, buminafos, busoxinone, butachlor,  
 butafenacil, butamifos, butenachlor, butralin, butroxydim, butylate, cafenstrole, carbaryl,  
 10 carbetamide, carfentrazone, carfentrazone-ethyl, carvone, chlorocholine chloride,  
 chlomethoxyfen, chloramben, chlorazifop, chlorazifop-butyl, chlorbromuron, chlorbufam,  
 chlorfenac, chlorfenac-sodium, chlorfenprop, chlorflurenol, chlorflurenol-methyl,  
 chloridazon, chlorimuron, chlorimuron-ethyl, chlormequat-chloride, chlornitrofen, 4-  
 chlorophenoxyacetic acid, chlorophthalim, chlorpropham, chlorthal-dimethyl, chlorotoluron,  
 15 chlorsulphuron, cinidon, cinidon-ethyl, cinmethylin, cinosulphuron, clethodim, clodinafop,  
 clodinafop-propargyl, clofencet, clomazone, clomeprop, cloprop, clopyralid, cloransulam,  
 cloransulam-methyl, cloxyfonac, cumyluron, cyanamide, cyanazine, cyclanilide, cycloate,  
 cyclosulphamuron, cycloxydim, cycluron, cyhalofop, cyhalofop-butyl, cyperquat, cyprazine,  
 cyprazole, cytokinine, 2,4-D, 2,4-DB, daimuron/dymron, dalapon, daminozide, dazomet, n-  
 20 decanol, desmedipham, desmetryn, detosyl-pyrazolate (DTP), diallate, diaminozide,  
 dicamba, dichlobenil, dichlorprop, dichlorprop-P, diclofop, diclofop-methyl, diclofop-P-  
 methyl, diclosulam, diethatyl, diethatyl-ethyl, difenoxuron, difenzoquat, diflufenican,  
 diflufenzopyr, diflufenzopyr-sodium, dikegulac-sodium, dimefuron, dimepiperate,  
 dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, dimethipin,  
 25 dimetrasulphuron, dinitramine, dinoseb, dinoterb, diphenamid, diisopropyl-naphthalene,  
 dipropetryn, diquat, diquat-dibromide, dithiopyr, diuron, DNOC, eglinazone-ethyl, endothal,  
 EPTC, esprocarb, ethalfluralin, ethametsulphuron, ethametsulphuron-methyl, ethyl  
 naphthyl acetate, ethephon, ethidimuron, ethiozin, ethofumesate, ethoxyfen, ethoxyfen-  
 ethyl, ethoxysulphuron, etobenzanid, F-5331, i.e., N-[2-chloro-4-fluoro-5-[4-(3-  
 30 fluoropropyl)-4,5-dihydro-5-oxo-1H-tetrazole-1-yl]phenyl]-ethanesulphonamide, F-7967,  
 i.e., 3-[7-chloro-5-fluoro-2-(trifluoromethyl)-1H-benzimidazole-4-yl]-1-methyl-6-  
 (trifluoromethyl)pyrimidine-2,4(1H,3H)-dione, fenoprop, fenoxaprop, fenoxaprop-P,  
 fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenoxasulphone, fentrazamide, fenuron, flamprop,  
 flamprop-M-isopropyl, flamprop-M-methyl, flazasulphuron, florasulam, fluazifop, fluazifop-

P, fluazifop-butyl, fluazifop-P-butyl, fluazolate, flucarbazone, flucarbazone-sodium, flucetosulphuron, fluchloralin, flufenacet (thiafluamide), flufenpyr, flufenpyr-ethyl, flumetralin, flumetsulam, flumiclorac, flumiclorac-pentyl, flumioxazin, flumipropyn, fluometuron, fluorodifen, fluoroglycofen, fluoroglycofen-ethyl, flupoxam, fluproacil,

5 flupropanate, flupyrsulphuron, flupyrsulphuron-methyl-sodium, flurenol, flurenol-butyl, fluridone, flurochloridone, fluroxypyr, fluroxypyr-meptyl, flurprimidol, flurtamone, fluthiacet, fluthiacet-methyl, fluthiamide, fomesafen, foramsulphuron, forchlorfenuron, fosamine, furyloxyfen, gibberellic acid, glufosinate, glufosinate-ammonium, glufosinate-P, glufosinate-P-ammonium, glufosinate-P-sodium, glyphosate, glyphosate-

10 isopropylammonium, H-9201, i.e., 0-(2,4-dimethyl-6-nitrophenyl)-O-ethyl isopropylphosphoramidothioate, halosafen, halosulphuron, halosulphuron-methyl, haloxyfop, haloxyfop-P, haloxyfop-ethoxyethyl, haloxyfop-P-ethoxyethyl, haloxyfop-methyl, haloxyfop-P-methyl, hexazinone, HW-02, i.e., 1-(dimethoxyphosphoryl)ethyl (2,4-dichlorophenoxy)acetate, imazamethabenz, imazamethabenz-methyl, imazamox,

15 imazamox-ammonium, imazapic, imazapyr, imazapyr-isopropylammonium, imazaquin, imazaquin-ammonium, imazethapyr, imazethapyr-ammonium, imazosulphuron, inabenfide, indanofan, indaziflam, indoleacetic acid (IAA), 4-indol-3-ylbutyric acid (IBA), iodosalphuron, iodosalphuron-methyl-sodium, iofensulphuron, iofensulphuron-sodium, ioxynil, ipfencarbazone, isocarbamid, isopropalin, isoproturon, isouron, isoxaben,

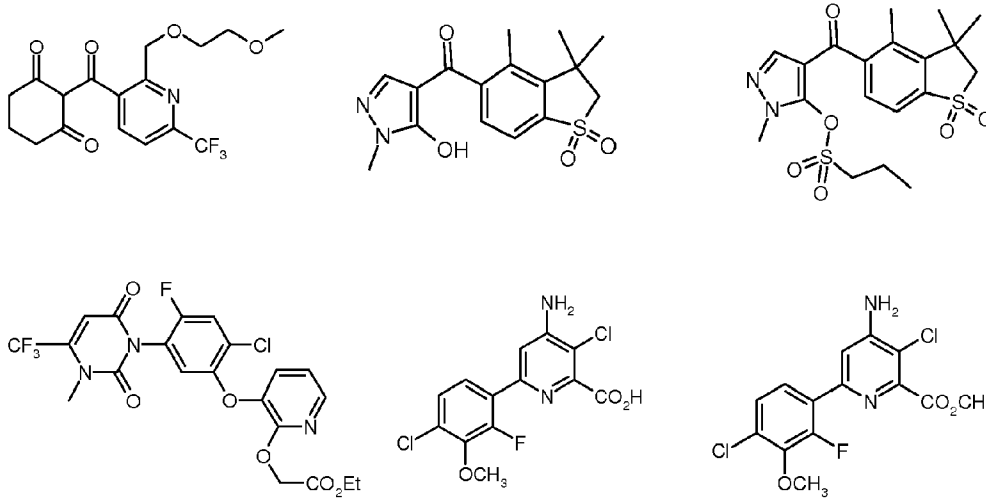
20 isoxachlortole, isoxaflutole, isoxapyrifop, KUH-043, i.e., 3-({[5-(difluoromethyl)-1-methyl-3-(trifluoromethyl)-1H-pyrazole-4-yl]methyl}sulphonyl)-5,5-dimethyl-4,5-dihydro-1,2-oxazole, karbutilate, ketospiradox, lactofen, lenacil, linuron, maleic hydrazide, MCPA, MCPB, MCPB-methyl, -ethyl and -sodium, mecoprop, mecoprop-sodium, mecoprop-butotyl, mecoprop-P-butotyl, mecoprop-P-

25 dimethylammonium, mecoprop-P-2-ethylhexyl, mecoprop-P-potassium, mefenacet, mefluidide, mepiquat-chloride, mesosalphuron, mesosalphuron-methyl, mesotrione, methabenzthiazuron, metam, metamifop, metamitron, metazachlor, metazasulphuron, methazole, methiopyrsulphuron, methiozolin, methoxyphenone, methylodymron, 1-methylcyclopropene, methyl isothiocyanate, metobenzuron, metobromuron, metolachlor,

30 S-metolachlor, metosulam, metoxuron, metribuzin, metsulphuron, metsulphuron-methyl, molinate, monalide, monocarbamide, monocarbamide dihydrogensulphate, monolinuron, monosalphuron, monosalphuron ester, monuron, MT-128, i.e., 6-chloro-N-[(2E)-3-chloroprop-2-en-1-yl]-5-methyl-N-phenylpyridazin-3-amine, MT-5950, i.e., N-[3-chloro-4-(1-methylethyl)phenyl]-2-methylpentanamide, NGGC-011, 1-naphthyl acetic acid (NAA),

naphthyl acetamide (NAAm), 2-naphthoxyacetic acid, naproanilide, napropamide,  
 naptalam, NC-310, i.e., 4-(2,4-dichlorobenzoyl)-1-methyl-5-benzoyloxy pyrazole, neburon,  
 nicosulphuron, nipyraclufen, nitralin, nitrofen, nitroguaiacolate, nitrophenolate-sodium  
 (isomer mixture), nitrofluorfen, nonanoic acid, norflurazon, orbencarb, orthosulphamuron,  
 5 oryzalin, oxadiargyl, oxadiazon, oxasulphuron, oxaziclomefone, oxyfluorfen,  
 paclobutrazole, paraquat, paraquat dichloride, pelargonic acid (nonanoic acid),  
 pendimethalin, pendralin, penoxsulam, pentanochlor, pentoxazone, perfluidone,  
 pethoxamid, phenisopham, phenmedipham, phenmedipham-ethyl, picloram, picolinafen,  
 pinoxaden, piperophos, pirifenop, pirifenop-butyl, pretilachlor, primisulphuron,  
 10 primisulphuron-methyl, probenazole, profluazole, procyazine, prodiamine, prifluraline,  
 profoxydim, prohexadione, prohexadione-calcium, prohydrojasnone, prometon,  
 prometryn, propachlor, propanil, propaquizafop, propazine, propham, propisochlor,  
 propoxycarbazone, propoxycarbazone-sodium, propyrisulphuron, propyzamide,  
 prosulphalin, prosulphocarb, prosulphuron, prynachlor, pyraclonil, pyraflufen, pyraflufen-  
 15 ethyl, pyrasulphotole, pyrazolynate (pyrazolate), pyrazosulphuron, pyrazosulphuron-ethyl,  
 pyrazoxyfen, pyribambenz, pyribambenz-isopropyl, pyribambenz-propyl, pyribenzoxim,  
 pyributicarb, pyridafol, pyridate, pyrifitalid, pyriminobac, pyriminobac-methyl, pyrimisulphan,  
 pyriothiobac, pyriothiobac-sodium, pyroxasulphone, pyroxsulam, quinclorac, quinmerac,  
 quinochloramine, quizalofop, quizalofop-ethyl, quizalofop-P, quizalofop-P-ethyl, quizalofop-P-  
 20 tefuryl, rimsulphuron, saflufenacil, sebumeton, sethoxydim, siduron, simazine, simetryn,  
 SN-106279, i.e., methyl (2R)-2-({7-[2-chloro-4-(trifluoromethyl)phenoxy]-2-  
 naphthyl}oxy)propanoate, sulcotrione, sulphallate (CDEC), sulphentrazone,  
 sulphometuron, sulphometuron-methyl, sulphosate (glyphosate-trimesium),  
 sulphosulphuron, SW-065, SYN-523, SYP-249, i.e., 1-ethoxy-3-methyl-1-oxobut-3-en-2-yl-  
 25 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate, SYP-300, i.e., 1-[7-fluoro-3-oxo-4-  
 (prop-2-yn-1-yl)-3,4-dihydro-2H-1,4-benzoxazin-6-yl]-3-propyl-2-thioxoimidazolidine-4,5-  
 dione, tebutam, tebuthiuron, tecnazene, tefuryltrione, tembotrione, tepraloxydim, terbacil,  
 terbucarb, terbuchlor, terbumeton, terbuthylazine, terbutryne, thenylchlor, thiaflumide,  
 thiazafluron, thiazopyr, thidiazimin, thidiazuron, thiencarbazone, thiencarbazone-methyl,  
 30 thifensulphuron, thifensulphuron-methyl, thiobencarb, tiocarbazil, topramezone,  
 tralkoxydim, triafamone, triallate, triasulphuron, triaziflam, triazofenamamide, tribenuron,  
 tribenuron-methyl, tribufos, trichloroacetic acid (TCA), triclopyr, tridiphane, trietazine,  
 trifloxysulphuron, trifloxysulphuron-sodium, trifluralin, triflusulphuron, triflusulphuron-  
 methyl, trimeturon, trinexapac, trinexapac-ethyl, tritosulphuron, tsitodef, uniconazole,

uniconazole-P, vernolate, ZJ-0862, i.e., 3,4-dichloro-N-{2-[(4,6-dimethoxypyrimidine-2-yl)oxy]benzyl}aniline, as well as the following compounds:



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**[0042]** Mentioned further as examples of plant growth regulators are natural plant hormones, such as abscisic acid, jasmonic acid, salicylic acid and their esters, kinetin, and brassinosteroids.

**[0043]** Mentioned as examples of plant nutrients are conventional inorganic or organic fertilisers for providing plants with macronutrients and/or micronutrients.

**[0044]** Mentioned as examples of repellents are diethyltolylamide, ethylhexanediol, and butopyronoxyl.

**[0045]** Preferred active agrochemical ingredients are butenolides, neonicotinoids, triazoles, and strobilurins - especially, flupyradifurone, imidacloprid, thiacloprid, cyproconazole, epoxiconazole, metconazole, prothioconazole, tebuconazole, as well as azoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, picoxystrobin, pyraclostrobin, and trifloxystrobin. Preferred also are all systemic leaf-applied or post-emergence herbicides and safeners - especially, amidosulphuron, bromoxynil, cyprosulphamide, 2,4-D, glufosinate, glyphosate, iodosulphuron-methyl, isoxadifen-ethyl, mefenpyr, mesosulphuron, mesotrione, metamitron, phenmedipham, sulcotrione, tembotrione, and thien carbazon-methyl.

25

**[0046]** The present invention furthermore relates to formulations and modes of application prepared therefrom as plant-protecting agents and/or pesticides, such as drench, drip, and spray liquids, comprising at least one of the active ingredients according to the invention. Where appropriate, the modes of application contain additional plant-protecting agents  
5 and/or pesticides and/or action-improving adjuvants, such as penetration enhancers, e.g., vegetable oils, such as rapeseed oil, sunflower oil, mineral oils, such as paraffin oils, alkyl esters of vegetative fatty acids, such as rapeseed oil methyl ester or soy bean oil methyl ester, or alkanol alkoxyates, and/or spreading agents, such as alkylsiloxanes, and/or salts, e.g., organic or inorganic ammonium or phosphonium salts, such as ammonium sulphate  
10 or diammonium hydrogen phosphate, and/or retention enhancers, such as dioctyl sulphosuccinate or hydroxypropyl guar polymers, and/or humectants, such as glycerol, and/or fertilisers, such as ammonium-, potassium-, or phosphorus-containing fertilisers.

**[0047]** Examples of conventional formulations are water-soluble liquids (SL), emulsifiable  
15 concentrates (EC), emulsions in water (EW), suspension concentrates (SC, SE, FS, OD), water-dispersible granules (WG), granules (GR), and capsule concentrates (CS); these and other possible formulation types are described by, for example, Crop Life International and in Pesticide Specifications, Manual on development and use of FAO and WHO specifications for pesticides, FAO Plant Production and Protection Papers - 173, prepared  
20 by the FAO/WHO Joint Meeting on Pesticide Specifications, 2004, ISBN: 9251048576. Where appropriate, the formulations contain further active agrochemical ingredients in addition to one or more active ingredients according to the invention.

**[0048]** These further ingredients are preferably formulations or modes of application which  
25 contain additives, such as extenders, solvents, spontaneity enhancers, carriers, emulsifiers, dispersants, anti-freezing agents, biocides, thickeners, and/or further additives, such as adjuvants. An adjuvant in this context is a component that enhances the biological effect of the formulation, without the component itself having any biological effect. Examples of adjuvants are agents that enhance retention, spreading behaviour,  
30 adhesion to the leaf surface, or penetration.

**[0049]** These formulations are produced in a known manner, e.g., by mixing the active ingredients with additives, such as extenders, solvents, and/or solid carriers and/or further

additives, such as surface-active agents. The formulations are produced either in suitable facilities or before or during application.

5 **[0050]** Substances that are suitable for imparting special properties, such as certain physical, technical, and/or biological properties, to the formulation of the active ingredient or to the modes of application prepared from these formulations (e.g., ready-to-use plant-protecting agents, such as spray liquids or seed dressing agents) may be used as additives.

10 **[0051]** Suitable as extenders are, for example, water, polar and non-polar organic chemical liquids, e.g., from the classes of the aromatic and non-aromatic hydrocarbons (such as paraffins, alkylbenzenes, alkylnaphthalenes, chlorobenzenes), the alcohols and polyols (which may, where appropriate, also be substituted, etherified, and/or esterified), the ketones (such as acetone, cyclohexanone), esters (including fats and oils), and (poly)ethers, simple and substituted amines, amides, lactams (such as N-  
15 alkylpyrrolidones) and lactones, sulphones and sulphoxides (such as dimethyl sulphoxide).

**[0052]** In case water is used as extender, it is also possible to use, for example, organic solvents as auxiliary solvents. Liquid solvents to be considered are, essentially: aromatics, such as xylene, toluene, or alkylnaphthalenes, chlorinated aromatics or chlorinated  
20 aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes, or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, e.g., crude oil fractions, mineral and vegetable oils, alcohols, such as butanol or glycol and their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone, or cyclohexanone, strongly polar solvents, such as dimethyl formamide and dimethyl sulphoxide, as well as  
25 water.

**[0053]** All suitable solvents may, in principle, be used. Examples of suitable solvents are aromatic hydrocarbons, such as xylene, toluene, or alkylnaphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzene, chloroethylene, or  
30 methylene chloride, aliphatic hydrocarbons, such as cyclohexane, paraffins, crude oil fractions, mineral and vegetable oils, alcohols, such as methanol, ethanol, isopropanol, butanol, or glycol and their ethers and esters, ketones, e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, or cyclohexanone, strongly polar solvents, such as dimethyl sulphoxide, as well as water.

**[0054]** All suitable carriers may, in principle, be used. Carriers to be considered are especially: e.g., ammonium salts and ground natural rocks, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite, or diatomaceous earth, and ground synthetic materials, such as highly dispersed silica, alumina, and natural or synthetic silicates, resins, waxes, and/or solid fertilisers. Mixtures of such carriers may also be used. Carriers for granules to be considered are: e.g., crushed and fractionated natural stone, such as calcite, marble, pumice, sepiolite, dolomite, as well as synthetic granules of inorganic and organic meals, as well as granules of organic material, such as sawdust, paper, coconut shells, maize cobs, and tobacco stalks.

**[0055]** Liquefied gaseous extenders or solvents may also be used. Extenders or carriers that are gaseous at standard temperature and standard pressure, e.g., aerosol propellant gases, such as halohydrocarbons, as well as butane, propane, nitrogen, and carbon dioxide, are particularly suitable.

**[0056]** Examples of emulsifiers and/or foamers, dispersants, or wetters with ionic or non-ionic properties, or mixtures of these surface-active agents, are salts of polyacrylic acid, salts of lignosulphonic acid, salts of phenolsulphonic acid or naphthalenesulphonic acid, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, with substituted phenols (preferably, alkylphenols or arylphenols), salts of sulphosuccinic esters, taurine derivatives (preferably, alkyl taurates), phosphoric esters of polyethoxylated alcohols or phenols, fatty acid esters of polyols, and derivatives of the compounds containing sulphates, sulphonates, and phosphates, e.g., alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates, protein hydrolysates, lignosulphite waste liquors, and methyl cellulose. The presence of a surface-active agent is advantageous if one of the active ingredients and/or one of the inert carriers is not soluble in water and if the application takes place in water.

**[0057]** Present as further additives in the formulations and the modes of application derived therefrom may be dyes, such as inorganic pigments, e.g., iron oxide, titanium oxide, and Prussian Blue, and organic dyes, such as alizarin dyes, azo dyes, and metal phthalocyanine dyes, and nutrients and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum, and zinc.

**[0058]** Also included may be stabilisers, such as cold stabilisers, preservatives, antioxidants, light stabilisers, or other agents improving chemical and/or physical stability. Foamers or defoamers may also be included.

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**[0059]** Moreover, the formulations and the modes of application derived therefrom may also include, as further additives, adhesives, such as carboxymethyl cellulose, natural and synthetic polymers, in the form of powders, granules, or lattices, such as gum arabic, polyvinyl alcohol, polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids. Further additives may be mineral and vegetable oils.

10

**[0060]** Where appropriate, further additives may be included in the formulations and the modes of application derived therefrom. Examples of such additives are fragrances, protective colloids, binders, adhesives, thickeners, thixotropic agents, penetration enhancers, retention enhancers, stabilisers, sequestering agents, complexing agents, humectants, and spreading agents. The active ingredients may generally be combined with any solid or liquid additive that is commonly used for formulation purposes.

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**[0061]** Retention enhancers to be considered are all substances that reduce the dynamic surface tension, such as dioctyl sulphosuccinate, or increase visco-elasticity, such as hydroxypropyl guar polymers.

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**[0062]** Penetration enhancers to be considered in the present context are all substances that are generally used to improve penetration of active agrochemical ingredients into plants. Penetration enhancers are defined in this context by their ability to penetrate from the (generally aqueous) application liquid and/or from the spray coating into the cuticle of the plant and thereby increase the mobility of active ingredients in the cuticle. The method described in the literature (Baur et al., 1997, Pesticide Science 51, 131-152) may be used to determine this property. Examples are alcohol alkoxyates, such as coconut fatty ethoxylate (10) or isotridecyl ethoxylate (12), fatty acid esters, such as rapeseed oil methyl ester or soy bean oil methyl ester, fatty amine alkoxyates, such as tallow amine ethoxylate (15), or ammonium and/or phosphonium salts, such as ammonium sulphate or diammonium hydrogen phosphate.

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**[0063]** The formulations preferably contain between 0.00000001 and 98 wt% active ingredient or, more preferably, between 0.01 and 95 wt% active ingredient - more preferably, between 0.5 and 90 wt% active ingredient - based upon the weight of the formulation.

**[0064]** The active ingredient content of the modes of application (plant-protecting agents) prepared from the formulations can vary within wide limits. The active ingredient concentration of the modes of application may typically be between 0.00000001 and 95 wt% active ingredient - preferably, between 0.00001 and 1 wt% - based upon the weight of the mode of application. Application takes place in a customary manner adapted to the modes of application.

**[0065]** The content of the individual components in the formulations according to the invention may be varied within a wider range.

**[0066]** The formulations according to the invention are produced by, for example, mixing the components with one another in the respectively desired ratios. If the active agrochemical ingredient is a solid substance, it is generally used either in finely ground form or in the form of a solution or suspension in an organic solvent or water. If the active agrochemical ingredient is liquid, there is often no need to use an organic solvent. It is also possible to use a solid active agrochemical ingredient in the form of a melt.

**[0067]** When executing the process, the temperatures may vary within a certain range. Working temperatures are generally between 0 °C and 80 °C - preferably, between 10 °C and 60 °C.

**[0068]** When executing the process according to the invention, the procedure is generally to mix the etherified lactate esters of the formula (I) with one or more active ingredients and, where appropriate, with additives. The sequence in which the components are mixed with one another is arbitrary.

**[0069]** Devices to be considered for executing the process according to the invention are customary devices used for production of agrochemical formulations.

**[0070]** Examples of modes of application are all the processes known as commonly used to the person skilled in the art: spraying, dipping, misting, as well as a number of specific processes for direct treatment below or above ground of whole plants or parts (seed, root, 5 stolons, stem, trunk, leaf), such as trunk injection, in the case of trees, or stem bandages, in the case of perennial plants, and a number of specific indirect application processes.

**[0071]** The term, "harmful organisms", includes all forms of organisms that cause economic and/or health damage in the respective field of use. Preferred are harmful plant 10 and animal organisms, as well as organisms that cause diseases; particularly preferred are terrestrial and aquatic weed grasses, and weeds, algae, mosses, insects, mites, nematodes, rodents, fungi, bacteria, and viruses.

**[0072]** The respective area-based and/or object-based application rate of the plant- 15 protecting agents of a wide variety of different formulation types for controlling the harmful organisms mentioned varies very strongly. For this purpose, the application media known to the person skilled in the art to be commonly used for the respective field of use are generally used in the customary amounts, such as several hundred litres of water per hectare, in the case of standard spraying processes, to a few litres of oil per hectare, in the 20 case of 'ultra low volume' aircraft application, and down to a few millilitres of a physiological solution, in the case of injection processes. The concentrations of the plant-protecting agents according to the invention in the respective application media therefore vary within a wide range and are dependent upon the respective field of use. Concentrations known to the person skilled in the art to be commonly used for the 25 respective field of use are generally used. Preferred are concentrations from 0.01 to 99 wt% - more preferably, from 0.1 to 90 wt%.

**[0073]** The plant-protecting agents according to the invention can be applied, for example, in the formulation forms customary for liquid preparations, either as such or after prior 30 dilution with water, i.e., for example, as emulsions, suspensions, or solutions. Application takes place by customary methods, i.e., for example, by spraying, pouring, or injecting.

**[0074]** The application rate of the plant-protecting agent according to the invention may be varied within a wider range. It is based upon the respective active agrochemical ingredients and on their content in the plant-protecting agents.

5 **[0075]** According to the invention, all plants and plant parts can be treated. Plants are understood in this case to mean all plants and plant populations, such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants may be plants that can be obtained by conventional breeding and optimisation methods or by biotechnological and genetic engineering methods or by combinations of these methods,  
10 including transgenic plants and including plant varieties that can or cannot be protected by plant variety rights. Plant parts are understood to mean all parts and organs of plants above and below the ground, such as shoot, leaf, flower, and root, examples of which are leaves, needles, stalks, stems, flowers, fruit bodies, fruits and seeds, as well as roots, tubers, and rhizomes. Plant parts also include harvested crop, as well as vegetative and  
15 generative propagation material, such as scions, tubers, rhizomes, sprigs, and seeds.

**[0076]** As already mentioned above, all plants and their parts can be treated according to the invention. In a preferred embodiment, wild plant species, and plant varieties or plant species and plant varieties obtained by conventional biological breeding methods, such as  
20 hybridisation or protoplast fusion, and their parts are treated. In another preferred embodiment, transgenic plants, or plant varieties obtained by genetic engineering methods and, where appropriate, in combination with conventional methods (genetically modified organisms), and their parts are treated. The term, "parts", or "parts of plants" or "plant parts", was explained above. More preferably treated according to the invention are plants  
25 of the respective commercially available or used plant varieties. Plant varieties are understood to be plants with new traits, which were bred not only by conventional breeding, but by mutagenesis, or by recombinant DNA techniques. They may be varieties, races, biotypes, and genotypes.

30 **[0077]** The preferred transgenic plants or plant varieties (those obtained by genetic engineering) to be treated according to the invention include all plants that, as a result of the genetic modification, acquired genetic material that imparts particularly advantageous, useful traits to these plants. Examples of such properties are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to

water or soil salinity, enhanced flowering performance, easier harvesting, accelerated ripening, higher yields, higher quality, and/or a higher nutritional value of the harvested products, longer storage life, and/or processability of the harvested products. Additional and particularly emphasised examples of such properties are an improved defense of the plants against animal and microbial pests, such as against insects, mites, plant pathogenic fungi, bacteria, and/or viruses, as well as increased tolerance of the plants to certain herbicidally active ingredients. Examples of transgenic plants are the important crop plants, such as cereals (wheat, rice), maize, soy beans, potatoes, sugar beets, tomatoes, peas, and other vegetable types, cotton, tobacco, rapeseed, as well as fruit plants (with the fruits, apples, pears, citrus fruits, and grapes), with particular emphasis on maize, soy beans, potatoes, cotton, tobacco, and rapeseed. Particularly emphasised as traits are the improved defense of the plants against insects, arachnids, nematodes, and snails by toxins formed in the plants - especially those produced in the plants by the genetic material from *Bacillus thuringiensis* (e.g., by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry9c, Cry2Ab, Cry3Bb, and CryIF, as well as their combinations) (referred to hereinafter as "Bt plants"). Particularly emphasised as traits are also the improved defense of plants against fungi, bacteria, and viruses by systemic acquired resistance (SAR), systemin, phytoalexins, elicitors, as well as resistance genes and correspondingly expressed proteins and toxins. Particularly emphasised as traits are, furthermore, the increased tolerance of the plants to certain active herbicidal ingredients, e.g., imidazolinones, sulphonylureas, glyphosate, or phosphinothricin (e.g., the "PAT" gene). The genes which impart the respective desired traits may also be present in the transgenic plants in combinations with one another. Examples of "Bt plants" are maize varieties, cotton varieties, soya varieties, and potato varieties which are sold under the trade names, YIELD GARD® (e.g., maize, cotton, soya), KnockOut® (e.g., maize), StarLink® (e.g., maize), Bollgard® (cotton), Nucofn® (cotton), and NewLeaf® (potato). Examples of herbicide-tolerant plants are maize varieties, cotton varieties, and soy bean varieties that are sold under the trade names, Roundup Ready® (tolerance to glyphosate, e.g., maize, cotton, soy beans), Liberty Link® (tolerance to phosphinothricin, e.g., rapeseed), IMI® (tolerance to imidazolinones), and STS® (tolerance to sulphonylureas, e.g., maize). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) also include the varieties sold under the Clearfield® name (e.g., maize). Of course, these statements also apply to plant varieties developed in the future or marketed in the future with these genetic traits or genetic traits developed in the future.

**[0078]** Preferred are plants from the group of useful plants, ornamental plants, grass types, generally used trees, which are utilised in public and private areas as ornamental plants, and forest stand. Forest stand include trees for the production of timber, cellulose, paper,  
5 and products made from parts of the trees.

**[0079]** The term, useful plants, as used here, refers to crop plants used as plants for obtaining foodstuffs, animal feeds, and fuels, or for industrial purposes.

**[0080]** Useful plants that can be treated according to the invention include, for example, the following plant species: turf, vines, cereals, e.g., wheat, barley, rye, oats, rice, maize, and millet; beets, e.g., sugar beets and fodder beets; fruits, e.g., pomaceous fruit, stone fruit, and soft fruit, e.g., apples, pears, plums, peaches, almonds, cherries, and berries, e.g., strawberries, raspberries, blackberries; legumes, e.g., beans, lentils, peas, and soy beans;  
15 oil crops, e.g., rapeseed, mustard, poppies, olives, sunflowers, coconuts, castor oil plants, cacao beans, and peanuts; cucurbits, e.g., pumpkin/squash, cucumbers, and melons; fibre plants, e.g., cotton, flax, hemp, and jute; citrus fruit, e.g., oranges, lemons, grapefruit, and tangerines; vegetables, e.g., spinach, lettuce, asparagus, cabbage varieties, carrots, onions, tomatoes, potatoes, and bell peppers; laurel family, e.g., avocado, cinnamomum,  
20 camphor, or also plants such as tobacco, nuts, coffee, eggplant, sugar cane, tea, pepper, grapevines, hops, bananas, latex plants as well as ornamentals, e.g., flowers, shrubs, deciduous trees, and conifers. This enumeration does not constitute a limitation.

**[0081]** The following plants are considered to be particularly suitable target crops for the  
25 application of the process according to the invention: cotton, eggplant, turf, pomaceous fruit, stone fruit, soft fruit, maize, wheat, barley, cucumber, tobacco, vines, rice, cereals, pear, beans, soy beans, rapeseed, tomato, bell pepper, melons, cabbage, potatoes, and apples.

**[0082]** Where the use of herbicides is concerned, the plants treated according to the  
30 invention are all kinds of weeds. With regard to the protection of crop plants by application of, for example, fungicides and insecticides, the application in economically important crops, e.g., also transgenic crops of useful plants and ornamentals, e.g., of cereals such as wheat, barley, rye, oats, millet, rice, manioc, and maize, or crops of sugar beet, cotton, soy bean, rapeseed, potato, tomato, peas, and other vegetables, is preferred.

[0083] The invention is illustrated in more detail by the examples.

### Examples

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#### Production of the etherified lactate esters according to the invention

##### Raw materials used:

- 10 [0084] Catalyst for the alkylene oxide addition (DMC catalyst):  
double metal cyanide catalyst containing zinc hexacyanocobaltate, tert-butanol, and  
polypropylene glycol with a number-average molecular weight of 1,000 g/mol; described in  
WO-A 01/80994, example 6.
- 15 [0085] 2-ethylhexyl lactate, acquired from the company, Galactic  
lauryl lactate (PURASOLV LL®) acquired from the company, PURAC  
IRGANOX® 1076: octadecyl-3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate. (BASF SE)

#### Production of the etherified lactate esters according to the invention, based upon 20 ethylhexyl lactate

##### A) 2-ethylhexyl lactate 2PO/2EO

- 25 [0086] 160.0 g (0.792 mol) of 2-ethylhexyl lactate and 0.067 g of DMC catalyst were placed in  
a 2 L laboratory autoclave at 100 °C under a nitrogen atmosphere. After 5-fold  
nitrogen/vacuum exchange between 0.1 and 3.0 bar (absolute), the temperature was  
increased to 130 °C. Then, 91.88 g (1.584 mol) of PO were metered into the reactor at this  
temperature while stirring over the course of 10 minutes, the pressure in the reactor rising  
from 0.21 bar (absolute) to 0.54 bar (absolute). After a subsequent reaction time of 25  
30 minutes, the reactor pressure was first adjusted with nitrogen to 2.15 bar (absolute) and,  
subsequently, while stirring at 130 °C, 69.68 g (1.584 mol) of EO were metered into the  
reactor over the course of 10 minutes, the pressure rising from 2.15 bar (absolute) to 2.37  
bar (absolute). After a subsequent reaction time of 45 minutes, volatile matters were  
removed by heating in vacuum at 90 °C for 30 minutes, and the reaction mixture was then

cooled to room temperature. 161 mg of IRGANOX® 1076 were, lastly, added to the product.

5 **[0087]** The products with the composition, "2-ethylhexyl lactate 2PO/5EO" and "2-ethylhexyl lactate 2PO/10EO" from table 1, were produced in a similar manner.

### **B) 2-ethylhexyl lactate 2EO**

10 **[0088]** 160.0 g (0.792 mol) of 2-ethylhexyl lactate and 0.07 g of DMC catalyst were placed in a 2 L laboratory autoclave at 100 °C under a nitrogen atmosphere. After 5-fold nitrogen/vacuum exchange between 0.1 and 3.0 bar (absolute), the temperature was increased to 130 °C, and the reactor pressure was then adjusted with nitrogen to 2.19 bar (absolute). Subsequently, 69.68 g (1.584 mol) of EO were metered into the reactor at 130 °C while stirring over the course of 30 minutes, the pressure in the reactor rising from 2.19  
15 bar (absolute) to 2.61 bar (absolute). After a subsequent reaction time of 60 minutes, volatile matters were removed by heating in vacuum at 90 °C for 30 minutes, and the reaction mixture was then cooled to room temperature. 115 mg of IRGANOX® 1076 were, lastly, added to the product.

20 **[0089]** The products with the composition, "2-ethylhexyl lactate 5EO" and "2-ethylhexyl lactate 10EO", as well as "2-ethylhexyl lactate 15EO" from table 1, were produced in an analogous manner.

25 **Production of the etherified lactate esters according to the invention, based upon lauryl lactate**

### **C) Lauryl lactate 5EO/2PO**

30 **[0090]** 50 g PURASOLV LL® were placed in a 2 L laboratory autoclave under a nitrogen atmosphere. After adding 2 mg of 85% phosphoric acid, the contents of the reactor were stirred at room temperature for 20 minutes (200 rpm, propeller stirrer). After adding 12 mg of DMC catalyst, the contents of the autoclave were heated to 130 °C and stripped for 30 minutes at this temperature while stirring at 800 rpm in vacuum at an absolute pressure of 100 to 120 mbar, with the introduction of 50 mL of nitrogen per minute via a distributor ring

lying beneath the level of the liquid. This distributor ring was then used to meter and add a total of 39.4 g of ethylene oxide over a period of 58 minutes, likewise at 130 °C while stirring at 800 rpm. After a subsequent reaction time of 17 minutes, 20.8 g of propylene oxide were metered and added at 130 °C over a period of 30 minutes, while stirring at 800 rpm. After a subsequent reaction time of 22 minutes, the product was heated for 30 minutes at an absolute pressure of 1 mbar and then cooled to 80 °C. The autoclave was depressurised with nitrogen to approximately 1 bar. 50 g of product were discharged from the autoclave and admixed with 30 mg of IRGANOX® 1076.

#### 10 **D) Lauryl lactate 5EO/5PO**

[0091] The remaining autoclave contents of the product from example C) were heated to 130 °C while stirring (800 rpm), after which a further 17.1 g of propylene oxide were metered and added over a period of 34 minutes. After a subsequent reaction time of 30 minutes, the product was heated for 30 minutes at an absolute pressure of 1 mbar. Then, depressurisation with nitrogen to approximately 1 bar and cooling to 80 °C took place. The product was discharged and admixed with 47 mg of IRGANOX® 1076.

#### 20 **E) Lauryl lactate 8EO/2PO**

[0092] 152.0 g PURASOLV LL® were placed in a 2 L laboratory autoclave under a nitrogen atmosphere. After adding 11 mg of 85% phosphoric acid, the contents of the reactor were stirred at room temperature for 20 minutes (200 rpm, propeller stirrer). After adding 56 mg of DMC catalyst, the contents of the autoclave were heated to 130 °C and stripped for 30 minutes at this temperature while stirring at 800 rpm in vacuum at an absolute pressure of 100 to 120 mbar, with the introduction of 50 mL of nitrogen per minute via a distributor ring lying beneath the level of the liquid. This distributor ring was then used to meter and add a total of 191.7 g of ethylene oxide over a period of 4.03 hours, likewise at 130 °C while stirring at 800 rpm. After a subsequent reaction time of 10 minutes, 63.2 g of propylene oxide were metered and added at 130 °C over a period of 2.0 hours while stirring at 800 rpm. After a subsequent reaction time of 30 minutes, the product was heated for 30 minutes at an absolute pressure of 1 mbar and then cooled to 80 °C. The autoclave was depressurised with nitrogen to approximately 1 bar. 76.9 g of product were discharged from the autoclave and admixed with 41 mg of IRGANOX® 1076.

**F) Lauryl lactate 8EO/5PO**

**[0093]** The remaining autoclave contents of the product from example E) were heated to 130 °C while stirring (800 rpm), after which a further 77.2 g of propylene oxide were metered and added over a period of 1.02 hours. After a subsequent reaction time of 26 minutes, the product was heated for 30 minutes at an absolute pressure of 1 mbar. Then, depressurisation with nitrogen to approximately 1 bar and cooling to 80 °C took place. The product was discharged and admixed with 204 mg of IRGANOX® 1076.

**Use**

**[0094]** The etherified lactate esters have very good properties as surfactants. Surfactants are used in plant protection as, among other things, wetters and stickers, as well as emulsifiers. Their suitability as wetters is characterised by, for example, the static surface tension, and their suitability as adhesives by the dynamic surface tension (see Adamson AW 1990. Physical Chemistry of Surfaces. London, Wiley / Berger PD & Berger CH, 1993. Effect of Surfactant Type and Order of Addition on Droplet Size and Dynamic Interfacial Properties. Pesticide formulations and application systems, 13th vol., Berger, PD, Debisetty, BN, Hall, FR, eds., American Society for Testing and Materials. / Knowles, DA 1998. Chemistry and Technology of Agrochemical Formulations, Kluwer Academic Publishers, Dordrecht).

**1) Static surface tension in aqueous systems**

**[0095]** The surface tension value achievable in equilibrium was determined via the pending drop method using a goniometer (DSA10 goniometer, Kruss). The table shows the results of the measurements on the etherified lactate esters at 0.3 and 3 g/L at room temperature (20 °C), in comparison to literature values for two frequently used surfactants.

Table 1

Test substance	Static surface tension (mN/m)	
	0.3 g/L	3 g/L

	Static surface tension (mN/m)	
Lauryl lactate 5EO/2PO	31.63	31.34
Lauryl lactate 5EO/5PO	31.65	30.14
Lauryl lactate 8EO/2PO	30.76	30.71
Lauryl lactate 8EO/5PO	31.38	31.51
2-ethylhexyl lactate 2PO/ 2EO	40.40	29.47
2-ethylhexyl lactate 2PO/ 5EO	43.35	28.48
2-ethylhexyl lactate 2PO/ 10EO	47.43	36.0
2-ethylhexyl lactate 2EO	45.34	28.19
2-ethylhexyl lactate 5EO	48.65	32.61
2-ethylhexyl lactate 10EO	52.99	35.18
2-ethylhexyl lactate 15EO	54.33	42.23
<b>Comparison (commercial)</b>		
Frigate * (tallow amine ethoxylate)	-	39.6
Tanemul HOT ** (ethylhexyl alkoxyate)	35.2	29.7
*ISK Biosciences, Diegem (Belgium), **Tanatex, Leverkusen (Germany)		

**[0096]** In this case, lauryl lactate 5EO/2PO, for example, means that, for this etherified lactate ester, in the notation of formula (I), R is lauryl and R1 is  $-(AO)_m-R'$ , wherein AO is a mixture of ethylene oxide (EO) radicals and propylene oxide (PO) radicals, wherein the first EO fraction bonds to the lactate ester group, and the subsequent PO fraction bonds to the EO radicals, m stands for  $5 + 2 = 7$ , and R' is hydrogen.

## 2) Dynamic surface tension (surface activity)

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**[0097]** The dynamic surface tension was determined via the bubble pressure method (BP2100 tensiometer, Krüss). With a timespan relevant for the spray application of agrochemicals in aqueous dilution (referred to as the surface age in the bubble pressure method) of 200 milliseconds, the value of the dynamic surface tension in [mN/m] correlates with the adherence on difficult-to-wet plants, such as barley (cereal). A value of 50 mN/m (at

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20-21 °C) produces, relative to water (72.8 mN/m), an improvement in the adherence from "zero adherence" to approximately 50% (Baur P, Pontzen R, 2007. Basic features of plant surface wettability and deposit formation and the impact of adjuvants. In: R E Gaskin, ed., Proceeding of the 8th International Symposium on Adjuvants for Agrochemicals. Publisher: International Society for Agrochemical Adjuvants (ISAA), Columbus, Ohio, USA). Table 2 shows that this value is already achieved by many etherified lactate esters at the low test concentration in water, and that all of them clearly fall below this value at 3 g/L. The etherified lactate esters are thus superbly suitable for enhancing the adherence of agrochemicals on cereals (with maize, rice, millet), bananas, cabbage/rapeseed, soy beans, and other difficult-to-wet crop plants and harmful plants. The positive wetting and sticking effects, naturally, also apply to other organisms and artificial surfaces and/or technical applications, e.g., for achieving thin coatings on surfaces or for cleaning surfaces.

Table 2

Test substance	Dynamic surface tension (mN/m)	
	0.3 g/L	3 g/L
Lauryl lactate 5EO/2PO	51.9	37.4
Lauryl lactate 5EO/5PO	52.7	36.5
Lauryl lactate 8EO/2PO	54.3	37.7
Lauryl lactate 8EO/5PO	50.9	36.2
2-ethylhexyl lactate 2PO/ 2EO	47.8	30.7
2-ethylhexyl lactate 2PO/ 5EO	50.7	29.6
2-ethylhexyl lactate 2PO/ 10EO	54.2	37.4
2-ethylhexyl lactate 2EO	50.9	26.8
2-ethylhexyl lactate 5EO	54.4	35.3
2-ethylhexyl lactate 10EO	56.6	46.6
2-ethylhexyl lactate 15EO	58.6	48.1
<b>Comparison (commercial)</b>		
Frigate* (tallow amine ethoxylate)	-	50.9
Tanemul HOT** (ethylhexyl alkoxyate)	44.3	31.5

	<b>Dynamic surface tension (mN/m)</b>
*ISK Biosciences, Diegem (Belgium), **Tanatex, Leverkusen (Germany)	

### 3) Enhancing penetration of active ingredients selected by way of example

**[0098]** Surfactants may also enhance the uptake of (active) ingredients through membranes, such as skin, films, or the plant cuticle. As a so-called "finite dose" application, it is known, for the single application or application of a solution, cream, gel, etc., to a membrane, that the uptake of active ingredients can be influenced by some additives, such as surfactants, even after wetting has taken place. This effect is independent of the surfactant activity, is often highly dependent upon the concentration, and occurs to a very large extent after volatilisisation of water and any solvents present as a consequence of interaction with, for example, active ingredient, membrane, and environmental factors. For various surfactants, it is observed that, following addition to active ingredient preparations, the penetration of a particular active ingredient is massively enhanced by some surfactants, while others are completely inactive (Cronfeld, P, Lader, K, Baur, P. (2001). Classification of Adjuvants and Adjuvant Blends by Effects on Cuticular Penetration, Pesticide Formulations and Application Systems: Twentieth Volume, ASTM STP 1400, A. K. Viets, R. S. Tann, J. C. Mueninghoff, Eds, American Society for Testing and Materials, West Conshohocken, PA 2001).

**[0099]** The potential, independent of the surfactant activity, of enhancing leaf uptake of active agrochemical ingredients was determined in membrane penetration experiments with apple leaf cuticles. The principle of the method has been published (e.g., WO-A-2005/194844), and only the specifics and methodological deviations are explained below. The leaf cuticles were isolated enzymatically in the manner described from apple leaves of field trees in a commercial pomaceous fruit orchard in Kriftel, to the west of Frankfurt, in 2010. The cuticles, which were first dried in air, were installed into stainless steel diffusion cells. After application to the original top leaf face and evaporation of the test liquid, i.e., of the aqueous preparations of the active ingredients with or without the etherified lactate esters, the diffusion cells were transferred to thermostatted blocks and were filled with aqueous liquid. The water used to prepare the aqueous test liquids was local tap water (of known composition). At regular intervals, samples were taken, and the penetrated fraction of active ingredient was determined, depending upon the test system, either by HPLC or

by scintillation measurement. In the system with radioactively marked active ingredient (thiacloprid and fluoxastrobin), the aqueous liquid was a phospholipid suspension, and the entire quantity was replaced. In the case of the HPLC variant (tebuconazole SC430), only one aliquot was removed. During the experiment, the temperature in the system (block, diffusion cells, liquids, etc.) and the atmospheric humidity over the spray coating on the cuticle were precisely known and monitored. In each of the experiments, the relative humidity was kept consistently at a constant 60%, but the temperature was increased after one day by 10 °C, viz., from 20 °C to 30 °C for thiacloprid and tebuconazole, and from 15 °C to 25 °C for fluoxastrobin. Depending upon the variant (active ingredient x, etherified lactate ester), 7-8 repetitions were arranged.

**[0100]** Shown by way of example below is the enhancement of the uptake by the etherified lactate esters upon tank-mix addition to

- 1) a solution of the insecticide thiacloprid with 0.5 g/L and 3 g/L etherified lactate ester
- 2) a suspension concentrate of the fungicide tebuconazole with 0.5 g/L and 2 g/L etherified lactate ester
- 3) a solution of the fungicide fluoxastrobin with 0.5 g/L and 2 g/L etherified lactate ester, in each case in comparison to the systems without addition of the etherified lactate esters.

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Table 3

Etherified lactate ester	Mean penetration of thiacloprid* in % (n= 4-8)			
	0.5 g/L		3 g/L	
	24 h**	48 h***	24 h**	48 h***
Thiacloprid dissolved in acetone/water without etherified lactate ester	<3	<5	<3	<5
Lauryl lactate 5EO/2PO	13.6	17.4	63.9	74.5
Lauryl lactate 5EO/5PO	18.6	24.0	67.4	76.3
Lauryl lactate 8EO/2PO	14.5	18.8	73.3	80.4
Lauryl lactate 8EO/5PO	20.5	27.3	72.0	82.9
2-ethylhexyl lactate 2PO/ 2EO	11.5	15.1	20.3	23.4

Etherified lactate ester	Mean penetration of thiacloprid* in % (n= 4-8)			
	0.5 g/L		3 g/L	
	24 h**	48 h***	24 h**	48 h***
2-ethylhexyl lactate 2PO/ 5EO	10.2	12.1	43.2	49.2
2-ethylhexyl lactate 2PO/ 10EO	8.1	10.0	36.9	47.2
2-ethylhexyl lactate 2EO	5.6	6.5	35.5	43.0
2-ethylhexyl lactate 5EO	12.1	14.1	31.4	39.9
2-ethylhexyl lactate 10EO	11.0	12.4	39.6	46.2
2-ethylhexyl lactate 15EO	10.5	14.0	29.9	41.9

\* 0.2 g/L thiacloprid; \*\*20 °C/60% relative humidity (RH); \*\*\*30 °C/60% RH

Table 4

Etherified lactate ester	Mean penetration of tebuconazole* in % (n= 4-8)			
	0.5 g/L		2 g/L	
	24 h**	48 h***	24 h**	48 h***
Tebuconazole SC 430 without etherified lactate ester	2.2	20.5	2.2	20.5
Lauryl lactate 5EO/2PO	27.6	75.1	57.1	68.3
Lauryl lactate 5EO/5PO	36.9	36.9	59.0	74.0
Lauryl lactate 8EO/2PO	25.4	62.9	62.9	73.3
Lauryl lactate 8EO/5PO	45.6	75.9	41.0	56.9
2-ethylhexyl lactate 2PO/ 2EO	23.2	58.1	27.0	36.5
2-ethylhexyl lactate 2PO/ 5EO	31.7	74.8	53.9	71.1
2-ethylhexyl lactate 2PO/ 10EO	-	-	52.2	79.3
2-ethylhexyl lactate 2EO	-	-	42.1	42.1
2-ethylhexyl lactate 5EO	-	-	45.0	63.8

Etherified lactate ester	Mean penetration of tebuconazole* in % (n= 4-8)			
	0.5 g/L		2 g/L	
2-ethylhexyl lactate 10EO	-	-	42.3	78.1
2-ethylhexyl lactate 15EO	-	-	30.5	53.6

\* 0.5 g/L tebuconazole; \*\*20 °C/60% RH; \*\*\*30 °C/60% RH

Table 5

Etherified lactate ester	Mean penetration of fluoxastrobine* in % (n= 4-8)			
	0.5 g/L		2 g/L	
	24 h**	48 h***	24 h**	48 h***
Fluoxastrobin dissolved in acetone/water without etherified lactate ester	2.6	6.9	2.6	6.9
Commercial fluoxastrobin EC formulation 3 g/L	1.8	7.3	1.8	7.3
Lauryl lactate 5EO/2PO	3.3	7.5	12.7	25.6
Lauryl lactate 5EO/5PO	4.7	10.0	12.2	23.1
Lauryl lactate 8EO/2PO	4.0	7.8	11.5	20.4
Lauryl lactate 8EO/5PO	3.9	9.6	6.8	19.8
2-ethylhexyl lactate 2PO/ 2EO	12.1	18.6	16.1	26.0
2-ethylhexyl lactate 2PO/ 5EO	9.9	16.2	14.4	24.2
2-ethylhexyl lactate 2PO/ 10EO	8.9	17.5	13.1	22.1
2-ethylhexyl lactate 2EO	10.6	35.2	11.4	18.9
2-ethylhexyl lactate 5EO	8.7	13.9	13.0	21.4
2-ethylhexyl lactate 10EO	9.7	15.9	16.8	26.9
2-ethylhexyl lactate 15EO	9.5	14.1	13.4	25.8

\* 0.3 g/L fluoxastrobin; \*\*15 °C/60% RH; \*\*\*25 °C/60% RH

**[0101]** Tables 3 through 5 show the superb suitability of the etherified lactate esters according to the invention, as a function of concentration, for greatly enhancing leaf penetration for a variety of active ingredients, active ingredient preparations (solutions, in the case of thiacloprid and fluoxastrobin; suspension concentrate, in the case of tebuconazole), and environmental factors. The relative independence of the degree of ethoxylation or alkoxylation with respect to the capacity to enhance penetration, and the difference in surface activity at the same time, mean that the etherified lactate esters are also components of interest to be incorporated into agrochemical formulations.

#### 10 **4) Foam behaviour**

**[0102]** The important properties of surface-active substances include the foam behaviour - particularly, in aqueous systems. Virtually all surfactants foam, and the time to collapse the foam has to be shortened in the case of critical (highly foaming) surfactants through the addition of defoamers to the formulation or the aqueous application preparation. The foam behaviour of some of the substances according to the invention was characterised using aqueous solutions at a concentration of 3 g/L, in accordance with the foam test of CIPAC method MT47. The values in the table show the percentage filling with foam in a cylinder over a period of 12 minutes. A value of 100 (%) thus denotes maximum foam and is obtained, for example, over the entire 12-minute period with lauryl ether sulphates (such as Genapol LRO).

**[0103]** Using the example of the etherified ethylhexyl lactate esters according to the invention, the following table shows that the foam behaviour of the substances must be classified as very favourable. At the relatively high concentration of 3 g/L - for use in agrochemical aqueous spray liquids, for example - collapse of the foam is very quick. It is also surprising, in the case of the ethoxylated ethylhexyl lactate esters according to the invention, that only the 5EO degree of ethoxylation shows an initially relatively strong foaming behaviour, whereas higher and lower degrees of ethoxylation produced little to no foam. The comparison is the result with the alkoxyated ethylhexyl lactate esters (mixed EO/PO) according to the invention, even though they are also stronger surfactants (see tables 1 and 2).

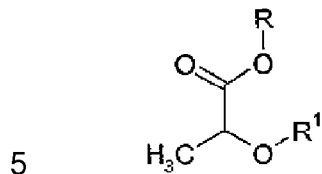
Table

Etherified lactate ester	Percentage foam volume*			
	10 s	60 s	3 min	12 min
Lauryl lactate 2PO/ 2EO	2	2	0	0
Lauryl lactate 2PO/ 5EO	25	10	10	10
Lauryl lactate 2PO/ 10EO	50	10	0	0
2-ethylhexyl lactate 2EO	5	5	5	5
2-ethylhexyl lactate 5EO	50	40	20	10
2-ethylhexyl lactate 10EO	10	5	5	0
2-ethylhexyl lactate 15EO	0	0	0	0

\* foam test in accordance with CIPAC MT47 with CIPAC D water (342 ppm); concentration of 3 g/L

### 5) Crop tolerance

- 5 **[0104]** At the concentrations in which the significantly enhancing effects on wetting and uptake of agrochemicals were found, the tolerance by crops of the etherified lactate esters (lactate ester ethoxylates) was very good.

**Patentkrav****1. Æteriserede lactatestere med formlen (I)**

hvor

R betegner 2-ethyl-hexyl eller lauryl,

10 R<sup>1</sup> betegner en alkoxyleret alkylrest med formlen  $-(\text{-AO})_m\text{-R}'$ , hvor AO betegner en ethylenoxid-rest, en propylenoxid-rest, en butylenoxid-rest eller betegner blandinger af ethylenoxid og propylenoxid-rester og m betegner tal fra 2 til 15,

R' betegner hydrogen eller betegner en forgrenet eller uforgrenet, mættet, delvist mættet eller umættet C<sub>1</sub>-C<sub>10</sub>-alkylrest.

15

**2. Æteriserede laktatestere ifølge krav 1, hvor R betegner lauryl, R<sup>1</sup> betegner  $-(\text{-AO})_m\text{-R}'$ , hvor R' betegner hydrogen og  $-(\text{-AO})_m$  er udvalgt fra gruppen bestående af de følgende alkyoxylat-rester:  $-(\text{EO})_5\text{-(PO)}_2$ ,  $-(\text{EO})_5\text{-(PO)}_5$ ,  $-(\text{EO})_8\text{-(PO)}_2$ ,  $-(\text{EO})_8\text{-(PO)}_5$ .**

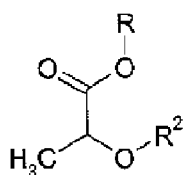
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**3. Æteriserede laktatestere ifølge krav 1, hvor R betegner ethylhexyl, R<sup>1</sup> betegner  $-(\text{-AO})_m\text{-R}'$ , hvor R' betegner hydrogen og  $-(\text{-AO})_m$  er udvalgt fra gruppen bestående af de følgende alkyoxylat-rester:  $-(\text{EO})_2\text{-(PO)}_2$ ,  $-(\text{EO})_2\text{-(PO)}_5$ ,  $-(\text{EO})_2\text{-(PO)}_{10}$ ,  $-(\text{EO})_2$ ,  $-(\text{EO})_5$ ,  $-(\text{EO})_{10}$ ,  $-(\text{EO})_{15}$ .**

25

**4. Fremgangsmåde til fremstilling af de æteriserede laktatestere ifølge et af kravene 1 til 3, ved hvilken man reagerer laktatestere med formlen (II), i hvilken R har den i krav 1 angivne betydning, og i hvilken R<sup>2</sup> betegner R', hvor R' har den i krav 1 angivne betydning**

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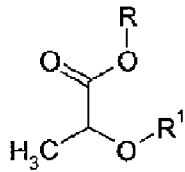


med alkylenoxider i nærvær af DMC-katalysatorer.

5. Anvendelse af de æteriserede laktatestere med formlen (I) ifølge krav 1 som tensid, som befugtnings- og hæftemiddel eller som emulgator.

5

6. Anvendelse af æteriserede laktatestere med formlen (I)



10

hvor

R betegner uforgrenet eller forgrenet, mættet eller umættet C<sub>1</sub>-C<sub>20</sub>-alkyl, og R<sup>1</sup> betegner en alkoxyleret alkylrest med formlen  $(-\text{AO})_m-\text{R}^1$ , hvor AO betegner en ethylenoxid-rest, en propylenoxid-rest, en butylenoxid-rest eller betegner blandinger af ethylenoxid og propylenoxid-rester eller blandinger af ethylenoxid og butylenoxid-rester og m betegner tal fra 2 til 30,

15

R' betegner hydrogen eller betegner en forgrenet eller uforgrenet, mættet, delvist mættet eller umættet C<sub>1</sub>-C<sub>20</sub>-alkylrest, til forbedring af virkningen af agrokemiske aktive stoffer i og på planter.

20

7. Anvendelse af de æteriserede laktatestere med formlen (I) ifølge krav 1 til reducere eller hindre skumdannelsen i agrokemiske formuleringer.