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(54) Title: BIOCIDES COMPOSITIONS COMPRISING ESTERS OF ETHOXYLATED ALCOHOLS

(57) Abstract: Suggested are biocide compositions, comprising (a) Esters of ethoxylated alcohols according to formula (I) $R^1CO(OCH_2CH_2)_nOR^2$ (I) In which R^1CO stands for a saturated or unsaturated acyl radical having 8 to 22 carbon atoms, R^2 represents an alkyl radical having 1 to 10 carbon atoms, n denominates an integer of from 1 to 100, on condition that said esters exhibit an HLB value within a range of 10 to 17: (b) Biocides and optionally (c) Oil components or co-solvents and/or (d) Emulsifiers. The compositions show high solubility for biocides and improved emulsification properties.



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Biocide compositions comprising esters of ethoxylated alcohols

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Field of the invention

10 The present invention relates to the area of agrochemicals and refers to biocide compositions comprising esters of ethoxylated alcohols and its use as a solvent for biocides.

Background of the invention

15 Biocides, and in particular pesticides such as fungicides, insecticides and herbicides, are important auxiliary agents for agriculture in order to protect and to increase crops yields. Depending on the various and often very specific needs a magnitude of actives exist which show very different chemical structures and behaviours. Nevertheless, it is well known from the state of the art that it remains difficult to prepare concentrates of these actives which are exhibiting a satisfying stability, especially if stored at very low or elevated temperatures over a longer period. As a matter of fact, the solutions show a strong tendency to either
20 separate or to form crystals, which makes it necessary to re-disperse the actives in the compositions prior to every application in order to obtain a homogenous product. In addition, many biocides, especially pesticides, do exhibit suboptimal biological efficacy because of insufficient retention, adhesion, wetting, or penetration. Therefore, there is a need for a corresponding adjuvant which allows access to a better biological performance.

25 In international patent application **WO 02/069705 A1** (Cognis), esters of ethoxylated alcohols are disclosed in combination with alkyl polyglycosides (APGs). The esters of ethoxylated alcohols are described by the formula $RO(EO)_n(PO)_mR'$, in which RO represents an alcohol component between 1 and 6 C atoms, R' represents hydrogen and/or an ester group $CO-R''$, in which R'' stands for an alkyl group comprising between 5 and 29 C atoms. **DE 19823252 A1** (Henkel) describes a water based composition containing at least one agrochemical with a solubility in water of less than 10%. This composition contains a compound corresponding to the formula $RO(EO)_n(PO)_mR'$ in which m is at least one. Their use is given as emulsifiers and dispersing additives. Finally, **WO 96/022109** (SEPPIC) teaches a self-emulsifiable composition consisting of an ethoxylated fatty acid ester having an HLB
30 value between 4 and 10.

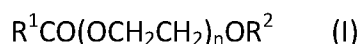
Products generally found in the market present either a limited content of biocides and /or hazardous labeling and a non favorable eco-toxicological profile. The problem underlying the present invention has been to identify suitable new adjuvants or additives for biocide compositions with better biological performance than obtainable in the market.

In this context a related problem associated with the present invention refers to the trend that active ingredients in crop protection assume a higher molecular weight and in parallel their water solubility decreases. Hence the penetration of the cuticular layer poses a barrier. As a result, adjuvants are needed enhancing the biological efficacy of crop protection products, acting also as emulsifiers, in particular for o/w emulsions, and requiring HLB values of about 8 to about 18.

Detailed description of the invention

The present invention refers to biocide compositions, comprising

- (a) Esters of ethoxylated alcohols



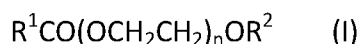
In which R^1CO stands for a saturated or unsaturated acyl radical having 8 to 22 carbon atoms, R^2 represents an alkyl radical having 1 to 10 carbon atoms, n denominates an integer of from 1 to 100, on condition that said esters exhibit an HLB value¹ within a range of 10 to 17;

- (b) Biocides and optionally
(c) Oil components and/or co-solvents and/or
(d) Emulsifiers.

Surprisingly it has been observed that esters of ethoxylated alcohols according to formula (I) represent efficient adjuvants or additives for various types of biocides. In particular, esters of ethoxylated isoamyl alcohol and unsaturated fatty acids, in particular oleic acid, are able to improve the biological performance a wide range of biocides. Furthermore, the esters can be water soluble or non water soluble depending on the alkyl chain and degree of alkoxylation, which offers flexibility with regard to the application and the pesticide to be formulated.

Esters of ethoxylated alcohols

The esters of ethoxylated alcohols forming compound (a) are following formula (I)



In which R^1CO stands for a saturated, preferably an unsaturated acyl radical having 8 to 22, preferably 16 to 22 carbon atoms, R^2 represents an alkyl radical having 1 to 10, preferably 1 to 6 and more preferably 2 to 4 carbon atoms, n denominates an integer of from 1 to about 100, preferably about 2 to about 25 and more preferably about 5 to about 15, on condition that said esters exhibit an HLB value within a range of about 10 to about 17, preferably about 12 to about 15. For example, suitable examples are esters based on lauric acid,

¹ The Hydrophilic-lipophilic balance of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, determined by calculating values for the different regions of the molecule, as described by Griffin in 1954 according to the equation $HLB = 20 * M_h / M$ where M_h is the molecular mass of the hydrophilic portion of the Molecule, and M is the molecular mass of the whole molecule, giving a result on an arbitrary scale of 0 to 20. An HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 would correspond to a molecule made up completely of hydrophilic components.

myristic acid, palmitic acid, stearic acid and preferably palmitoleic acid, oleic acid, linolic acid, linoleic acid, conjugated linoleic acid, erucic acid and their technical mixtures, such as for example sunflower fatty acid, olive fatty acid, soybean fatty acid and the like with adducts of 1 to 100, preferably 2 to 25 and more preferably 5 to 15 moles ethylene oxide to methanol, ethanol, propanol, isopropyl alcohol, the isomeric butanols, pentanols and hexanols and in particular isoamyl alcohol. The most preferred species are esters of oleic and/or stearic acid and adducts of 2 to 25, more particularly about 5 to about 15 moles ethylene oxide to isoamyl alcohol, given that the HLB value of said esters ranges between about 10 and about 17, preferably about 12 to about 15. Instead of pure isoamyl alcohol fusel alcohol can also be used, comprising minor traces of 1-propanol, 2-propanol and various butanol isomers. The use of fusel alcohol as a source for the isoamyl component is preferred since it represents a renewable source which fits into the concept of a true "green" additive.

Biocides

A biocide (component b) in the context of the present invention is a plant protection agent, more particular a chemical substance capable of killing different forms of living organisms used in fields such as medicine, agriculture, forestry, and mosquito control. Also counted under the group of biocides are so-called plant growth regulators. Usually, biocides are divided into two sub-groups:

- pesticides, which includes fungicides, herbicides, insecticides, algicides, molluscicides, miticides and rodenticides, (here, The Pesticide Manual, 14th edition, BCPC 2006 is included as a reference, it provides information about the individual mode of actions of active ingredients) and
- antimicrobials, which includes germicides, antibiotics, antibacterials, antivirals, antifungals, antiprotozoals and antiparasites.

Biocides can also be added to other materials (typically liquids) to protect the material from biological infestation and growth. For example, certain types of quaternary ammonium compounds (quats) can be added to pool water or industrial water systems to act as an algicide, protecting the water from infestation and growth of algae.

a) Pesticides

The U.S Environmental Protection Agency (EPA) defines a pesticide as "any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest". A pesticide may be a chemical substance or biological agent (such as a virus or bacteria) used against pests including insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes (roundworms) and microbes that compete with humans for food, destroy property, spread disease or are a nuisance. In the following examples, pesticides suitable for the agrochemical compositions according to the present invention are given:

b) Fungicides

A fungicide is one of three main methods of pest control – the chemical control of fungi in this case. Fungicides are chemical compounds used to prevent the spread of fungi in gardens and crops. Fungicides are also used to fight fungal infections. Fungicides can either be contact or systemic. A contact fungicide kills fungi when sprayed on its surface. A systemic fungicide has to be absorbed by the fungus before the fungus dies. Examples for suitable fungicides, according to the present invention, encompass the following chemical classes and corresponding examples:

- Aminopyrimidines such as bupirimate,
- Anilinopyrimidines such as cyprodinil, mepanipyrim, pyrimethanil,
- Heteroaromatics such as hymexazol,
- Heteroaromatic hydrocarbons such as etridiazole,
- Chlorophenyls/Nitroanilines such as chloroneb, dicloran, quintozone, tecnazene, tolclofos-methyl,
- Benzamide fungicides such as zoxamide,
- Benzenesulfonamides such as flusulfamide,
- Benzimidazoles such as acibenzolar, benomyl, benzothiazole, carbendazim, fuberidazole, metrafenone, probenazole, thiabendazole, triazoxide, and benzimidazole precursor fungicides,
- Carbamates such as propamocarb, diethofencarb,
- Carboxamides such as boscalid, diclocymet, ethaboxam, flutolanil, penthiopyrad, thifluzamide
- Chloronitriles such chlorothalonil,
- Cinnamic acid amides such as dimethomorph, flumorph,
- Cyanoacetamide oximes such as cymoxanil,
- Cyclopropanecarboxamides such as carpropamid,
- Dicarboximides such as iprodione, octhilinone, procymidone, vinclozolin
- Dimethyldithiocarbamates such as ferbam, metam, thiram, ziram,
- Dinitroanilines such as fluazinam,
- Dithiocarbamates such as mancozeb, mancozeb, maneb, metiram, nabam, propineb, zineb,
- Dithiolanes such as isoprothiolane,
- Glucopyranosyl antibiotics such as streptomycin, validamycin,
- Guanidines such as dodine, guazatine, iminoctadine,
- Hexopyranosyl antibiotics such as kasugamycin,
- Hydroxyanilides such as fenhexamid,

- Imidazoles such as imazalil, oxpoconazole, pefurazoate, prochloraz, triflumizole,
- Imidazolinones such as fenamidone,
- Inorganics such as Bordeaux mixture, copper hydroxide, copper naphthenate, copper oleate, copper oxychloride, copper(II) sulfate, copper sulfate, copper(II) acetate, copper(II) carbonate, cuprous oxide, sulfur,
- Isobenzofuranones such as phthalide,
- Mandelamides such as mandipropamide,
- Morpholines such as dodemorph, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine, aldimorph
- Organotins such as fentin,
- Oxazolidinones such as oxadixyl,
- Phenylamides such as benalaxyl, benalaxyl-M, furalaxyl, metalaxyl, metalaxyl-M, ofurace,
- Phenylpyrazoles such as fipronil,
- Phenylpyrroles such as fludioxonil,
- Phenylureas such as pencycuron,
- Phosphonates such as fosetyl,
- Phthalamic acids such as tecloftalam,
- Phthalimides such as captafol, captan, folpet,
- Piperazines such as triforine,
- Propionamides such as fenoxanil,
- Pyridines such as pyrifenoxy,
- Pyrimidines such as fenarimol, nuarimol,
- Pyrroloquinolinones such as pyroquilon,
- Qils such as cyazofamid,
- Quinazolinones such as proquinazid,
- Quinolines such as quinoxifen,
- Quinones such as dithianon,
- Sulfamides such as tolylfluanid, dichlofluanid,
- Strobilurines such as azoxystrobin, dimoxystrobin, famoxadone, fluoxastrobin, kresoxim-methyl, metominostrobin, picoxystrobin, pyraclostrobin, trifloxystrobin, orysastrobin,
- Thiocarbamates such as methasulfocarb,
- Thiophanates such as thiophanate-methyl,
- Thiophencarboxamides such as silthiofam,

- Triazole fungicides such as azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, fluotrimazole, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, quinconazole
- Triazolobenzothidazoles such as tricyclazole,
- Valinamide carbamates such as iprovalicarb, benthiavalicarb
- Fluopicolide
- Pentachlorophenol

and their mixtures.

c) Herbicides

An herbicide is a pesticide used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often based on plant hormones. Herbicides used to clear waste ground are nonselective and kill all plant material with which they come into contact. Herbicides are widely used in agriculture and in landscape turf management. They are applied in total vegetation control (TVC) programs for maintenance of highways and railroads. Smaller quantities are used in forestry, pasture systems, and management of areas set aside as wildlife habitat. In general, active ingredients representing including various chemical classes and corresponding examples can be used

- Anilides such as propanil
- Aryloxycarboxylic acids e.g. MCPA-thioethyl
- Aryloxyphenoxypropionates e.g. clodinafop-propargyl, cyhalofop-butyl, diclofops, fluazifops, haloxyfops, quizalofops,
- Chloroacetamides e.g. acetolochlor, alachlor, butachlor, dimethenamid, metolachlor, propachlor
- Cyclohexanedione oximes e.g. clethodim, sethoxydim, tralkoxydim,
- Benzamides such as isoxaben
- Benzimidazoles such as dicamba, ethofumesate
- Dinitroanilines e.g. trifluralin, pendimethalin,
- Diphenyl ethers e.g. aclonifen, oxyfluorfen,
- The glycine derivative glyphosate, a systemic nonselective (it kills any type of plant) herbicide used in no-till burndown and for weed control in crops that are genetically modified to resist its effects,
- Hydroxybenzonitriles e.g. bromoxynil,
- Imidazolinones e.g. fenamidone, imazapic, imazamox, imazapic, imazapyr, imazaquin,

- Isoxazolidinones e.g. clomazone
 - Paraquat as bipyridylium,
 - Phenyl carbamates e.g. desmedipham, phenmedipham,
 - Phenylpyrazoles e.g. pyraflufen-ethyl
 - 5 ○ Phenylpyrazolines e.g. pinoxaden,
 - Pyridinecarboxylic acids or synthetic auxins e.g. picloram, clopyralid, and triclopyr,
 - Pyrimidinyloxybenzoics e.g. bispyrtbac-sodium
 - Sulfonyureas e.g. amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorsulfuron, flazasulfuron, foramsulfuron, flupyrsulfuron-methyl-sodium, nicosulfuron, rim-
 - 10 sulfuron, sulfosulfuron, tribenuron-methyl, trifloxysulfuron-sodium, triflusulfuron, tritosulfuron,
 - Triazolopyrimidines e.g. penoxsulam, metosulam, florasulam,
 - Triketones e.g. mesotriones, sulcotrione,
 - Ureas e.g. diuron, linuron,
 - 15 ○ Phenoxy-carboxylic acids such as 2,4-D, MCPA, MCPB, mecoprop,
 - Triazines such as atrazine, simazine, terbutylazine,
- and their mixtures.

d) Insecticides

- 20 An insecticide is a pesticide used against insects in all developmental forms. They include ovicides and larvicides used against the eggs and larvae of insects. Insecticides are used in agriculture, medicine, industry and the household. In the following, suitable chemical classes and examples of insecticides are mentioned:
- Abamectin, emamectin,
 - 25 ○ Anthranilic diamides such as rynaxypyr
 - Synthetic auxins such as avermectin,
 - Amidines such as amitraz,
 - Anthranilic diamide such as rynaxypyr,
 - Carbamates such as aldicarb, carbofuran, carbaryl, methomyl, 2-(1-
 - 30 methylpropyl)phenyl methylcarbamate,
 - Chlorinated insecticides such as, for example, Camphechlor, DDT, Hexachlorocyclohexane, gamma-Hexachlorocyclohexane, Methoxychlor, Pentachlorophenol, TDE, Aldrin, Chlordane, Chlordanecone, Dieldrin, Endosulfan, Endrin, Heptachlor, Mirex,
 - Juvenile hormone mimics such as pyriproxyfen,
 - 35 ○ Neonicotinoids such as imidacloprid, clothianidin, thiacloprid, thiamethoxam,

- Organophosphorus compounds such as acephate, azinphos-methyl, bensulide, chlorethoxyfos, chlorpyrifos, chlorpyrifos-methyl, diazinon, dichlorvos (DDVP), dicrotophos, dimethoate, disulfoton, dthoprop, fenamiphos, fenitrothion, fenthion, fosthiazate, malathion, methamidophos, methidathion, methyl-parathion, mevinphos, naled, omethoate, oxydemeton-methyl, parathion, phorate, phosalone, phosmet, phostebupirim, pirimiphos-methyl, profenofos, terbufos, tetrachlorvinphos, tribufos, trichlorfon,
- Oxadiazines such as indoxacarb,
- Plant toxin derived compounds such as derris (rotenone), pyrethrum, neem (azadirachtin), nicotine, caffeine,
- Pheromones such as cuellure, methyl eugenol,
- Pyrethroids such as, for example, allethrin, bifenthrin, deltamethrin, permethrin, resmethrin, sumithrin, tetramethrin, tralomethrin, transfluthrin,
- Selective feeding blockers such as flonicamid, pymetrozine,
- Spinosyns e.g. spinosad

and their mixtures.

e) Plant Growth Regulators

Plant hormones (also known as phytohormones) are chemicals that regulate plant growth. Plant hormones are signal molecules produced within the plant, and occur in extremely low concentrations. Hormones regulate cellular processes in targeted cells locally and when moved to other locations, in other locations of the plant. Plants, unlike animals, lack glands that produce and secrete hormones. Plant hormones shape the plant, affecting seed growth, time of flowering, the sex of flowers, senescence of leaves and fruits. They affect which tissues grow upward and which grow downward, leaf formation and stem growth, fruit development and ripening, plant longevity and even plant death. Hormones are vital to plant growth and lacking them, plants would be mostly a mass of undifferentiated cells. In the following, suitable plant growth regulators are mentioned:

- Aviglycine,
- Cyanamide,
- Gibberellins such as gibberellic acid,
- Quaternary ammoniums such as chlormequat chloride, mepiquat chloride,
- Ethylene generators such as ethephone,

f) Rodenticides

Rodenticides are a category of pest control chemicals intended to kill rodents. Rodents are difficult to kill with poisons because their feeding habits reflect their place as scavengers. They would eat a small bit of something and wait, and if they do not get sick, they would continue eating. An effective rodenticide must be tasteless and odorless in lethal

concentrations, and have a delayed effect. In the following, examples for suitable rodenticides are given:

Anticoagulants are defined as chronic (death occurs after 1 - 2 weeks post ingestion of the lethal dose, rarely sooner), single-dose (second generation) or multiple dose (first generation) cumulative rodenticides. Fatal internal bleeding is caused by lethal dose of anticoagulants such as brodifacoum, coumatetralyl or warfarin. These substances in effective doses are antivitamins K, blocking the enzymes K_1 -2,3-epoxide-reductase (this enzyme is preferentially blocked by 4-hydroxycoumarin/4-hydroxythiacoumarin derivatives) and K_1 -quinone-reductase (this enzyme is preferentially blocked by indandione derivatives), depriving the organism of its source of active vitamin K_1 . This leads to a disruption of the vitamin K cycle, resulting in an inability of production of essential blood-clotting factors (mainly coagulation factors II (prothrombin), VII (proconvertin), IX (Christmas factor) and X (Stuart factor)). In addition to this specific metabolic disruption, toxic doses of 4-hydroxycoumarin/4-hydroxythiacoumarin and indandione anticoagulants are causing damage to tiny blood vessels (capillaries), increasing their permeability, causing diffuse internal bleedings (haemorrhagias). These effects are gradual; they develop in the course of days and are not accompanied by any nociceptive perceptions, such as pain or agony. In the final phase of intoxication the exhausted rodent collapses in hypovolemic circulatory shock or severe anemia and dies calmly. Rodenticidal anticoagulants are either first generation agents (4-hydroxycoumarin type: warfarin, coumatetralyl; indandione type: pindone, diphacinone, chlorophacinone), generally requiring higher concentrations (usually between 0.005 and 0.1%), consecutive intake over days in order to accumulate the lethal dose, poor active or inactive after single feeding and less toxic than second generation agents, which are derivatives of 4-hydroxycoumarin (difenacoum, brodifacoum, bromadiolone and flocoumafen) or 4-hydroxy-1-benzothiin-2-one (4-hydroxy-1-thiacoumarin, sometimes incorrectly referred to as 4-hydroxy-1-thiocoumarin, for reason see heterocyclic compounds), namely difethialone. Second generation agents are far more toxic than first generation agents, they are generally applied in lower concentrations in baits (usually in the order of 0.001 - 0.005%), and are lethal after single ingestion of bait and are effective also against strains of rodents that have become resistant against first generation anticoagulants; thus the second generation anticoagulants are sometimes referred to as "superwarfarins". Sometimes, anticoagulant rodenticides are potentiated by an antibiotic, most commonly by sulfaquinoxaline. The aim of this association (e.g. warfarin 0.05% + sulfaquinoxaline 0.02%, or difenacoum 0.005% + sulfaquinoxaline 0.02% etc.) is that the antibiotic/bacteriostatic agent suppresses intestinal/gut symbiotic microflora that represents a source of vitamin K. Thus the symbiotic bacteria are killed or their metabolism is impaired and the production of vitamin K by them is diminished, an effect which logically contributes to the action of anticoagulants. Antibiotic agents other than sulfaquinoxaline may be used, for example co-trimoxazole, tetracycline, neomycin or metronidazole. A further synergism used in rodenticidal baits is that of an association of an anticoagulant with a compound with vitamin D-activity, i.e. cholecalciferol or ergocalciferol (see below). A typical formula used is, e. g., warfarin 0.025 - 0.05% + cholecalciferol 0.01%. In some countries there are even fixed three-component rodenticides, i.e. anticoagulant + antibiotic + vitamin D, e. g. difenacoum 0.005% + sulfaquinoxaline 0.02% + cholecalciferol 0.01%. Associations of a second-generation anticoagulant with an antibiotic and/or vitamin D are considered to be effective even against the most resistant strains of rodents, though some second generation anticoagulants

(namely brodifacoum and difethialone), in bait concentrations of 0.0025 - 0.005% are so toxic that no known resistant strain of rodents exists and even rodents resistant against any other derivatives are reliably exterminated by application of these most toxic anticoagulants.

Vitamin K₁ has been suggested and successfully used as an antidote for pets or humans, which/who were either accidentally or intentionally (poison assaults on pets, suicidal attempts) exposed to anticoagulant poisons. In addition, since some of these poisons act by inhibiting liver functions and in progressed stages of poisoning, several blood-clotting factors as well as the whole volume of circulating blood lacks, a blood transfusion (optionally with the clotting factors present) can save a person's life who inadvertently takes them, which is an advantage over some older poisons.

Metal phosphides have been used as a means of killing rodents and are considered single-dose fast acting rodenticides (death occurs commonly within 1-3 days after single bait ingestion). A bait consisting of food and a phosphide (usually zinc phosphide) is left where the rodents can eat it. The acid in the digestive system of the rodent reacts with the phosphide to generate the toxic phosphine gas. This method of vermin control has possible use in places where rodents are resistant to some of the anticoagulants, particularly for control of house and field mice; zinc phosphide baits are also cheaper than most second-generation anticoagulants, so that sometimes, in cases of large infestation by rodents, their population is initially reduced by copious amounts of zinc phosphide bait applied, and the rest of the population that survived the initial fast-acting poison is then eradicated by prolonged feeding on anticoagulant bait. Inversely, the individual rodents that survived anticoagulant bait poisoning (rest population) can be eradicated by pre-baiting them with nontoxic bait for a week or two (this is important to overcome bait shyness, and to get rodents used to feeding in specific areas by offering specific food, especially when eradicating rats) and subsequently applying poisoned bait of the same sort as used for pre-baiting until all consumption of the bait ceases (usually within 2-4 days). These methods of alternating rodenticides with different modes of action provides a factual or an almost 100% eradication of the rodent population in the area if the acceptance/palatability of bait is good (i.e., rodents readily feed on it).

Phosphides are rather fast acting rat poisons, resulting in that the rats are dying usually in open areas instead of the affected buildings. Typical examples are aluminum phosphide (fumigant only), calcium phosphide (fumigant only), magnesium phosphide (fumigant only) and zinc phosphide (in baits). Zinc phosphide is typically added to rodent baits in amounts of around 0.75-2%. The baits have a strong, pungent garlic-like odor characteristic for phosphine liberated by hydrolysis. The odor attracts (or, at least, does not repulse) rodents, but has a repulsive effect on other mammals; birds, however (notably wild turkeys), are not sensitive to the smell and feed on the bait thus becoming collateral damage.

Hypercalcemia. Calciferols (vitamins D), cholecalciferol (vitamin D₃) and ergocalciferol (vitamin D₂) are used as rodenticides, which are toxic to rodents for the same reason that they are beneficial to mammals: they are affecting calcium and phosphate homeostasis in the body. Vitamins D are essential in minute quantities (few IUs per kilogram body weight daily, which is only a fraction of a milligram), and like most fat soluble vitamins they are toxic in larger doses as they readily result in the so-called hypervitaminosis, which is, simply said, poisoning by the vitamin. If the poisoning is severe enough (that is, if the dose of the toxicant is high enough), it eventually leads to death. In rodents consuming the rodenticidal

bait it causes hypercalcemia by raising the calcium level, mainly by increasing calcium absorption from food, mobilising bone-matrix-fixed calcium into ionised form (mainly monohydrogencarbonate calcium cation, partially bound to plasma proteins, $[\text{CaHCO}_3]^+$), which circulates dissolved in the blood plasma, and after ingestion of a lethal dose the free calcium levels are raised sufficiently so that blood vessels, kidneys, the stomach wall and lungs are mineralised/calcified (formation of calcificates, crystals of calcium salts/complexes in the tissues thus damaging them), leading further to heart problems (myocard is sensitive to variations of free calcium levels that are affecting both myocardial contractibility and excitation propagation between atrias and ventriculas) and bleeding (due to capillary damage) and possibly kidney failure. It is considered to be single-dose, or cumulative (depending on concentration used; the common 0.075% bait concentration is lethal to most rodents after a single intake of larger portions of the bait), sub-chronic (death occurring usually within days to one week after ingestion of the bait). Applied concentrations are 0.075% cholecalciferol and 0.1% ergocalciferol when used alone. There is an important feature of calciferols toxicology which is that they are synergistic with anticoagulant toxicants. This means that mixtures of anticoagulants and calciferols in the same bait are more toxic than the sum of toxicities of the anticoagulant and the calciferol in the bait so that a massive hypercalcemic effect can be achieved by substantially lower calciferol content in the bait and vice-versa. More pronounced anticoagulant/hemorrhagic effects are observed if calciferol is present. This synergism is mostly used in baits low in calciferol because effective concentrations of calciferols are more expensive than effective concentrations of most anticoagulants. The historically very first application of a calciferol in rodenticidal bait was, in fact, the Sorex product Sorexa[®] D (with a different formula than today's Sorexa[®] D) back in the early 1970's, containing warfarin 0.025% + ergocalciferol 0.1%. Today, Sorexa[®] CD contains a 0.0025% difenacoum + 0.075% cholecalciferol combination. Numerous other brand products containing either calciferols 0.075 - 0.1% (e. g. Quintox[®], containing 0.075% cholecalciferol) alone, or a combination of calciferol 0.01 - 0.075% with an anticoagulant are marketed.

g) Miticides, molluscicides and nematicides

Miticides are pesticides that kill mites. Antibiotic miticides, carbamate miticides, formamidine miticides, mite growth regulators, organochlorine, permethrin and organophosphate miticides all belong to this category. Molluscicides are pesticides used to control mollusks, such as moths, slugs and snails. These substances include metaldehyde, methiocarb and aluminium sulfate. A nematicide is a type of chemical pesticide used to kill parasitic nematodes (a phylum of worm). A nematicide is obtained from a neem tree's seed cake; which is the residue of neem seeds after oil extraction. The neem tree is known by several names in the world but was first cultivated in India since ancient times.

h) Antimicrobials

In the following examples, antimicrobials suitable for agrochemical compositions according to the present invention are given. Bactericidal disinfectants mostly used are those applying

- active chlorine (i.e., hypochlorites, chloramines, dichloroisocyanurate and trichloroisocyanurate, wet chlorine, chlorine dioxide, etc.),

- active oxygen (peroxides such as peracetic acid, potassium persulfate, sodium perborate, sodium percarbonate and urea perhydrate),
- iodine (iodopovidone (povidone-iodine, Betadine), Lugol's solution, iodine tincture, iodinated nonionic surfactants),
- 5 ○ concentrated alcohols (mainly ethanol, 1-propanol, called also n-propanol and 2-propanol, called isopropanol and mixtures thereof; further, 2-phenoxyethanol and 1- and 2-phenoxypropanols are used),
- phenolic substances (such as phenol (also called "carbolic acid"), cresols (called "Lysol" in combination with liquid potassium soaps), halogenated (chlorinated, brominated) phenols, such as hexachlorophene, triclosan, trichlorophenol, tribromophenol, pentachlorophenol, Dibromol and salts thereof),
- 10 ○ cationic surfactants such as some quaternary ammonium cations (such as benzalkonium chloride, cetyl trimethylammonium bromide or chloride, didecyldimethylammonium chloride, cetylpyridinium chloride, benzethonium chloride) and others, non-quaternary compounds such as chlorhexidine, glucoprotamine, octenidine dihydrochloride, etc.),
- 15 ○ strong oxidizers such as ozone and permanganate solutions;
- heavy metals and their salts such as colloidal silver, silver nitrate, mercury chloride, phenylmercury salts, copper sulfate, copper oxide-chloride etc. Heavy metals and their salts are the most toxic and environmentally hazardous bactericides and, therefore, their use is strongly suppressed or forbidden; further, also
- 20 ○ properly concentrated strong acids (phosphoric, nitric, sulfuric, amidosulfuric, toluenesulfonic acids) and
- alkalis (sodium, potassium, calcium hydroxides) between pH < 1 or > 13, particularly below elevated temperatures (above 60°C) kill bacteria.
- 25

As antiseptics (i.e., germicide agents that can be used on human or animal body, skin, mucosae, wounds and the like), few of the above mentioned disinfectants can be used under proper conditions (mainly concentration, pH, temperature and toxicity toward man/animal). Among them, important are

- 30 ○ Some properly diluted chlorine preparations (e. g. Daquin's solution, 0.5% sodium or potassium hypochlorite solution, pH-adjusted to pH 7 - 8, or 0.5 - 1% solution of sodium benzenesulfochloramide (chloramine B)), some
- iodine preparations such as iodopovidone in various galenics (ointments, solutions, wound plasters), in the past also Lugol's solution,
- 35 ○ peroxides as urea perhydrate solutions and pH-buffered 0.1 - 0.25% peracetic acid solutions,
- alcohols with or without antiseptic additives, used mainly for skin antiseptics,
- weak organic acids such as sorbic acid, benzoic acid, lactic acid and salicylic acid
- some phenolic compounds such as hexachlorophene, triclosan and Dibromol, and

- cation-active compounds such as 0.05 - 0.5% benzalkonium, 0.5 - 4% chlorhexidine, 0.1 - 2% octenidine solutions.

Bactericidal antibiotics kill bacteria; bacteriostatic antibiotics only slow down their growth or reproduction. Penicillin is a bactericide, as are cephalosporins. Aminoglycosidic antibiotics can act in both a bactericidal manner (by disrupting cell wall precursor leading to lysis) or bacteriostatic manner (by connecting to 30s ribosomal subunit and reducing translation fidelity leading to inaccurate protein synthesis). Other bactericidal antibiotics according to the present invention include the fluoroquinolones, nitrofurans, vancomycin, monobactams, co-trimoxazole, and metronidazole Preferred actives are those with systemic or partially systemic mode of action such as for example azoxystrobin.

Overall preferred are biocides selected either

- (i) from the group consisting of azoles, strobilurines, diphenyl ethers, anilides, organophosphates, synthetic pyrethroids, neonicotinoids, oxadiazines, benzoyl-ureas, phenyl carbamates, chloroacetamides, triketones, pyridinecarboxylic acids, cyclohexanedione oximes, phenylpyrazoles, glyphosate and its salts, and their mixtures, or
- (ii) from the group consisting of oxyfluorfen, propanil, chlorpyrifos, bifenthrin, deltamethrin, azoxystrobin, kresoxim-methyl, lambda-cyhalothrin, novaluron, lufenuron, imidacloprid, thiacloprid, indoxacarb, oxyfluorfen, fluroxypyr and its esters, phenmedipham, desmedipham, acetochlor, tebuconazole, epoxiconazole, propiconazole, fenbuconazole, triadimenol, fipronil, and their mixtures.

Oil components or co-solvents

Suitable oil components or co-solvents (component c) are, for example, Guerbet alcohols based on fatty alcohols having 6 to 18, preferably 8 to 10, carbon atoms, esters of linear C₆-C₂₂-fatty acids with linear or branched C₆-C₂₂-fatty alcohols or esters of branched C₆-C₁₃-carboxylic acids with linear or branched C₆-C₂₂-fatty alcohols, such as, for example, myristyl myristate, myristyl palmitate, myristyl stearate, myristyl isostearate, myristyl oleate, myristyl behenate, myristyl erucate, cetyl myristate, cetyl palmitate, cetyl stearate, cetyl isostearate, cetyl oleate, cetyl behenate, cetyl erucate, stearyl myristate, stearyl palmitate, stearyl stearate, stearyl isostearate, stearyl oleate, stearyl behenate, stearyl erucate, isostearyl myristate, isostearyl palmitate, isostearyl stearate, isostearyl isostearate, isostearyl oleate, isostearyl behenate, isostearyl oleate, oleyl myristate, oleyl palmitate, oleyl stearate, oleyl isostearate, oleyl oleate, oleyl behenate, oleyl erucate, behenyl myristate, behenyl palmitate, behenyl stearate, behenyl isostearate, behenyl oleate, behenyl behenate, behenyl erucate, erucyl myristate, erucyl palmitate, erucyl stearate, erucyl isostearate, erucyl oleate, erucyl behenate and erucyl erucate. Also suitable are esters of linear C₆-C₂₂-fatty acids with branched alcohols, in particular 2-ethylhexanol, esters of C₁₈-C₃₈-alkylhydroxy carboxylic acids with linear or branched C₆-C₂₂-fatty alcohols, in particular Dioctyl Malate, esters of linear and/or branched fatty acids with polyhydric alcohols (such as, for example, propylene glycol, dimerdol or trimetriol) and/or Guerbet alcohols, triglycerides based on C₆-C₁₀-fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆-C₁₈-fatty acids, esters of C₆-C₂₂-fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, in particular benzoic acid, esters of C₂-C₁₂-dicarboxylic acids with linear or branched alcohols having 1 to 22

- carbon atoms (Cetiol® B) or polyols having 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C₆-C₂₂-fatty alcohol carbonates, such as, for example, Dicaprylyl Carbonate (Cetiol® CC), Guerbet carbonates, based on fatty alcohols having 6 to 18, preferably 8 to 10, carbon atoms, esters of benzoic acid with linear and/or branched C₆-C₂₂-alcohols (e.g. Cetiol® AB), linear or branched, symmetrical or asymmetrical dialkyl ethers having 6 to 22 carbon atoms per alkyl group, such as, for example, dicaprylyl ether (Cetiol® OE), ring-opening products of epoxidized fatty acid esters with polyols, silicone oils (cyclomethicones, silicone methicone grades, etc.), aliphatic or naphthenic hydrocarbons, such as, for example,
- 10 The preferred oil components or co-solvents show an ester or an amide structure. Particularly preferred are adipates (Cetiol® B, Agnique® DiME 6), methyl esters of vegetable oils (Agnique ME 18RD-F, Agnique® ME 12C-F), alkyl esters (Agnique® AE 3-2EH = 2-Ethylhexylamide) alkyl amides (Agnique® AMD 10), lactates, succinates, lactamides, succinamides and their mixtures – all products available in the market from Cognis GmbH,
- 15 Düsseldorf.

Emulsifiers

Suitable emulsifiers (component d) include non-ionic and anionic surfactants and their mixtures. Non-ionic surfactants include for example:

- 20 ○ products of the addition of 2 to 30 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear C₈₋₂₂ fatty alcohols, onto C₁₂₋₂₂ fatty acids and onto alkyl phenols containing 8 to 15 carbon atoms in the alkyl group;
- C_{12/18} fatty acid monoesters and diesters of addition products of 1 to 80, preferably 10 – 60 mol ethylene oxide onto glycerol;
- 25 ○ glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide addition products thereof;
- addition products of 15 to 60 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;
- 30 ○ polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxystearate or polyglycerol dimerate isostearate. Mixtures of compounds from several of these classes are also suitable;
- addition products of 2 to 15 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;
- 35 ○ partial esters based on linear, branched, unsaturated or saturated C_{6/22} fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol, polyglycerol, pentaerythritol, -dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);
- 40 ○ mono-, di and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;

- wool wax alcohols;
- polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;
- mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol and/or mixed esters of C₆₋₂₂ fatty acids, methyl glucose and polyols, preferably glycerol or polyglycerol,
- polyalkylene glycols and
- carbonates.

The addition products of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkylphenols, glycerol mono- and diesters and sorbitan mono- and diesters of fatty acids or onto castor oil are known commercially available products. They are homologue mixtures of which the average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C_{12/18} fatty acid monoesters and diesters of addition products of ethylene oxide onto glycerol are known as lipid layer enhancers for cosmetic formulations. The preferred emulsifiers are described in more detail as follows:

a) Partial glycerides

Typical examples of suitable partial glycerides are hydroxystearic acid monoglyceride, hydroxystearic acid diglyceride, isostearic acid monoglyceride, isostearic acid diglyceride, oleic acid monoglyceride, oleic acid diglyceride, ricinoleic acid monoglyceride, ricinoleic acid diglyceride, linoleic acid monoglyceride, linoleic acid diglyceride, linolenic acid monoglyceride, linolenic acid diglyceride, erucic acid monoglyceride, erucic acid diglyceride, tartaric acid monoglyceride, tartaric acid diglyceride, citric acid monoglyceride, citric acid diglyceride, malic acid monoglyceride, malic acid diglyceride and technical mixtures thereof which may still contain small quantities of triglyceride from the production process. Addition products of 1 to 30, and preferably 5 to 10, mol ethylene oxide onto the partial glycerides mentioned are also suitable.

b) Sorbitan esters

Suitable sorbitan esters are sorbitan monoisostearate, sorbitan sesquiisostearate, sorbitan diisostearate, sorbitan triisostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan dioleate, sorbitan trioleate, sorbitan monoerucate, sorbitan sesquierucate, sorbitan dierucate, sorbitan trierucate, sorbitan monoricinoleate, sorbitan sesquiricinoleate, sorbitan diricinoleate, sorbitan triricinoleate, sorbitan monohydroxystearate, sorbitan sesquihydroxystearate, sorbitan dihydroxystearate, sorbitan trihydroxystearate, sorbitan monotartrate, sorbitan sesquitartrate, sorbitan ditartrate, sorbitan tritartrate, sorbitan monocitrate, sorbitan sesquicitrate, sorbitan dicitrate, sorbitan tricitrate, sorbitan monomaleate, sorbitan sesquimaleate, sorbitan dimaleate, sorbitan trimaleate and technical mixtures thereof. Addition products of 1 to 30, and preferably 5 to 10, mol ethylene oxide onto the sorbitan esters mentioned are also suitable.

c) Alk(en)yl oligoglycosides

The alkyl or alkenyl oligoglycosides representing also preferred emulsifiers may be derived from aldoses or ketoses containing 5 or 6 carbon atoms, preferably glucose. Accordingly, the preferred alkyl and/or alkenyl oligoglycosides are alkyl or alkenyl oligoglucosides. These materials are also known generically as "alkyl polyglycosides" (APG). The alk(en)yl oligoglycosides according to the invention correspond to formula (II) :



wherein R^3 is an alkyl or alkenyl radical having from 6 to 22 carbon atoms, G is a sugar unit having 5 or 6 carbon atoms and p is a number from 1 to 10. The index p in general formula (II) indicates the degree of oligomerisation (DP degree), i.e. the distribution of mono- and oligoglycosides, and is a number of 1 to 10. Whereas p in a given compound must always be an integer and, above all, may assume a value of 1 to 6, the value p for a certain alkyl oligoglycoside is an analytically determined calculated quantity which is mostly a broken number. Alk(en)yl oligoglycosides having an average degree of oligomerisation p of 1.1 to 3.0 are preferably used. Alk(en)yl oligoglycosides having a degree of oligomerisation below 1.7 and, more particularly, between 1.2 and 1.4 are preferred from the applicational point of view. The alkyl or alkenyl radical R^3 may be derived from primary alcohols containing 4 to 22 and preferably 8 to 16 carbon atoms. Typical examples are butanol, caproic alcohol, caprylic alcohol, capric alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and technical mixtures thereof such as are formed, for example, in the hydrogenation of technical fatty acid methyl esters or in the hydrogenation of aldehydes from Roelen's oxo synthesis. Alkyl oligoglucosides based on hydrogenated C_8 - C_{16} coconut oil alcohol having a DP of 1 to 3 are preferred. Also suitable are alkoxylation products of alkyl oligoglucosides, for example adducts of 1 to 10 moles ethylene oxide and/or 1 to 5 moles propylene oxide to C_8 - C_{10} or C_{12} - C_{18} alkyl oligoglucoside having a DP between 1.2 and 1.4.

d) Alkoxylated vegetable oils

Suitable emulsifiers are castor oil, rape seed oil, soy been oil ethoxylated with 3 to 80 moles ethylene oxide (Agnique® CSO 35, Agnique® SBO 10, Agnique® SBO 60))

e) Alkoxylated copolymers

Typical copolymers are ethoxylated and propoxylated block and/or random polymers of C_2 - C_{22} linear or branched alcohols, alkoxyated oligosaccharides and alkoxyated oligoglycerol esters.

f) Anionic emulsifiers

Typical anionic emulsifiers encompass alkylbenzene sulfonic acids and their salts, as for example calcium dodecylbenzene sulfonate dissolved in isobutanol (Agnique® ABS 65C) or 2-ethylhexanol (Agnique® ABS 60C-EH), dialkyl sulfosuccinates, as for example di-2-ethylhexyl sulfosuccinate or dioctyl sulfosuccinate, and polyacrylates having a molar weight of from 1,000 to 50,000.

g) Miscellaneous emulsifiers

Other suitable emulsifiers are zwitterionic surfactants. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Ampholytic surfactants are also suitable emulsifiers. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8/18} alkyl or acyl group, contain at least one free amino group and at least one –COOH- or –SO₃H- group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethyl aminopropionate and C_{12/18} acyl sarcosine.

Biocide compositions

Depending on the nature of the biocide the products may show the following compositions:

- (a) about 0.1 % b.w. to about 99 % b.w., preferably about 15 % b.w. to about 70 % b.w., and most preferably about 20 % b.w. to about 45 % b.w. esters of ethoxylated alcohols according to formula (I);
- (b) about 1 % b.w. to about 99.1 % b.w., preferably about 5 % b.w. to about 75 % b.w., and most preferably about 15 % b.w. to about 40 % b.w. biocides,
- (c) 0 to about 50 % b.w., preferably about 5 % b.w. to about 30 % b.w. and more preferably about 10 % b.w. to about 25 % b.w. oil components or co-solvents and
- (d) 0 to about 15 % b.w., and preferably about 5 % b.w. to about 10 % b.w., emulsifiers

on the condition that the numbers optionally together with water add to 100 % b.w. The compositions represent concentrates to be diluted with water to give aqueous formulations for end-users comprising about 0.5 to about 5, preferably about 0.5 to about 1 % of the active matter represented by the concentrate.

Industrial application

Another embodiment of the present invention is related to the use of esters of ethoxylated alcohols according to formula (I) as adjuvants or additives, for example green solvents, dispersants, carrier oils and the like, for enhancing the biological efficacy of biocides. Finally,
5 the present invention also encompasses spray solutions comprising at least one pesticide and esters of ethoxylated alcohols according to formula (I).

Examples

Examples 1 to 5, Comparative Examples C1 to C5

- 5 Opus SC125, a commercial available pesticide sold by BASF, was tested to control barley powdery mildew (BPM) in a curative greenhouse trial, Azoxystrobin SC 250 in a protective trial. In each case, barley was cultivated in a substrate "Frustorder Erde" for three weeks. Each treatment was replicated 14 times. The adjuvant dose rate in each treatment was 50 ml/ha.

10

Curative trial with Opus

- Inoculation of the leaves with powdery mildew (*Blumeria graminis f. sp. hordei*) was done 2 days prior to application to test Opus' curative action. From the stem, leaf segments were cut off with a length of 10 cm using the flag leaf (F) and 2nd leaf (F-1). Altogether, the leaves of each stem were placed on benzimidazol agar i.e. 0.5% Agar with 40 ppm benzimidazol. The concentration of Opus for the leaf application was 10 g/ha. Assessment 14 days after treatment (14 DAT) of the efficacy against powdery mildew was done by counting the mildew pustules per leaf on a length of 7 cm. The assessment of the infection rate was conducted by a trained biologist.

20

Protective trial with Amistar

- 5 h after application with the equivalent of 5 g/ha azoxystrobin, leaf segments were cut off at a length of 7 cm from the stem. The leaves of the F and F-1 leaf were placed on agar. After the inoculation, the incubation time was 10 d. The assessment of the infection rate was conducted by a trained biologist.

- 25 The results are summarized in Table 1. Examples 1 to 5 are according to the inventions, examples C1 to C5 serve for comparison.

- By considering the performance in both trials, the results clearly indicate that isoamyl-20 oleate gave the best adjuvancy effect. By increasing the alkyl chain to 10 carbons, the sum of the infection rate increases. If the HLB is too low, for example in case of isoamyl-5EO oleate, even the use of isoamyl as starting alcohol for the ester does not give acceptable results.

30

Table 1:

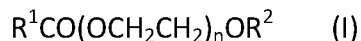
Infection rate [%] of barley powdery mildew after treatment with fungicides

Example	Adjuvant	OPUS	AMISTAR	Sum of infection rates	HLB Value
0	Control (no adjuvant)	38	51	89	-
1	Isoamyl+20EO oleate	7	0	7	14.6
2	Isoamyl+20EO laurate	12	0	12	15.7
3	Isoamyl+10EO laurate	4	14	18	13.0
4	Decyl+10EO-C _{8/10} Ester	22	0	22	12.5
5	Decyl+20EO-C _{8/10} Ester	11	12	23	15.0
C1	Isodecyl+6EO-C _{8/10} Ester	21	5	26	4.0
C2	C _{12/14} +5EO-C _{8/10} Ester	24	3	27	8.3
C3	C _{12/14} +10EO-C _{8/10} Ester	29	2	31	11.8
C4	C _{12/14} +20EO-C _{8/10} Ester	15	18	33	14.8
C5	Isoamyl+5EO oleate	17	17	34	8.1

Claims

1. Biocide compositions, comprising

(a) Esters of ethoxylated alcohols according to formula (I)



In which R^1CO stands for an saturated or unsaturated acyl radical having 8 to 22 carbon atoms, R^2 represents an alkyl radical having 1 to 10 carbon atoms, n denominates an integer of from 1 to 100, on condition that said esters exhibit an HLB value within a range of 10 to 17,

(b) Biocides and optionally

(c) Oil components or co- solvents and/or,

(d) Emulsifiers.

2. Compositions according to Claim 1, **characterised in** that they comprise esters of ethoxylated alcohols according to formula (I) in which R^1CO stands for an unsaturated acyl radical having 8 to 22 carbon atoms, R^2 represents an alkyl radical having 1 to 6 carbon atoms and n denominates an integer of from 2 to 25.

3. Compositions according to Claims 1 and/or 2, **characterised in** that they comprise esters of ethoxylated isoamyl alcohol according to formula (I) in which R^1CO stands for an unsaturated acyl radical having 12 to 22 carbon atoms.

4. Compositions according to Claims 1 to 3, **characterised in** that they comprise as component (a) oleyl and/or stearyl esters of ethoxylated isoamyl alcohol.

5. Compositions according to any of the preceding Claims 1 to 4, **characterised in** that they comprise biocides (component b) selected from the group consisting of herbicides, fungicides, insecticides and plant growth regulators.

6. Compositions according to any of the preceding Claims 1 to 5, **characterised in** that they comprise biocides (component b) selected from the group consisting of azoles, strobilurines, diphenyl ethers, anilides, organophosphates, synthetic pyrethroids, neonicotinoids, oxadiazines, benzoylureas, phenyl carbamates, chloroacetamides, triketones, pyridinecarboxylic acids, cyclohexanedione oximes, phenylpyrazoles, glyphosate and its salts, and their mixtures.

7. Compositions according to any of the preceding Claims 1 to 6, **characterised in** that they comprise biocides (Component b) selected from the group consisting of oxyfluorfen, propanil, chlorpyrifos, bifenthrin, deltamethrin, azoxystrobin, kresoxim-methyl, lambda-cyhalothrin, novaluron, lufenuron, imidacloprid, thiacloprid, indoxacarb, oxyfluorfen, fluroxypyr and its esters, phenmedipham, desmedipham, acetochlor, tebuconazole, epoxiconazole, propiconazole, fenbuconazole, triademamol, fipronil, and their mixtures.

8. Compositions according to any of the preceding Claims 1 to 7, **characterised in** that they comprise oil components or co-solvents (component c) selected from the group consisting of Guerbet alcohols based on fatty alcohols having 6 to 18 carbon atoms, esters of linear C₆-C₂₂-fatty acids with linear or branched C₆-C₂₂-fatty alcohols or esters of branched C₆-C₁₃-carboxylic acids with linear or branched C₆-C₂₂-fatty alcohols, methyl esters of C₆-C₂₂ fatty acids, esters of linear C₆-C₂₂-fatty acids with branched alcohols, esters of C₁₈-C₃₈- alkyl hydroxy carboxylic acids with linear or branched C₆-C₂₂-fatty alcohols, esters of linear and/or branched fatty acids with polyhydric alcohols and/or Guerbet alcohols, triglycerides based on C₆-C₁₀-fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆-C₁₈-fatty acids, esters of C₆-C₂₂-fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, esters of C₂-C₁₂-dicarboxylic acids with linear or branched alcohols having 1 to 22 carbon atoms or polyols having 2 to 10 carbon atoms and 2 to 6 hydroxyl groups, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear and branched C₆-C₂₂-fatty alcohol carbonates, Guerbet carbonates, based on fatty alcohols having 6 to 18, preferably 8 to 10, carbon atoms, esters of monopropylene glycol with C₂-C₁₈ acids and benzoic acid, esters of benzoic acid with linear and/or branched C₆-C₂₂-alcohols, linear or branched, symmetrical or asymmetrical dialkyl ethers having 6 to 22 carbon atoms per alkyl group, ring-opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons, mineral oils and their mixtures.
9. Compositions according to any of the preceding Claims 1 to 7, **characterised in** that said oil components or co-solvents show an ester or amide structure.
10. Compositions according to any of the preceding Claims 1 to 7, **characterised in** that said oil components or co-solvents are selected from the group consisting of adipates, methyl esters of vegetable oils, alkyl esters, fatty acid alkylamides, lactates, succinates lactamides, succinamides or their mixtures.
11. Compositions according to any of the preceding Claims 1 to 10, **characterised in** that they comprise emulsifiers (component d) selected from the group consisting of non-ionic and anionic surfactants or their mixtures.
12. Compositions according to any of the preceding Claims 1 to 11, **characterised in** that they comprise:
 - (a) 0.1 to 99 % b.w. esters of ethoxylated alcohols;
 - (b) 1 to 99.1 % b.w. biocides;
 - (c) 0 to 50 % b.w. oil components or co-solvents and
 - (d) 0 to 15 % b.w emulsifiers,
 on the condition that the numbers add optionally together with water to 100 % b.w.
13. Use of esters of ethoxylated alcohols as green solvents, carrier oils or dispersants for biocides.
14. Use of esters of ethoxylated alcohols as adjuvants.
15. Spray solutions comprising at least one biocide and esters of ethoxylated alcohols according to formula (I)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/068529

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N43/653 A01N43/54 A01N25/30
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	column 2, line 14 - line 67; claims; example 1; tables IX,X -----	1-15
Y	DE 101 07 714 A1 (COGNIS DEUTSCHLAND GMBH [DE]) 22 August 2002 (2002-08-22) paragraphs [0005], [0015]; claims ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

16 November 2011

Date of mailing of the international search report

01/12/2011

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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