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(54) Title: SOLID AGRICULTURAL COMPOSITIONS

(57) Abstract: Suggested are solid agricultural compositions, comprising: (a1) at least one alkoxyated alcohol according to general formula (I) $R^1O(AO)_nH$ (I) in which R1 stands for an unsaturated, linear hydrocarbon residue having 12 to 22 carbon atoms and 1, 2 or 3 double bonds, AO stands for an ethylene oxide, propylene, oxide and/or butylene oxide unit, and n represents an integer of from 1 to 60; (a2) at least one alkoxyated alcohol according to general formula (II) $R^2O(AO)_mH$ (II) in which R2 stands for a saturated, branched hydrocarbon residue having 8 to 36 carbon atoms, AO stands for an ethylene oxide, propylene, oxide and/or butylene oxide unit, and m represents an integer of from 1 to 60; (b) at least one biocide, and optionally (c) at least one inert Broenstedt base and/or (d) at least one solvent, emulsifier, polymer or filler, on condition that said compositions represent granules with a water content of less than 10 % b.w.

5 Solid agricultural compositions

Field of invention

The present invention belongs to the area of agriculture and refers to new solid biocide compositions comprising special types of surfactants with improved performance.

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State of the art

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. Depending on the various and often very specific needs, a magnitude of actives exist, which show very different chemical structures and behaviors.

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Pesticide products may be formulated as liquids, powders, or granules. Solvents, emulsifiers, dispersing agents and wetting agents are normally incorporated into such compositions in order to ensure that a uniform pesticide formulation has been prepared. Successful employment of any pesticide depends upon its proper formulation into a preparation that can be easily diluted with water into ready-to-use mixtures for application onto a targeted pest and/or agricultural substrate. In addition, the market requires additives - so-called "adjuvants" – providing additional benefit to the formulation by increasing the performance of the biocides in a synergistic way.

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Supply industry offers a wide spectrum of products, especially formulations, intending to fulfill all requirements of the end users. Of particular interest are surfactants working at the same time as adjuvants and solvents, wetting agents or emulsifiers. For example, **US 6,432,884** (Cognis) also refers to adjuvant compositions comprising fatty acid alkyl esters, like for example oleic acid ethyl ester, and non-ionic surfactants, like for example sorbitan esters. International patent application **WO 2004/080177 A1** (Cognis) discloses adjuvant compositions comprising fatty acid alkyl esters and a mixture of hydrophilic and hydrophobic emulsifiers. European patent **EP 0765602 B1** (Kao) recommends ethoxylated esters of glycerol or polyglycerol as adjuvants for herbicides. **WO 2010 145772 A1** (Cognis) recommends ethoxylates of unsaturated fatty alcohols as additives for aqueous solutions of biocides, in particular for tank mixes comprising glyphosate.

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While biocide compositions typically are offered in liquid forms, the solid, in particular granular form has benefits over the liquid form in easy transportation as it contains none or very little solvent or water. The granular form also has advantages of low dust in production, transportation and in application. Granular compositions of biocides, namely of glyphosate, are well known from the state of the art.

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For example, **WO 2009 09711 A1** (Excel) discloses a granular formulation comprising 70-72 % b.w. of ammonium glyphosate, 11-22 % b.w. ammonium sulfate, 5-12.5 % b.w. alkyl polyglucosides and 1-3 % b.w. acrylate based copolymers.

According to **WO 2006 133788 A1** (Sipcam) solid glyphosate compositions are obtainable, by adding solid Broenstedt bases like e.g. ammonium sulfate and liquid surfactants to the herbicide in order to obtain a wet cake and subsequently drying and granulation of the mass. Suitable surfactants are chosen from the group consisting of alkanol amides, betaine derivatives, ethoxylated-propoxylated block copolymers, glycerol esters, glycolic esters, imidazolines and its derivatives, lanolin and lecithin derivatives, tertiary and quaternary polyoxyalkylenalkyl amines, polyoxyalkylen alkyl ethers, polyoxyalkylen alkyl aryl ethers, polyoxyalkylen alkyl esters, alkoxyated and non alkoxyated sorbitan esters alkyl glycosides, alkyl polyglycosides, alkyl sulfates, alkyl phosphates, sulfonated olefins, alkyl aryl sulfonates, polyoxyalkylen alkyl ether sulfates, polyoxyalkylen alkyl ether phosphates, sulfosuccinate derivatives, and taurates.

Very similar is the content of **US 2004 102323 A1** (Vigil et al.) claiming a solid herbicidal formulation of N-(phosphonomethyl)glycine, in powder, rule or flake form, soluble or dispersible in water, comprising glyphosate (N-(phosphonomethyl)glycine) in the form of hydrosoluble salt and 5% to 30% in weight of one or more hydrosoluble tension-active agents, which are compatible with glyphosate and solids at ambient temperature, said tension-active agents being selected from the group consisting of alkanol amides, alkyl aryl sulfonates, sulfonated amines and amides, ethoxylated alkyl phenols, carboxylated alcohols, ethoxylated fatty acids, ethoxylated alcohols, sulfated alcohols, sugar and glucose derivatives, sorbitol derivatives, phosphate esters, imidazoline and its derivatives, lecithin and its derivatives, lignin and its derivatives, ethylene and propylene oxide block polymers, ethoxylated alcohol sulfates, fatty acid sulfates, naphthalene and alkyl naphthalene sulfonates, dodecyl and tridecyl benzene sulfonates, taurates and their derivatives.

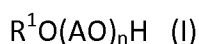
Nevertheless, solid formulations have additional challenges compared to liquid forms, which are not satisfied by the products found in the market and known from the state of the art. In particular, granular formulations are required exhibiting a better physical stability, water dispersibility and lower foaming.

Therefore, the problem underlying the present invention has been to provide new granular formulations of biocides, in particular granular formulations of glyphosate comprising tailor-made surfactant additives, in order to overcome the disadvantages explained above.

Description of the invention

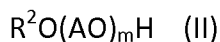
Object of the present invention are solid agricultural compositions, comprising:

(a1) at least one alkoxyated alcohol according to general formula (I)



In which R^1 stands for an unsaturated, linear hydrocarbon residue having 12 to 22 carbon atoms and 1, 2 or 3 double bonds, AO stands for an ethylene oxide, propylene oxide and/or butylene oxide unit, and n represents an integer of from 1 to 60;

(a2) at least one alkoxyated alcohol according to general formula (II)



In which R^2 stands for a saturated or an unsaturated, branched hydrocarbon residue having 8 to 36 carbon atoms, AO stands for an ethylene oxide, propylene oxide and/or butylene oxide unit, and m represents an integer of from 1 to 60;

(b) at least one biocide,

and optionally

(c) at least one inert Broenstedt base and/or

(d) at least one solvent, emulsifier or polymer,

on condition that said compositions represent granules with a water content of less than about 5 and preferably less than about 2.5 % b.w.

Surprisingly, it has been observed that the mixture of adducts of alkylene oxide, in particular about 2 to about 60 mol ethylene oxide and/or propylene oxide to (a1) unsaturated, linear alcohols and (a2) saturated, but branched alcohols provides a much better stability and dispersibility to the biocide granules compared of standard surfactants, like for example tallow amine ethoxylates. At the same time, foaming is also significantly reduced.

Alkoxyated alcohols

Alkoxyated unsaturated and/or branched alcohols forming compounds (a1) and (a2) represent known products which are obtainable according to standard procedures of organic chemistry. Typically, the alcohols are subjected to alkoxylation in the presence of an alkaline catalyst at temperatures of about 100 to 180 °C and pressures of up to 5 bar. It is possible to conduct alkoxylation using an individual alkylene oxide, that means either ethylene oxide, propylene oxide or butylene oxide or to use mixtures (random distribution). Also possible is to add them block-wise.

Suitable alcohols for obtaining compounds (a1) encompass unsaturated fatty alcohols having 12 to 22, preferably 18 carbon atoms, like for example palmoleyl alcohol, oleyl alcohol, elaidyl alcohol, linolyl alcohol, linolenyl alcohol, ricinoleyl alcohol, erucyl alcohol and their technical mixtures. Typically, oleyl alcohol is chosen showing a technical grade of purity defined by its iodine value. Suitable oleyl alcohols typically represent mixtures of unsaturated C_{18} and C_{22} fatty alcohols and saturated C_{12} - C_{22} fatty alcohols, showing iodine numbers between about 50 and about 125, preferably between about 90 and about 100, and are obtainable from vegetable oils or animal fats.

Suitable alcohols for obtaining compounds (a2) typically include guerbet alcohols, obtained by guerbet reaction of linear alcohols, preferably linear C_5 to C_{18} alcohols. These alcohols are branched in the beta-position to the hydroxyl group. A very prominent example is 2-ethylhexanol, but also 2-hexyldecanol and 2-octyldecanol are well-known sources. Nevertheless, also other branched alcohols can serve as starting material, as for example isostearyl alcohol or the monomer fraction obtained from the dimerization of unsaturated fatty alcohols.

The preferred compound (a1), however, represents an adduct of on average about 2 to about 15 mol ethylene oxide to oleyl alcohol, the preferred compound (a2) represents an adduct of on average about 2 to about 15 mol ethylene oxide and/or propylene oxide to guerbet alcohol having about 10 to about 24 carbon atoms. These two groups are individually preferred, but also in combination.

The compounds (a1) and (a2) can be added to the biocide composition within wide ranges, for example in weight ratios of unsaturated alcohol alkoxylates and said branched alcohol alkoxylates a1:a2 = about 20:80 to about 80:20. The best results are obtained in ratios by weight of a1:a2 = about 50:50 to about 30:70. The alcohols may be prepared individually and blended later, but it is also possible to subject a mixture of an appropriate unsaturated alcohol and an appropriate branched alcohol to joint alkoxylation.

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, moluscicides, 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, molluscs, 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,
- 10 ○ 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,
- 15 ○ 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,
- 20 ○ Carbamates such as propamocarb, diethofencarb,
- Carboxamides such as boscalid, diclocymet, ethaboxam, flutolanil, penthiopyrad, thifluzamide
- Chloronitriles such chlorothalonil,
- Cinnamic acid amides such as dimethomorph, flumorph,
- 25 ○ Cyanoacetamide oximes such as cymoxanil,
- Cyclopropanecarboxamides such as carpropamid,
- Dicarboximides such as iprodione, octhilinone, procymidone, vinclozolin
- Dimethyldithiocarbamates such ferbam, metam, thiram, ziram,
- Dinitroanilines such as fluazinam,
- 30 ○ 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,
- 35 ○ 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,
- 5 ○ Isobenzofuranones such as phthalide,
- Mandelamides such as mandipropamide,
- Morpholines such as dodemorph, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine, aldimorph
- Organotins such as fentin,
- 10 ○ Oxazolidinones such as oxadixyl,
- Phenylamides such as benalaxyl, benalaxyl-M, furalaxyl, metalaxyl, metalaxyl-M, ofurace,
- Phenylpyrazoles such as fipronil,
- Phenylpyrroles such as fludioxonil,
- 15 ○ Phenylureas such as pencycuron,
- Phosphonates such fosetyl,
- Phthalamic acids such as tecloftalam,
- Phthalimides such as captafol, captan, folpet,
- Piperazines such as triforine,
- 20 ○ Propionamides such as fenoxanil,
- Pyridines such as pyrifenox,
- Pyrimidines such as fenarimol, nuarimol,
- Pyrroloquinolinones such as pyroquilon,
- Qils such as cyazofamid,
- 25 ○ 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,
- 30 ○ Thiocarbamates such as methasulfocarb,
- Thiophanates such as thiophanate-methyl,
- Thiophencarboxamides such 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, bentiavalicarb
 - Fluopicolide
 - Pentachlorophenol
- 10 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 non-selective 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
- Aryloxy-carboxylic 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,
- Hydroxybenzotrioles e.g. bromoxynil,
- Imidazolinones e.g. fenamidone, imazapic, imazamox, imazapic, imazapyr, imazaquin,
- Isoxazolidinones e.g. clomazone

- Paraquat as bypyridylium,
 - Phenyl carbamates e.g. desmedipham, phenmedipham,
 - Phenylpyrazoles e.g. pyraflufen-ethyl
 - Phenylpyrazolines e.g. pinoxaden,
 - 5 ○ 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, rimsulfuron, sulfosulfuron, tribenuron-methyl, trifloxysulfuron-sodium, triflusulfuron, tritosulfuron,
 - 10 ○ Triazolopyrimidines e.g. penoxsulam, metosulam, florasulam,
 - Triketones e.g. mesotriones, sulcotrione,
 - Ureas e.g. diuron, linuron,
 - Phenoxy-carboxylic acids such as 2,4-D, MCPA, MCPB, mecoprops,
 - 15 ○ Triazines such as atrazine, simazine, terbuthylazine,
- and their mixtures.

d) Insecticides

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,
- Anthranilic diamides such as rynaxypyr
- 25 ○ Synthetic auxins such as avermectin,
- Amidines such as amitraz,
- Anthranilic diamide such as rynaxypyr,
- Carbamates such as aldicarb, carbofuran, carbaryl, methomyl, 2-(1-methylpropyl)phenyl methylcarbamate,
- 30 ○ Chlorinated insecticides such as, for example, Camphechlor, DDT, Hexachlorocyclohexane, gamma-Hexachlorocyclohexane, Methoxychlor, Pentachlorophenol, TDE, Aldrin, Chlordane, Chlordecone, Dieldrin, Endosulfan, Endrin, Heptachlor, Mirex,
- Juvenile hormone mimics such as pyriproxyfen,
- Neonicotinoids such as imidacloprid, clothianidin, thiacloprid, thiamethoxam,
- 35 ○ Organophosphorus compounds such as acephate, azinphos-methyl, bensulide, chloroxyfos, chlorpyrifos, chlorpyrifos-methyl, diazinon, dichlorvos (DDVP), dicrotophos, dimethoate, disulfoton, dthoprop, fenamiphos, fenitrothion, fenthion, fosthi-

azate, malathion, methamidophos, methidathion, methyl-parathion, mevinphos, naled, omethoate, oxydemeton-methyl, parathion, phorate, phosalone, phosmet, phostebupirim, pirimiphos-methyl, profenofos, terbufos, tetrachlor-vinphos, tribufos, trichlorfon,

- 5 ○ Oxadiazines such as indoxacarb,
- Plant toxin derived compounds such as derris (rotenone), pyrethrum, neem (azadirachtin), nicotine, caffeine,
- Pheromones such cuellure, methyl eugenol,
- Pyrethroids such as, for example, allethrin, bifenthrin, deltamethrin, permethrin,
- 10 resmethrin, sumithrin, tetramethrin, tralomethrin, transluthrin,
- Selective feeding blockers such as flonicamid, pymetrozine,
- Spinosyns e.g. spinosad

and their mixtures.

15 ***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

20 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

25 following, suitable plant growth regulators are mentioned:

- Aviglycine,
- Cyanamide,
- Gibberellins such gibberellic acid,
- Quaternary ammoniums such as chlormequat chloride, mepiquat chloride,
- 30 ○ Ethylene generators such 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, chlorphacinone), 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% + cholecal-

ciferol 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 monohydrogen-carbonate calcium cation, partially bound to plasma proteins, $[CaHCO_3]^+$), 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/calcalcified (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 Sorex[®] D (with a different formula than today's Sorex[®] D) back in the early 1970's, containing warfarin 0.025% + ergocalciferol 0.1%. Today, Sorex[®] 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, moluscicides and nematocides

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 nematocide is a type of chemical pesticide used to kill parasitic nematodes (a phylum of worm). A nematocide 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.),
- 5 ○ 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),
- 10 ○ 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 "Lysole" in combination with liquid potassium soaps), halogenated (chlorinated, brominated) phenols, such as hexachlorophene, triclosan, trichlorophenol, tribromophenol, pentachlorophenol, Dibromol and salts thereof),
- 15 ○ 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.),
- 20 ○ 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
- 25 ○ 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.

30 As antiseptics (i.e., germicide agents that can be used on human or animal body, skin, mucoses, 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

- 35 ○ 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,
- peroxides as urea perhydrate solutions and pH-buffered 0.1 - 0.25% peracetic acid solutions,
- 40 ○ 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.

5 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, 10 co-trimoxazole, and metronidazole Preferred actives are those with systemic or partially systemic mode of action such as for example azoxystrobin.

Overall preferred are non-selective herbicides and in particular biocides selected either

- 15 (i) from the group consisting of paraquat, diquat, glufosinate, glyphosate and its salts, and their mixtures; or
- (ii) 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, and their mixtures; or
- 20 (iii) from the group consisting of oxyflurofen, propanil, chlorpyrifos, bifenthrin, deltamethrin, azoxystrobin, krexoxim-methyl, lambda-cyhalothrin, novaluron, lufenuron, imidacloprid, thiacloprid, indoxacarb, oxyfluorfen, fluroxypyr and its esters, phenmedipham, desmedipham, acetochlor, tebuconazole, epoxiconazole, propiconazole, fenbuconazole, triademenol, fipronil, and their mixtures.

25 The most preferred biocides, however, are glyphosates including their esters and salts, in particular its sodium, potassium, ammonium and isopropylammonium salt and their mixtures.

Inert Broenstedt bases

30 Typically, the inert Broenstedt bases (component c) represent alkaline, ammonium and/or alkaline earth sulfates, preferably ammonium sulfate, potassium sulfate, sodium sulfate, or their mixtures. Optionally small amounts of anti-packing agents as, for example, magnesium carbonate are added. Preferably the inert agent is milled before being added to the other components so as to have particle size lower than 500 micron.

35

Solvents

Suitable solvents (component d1) 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 40 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, dimerdiol or trimertriol) 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.

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-Ethylhexyl Lactate) and alkyl amides (Agnique[®] AMD 10) – all products available in the market from Cognis GmbH, Düsseldorf.

Emulsifiers

Suitable emulsifiers (component d2) include non-ionic and anionic surfactants and their mixtures. Non-ionic surfactants include for example:

- 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 30 mol ethylene oxide onto glycerol;
- 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 hydrogen-

- ated castor oil;
- 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;
 - 5 ○ addition products of 2 to 15 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;
 - 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);
 - 10 ○ mono-, di and trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;
 - wool wax alcohols;
 - 15 ○ 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, and
 - polyalkylene glycols.
- 20 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
- 25 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

- 30 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
- 35 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.

40

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 (III) :



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 (III) 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^1 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) Alkoxyated vegetable oils and copolymers

Suitable emulsifiers are castor oil, rape seed oil, soy bean oil ethoxylated with 3 to 80 moles ethylene oxide (Agnique[®] CSO 35, Agnique[®] SBO 10, Agnique[®] SBO 60). Typical copolymers are ethoxylated and propoxylated block and/or random polymers of C₂-C₂₂ linear or branched alcohols.

e) 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.

f) 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-alkylamino-butyrac 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.

Polymers

Also the polymers (component d3) represent optional ingredients which are added to the formulation to increase stability of the granules. Examples are polyacrylates, polymethacrylates and condensation products of naphthalene sulfonic acid.

Biocide compositions

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

- (a) about 1 to about 30, and preferably about 8 to about 12 % b.w. mixtures of alkoxy-lated alcohols according to formula (I) and (II)
- 5 (b) about 3 to about 95, and preferably about 50 to 90 and more preferably about 70 to about 85 % b.w. biocides;
- (c) 0 to about 15, and preferably about 2 to about 8 % b.w. inert Broenstedt bases;
- (d1) 0 to about 5, and preferably about 2 to about 4 % b.w. solvents;
- (d2) 0 to about 5, and preferably about 2 to about 4 % b.w. emulsifiers; and
- 10 (d3) 0 to about 5, and preferably about 2 to about 4 % b.w. polymers;
- (d4) 0 to about 5, and preferably about 2 to about 4 % b.w. fillers, such as clay.

on condition that the numbers add optionally together with not more than about 10 , and preferably about 3 to 5 % b.w. water to 100 % b.w.

15 Industrial application

A final embodiment of the present invention is related to the use of mixtures of alkoxy-lated unsaturated and branched alcohols as defined above as additives and or adjuvants for bio-cides and biocide compositions, preferably for compositions representing granules with a water content of less than about 10 % b.w. , and preferably less than about 5 % b.w.

20

Examples

Examples 1 to 6, Comparative Example C1

5 Various surfactant blends were used for making glyphosate granules and the resulting products were evaluated for its properties. Foam height was determined according to the Ross-Miles Test, appearance, hardness, solubility and stability by observation. The results are compiled in the following Table 1. Examples 1 to 6 are according to the invention, Example C1 serves for comparison.

Table 1

10 Properties of glyphosate granules

Composition	C1	1	2	3	4	5	6
Surfactant blend for water soluble granule (WG) formula							
Agnique® GPC ¹	100.0	-	-	-	-	-	-
Agnique® FOH 90C-5 ²	-	-	-	50.0	45.0	-	-
Agnique® FOH 90C-10 ³	-	50.0	45.0	-	-	30.0	30.0
Lutensol® XP 60 ⁴	-	50.0	45.0	-	-	40.0	35.0
Lutensol® XP 100 ⁵	-	-	-	50.0	45.0	30.0	30.0
Hydropalat® 5040 ⁶	-	-	10.0	-	10.0	-	10.0
WG formula							
Surfactant blend (above)	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Sodium sulfate	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Ammonium sulfate	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Glyphosate ammonium salt (96.2 %)	83.4	83.4	83.4	83.4	83.4	83.4	83.4
Tamol® NN 8906 ⁷	1.5	1.5	1.5	1.5	1.5	1.5	1.5
WG properties (after adding 2.0 % water to the granules)							
Appearance	Granule	Granule	Granule	Granule	Granule	Granule	Granule
Hardness	Soft	Good	Good	Good	Good	Good	good
Collapsibility	25.0	5.0	5.0	5.0	5.0	5.0	5.0
Foam height [ml]	> 10	< 5	< 10	< 5	< 5	< 5	< 10
Solubility	Poor	Good	Good	Good	Good	Good	Good
Stability (54 °C, 2 weeks)	Average	Good	Good	Good	Good	Good	Good

1) Tallow amine+15EO; 2) Oleyl alcohol+5EO; 3) Oleyl alcohol+10 EO; 4) C₁₀ Guerbet alcohol+6EO; 5) C₁₀ Guerbet alcohol+10EO; 6) Polyacrylate; 7) Naphthalene sulfonic acid polycondensate, sodium salt

Claims

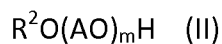
1. Solid agricultural compositions, comprising:

(a1) at least one alkoxyated alcohol according to general formula (I)



In which R^1 stands for an unsaturated, linear hydrocarbon residue having 12 to 22 carbon atoms and 1, 2 or 3 double bonds, AO stands for an ethylene oxide, propylene, oxide and/or butylene oxide unit, and n represents an integer of from 1 to 60;

10 (a2) at least one alkoxyated alcohol according to general formula (II)



In which R^2 stands for a saturated, branched hydrocarbon residue having 8 to 36 carbon atoms, AO stands for an ethylene oxide, propylene, oxide and/or butylene oxide unit, and m represents an integer of from 1 to 60;

15 (b) at least one biocide,
and optionally

(c) at least one inert Broenstedt base and/or

(d) at least one solvent, emulsifier, polymer or filler,

20 on condition that said compositions represent granules with a water content of less than 10 % b.w.

2. Compositions according to Claim 1, **characterized in** that compound (a1) represents an adduct of on average 2 to 15 mol ethylene oxide to oleyl alcohol

3. Compositions according to Claim 1, **characterized in** that compound (a2) represents an adduct of on average 2 to 15 mol ethylene oxide and/or propylene oxide to guerbet alcohol having 10 to 24 carbon atoms.

4. Compositions according to any of the preceding Claims 1 to 3, **characterized in** that said unsaturated alcohol alkoxyates and said branched alcohol alkoxyates are present in a ratio by weight $a1:a2 = 20:80$ to $80:20$.

5. Compositions according to any of the preceding Claims 1 to 4, **characterized in** that said solid compositions contain less than 5 % water.

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 herbicides, fungicides, insecticides and plant growth regulators.

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 non-selective herbicides.

8. Compositions according to any of the preceding Claims 1 to 7, **characterised in** that they comprise biocides (component b) selected from the group consisting of paraquat, diquat, glufosinate, glyphosate and its salts, and their mixtures.
- 5 9. Compositions according to any of the preceding Claims 1 to 8, **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, and their mixtures.
- 10 10. Compositions according to any of the preceding Claims 1 to 9, **characterised in** that they comprise biocides (component b) selected from the group consisting of oxyfluorfen, propanil, chlorpyrifos, bifenthrin, deltamethrin, azoxystrobin, krexoxim-methyl, lambda-cyhalothrin, novaluron, lufenuron, imidacloprid, thiacloprid, indoxacarb, oxyfluorfen, fluroxypyr and its esters, phenmedipham, desmedipham, acetochlor, tebuconazole, epoxiconazole, propiconazole, fenbuconazole, triademenol, fipronil, and their mixtures.
- 15 11. Compositions according to any of the preceding Claims 1 to 10, **characterised in** that they comprise as biocides glyphosate or one of its esters or salts.
- 20 12. Compositions according to any of the preceding Claims 1 to 11, **characterised in** that they comprise as inert Broensted bases (component c) alkaline, ammonium and/or alkaline earth sulfates.
- 25 13. Compositions according to any of the preceding Claims 1 to 12, **characterised in** that they comprise solvents (component d1) 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 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.
- 30 35 40 14. Compositions according to any of the preceding Claims 1 to 13, **characterised in** that they comprise emulsifiers (component d2) selected from the group consisting of non-ionic and anionic surfactants or their mixtures.

15. Compositions according to any of the preceding Claims 1 to 14, **characterised in** that they comprise polymers (component d3) selected from the group consisting of polyacrylates, polymethacrylates and polycondensation products of naphthalene sulfonic acid.
- 5 16. Compositions according to any of the preceding Claims 1 to 15, **characterised in** that they comprise:
- (a) 1 to 30 % b.w. mixtures of alkoxyated alcohols according to formula (I) and (II)
 - (b) 3 to 95 % b.w. biocides;
 - (c) 0 to 15 % b.w. inert Broenstedt bases;
 - 10 (d1) 0 to 5 % b.w. solvents;
 - (d2) 0 to 5 % b.w emulsifiers; and
 - (d3) 0 to 5 % b.w. polymers;
 - (d4) 0 to 5 % b.w. fillers;
- 15 on condition that the numbers add optionally together with not more than 10 % b.w. water to 100 % b.w.
17. Use of mixtures of alkoxyated unsaturated and branched alcohols according to Claim 1 as additives for biocides and biocide compositions.
18. Use of mixtures of alkoxyated unsaturated and branched alcohols according to Claim 1 as adjuvants for biocides and biocide compositions.
- 20 19. Use according to Claims 17 and/or 18, **characterized in** that said biocide compositions represent granules with a water content of less than 5 % b.w.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/080233

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: A01N 25/00; A01N 25/12; A01N 25/30; A01N 57/20; A01P 13/00

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 practicable, search terms used)

CNABS, CPRSABS, DWPI, SIPOABS, CJFD, CAB ABSTRACT, Roundup, glyphosate, AE, AEO, Alcoholalkoxylate, Alkoxylated alcohol, Genapol, Softanol, Tergitol, alcohol, ethylhexanol, guerbet alcohol, hexyldecanol, octyldodecanol, ol, oleyl alcohol, granule, granules

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1241114 A (MONSANTO COMPANY), 12 January 2000 (12.01.2000), see page 4, lines 21-25; page 7, lines 16-24; page 17, lines 14-20; page 18, line 30; page 19, lines 8-10; table of pages 24-25; page 73, table 15a	1-19
Y	CN 1241114 A (MONSANTO COMPANY), 12 January 2000 (12.01.2000), see page 4, lines 21-25; page 7, lines 16-24; page 17, lines 14-20; page 18, line 30; page 19, lines 8-10; table of pages 24-25; tables of Pages 21-22; tables 13a-16a; tables 18a-19a; tables 24a; tables 27a-34a; tables 37a; tables 39a-42a; tables 45a; tables 48a; tables 50a; tables 60a; tables 62a-64a; tables 66a; tables 68a-70a	1-19
X	WO 9600010 A1 (ZENECA LIMITED), 4 January 1996 (04.01.1996), see page 2, paragraph 3 to page 5, paragraph 3	1-19
Y	WO 9814060 A1 (ALBEMARLE CORPORATION), 9 April 1998 (09.04.1998), see page 2, line 16 to page 3, line 21; page 12, lines 23-31	1-19

Further documents are listed in the continuation of Box C.

See patent family annex.

<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p>	<p>“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</p> <p>“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</p> <p>“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</p> <p>“&” document member of the same patent family</p>
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<p>Date of the actual completion of the international search</p> <p style="text-align: center;">19 June 2012 (19.06.2012)</p>	<p>Date of mailing of the international search report</p> <p style="text-align: center;">05 Jul. 2012 (05.07.2012)</p>
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<p>Name and mailing address of the ISA/CN</p> <p>The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451</p>	<p>Authorized officer</p> <p style="text-align: center;">KANG Endai</p> <p>Telephone No. (86-10)62084338</p>
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International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 9736493 A1 (ALBEMARLE CORPORATION), 9 October 1997 (09.10.1997), see page 3, paragraphs 1-4; page 4, paragraph 2 to page 8, paragraph 2; claims 25-30	1-19
Y	WO 2008070947 A2 (RICARDO AMARAL BEMER), 19 June 2008 (19.06.2008), see claims 12-16	1-19
Y	US 6337078 A (RICHARD LEVY), 8 January 2002 (08.01.2002), see column 9, lines 48-55	1-19
A	WO 2006133788 A (SIPCAM S.P.A), 21 December 2006 (21.12.2006), see page 13, line 3 to page 14, line 12	1-19

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/080233

CLASSIFICATION OF SUBJECT MATTER:

A01N 25/12 (2006.01)i

A01N 25/30 (2006.01)i

A01N 57/20 (2006.01)n

A01P 13/00 (2006.01)n