The compositions exhibit an improved stability even if stored at temperatures between 5° and 40° C. over a longer period.
BIOCIDE COMPOSITIONS (I)

FIELD OF THE INVENTION

[0001] The present invention relates to the area of agrochemicals and refers to biocide compositions comprising certain dialkylamides and their use as solvents or dispersants for biocides.

BACKGROUND OF THE INVENTION

[0002] 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 behaviours. Nevertheless, it is well known from the state of the art that it remains difficult to prepare aqueous solutions of these actives exhibiting a satisfying stability, especially if stored over a longer time at very low or elevated temperatures. As a matter of fact, the solutions show a strong tendency to either separate or 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. Due to the fact that in spray equipments, which are customarily used for the application of aqueous formulations of plant treatment agents, several filters and nozzles are present, an additional problem appears which is related to the blocking of these filters and nozzles as a result of crystallizing active compound during the application of aqueous spray liquors based on solid active compounds.

[0003] European patent application EP 0453899 B1 (Bayer) discloses the use of dimethylamides derived from saturated C_2-C_20 fatty acids as crystallisation inhibitors for azol derivatives which can be applied as fungicides. Unfortunately, the dimethylamides suggested in the patent are useful for a limited number of actives. Even in case of azols and azol derivatives the ability to inhibit unwanted crystallisation is limited to ambient temperatures, while the products are close to being useless in case the solutions have to be used at temperatures of about 5 to 10°C.

[0004] Therefore the problem underlying the present invention has been to avoid the disadvantages of the state of the art and develop new compositions with improved storage stability and reduced tendency to form crystals for a wide range of biocides within a temperature range between 5 and 40°C.

DETAILED DESCRIPTION OF THE INVENTION

[0005] The present invention refers to biocide compositions, comprising

[0006] (a) at least one dialkylamide based on a hydroxy-carboxylic acid, and

[0007] (b) at least one biocide.

[0008] Surprisingly it has been observed that dialkylamides, and preferably dimethylamides, obtained from hydroxyacaboxylic acid, in particular lactic acid dimethylamide, show an improved solubilising power compared to dimethylamides from fatty acids as known from the state of the art. Applicant has found that the hydroxyacaboxylic acid dialkylamides are able to dissolve or disperse a wide range of biocides even under drastic conditions, which means storage times of at least 4 weeks at temperatures between 5 and 40°C. without phase separation or sedimentation.

Dialkylamides

[0009] Dialkylamides according to the present invention (component a) can be derived from hydroxy-substituted mono-, di- or triacetic acid. In case the carboxylic acid has two or three acid groups, the amide may be a mono-, di- or triamide or represent a statistical mixture. In a first embodiment of the present invention, dialkylamides follow the general formula (I),

\[ R^1\text{CO} - \text{NR}^2\text{R}^3 \]  

in which \( R^1\text{CO} \) stands for a hydroxy-substituted acyl radical having 1 to 22 carbon atoms, and \( R^2\text{and R}^3 \) independently represent hydrogen or alkyl groups having 1 to 4 carbon atoms. Typical examples are dialkylamides of lactic acid, ricinoleic acid or 12-hydroxy stearic acid. Other suitable dialkylamides can be derived from citric acid or tartaric acid or their mixtures. The preferred dialkylamides represent dimethylamides. The most preferred species exhibiting the best performance in dissolving or dispersing a wide number of different biocides over a long period and both at low and high temperatures is lactic acid dimethylamide.

Biocides

[0010] A biocide (component b) is a chemical substance capable of killing different forms of living organisms used in fields such as medicine, agriculture, forestry, and mosquito control. Usually, biocides are divided into two sub-groups:

[0011] pesticides, which includes fungicides, herbicides, insecticides, algalicides, molluscicides, miticides and rodenticides, and

[0012] antimicrobials, which includes germicides, antibiotic, antibacterial, antiviral, antifungal, antiprotential and antiparasites.

[0013] 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.

Pesticides

[0014] 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:

[0015] Fungicides

[0016] A fungicide is one of three methods of pest control—the chemical control of fungi in this case. Fungicides are chemical compounds used to prevent the growth 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 species: (3-ethoxypropyl)mercury bromide, 2-methi-
oxyethylmercury chloride, 2-phenylphenol, 8-hydroxyquinoline sulfate, 8-phenylmercuricxyquinoline, acibenzolar, acylamino acid fungicides, acypetac, aldorph, aliphatic nitrogen fungicides, allyl alcohol, amide fungicides, ampropylfos, anilide, anilide fungicides, antibiotic fungicides, aromatic fungicides, aurofungin, azoxystrobin, bariun polysulfide, benalaxyl, benzaldehyde, benzalkonium chloride, benzenacril, benzamide fungicides, benzamidazon, benzamide fungicides, benzimidazole fungicides, benzimidazole precursor fungicides, benzimidazolylcarbamate fungicides, benzothiazole fungicides, bethoxazin, binaflur, bilanox, bithionol, blasticidin-S, Bordeaux mixture, bosalid, bridged diphenyl fungicides, bromocarpace, buxinate, Burgundy mixture, buthiobate, butylamine, calcium polysulfide, captfol, captan, carbamate fungicides, carboramorph, carbonatite fungicides, carbendazim, carboxin, carprofamid, carveone, Cheshnut mixture, chlorimethoan, chlobenziazole, chlorimuron, chlorimuron-ethyl, chlorimuron-ethyl, chlorodinitrifenethyl, chloroneb, chloropicrin, chlorothalonil, chlorquin, chloroxone, ciploxipox, clmbazole, clortimazole, conazole fungicides, conazole fungicides (imidazoles), conazolefungicides (triazoles), copper (II) acetate, copper(II) carbonate, basic, copper fungicides, copper hydroxide, copper naphthenate, copper oxide, copper oxychloride, copper(II) sulfide, copper sulfate, basic, copper zinc chromate, cresol, cutane, cuprobam, cupric oxide, cyazofamid, cyflurafuran, cyclic dithiocarbamate fungicides, cycloheximide, cyflufenamid, cyprofamid, cyprozazole, cypropol, dazomet, DBCP, debacar, decaflan, dehydroacetic acid, dicarboximide fungicides, dichlofluanid, dichlone, dichloronphene, dichloromethyl, dichloromide fungicides, dichlozoline, dicyclotrazol, diclofenac, diclofrocarbonate, difenconazole, diflumetrol, dimetrimol, dimethomorph, dimoxystrobin, diniconazole, dinotrophenol fungicides, dinobuten, dinocap, dinocut, dinonet, dinonit, dino, dinitrofen, diphenylamine, diphenylamine, disulfiram, ditianilam, dithioan, dithiocarbamate fungicides, DNOC, dodemorph, doquin, dodec, DONATODINE, droxolanol, edifenphos, epoxiconazole, etaconazole, etem, etixobam, ethirimol, ethoxyquin, ethylmercury, ethylmercury acetate, ethylmercury bromide, ethylmercury chloride, ethylmercury phosphate, etridiazole, famoxadone, fenamidone, fenaminoic acid, fenapanil, fenamiphos, fenhexamid, fenitropan, fenoxaprid, fenchlorphos, fenpropidin, fenpropimorph, fentin, ferbam, ferbam, fluazinam, floriloxone, fludioxonil, flumeten, flumorph, fluphenicol, fluoroacide, fluoroacetamide, fluoroacetamide, fluoroacetamide, fluoroacetamide, flusoxytriazin, flusilazole, flutolanil, flutriafol, folpet, formaldehyde, fosetyl, furadiazin, furfural, furamidone, furamidone, furamido fungicides, furamidone fungicides, furfuracil, furconazole, furconazole-cis, furconazole, furconazole-cis, fumazin, furofuran, glyoxin, glyoxin, griseofulvin, guazatine, halacrine, hexachlorobenzene, hexachlorobutadiene, hexachlorophene, hexaconazole, hexythiofos, hydrargaphen, hymexazol, imazalil, imibenconazole, imidazole fungicides, iminoconazole, inorganic fungicides, inorganic mercury fungicides, iodomethane, iopconazole, iprobenfos, iprodione, iprovalicarb, isoprothiolane, kasugamycin, kresoxim-methyl, l-methyl sulfox, mancozeb, mancozeb, maneb, meibenil, mecinonil, mepronil, mercuric chloride, mercuric oxide, mercurous chloride, mercury fungicides, metalaril, metalaxyl-M, metan, metalaxyl, metconazole, methanofurcar, methfuroxam, methyl bromide, methyl isothiocyanate, methylmercury benzoate, methylmercury dicyandiamide, methylmercury pentachlorophenoxide, metiram, metomicrob, metofenone, mercury, n-(ethylmercury)-p-toluenesulphonanilide, naph, natacam, nitrolystene, nitronil-isopropyl, nustrol, OCH, ochtholine, oflurine, organomercury fungicides, organophosphorus fungicides, organotin fungicides, orydatazol, oxadiazin, oxathiin fungicides, oxazole fungicides, oxxine copper, oxoproconazole, oxybaroxin, peflurazole, penconazole, pencycuron, penteclophenol, penthiapryn, phenylmercury acetate, phenylmercury chloride, phenylmercury derivative of pyrocatechol, phenylmercury nitrate, phenylmercury salicylate, phenylsulfa- mide fungicides, phosphene, phthalide, phthalide fungicides, picocarbos, piperonyl, polybrominated, polymeric dithiocarbamate fungicides, polyoxins, pentaerythrol, polysulfide fungicides, potassium azide, potassium polsulfide, potassium thioanate, probenazole, prociloraz, proconazole, propamocar, propiconazole, propine, propinoxad, prothioctocar, prothioconazole, pyracarbolid, pyraclostrobin, pyrazole fungicides, pyrazoles, pyridzine fungicides, pyrimidin, pyridox, pyrimethanil, pyrimidine fungicides, pyrquinol, pyrophos, pyrrol, pyrrole fungicides, quinacetol, quinazamid, quinalconazole, quinoline fungicides, quinone fungicides, quinoxaline fungicides, quinone oxygen, quinone, resanazole, salicylanilide, stilbione, simconazole, sodium azide, sodium orthophenylhydroxide, sodium pentachlorophenoxide, sodium polysulfide, spiroxamine, streptomycin, streptoburin fungicides, sulfonanilide fungicides, sulfur, sulproth, TCMB, tebuconazole, teclofatan, tecanze, tecoran, teconazole, thiabenda, thiadifluor, thiacylene, thiacarbanate fungicides, thiochlorphen, thioamidal, thioanilide fungicides, thioconazole, thiram, thiolut, thioylmethyl, tolylfluron, tolylmercury acetate, triadimefon, triadimenol, triamidol, triallol, tricarbaloxy, triazole fungicides, triazole fungicides, triazoline fungicides, trichlorome, trietradecyl, trilixyl, triloxynostrobin, triflumizole, trifloride, triticonazole, unclassified fungicides, unspecific acid, uniconazole, urea fungicides, validamycin, valinamide fungicides, vinclozolin, zarilamid, zinc naphthenate, zineb, ziram, zoxamide and their mixtures.

[0017] Herbicides

[0018] 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 the following, a number of suitable herbicides are compiled:

[0019] 2,4-D, a broadleaf herbicide in the phenoxy group used in turf and in no-till field crop production. Now mainly used in a blend with other herbicides that act as synergists, it is the most widely used herbicide in the
world, third most commonly used in the United States. It is an example of synthetic auxin (plant hormone).

[0020] Atrazine, a triazine herbicide used in corn and sorghum for control of broadleaf weeds and grasses. It is still used because of its low cost and because it works as a synergist when used with other herbicides, it is a photosystem H inhibitor.

[0021] Clopyralid, a broadleaf herbicide in the pyridine group, used mainly in turf, rangeland, and for control of noxious thistles. Notorious for its ability to persist in compost. It is another example of synthetic auxin.

[0022] Dicamba, a persistent broadleaf herbicide active in the soil, used on turf and field corn. It is another example of synthetic auxin.

[0023] Glyphosate, a systemic nonselective (it kills all type of plant) herbicide used in no-till burndown and for weed control in crops that are genetically modified to resist its effects. It is an example of an EPSPS inhibitor.

[0024] Imazapic, a nonselective herbicide used for the control of a broad range of weeds including terrestrial and perennial grasses and broad-leaved herbs, woody species, and riparian and emergent aquatic species.

[0025] Imazapic, a selective herbicide for both the pre- and post-emergent control of some annual and perennial grasses and some broadleaf weeds. Imazapic kills plants by inhibiting the production of branched chain amino acids (valine, leucine, and isoleucine), which are necessary for protein synthesis and cell growth.

[0026] Metolachlor, a pre-emergent herbicide widely used for control of annual grasses in corn and sorghum; it has largely replaced atrazine for these uses.

[0027] Paraquat, a nonselective contact herbicide used for no-till burndown and in aerial destruction of marijuana and coca plantings. More acutely toxic to people than any other herbicide in widespread commercial use.

[0028] Picolam, a pyridine herbicide mainly used to control unwanted trees in pastures and edges of fields. It is another synthetic auxin.


[0030] Insecticides.

[0031] 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 insecticides are mentioned:

[0032] Chlorinated insecticides such as, for example, Camphechlor, DDT, Hexachlorocyclohexane, gamma-Hexachlorocyclohexane, Methoxychlor, Pentachlorophenol, TDE, Aldrin, Chlordane, Chloredcone, Dieldrin, Endosulfan, Endrin, Heptachlor, Mirex and their mixtures;

[0033] Organophosphorus compounds such as, for example, Acephate, Azinphos-methyl, Bensulide, Chloroaryl, Chlorpyrifos, Chlorpyrifos-methyl, Diazinon, Dichlorvos (DDVP), Dicrotophos, Dimethoate, Disulfoton, Ethoprop, Fenamiphos, Fenithion, Fenphos, Fosthiazate, Malathion, Methamidophos, Methidathion, Methion-methyl-parathion, Mevinphos, Naled, Omethoate, Oxydemeton-methyl, Parathion, Phorate, Phosalone, Phosmet, Phosteburon, Pirimiphos-methyl, Profenofos, Terbufos, Tetrachlorvinphos, Tribufos, Trichlorfon and their mixture; [0034] Carbamates such as, for example, Aldicarb, Carbophur, Carbaryl, Methomyl, 2-(1-Methylpropyl)phenyl methylcarbamate and their mixtures;

[0035] Pyrethroids such as, for example, Allethrin, Bifentrin, Deltamethrin, Permethrin, Resmethrin, Sumithrin, Tetramethrin, Tralomethrin, Transfluthrin and their mixtures; Plant toxin derived compounds such as, for example, Derris (rotenone), Pyrethrum, Neem (Azadirachtin), Nicotine, Caffeine and their mixtures.

[0036] Rodenticides.

[0037] 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:

[0038] 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$_2$,3-epoxide-reductase (this enzyme is preferentially blocked by 4-hydroxyocoumarin/4-hydroxythiacoumarin derivatives) and K$_1$-quinoine-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 (Smart factor)). In addition to this specific metabolic disruption, toxic doses of 4-hydroxyocoumarin/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, diphenacinone, chloroplicacine), 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-benzothien-2-one (4-hydroxy-1-thiacoumarin, sometimes incorrectly referred to as 4-hydroxy-1-thiacoumarin, 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 sulfaquinocarcin. The aim of this association (e.g. warfarin 0.05%+sulfaquinocarcin 0.02%, or difenacoum 0.005%+sulfaquinocarcin 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 sulfaquinocarcin may be used, for example co-trimoxazole, tetracycline, neomycin or metronida-zole. 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%+sulfaquinocarcin 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 derivates are reliably exterminated by application of these most toxic anticoagulants.

Vitamin K 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. Conversely, 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 provide 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 most cases of rats 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.

Hypercacemia. Calciferols (vitamins D), cholecalciferol (vitamin D$_1$) and ergocalciferol (vitamin D$_2$) 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 Ws 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 calcifi-
erol in the bait so that a massive hypercalcemic effect can be achieved by a substantially lower calciferol content in the bait and vice-versa. More pronounced anticoagu-lant/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% difenaconum + 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.

[0043] Miticides, Moltuscides and Nematicides

[0044] 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.

[0045] Moltuscides are pesticides used to control mol-lusks, such as mosls, slugs and snails. These substences include metaldehyde, methiocarb and aluminium sulfate. A nematicide is a type of chemical pesticide used to kill parasitic nematodes (a phylum of worm).

[0046] 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.

[0047] Antimicrobials

[0048] In the following examples, antimicrobials suitable for agrochemical compositions according to the present invention are given. Bactericidal disinfectants mostly used are those applying

[0049] active chlorine (i.e., hypochlorites, chloramines, dichloroisocyanurate and trichloroisocyanurate, wet chlorine, chlorine dioxide, etc.),

[0050] active oxygen (peroxides such as peracetic acid, potassium persulfate, sodium perborate, sodium percarbonate and urea perhydrate),

[0051] iodine (povidone iodine, Betadine), Lugol’s solution, iodine tincture, iodinated non-ionic surfactants,

[0052] 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-phenoxypipropanols are used),

[0053] phenolic substances (such as phenol (also called “carbolic acid”), cresols (called “Lysole” in combination with liquid potassium soaps), halogenated (chlorin-ated, brominated) phenols, such as hexachlorophene, triclosan, trichlorophenol, tribromophenol, pentachlorophenol, Dibromol and salts thereof),

[0054] cationic surfactants such as some quaternary ammonium cations (such as benzalkonium chloride, cetaryl trimethylammonium bromide or chloride, dide-cyldimethylammonium chloride, cetylpyridinium chloride, benzethonium chloride) and others, non-quar-tierary compounds such as chlorhexidine, glycopyrrolamine, octenidine dihydrochloride, etc.);

[0055] strong oxidizers such as ozone and permanganate solutions;

[0056] 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

[0057] properly concentrated strong acids (phosphoric, nitric, sulfuric, amidosulfuric, thioenesulfonic acids) and

[0058] alkalis (sodium, potassium, calcium hydroxides) between pH <1 or >13, particularly below elevated temperatures (above 60°C) kill bacteria.

[0059] 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

[0060] 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 benzenesulfonate (chloramine B)), some

[0061] iodine preparations such as iopodovivone in various galencies (ointments, solutions, wound plasters), in the past also Lugol’s solution,

[0062] peroxides as urea perhydrate solutions and pH-buffered 0.1-0.25% peracetic acid solutions,

[0063] alcohols with or without antiseptic additives, used mainly for skin antisepsis,

[0064] weak organic acids such as sorbic acid, benzoic acid, lactic acid and salicylic acid

[0065] some phenolic compounds such as hexachloro-phenol, tricosan and Dibromol, and

[0066] cation-active compounds such as 0.05-0.5% benzalkonium, 0.5-4% chlorhexidine, 0.1-2% cetrimide solutions.

[0067] 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 bacterio-static 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.

Emulsifiers

[0068] In a number of cases it is advantageous to add emul-sifiers (component c) to the biocide compositions in order to support the stability of the products. A first preferred group of emulsifiers encompasses non-ionic surfactants such as, for example:

[0069] products of the addition of 2 to 30 mol ethylene oxide and/or 0 to 5 mol propylene oxide onto linear or branched, saturated or unsaturated C₈₋₂₂ fatty alcohols, onto C₁₂₋₁₈ fatty acids and onto alkyl phenols containing 8 to 15 carbon atoms in the alkyl group;

[0070] C₁₂₋₁₈ fatty acid monoesters and diesters of addition products of 1 to 30 mol ethylene oxide onto glycerol;
[0071] 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;

[0072] addition products of 15 to 60 mol ethylene oxide onto castor oil and/or hydrogenated castor oil;

[0073] polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate, polyglycerol poly-12-hydroxy stearate or polyglycerol dimannate isostearate. Mixtures of compounds from several of these classes are also suitable;

[0074] addition products of 2 to 15 mol ethylene oxide onto castor oil and/or hydrogenated castor oil and/or other vegetable oils;

[0075] partial esters based on linear, branched, unsaturated or saturated C_{12-22} fatty acids, ricinoleic acid and 12-hydroxy stearic acid and glycerol, polyglycerol, pentaoxythritol, dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl gluco side) and polyglycides (for example cellulose);

[0076] mono-, di and triacyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates and salts thereof;

[0077] wool wax alcohols;

[0078] polyisoxazoline/polyalkyl polye ther copolymers and corresponding derivatives;

[0079] mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol and/or mixed esters of C_{12-22} fatty acids, methyl glucose and polyols, preferably glycerol or polyglycerol;

[0080] polyalkylene glycols and

[0081] alkyl and glycerol carbonates.

[0082] The addition products of ethylene oxide and/or propylene oxide onto fatty alcohols, fatty acids, alkyl phenols, 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 alkylation 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:

[0083] Partial Glycerides

[0084] Typical examples of suitable partial glycerides are hydroxy stearic 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 mol, and preferably 5 to 10 mol ethylene oxide onto the partial glycerides mentioned are also suitable.

[0085] Sorbitan Esters

[0086] Suitable sorbitan esters are sorbitan monoestearate, sorbitan sesquisostearate, sorbitan diestearate, sorbitan triestearate, sorbitan monooleate, sorbitan sesqui olate, sorbitan dioleate, sorbitan trioleate, sorbitan monoerucate, sorbitan sesqui erucate, sorbitan dierucate, sorbitan trierucate, sorbitan monoricinoleate, sorbitan sesquiricinoleate, sorbitan diricinoleate, sorbitan triricinoleate, sorbitan monohydroxy stearate, sorbitan sesqui hydroxy stearate, sorbitan dihydroxy stearate, sorbitan trihydroxy stearate, sorbitan monoartrate, sorbitan sesquiartate, sorbitan diartate, sorbitan triartate, sorbitan monocitrate, sorbitan sesquicitrate, sorbitan dicitrate, sorbitan tricitrate, sorbitan monomannate, sorbitan sesquimannate, sorbitan dimanlate, sorbitan trimanneate and technical mixtures thereof. Addition products of 1 to 30 mol, and preferably 5 to 10 mol ethylene oxide onto the sorbitan esters mentioned are also suitable.

[0087] Polyglycerol Esters

[0088] Typical examples of suitable polyglycerol esters are Polyglyceryl-2 Dipolyhydroxy stearate (Dehyms&® PGPH), Polyglycerin-3 Diostearate (Lameform® TGI), Polyglyceryl-4 Isostearate (Isolan® GI 34), Polyglyceryl-3 Oleate, Diisostearoyl Polyglyceryl-3 Distearate (Isolan® PDI), Polyglyceryl-3 Methylglucose Distearate (Tego Care® 450), Polyglyceryl-3 Beeswax (Cera Bellinai®), Polyglyceryl-4 Caprate (Polyglycerol Caprate T2010/90), Polyglyceryl-3 Cety1 Ether (Chimexane® NL), Polyglyceryl-3 Distearate (Cremophor® GS 32) and Polyglyceryl Polyricinoleate (Admuls® WOL 1403), Polyglyceryl Dimerate Isostearate and mixtures thereof. Examples of other suitable polyesters are the mono-, di- and triesters of trimethy l propone or pentaoxythritol with lauric acid, cocoytafatity, tallow fatty acid, palmitic acid, stearic acid, oleic acid, behenic acid and the like, optionally reacted with 1 to 30 mol ethylene oxide.

[0089] Typical anionic emulsifiers are aliphatic C_{12-22} fatty acids such as palmitic acid, stearic acid or behenic acid, for example, and C_{12-22} dicarboxylic acids such as azelaid acid or sebacic acid for example.

[0090] 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, N-acylammonopropyl-N,N-dimethyl ammonium glycinate, for example cocoaceyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoaceylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoaceylaminoethyl hydroxyethyl carboxymethyl glycinate. The fatty acid amide derivative known under the CTFA name of Cocamidopropyl Betaine is particularly preferred. Amphoteric surfactants are also suitable emulsifiers. Amphoteric surfactants are surface-active compounds which, in addition to a C_{6-18} alkyl or acyl group, contain at least one free amino group and at least one —COOH — or —SO_3H — group in the molecule and which are capable of forming inner salts. Examples of suitable amphoteric surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkylaminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyltaurines, N-alkyl sarcosines, 2-alkyl-ammonopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred amphoteric surfactants are N-cocoaceylaminopropionate, cocoaceylaminoethyl aminopropionate and C_{12-18} acyl sarcosine.
Biocide Compositions

Typically, the compositions according to the present invention comprise:

(a) about 0.1% b.w. to about 99% b.w., preferably about 5% b.w. to about 90% b.w., and most preferably about 15% b.w. to about 25% b.w., dialkylamides derived from hydroxy carboxylic acids.

(b) about 1% b.w. to about 99.1% b.w., preferably about 2% b.w. to about 80% b.w., and most preferably about 5% b.w. to about 15% b.w., biocides, and

(c) 0% b.w. to about 10% b.w., and preferably 1 to 5% b.w., emulsifiers

on condition that the amounts add with water to 100% b.w. Usually, the active matter content (which means the sum of components a+b+c) is about 5% b.w. to about 50% b.w., and preferably about 10% b.w. to about 25% b.w., calculated on the total of the aqueous composition.

INDUSTRIAL APPLICATION

A final embodiment of the present invention relates to the use of dialkylamides based on hydroxy carboxylic acids, in particular of the dimethylamide of lactic acid as solvents or dispersants for biocides.

EXAMPLES

Examples 1 to 6, Comparative Examples C1 and C2

Several aqueous concentrates were prepared by mixing biocides, dimethylamides and emulsifiers in water until a homogenous solution was obtained. The concentrates were subsequently diluted with water in order to achieve an active matter concentration of 10% b.w. The products thus obtained were stored over a period of 10 to 40 days at temperatures of 5, 20 and 40°C. The stability of the mixtures was observed by inspection and determined according to the following scale: (+)=stable; (+)=slight phase separation/formation of some crystals; (o)=significant phase separation/settling/sedimentation; (-) phases clearly separated/strong sedimentation of crystals. The results are compiled in Table 1. The amounts reflect the composition of the concentrates.

<table>
<thead>
<tr>
<th>TABLE 1-continued</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stability of biocide compositions</td>
</tr>
<tr>
<td>Composition [% b.w.]</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Bipheryl</td>
</tr>
<tr>
<td>Glyphosphate</td>
</tr>
<tr>
<td>Delta star</td>
</tr>
<tr>
<td>Glucostein</td>
</tr>
<tr>
<td>Lactic acid dimethylamide</td>
</tr>
<tr>
<td>Stearic acid dimethylamide</td>
</tr>
<tr>
<td>Sorbitan mono/stearate + 2EO</td>
</tr>
<tr>
<td>Polyglycerol-2</td>
</tr>
<tr>
<td>Dipolyhydroxyesterate</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Stability</td>
</tr>
<tr>
<td>after 10 days, 5°C.</td>
</tr>
<tr>
<td>after 20 days, 5°C.</td>
</tr>
<tr>
<td>after 40 days, 5°C.</td>
</tr>
<tr>
<td>after 10 days, 20°C.</td>
</tr>
<tr>
<td>after 20 days, 20°C.</td>
</tr>
<tr>
<td>after 40 days, 20°C.</td>
</tr>
<tr>
<td>after 10 days, 40°C.</td>
</tr>
</tbody>
</table>

1.-10. (canceled)

11. A biocide composition comprising:

(a) at least one dialkylamide of a hydroxy carboxylic acid selected from the group consisting of lactic acid, citric acid, tartaric acid, rinooleic acid, 12-hydroxy stearic acid, and mixtures thereof; and

(b) at least one fungicide selected from the group consisting of acylaminio acid fungicides, aliphatic nitrogen fungicides, amide fungicides, anilide fungicides, benzamide fungicides, benzanilide fungicides, benzimidazole fungicides, benzimidazole precursor fungicides, benzimidazolylcarbamate fungicides, benzoiazole fungicides, bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, copper fungicides, cyclic dithiocarbamate fungicides, dicarboximide fungicides, dinitrophenyl fungicides, dithiocarbamate fungicides, furamide fungicides, furanilide fungicides, imidazole fungicides, inorganic fungicides, inorganic mercury fungicides, morpholine fungicides, organomercury fungicides, organophosphorus fungicides, organotin fungicides, oxathin fungicides, oxazole fungicides, phenyl-sulfamide fungicides, phthalimide fungicides, polymeric dithiocarbamate fungicides, polysulfide fungicides, pyrazole fungicides, pyridine fungicides, pyrimidinyl fungicides, pyrrole fungicides, quinolone fungicides, quinone fungicides, quinoxaline fungicides, stroblurin fungicides, sulfonamide fungicides, thiabazole fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, urea fungicides, valinamide fungicides, metalaxyl, metalaxyl-M, flupicilide or boscalid, and combinations thereof.

12. The composition of claim 11, wherein component (a) comprises lactic acid dimethylamide.

13. The composition of claim 11, further comprising as component (c) at least one emulsifier.

14. A biocide composition comprising:

(a) 0.1% to 99% by weight, based on the composition, of at least one dialkylamide of a hydroxy carboxylic acid selected from the group consisting of lactic acid, citric acid, tartaric acid, rinooleic acid, 12-hydroxy stearic acid, and mixtures thereof; and

(b) 0.1% to 99.1% by weight, based on the composition, of at least one fungicide selected from the group consisting of acylaminio acid fungicides, aliphatic nitrogen fungicides, amide fungicides, anilide fungicides, benzamide fungicides, benzanilide fungicides, benzimidazole fungicides, benzimidazole precursor fungicides, benzimidazolylcarbamate fungicides, benzoiazole fungicides, bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, copper fungicides, cyclic dithiocarbamate fungicides, dicarboximide fungicides, dinitrophenyl fungicides, dithiocarbamate fungicides, furamide fungicides, furanilide fungicides, imidazole fungicides, inorganic fungicides, inorganic mercury fungicides, morpholine fungicides, organomercury fungicides, organophosphorus fungicides, organotin fungicides, oxathin fungicides, oxazole fungicides, phenyl-sulfamide fungicides, phthalimide fungicides, polymeric dithiocarbamate fungicides, polysulfide fungicides, pyrazole fungicides, pyridine fungicides, pyrimidinyl fungicides, pyrrole fungicides, quinolone fungicides, quinone fungicides, quinoxaline fungicides, stroblurin fungicides, sulfonamide fungicides, thiabazole fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, urea fungicides, valinamide fungicides, metalaxyl, metalaxyl-M, flupicilide or boscalid, and combinations thereof.
cides, oxathiin fungicides, oxazole fungicides, phenyl-sulfamide fungicides, phthalimide fungicides, polymeric dithiocarbamate fungicides, polysulfide fungicides, pyrazole fungicides, pyridine fungicides, pyrimidine fungicides, pyrrole fungicides, quinolone fungicides, quinone fungicides, quinoxaline fungicides, strobilurin fungicides, sulfanilamide fungicides, thiadiazole fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, urea fungicides, valinamide fungicides, metalaxyl, metalaxyl-M, fluopicolide or bosalid, and combinations thereof; and

(c) 0% to 10% by weight, based on the composition of at least one emulsifier,

wherein the amounts, including water, total 100%.

15. The composition of claim 14, wherein the sum components (a)+(b)+(c) equals 5% to 50% by weight, based on the composition.

16. A method of dissolving or dispersing fungicides, the method comprising adding at least one dialkylamide of a hydroxy carbonylic acid selected from the group consisting of lactic acid, citric acid, tartaric acid, ricinoleic acid, 12-hydroxy stearic acid, and mixtures thereof to aid in dissolving or dispersing at least one fungicide selected from the group consisting of acylamino acid fungicides, aliphatic nitrogen fungicides, amide fungicides, aniline fungicides, benzanilide fungicides, benzimidazole fungicides, benzimidazole precursor fungicides, benzimidazolyl-carbamate fungicides, benzothiazole fungicides, bridged diphenyl fungicides, carbamate fungicides, carbanilate fungicides, copper fungicides, cyclic dithiocarbamate fungicides, dicarboximide fungicides, dinitrophenol fungicides, dithiocarbamate fungicides, furamide fungicides, furanilide fungicides, imidazole fungicides, inorganic fungicides, inorganic mercury fungicides, morpholine fungicides, organo-mercury fungicides, organophosphorus fungicides, organotin fungicides, oxathiin fungicides, oxazole fungicides, phenyl-sulfamide fungicides, phthalimide fungicides, polymeric dithiocarbamate fungicides, polysulfide fungicides, pyrazole fungicides, pyridine fungicides, pyrimidine fungicides, pyrrole fungicides, quinolone fungicides, quinone fungicides, quinoxaline fungicides, strobilurin fungicides, sulfanilamide fungicides, thiadiazole fungicides, thiocarbamate fungicides, thiophene fungicides, triazine fungicides, urea fungicides, valinamide fungicides, metalaxyl, metalaxyl-M, fluopicolide or bosalid, and combinations thereof.

17. The composition of claim 11, wherein the composition has a mean storage time of at least 4 weeks at temperatures between 5 and 40°C without phase separation or sedimentation.

18. The composition of claim 11, wherein the composition is effective to reduce formation of crystals during storage.

* * * * *