AN AGROCHEMICAL COMPOSITION COMPRISING A PESTICIDE AND SUBMICRON PARTICLES CONTAINING A LIGHT STABILIZER

Subject matter of the present invention relates to an agrochemical composition comprising a) a water-insoluble pesticide, and b) submicron particles containing an organic light stabilizer as defined herein. The invention further relates to a process for the preparation of said composition; an emulsion obtainable by high shear mixing water, and the components a) and b); and to a method for controlling an undesired attack by insects or mites, where the composition or the emulsion is allowed to act on the respective pests, their environment or on the crop plants to be protected from the respective pests.
An Agrochemical Composition Comprising A Pesticide And Submicron Particles Containing A Light Stabilizer

BACKGROUND OF THE INVENTION

[001] Agrochemical oil-in-water emulsion (also referred to as pre-mix concentrates or application ready solutions) are widely used formulations in crop protection. Some pesticidal active ingredients (a.i.) are susceptible to ultraviolet radiation (UV) breakdown (e.g. photodegradation), which reduces the efficacy of the active ingredient. Some pesticidal active ingredients are also poorly water soluble. The disadvantage of the known agrochemical oil-in-water emulsion is the poor cold stability, the pronounced tendency to crystallize and the low pesticide concentration. An additional disadvantage is that poorly soluble, photodegradable can be unstable when exposed to light.

SUMMARY OF THE INVENTION

[002] Subject matter of the present invention relates to agrochemical oil-in-water emulsion comprising a) a water-insoluble pesticide and b) submicron particles containing an organic light stabilizer. In an embodiment, the present invention relates to agrochemical oil-in-water emulsions that are used to stabilize a photodegradable pesticidal active ingredient (a.i.). More specifically, this invention relates to an agrochemical oil-in-water emulsion, where the photodegradable active ingredient is dissolved in the oil phase, which is encircled by a polymer matrix formed by a film of submicron particles encapsulating the oil droplet surface, with an organic light stabilizer within the submicron particles. More specifically, the present invention relates to oil-in-water emulsions comprising a) an isothiazoline insecticide, and b) submicron particles as defined herein.

[003] The invention further relates to a process for the preparation of said oil-in-water emulsion; and to a method for controlling undesired attack by insects or mites, where the oil-in-water emulsion is allowed to act on the respective pests, their environment or on the crop plants to be protected from the respective pests. The present invention comprises combinations of certain features with other additional features.

DETAILED DESCRIPTION OF THE INVENTION

[004] It was an object of the present invention to provide an agrochemical oil-in-water emulsion which overcomes the disadvantages described supra.

[005] The object was achieved by an agrochemical oil-in-water emulsion comprising pesticide, which is susceptible to photodegradation and/or which is water-insoluble, e.g an
isothiazoline insecticide, and submicron particles containing an organic light stabilizer as defined herein.

[006] Usually, an oil-in-water emulsion is taken to mean compositions which maintains an oil-in-water emulsion upon mixing with water (e.g. in a weight ratio of 1 part concentrate to 99 parts water). The emulsion usually forms under shear mixing. In various embodiments, the resulting emulsion may have an average oil droplet size around 1-3 microns. The average droplet size may be determined by laser diffraction, e.g. with a Malvern Mastersizer 2000.

[007] The isothiazoline insecticide suitable for the formulation of the present invention is a compound of the formula I:

\[
\begin{array}{c}
\text{B}^1 \\
\text{B}^2 \\
\text{B}^3 \\
\text{S} \\
\text{N} \\
\text{G}^1 \\
\text{G}^2 \\
\text{G}^3 \\
\text{G}^4 \\
\text{A} \\
\end{array}
\]

wherein

\( A \) is a group \( A^1, A^2, A^3 \) or \( A^4 \);

wherein

\( A^1 \) is selected from the group consisting of \(-\text{C}(=\text{NR}^6)\text{R}^8, -\text{S}(\text{O})_n\text{R}^9 \) and \(-\text{N(}\text{R}^5)\text{R}^8;\)

\( A^2 \) is a group of following formula:

\[
\begin{array}{c}
\# \\
\text{W} \\
\text{Y} \\
\text{(A}^2\text{)} \\
\end{array}
\]

wherein

\( \# \) denotes the bond to the aromatic ring of formula (I);
W is selected from O and S;

Y is selected from hydrogen, -N(R^5)R^6 and -OR^9;

A^3 is a group of following formula:

\[
\begin{array}{c}
\text{R}^7a \\
\text{R}^7b \\
\text{N}^6 \\
\text{R}^5 \\
\end{array}
\]

\[\text{(A}^3\text{)}\]

wherein

# denotes the bond to the aromatic ring of formula (I);

A^4 is a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heteromonocyclic ring containing 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO_2, as ring members, or is a 8-, 9- or 10-membered saturated, partially unsaturated or maximally unsaturated heterobicyclic ring containing 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO_2, as ring members, where the heteromonocyclic or heterobicyclic ring is optionally substituted with one or more substituents R^{11};

B^1, B^2 and B^3 are each independently selected from the group consisting of N and CR^2, with the proviso that at most two of B^1, B^2 and B^3 are N;

G^1, G^2, G^3 and G^4 are each independently selected from the group consisting of N and CR^4, with the proviso that at most two of G^1, G^2, G^3 and G^4 are N;

R^1 is selected from the group consisting of Ci-C_4-alkyl, CrC_4-haloalkyl, CrC_4-alkoxy-CrC_4-alkyl, Ci-C_4-haloalkoxy-CrC_4-alkyl-, C_2-C_4-alkenyl, C_2-C_4-haloalkenyl, C_2-C_4-alkynyl, C_2-C_4-haloalkynyl, C_3-C_6-cycloalkyl, C_3-C_6-halocycloalkyl and -C(=O)OR^{15};

each R^2 is independently selected from the group consisting of hydrogen, halogen, cyano, azido, nitro, -SCN, -SF_5, Ci-C_6-alkyl, Cs-Cs-cycloalkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl, wherein the four last mentioned aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or may be substituted by one or more radicals R^8,

- Si(R_{12})_3, -OR^{9}, -S(O)_{n}R^9, -NR^{10a}R^{10b},
phenyl which may be substituted by 1, 2, 3, 4 or 5 radicals \( R^{11} \), and a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated, partially unsaturated or maximally unsaturated heteromonocyclic or heterobicyclic ring containing 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO\(_2\), as ring members, where the heteromonocyclic or heterobicyclic ring may be substituted by one or more radicals \( R^{11} \);

\( R^{3a}, R^{3b} \) are each independently selected from the group consisting of hydrogen, halogen, hydroxyl, \(-\text{CO}_{2} -R^{3d}\), \( \text{CrC}_{3}\)-alkyl, \( \text{CrC}_{3}\)-haloalkyl, \( C_{2}\)-C\(_{3}\)-alkenyl, \( C_{2}\)-C\(_{3}\)-alkynyl, \( \text{CrC}_{3}\)-alkoxy, \( \text{CrC}_{3}\)-haloalkoxy, \( \text{CrC}_{3}\)-alkylthio, \( \text{CrC}_{3}\)-haloalkylthio, \( \text{CrC}_{3}\)-alkylsulfonyl and \( \text{CrC}_{3}\)-haloalkylsulfonyl; or

\( R^{3a} \) and \( R^{3b} \) together form a group \( \equiv 0, \equiv \text{C}(R^{3c})_{2}, \equiv \text{NOH} \) or \( \equiv \text{NOCH}_{3} \); each \( R^{3c} \) is independently selected from the group consisting of hydrogen, halogen, \( \text{CH}_{3} \) and \( \text{CF}_{3} \);

\( R^{3d} \) is selected from the group consisting of hydrogen, \( \text{CrC}_{6}\)-alkyl and \( \text{CrC}_{3}\)-alkyloxy-\( \text{CrC}_{3}\)-alkyl; each \( R^{4} \) is independently selected from the group consisting of hydrogen, halogen, cyano, azido, nitro, \(-\text{SCN}, -\text{SF}_{5}\), \( \text{CrC}_{6}\)-alkyl which may be partially or fully halogenated and/or may be substituted by one or more radicals \( R^{8}, C_{1}, C_{6} \) -cycloalkyl which may be partially or fully halogenated and/or may be substituted by one or more radicals \( R^{8}, C_{1}, C_{6} \) -alkenyl which may be partially or fully halogenated and/or may be substituted by one or more radicals \( R^{8}, C_{1}, C_{6} \) -alkynyl which may be partially or fully halogenated and/or may be substituted by one or more radicals \( R^{8} \),

\[-\text{S}(R^{11})_{3}, -\text{OR}^{8}, -\text{S}(O)nR^{9}, -\text{NR}^{10a}R^{10b}, \]

phenyl which may be substituted by 1, 2, 3, 4 or 5 radicals \( R^{11} \), and a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated, partially unsaturated or maximally unsaturated heteromonocyclic or heterobicyclic ring containing 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO\(_2\), as ring members, where the heteromonocyclic or heterobicyclic ring may be substituted by one or more radicals \( R^{11} \);

each \( R^{5} \) is independently selected from the group consisting of hydrogen, \( \text{Ci-C}_{10}\) -alkyl, \( C_{3}\)-C\(_{3}\) -cycloalkyl, \( C_{2}\)-C\(_{10}\)-alkenyl, \( C_{2}\)-C\(_{10}\)-alkynyl, wherein the four last-mentioned aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or may be substituted with one or more substituents \( R^{8} \), and

\[-\text{S}(0)_{n}R^{9}, \]

each \( R^{6} \) is independently selected from the group consisting of hydrogen, cyano, \( \text{Ci-C}_{10}\)-alkyl, \( C_{3}\)-C\(_{6}\)-cycloalkyl, \( C_{2}\)-C\(_{10}\)-alkenyl, \( C_{2}\)-C\(_{10}\)-alkynyl, wherein the four last-mentioned aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or may be substituted by one or more substituents \( R^{8} \),
phenyl which may be substituted with 1, 2, 3, 4, or 5 substituents $R^{11}$, and

a 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-membered saturated, partially unsaturated or maximally unsaturated heteromonocyclic or heterobicyclic ring containing 1, 2, 3 or 4 heteroatoms or heteroatom groups independently selected from N, O, S, NO, SO and SO$_2$, as ring members, where the heteromonocyclic or heterobicyclic ring may be substituted with one or more substituents $R^{11}$;

or $R^6$ and $R^6$, together with the nitrogen atom to which they are bound, form a 3-, 4-, 5-, 6-, 7- or 8-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring, where the ring may further contain 1, 2, 3 or 4 heteroatoms or heteroatom-containing groups selected from O, S, N, SO, SO$_2$. $C=O$ and $C=S$ as ring members, wherein the heterocyclic ring may be substituted with 1, 2, 3, 4 or 5 substituents independently selected from the group consisting of halogen, cyano, d-d-alkyl, d-d-haloalkyl, d-d-alkoxy, d-d-haloalkoxy, d-d-alkylthio, d-d-haloalkylthio, d-d-cycloalkyl, d-d-halocycloalkyl, d-d-alkenyl, d-d-haloalkenyl, d-d-alkynyl, d-d-haloalkynyl, wherein the aliphatic or cycloaliphatic moieties in the twelve last-mentioned radicals may be substituted by one or more radicals $R^8$, and phenyl which may be substituted with 1, 2, 3, 4 or 5 substituents $R^{11}$;

or $R^6$ and $R^6$, together form a group $=C(R^8)_2$, $=S(0)=C(R^9)$, $=NR^{10a}$ or $=NOR^9$;

$R^{10a}, R^{10b}$ are each independently selected from the group consisting of hydrogen, halogen, cyano, d-d-alkyl, d-d-cycloalkyl, d-d-alkenyl and d-d-alkynyl, wherein the four last-mentioned aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or may be substituted by one or more radicals $R^8$;

each $R^8$ is independently selected from the group consisting of cyano, azido, nitro, -SCN, -SF$_5$, d-d-cycloalkyl, d-d-halocycloalkyl, where the cycloaliphatic moieties in the two last-mentioned radicals may be substituted by one or more radicals $R^{13}$;

$-Si(R^{12})_3$, $-OR^8$, $-OSO_2R^9$, $-S(0)nR^9$, $-N(R^{10a})R^{10b}$, $-C(=O)N(R^{10a})R^{10b}$, $-C(=S)N(R^{10a})R^{10b}$, $-C(=O)OR^9$,

phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents $R^{16}$, and

a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring comprising 1, 2 or 3 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO$_2$, as ring members, where the heterocyclic ring is optionally substituted with one or more substituents $R^{16}$,
two R⁸ present on the same carbon atom of an alkyl, alkenyl, alkynyl or cycloalkyl group together form a group =0, =C(R¹ʳ)₂; =S; =S(0)ₙ(R¹₅)₂, =S(0)ₙR¹⁵N(R¹₄₉)R¹⁴ᵇ, =NR¹₀α, =NOR₉; or =NN(R¹₀α)R¹₀ᵇ;

or
two radicals R⁸, together with the carbon atoms of an alkyl, alkenyl, alkynyl or cycloalkyl group which they are bonded to, form a 3-, 4-, 5-, 6-, 7- or 8-membered saturated or partially unsaturated carbocyclic or heterocyclic ring, where the heterocyclic ring comprises 1, 2, 3 or 4 heteroatoms or heteroatom groups independently selected from N, O, S, NO, SO and SO₂, as ring members, and where the carbocyclic or heterocyclic ring is optionally substituted with one or more substituents R¹⁶; and

R⁸ as a substituent on a cycloalkyl ring is additionally selected from the group consisting of C₁-C₆-alkyl, Cᵡ-C₆-haloalkyl, C₂-C₆-alkenyl, C₂-C₆-haloalkenyl, C₂-C₆-alkynyl and C₂-C₆-haloalkynyl, where the aliphatic moieties in these six radicals may be substituted by one or more radicals R¹³; and

R⁸ in the groups -C(=NR₉)R⁸, -C(=0)R⁸ and =C(R⁸)₂ is additionally selected from the group consisting of hydrogen, halogen, Ci-C₆-alkyl, Cr₆-haloalkyl, C₂-C₆-alkenyl, C₂-C₆-haloalkenyl, C₂-C₆-alkynyl and C₂-C₆-haloalkynyl, where the aliphatic moieties in the six last-mentioned radicals may be substituted by one or more radicals R¹₃;

each R⁹ is independently selected from the group consisting of hydrogen, cyano, Ci-C₆-alkyl, Cr Ce-haloalkyl, Cs-Cs-cycloalkyl, c₃-c₉ -cycloalkyl-CrC₄-alkyl-, Cs-Cs-halocycloalkyl, C₂-Ce-alkenyl, C₂-C₆-haloalkenyl, C₂-C₆-alkenyl, C₂-C₆-haloalkynyl, where the aliphatic and cycloaliphatic moieties in the nine last-mentioned radicals may be substituted by one or more radicals R¹₃,

-Cr₆-alkyl-C(=0)OR₁⁵, -Cr₆-alkyl-C(=0)N(R¹₄₉)R¹⁴ᵇ,

-Cr₆-alkyl-C(=S)N(R¹₄₉)R¹⁴ᵇ, -Cr₆-alkyl-C(=NR¹₄)N(R¹₄₉)R¹⁴ᵇ,

-Si(R¹₂)₃, -S(0)ₙR¹₅, -S(0)ₙN(R¹₄₉)R¹⁴ᵇ, -N(R¹₀α)R¹₀ᵇ, -NₙC(R¹₃)₂, -C(=0)R¹₃,

-C(=0)N(R¹₄₉)R¹⁴ᵇ, -C(=S)N(R¹₄₉)R¹⁴ᵇ, -C(=0)OR₁⁵,

phenyl, optionally substituted with one or more substituents R¹⁶; and

a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring comprising 1, 2 or 3 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO₂, as ring members, where the heterocyclic ring is optionally substituted with one or more substituents R¹⁶; and
R₉ in the groups - S (0)ₙR₉ and -OSO₂R₉ is additionally selected from the group consisting of d-d-alkoxy and C₆-C₆-haloalkoxy;

R¹₀α, R¹₀β are selected independently from one another from the group consisting of hydrogen, d-d-alkyl, d-haloalkyl, d-d-cycloalkyl, d-d-halocycloalkyl, d-d-alkenyl, d-d-haloalkenyl, C₂-C₆-alkynyl, C₂-C₆-haloalkynyl, where the aliphatic and cycloaliphatic moieties in the eight last-mentioned radicals may be substituted by one or more radicals R₁₃;

-C₁₋C₆-alkyl-C(=O)OR¹₅, -C₁₋C₆-alkyl-C(=O)N(R¹₄α)R¹₄β, -C₁₋C₆-alkyl-C(=S)N(R¹₄α)R¹₄β, -d-d-alkyl-C(=NR₁₅)mN(R¹₄a)R¹₄b, -C₂-C₆-alkylthio, C₆-C₆-haloalkoxy, C₆-C₆-alkylthio,

-S (0)ₙR₁₅, -S (0)ₙN(R¹₄a)R¹₄b, -C (≡0)R₁₃, -C (≡0)OR¹₅, -C (≡0)N(R¹₄a)R¹₄b, -C(=S)R₁₅, -C(=S)SR₁₅, -C(=S)N(R¹₄a)R¹₄b, -C(=N)R₁₄R₁₃;

phenyl, optionally substituted with 1, 2, 3 or 4, substituents R₁₆; and

a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring comprising 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO, and SO₂, as ring members, where the heterocyclic ring is optionally substituted with one or more substituents R₁₆;

or

R¹₀α and R¹₀β form together with the nitrogen atom they are bonded to a 3-, 4-, 5-, 6-, 7- or 8-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring, wherein the heterocyclic ring may additionally contain one or two heteroatoms or heteroatom groups selected from N, O, S, NO, SO, and SO₂, as ring members, where the heterocyclic ring optionally carries one or more substituents selected from halogen, d-C₆-alkyl, d-d-haloalkyl, d-d-alkoxy, C₆-C₆-haloalkoxy, d-d-alkylthio, d-d-haloalkylthio, d-d-cycloalkyl, d-d-halocycloalkyl, d-d-alkenyl, d-d-haloalkenyl, d-d-alkynyl, d-d-haloalkynyl, phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R₁₆; and a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring comprising 1, 2 or 3 heteroatoms or heteroatom groups selected from N, O, S, NO, SO, and SO₂, as ring members, where the heterocyclic ring optionally carries one or more substituents R₁₆;

or R¹₀α and R¹₀β together form a group =C(R¹₃)₂; =S(0)ₙ(R¹₅)₂; =S(0)ₙR₁₅N(R¹₄a)R¹₄b, =NR¹₄ or =NOR¹₅;

R¹¹ is independently selected from the group consisting of halogen, cyano, azido, nitro, -SCN, -SF₅, d-do-alkyl, d-d-cycloalkyl, d-do-alkenyl, d-do-alkynyl, wherein the four last-mentioned aliphatic and cycloaliphatic radicals may be partially or fully halogenated and/or may be substituted with one or more radicals R₈;
phenyl, optionally substituted with 1, 2, 3, 4, or 5 substituents selected independently from \( R^{16} \); and

a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated aromatic heterocyclic ring comprising 1, 2, 3 or 4 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO2, as ring members, where the heterocyclic ring is optionally substituted with one or more substituents selected independently from \( R^{16} \);

or two \( R^{11} \) present on the same ring carbon atom of an unsaturated or partially unsaturated heterocyclic ring may together form a group \( =0, =C(R^{13})_2, =S, =S(0)_m(R^{15})_2, =S(0)_mR^{15}N(R^{14b})R^{14b}, =N(R^{14}, =NOR^{15}, or =NN(R^{14b})R^{14b};

or two \( R^{11} \) bound on adjacent ring atoms form together with the ring atoms to which they are bound a saturated 3-, 4-, 5-, 6-, 7-, 8- or 9-membered ring, wherein the ring may contain 1 or 2 heteroatoms or heteroatom groups selected from O, S, N, \( R^{14} \), NO, SO and SO2 and/or 1 or 2 groups selected from \( C=O, C=S \) and \( C=N \) as ring members, and wherein the ring may be substituted by one or more radicals selected from the group consisting of halogen, \( C\text{r}C\text{e}-\text{alkyl}, d-C\text{e}-\text{haloalkyl}, d-C\text{e}-\text{alkoxy}, C\text{r}C\text{e}-\text{alkoxy}, C\text{r}C\text{e}-\text{alkylthio}, C\text{r}C\text{e}-\text{haloalkylthio}, d-C\text{e}-\text{cyloalkyl}, C\text{e}-C\text{e}-\text{halocycloalkyl}, d-C\text{e}-\text{alkenyl}, d-C\text{e}-\text{haloalkenyl}, d-C\text{e}-\text{alkynyl}, d-C\text{e}-\text{haloalkynyl}, phenyl which may be substituted by 1, 2, 3, 4 or 5 radicals \( R^{16} \), and a 3-, 4-, 5-, 6- or 7-membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring containing 1, 2 or 3 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO2, as ring members, where the heterocyclic ring may be substituted by one or more radicals \( R^{16} \);

each \( R^{12} \) is independently selected from the group consisting of hydrogen, halogen, \( C\text{r}C\text{e}-\text{alkyl}, C\text{r}C\text{e}-\text{haloalkyl}, C\text{r}C\text{e}-\text{alkoxy}, C\text{r}C\text{e}-\text{haloalkoxy}, d-C\text{e}-\text{alkenyl}, d-C\text{e}-\text{haloalkenyl}, d-C\text{e}-\text{alkynyl}, d-C\text{e}-\text{haloalkynyl}, d-C\text{e}-\text{cyloalkyl}, d-C\text{e}-\text{halocycloalkyl}, C\text{r}C\text{e}-\text{alkoxy}-C\text{r}C\text{e}-\text{alkyl}, d-C\text{e}-\text{haloalkoxy}-d-C\text{e}-\text{alkyl}, and

phenyl, optionally substituted with 1, 2, 3, 4, or 5 substituents \( R^{16} \);

each \( R^{13} \) is independently selected from the group consisting of cyano, nitro, \(-\text{OH}, -\text{SH}, -\text{SCN}, -\text{S}_\text{F}_\text{e}, d-C\text{e}-\text{alkoxy}, d-C\text{e}-\text{haloalkoxy}, d-C\text{e}-\text{alkylthio}, d-C\text{e}-\text{haloalkylthio}, d-C\text{e}-\text{alkylsulfinyl}, d-C\text{e}-\text{haloalkylsulfinyl}, d-C\text{e}-\text{alkylsulfonyl}, d-C\text{e}-\text{haloalkylsulfonyl}, \text{trimethylsilyl}, \text{triethylsilyl}, \text{ferf-butyldimethylsilyl}, C\text{e}-C\text{e}-\text{cyloalkyl} which may be unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from \( d-d\text{-alkyl}, d-d\text{-cyloalkyl}, d-d\text{-alkoxy}, d-d\text{-haloalkoxy} \) and/or oxo; phenyl, benzyl, phenoxy, where the phenyl moiety in the three last-mentioned radicals may be unsubstituted or carry 1, 2, 3, 4 or 5 substituents \( R^{16} \); and a 3-, 4-, 5-, 6- or 7-membered saturated,
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partially unsaturated or maximally unsaturated heterocyclic ring containing 1, 2 or 3 heteroatoms or
heteroatom groups selected from N, O, S, NO, SO and SO2, as ring members, where the
heterocyclic ring may be substituted by 1, 2 or 3 substituents \( R_{16} \);

or

two \( R_{13} \) present on the same carbon atom of an alkyl, alkenyl, alkynyl or cycloalkyl group may
together be \( =0, =C(R_4^3\text{C}-\text{alkyl}), =C(C_1-C_4^4-\text{alkyl})C_1-C_4^4-\text{alkyl}, =N(C_1-C_6^6-\text{alkyl}) \) or \( =\text{NO}(C_1-C_6^6-\text{alkyl}) \);

and

\( R_{13} \) as a substituent on a cycloalkyl ring is additionally selected from the group consisting of C1-C6-
alkyl, C2-C6 -alkenyl and C2-C6 -alkynyl, wherein the three last-mentioned aliphatic radicals may be
unsubstituted, partially or fully halogenated and/or may carry 1 or 2 substituents selected from CN, C3-C4-cycloalkyl, CrC4-alkoxy, Ci-C4 -haloalkoxy and oxo;

and

\( R_{13} \) in the groups \( =\text{C}(R_{13}^3_2), -N=C(R_{13}^3_2), -C(=0)R_{13}^3, -C(=S)R_{13}^3 \) and
\( -C(=N \text{R}_{14}^4) \) \( R_{13}^3 \) is additionally selected from the group consisting of hydrogen, halogen, Ci-C6 -alkyl, C2-C6 -alkenyl and C2-C6 -alkynyl, wherein the three last-mentioned aliphatic radicals may be
unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from CN, C3-
C4-cycloalkyl, CrC4 -alkoxy, Ci-C4 -haloalkoxy and oxo;

each \( R_{14} \) is independently selected from the group consisting of hydrogen, cyano, Ci-C6 -alkoxy, Ci-
C6 -haloalkoxy, Ci-C6 -alkylthio, CrC6-haloalkylthio, CrC6-alkylsulfinyl, CrC6-haloalkylsulfinyl, Cr-
C6-alkylsulfonyl, Ci-C6 -haloalkylsulfonyl, trimethylsilyl, triethyisilyl, iert-butyidimethylsilyl, Ci-C6 -alkyl, C2-C6 -alkenyl, C2-C6 -alkynyl, wherein the three last-mentioned aliphatic radicals may be
unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from CN, Ci-
C4 -alkoxy, Ci-C4 -haloalkoxy, Ci-C4 -alkylthio, Ci-C4 -alkylsulfinyl, Ci-C4 -alkylsulfonyl, C3-C4-
cycloalkyl which may be substituted by 1 or 2 substituents selected from halogen and cyano; and oxo;

C3-C8-cycloalkyl which may be unsubstituted, partially or fully halogenated and/or may carry 1 or 2
radicals selected from Ci-C4 -alkyl, Ci-C4 -alkoxy, CrC4 -haloalkoxy, Ci-C4 -alkylthio, C1-C4-
alkylsulfinyl, Ci-C4 -alkylsulfonyl, C3-C4-cycloalkyl, C3-C4-cycloalkyl-Ci-C4-alkyl, where the
cycloalkyl moiety in the two last-mentioned radicals may be substituted by 1 or 2 substituents
selected from halogen and cyano; and oxo;

phenyl, benzyl, pyridyl, phenaxy, wherein the cyclic moieties in the four last-mentioned radicals
may be unsubstituted and/or carry 1, 2 or 3 substituents selected from halogen, Ci-C6 -alkyl, C1-C6-
haloalkyl, d-Ce-alkoxy, d-Ce-haloalkoxy and (CrC6-alkoxy)carbonyl; and a 3-, 4-, 5- or 6-
membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring comprising 1
or 2 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO2, as ring members,
where the heterocyclic ring is optionally substituted with one or more substituents R16;

R14a and R14b, independently of each other, have one of the meanings given for R14; or

R14a and R14b, together with the nitrogen atom to which they are bound, form a 3-, 4-, 5-, 6- or 7-
membered saturated, partially unsaturated or maximally unsaturated heterocyclic ring, wherein the
heterocyclic ring may additionally contain 1 or 2 heteroatoms or heteroatom groups selected from
N, O, S, NO, SO and SO2, as ring members, where the heterocyclic ring optionally carries one or
more substituents selected from halogen, CrC4-alkyl, Cl-C4 -haloalkyl, Cl-C4 -alkoxy and C1-C4-
haloalkoxy;

or

R14a and R14 or R14b and R14, together with the nitrogen atoms to which they are bound in the group
-C(=NR14)N(R14a)R14b, form a 3-, 4-, 5-, 6- or 7-membered partially unsaturated or maximally
unsaturated heterocyclic ring, wherein the heterocyclic ring may additionally contain 1 or 2
heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO2, as ring members,
where the heterocyclic ring optionally carries one or more substituents selected from halogen, Cl-
C4-haloalkyl, Cl-C4 -alkoxy and C1-C4 -haloalkoxy;

each R15 is independently selected from the group consisting of hydrogen, cyano, trimethylsilyl, triethylsilyl, tert-butylimethylsilyl,

Cl-C6 -alkyl, C2-C6 -alkenyl, C2-C6 -alkynyl, wherein the three last-mentioned aliphatic radicals may
be unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from C3-
C4-cycloalkyl, CrC4-alkoxy, Cl-C4 -haloalkoxy, Cl-C4 -alkylthio, CrC4-alkylsulfinyl, C1-C4-
alkylsulfonyl and oxo;

C3-C8 -cycloalkyl which may be unsubstituted, partially or fully halogenated and/or may carry 1 or 2
radicals selected from Cl-C4 -alkyl, C3-C4 -cycloalkyl, Cl-C4 -alkoxy, Cl-C4 -haloalkoxy, Cl-C4-
alkylthio, C1-C4 -alkylsulfinyl, Cl-C4 -alkylsulfonyl and oxo;

phenyl, benzyl, pyridyl and phenoxy, wherein the four last-mentioned radicals may be
unsubstituted, partially or fully halogenated and/or carry 1, 2 or 3 substituents selected from C1-C6-
alkyl, d-Ce-haloalkyl, d-Ce-alkoxy, d-Ce-haloalkoxy and (d-C6-alkoxy)carbonyl;

each R16 is independently selected from the group consisting of halogen, nitro, cyano, -OH , -S.H ,
d-Ce-alkoxy, d-Ce-haloalkoxy, d-Ce-alkylthio, d-Ce-haloalkylthio, C1-Ce -alkylsulfinyl, d-Ce-
haloalkylsulfinyl, C₁-C₆ -alkylsulfonyl, C₁-C₆ -haloalkylsulfonyl, trimethylsilyl, triethylsilyl, tert-butyldimethylsilyl;

C₁-C₆ -alkyl, C₂-C₆ -alkenyl, C₂-C₆ -alkynyl, wherein the three last-mentioned aliphatic radicals may be unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from C₃-C₄-cycloalkyl, CrC₄-alkoxy, C₁-C₄-haloalkoxy and oxo;

c₃-C₆ -cycloalkyl which may be unsubstituted, partially or fully halogenated and/or may carry 1 or 2 radicals selected from C₁-C₄-alkyl, C₃-C₄-cycloalkyl, C₁-C₄-alkoxy, CrC₄-haloalkoxy and oxo;

phenyl, benzyl, pyridyl and phenoxy, wherein the four last mentioned radicals may be unsubstituted, partially or fully halogenated and/or carry 1, 2 or 3 substituents selected from C₁-C₆-alkyl, d-C₆-haloalkyl, d-C₆-alkoxy, d-C₆-haloalkoxy and (C₁-C₆ -alkoxy)carbonyl;

or
two R¹⁶ present together on the same atom of an unsaturated or partially unsaturated ring may be =0, =S, =N(CrC₆-alkyl), =NO(C₃-C₆-alkyl), =CH(C₃-C₆-alkyl) or =C(C₃-C₆-alkyl)C₃-C₆-alkyl;

or
two R¹⁶ on two adjacent carbon atoms form together with the carbon atoms they are bonded to a 4-, 5-, 6-, 7- or 8-membered saturated, partially unsaturated or maximally unsaturated ring, wherein the ring may contain 1 or 2 heteroatoms or heteroatom groups selected from N, O, S, NO, SO and SO₂ as ring members, and wherein the ring optionally carries one or more substituents selected from halogen, C₁-C₄-haloalkyl, CrC₄-alkoxy and C₁-C₄-haloalkoxy;

each n is independently 0, 1 or 2; and

each m is independently 0 or 1;

and the N-oxides, stereoisomers and agriculturally or veterinarily acceptable salts thereof.

[008] Thus, the present invention relates to agrochemical oil-in-water emulsions comprising a) a photodegradation-sensitive and/or water-insoluble pesticide and b) submicron particles as defined herein below.

[009] Thus, in one embodiment the present invention relates to agrochemical oil-in-water emulsions comprising a) an isothiazoline insecticide of formula I, and b) submicron particles as defined herein below.

[0010] In one form, the isothiazoline insecticide is a compound of formula I.1.
wherein

$R^1$ is $\text{Cl-C}_4\text{-haloalkyl}$ and is in particular $\text{CF}_3$;

$R^{2a}$, $R^{2b}$ and $R^{2c}$ are selected independently from one another from hydrogen, halogen and $\text{C}_1\text{-C}_2\text{-haloalkyl}$, preferably from hydrogen, F, Cl, Br and $\text{CF}_3$;

$R^4$ is selected from hydrogen, halogen, cyano, $\text{Cl-C}_4\text{-alkyl}$, $\text{Cl-C}_4\text{-haloalkyl}$, $\text{Cl-C}_4\text{-alkoxy}$, $\text{Cl-C}_4\text{-haloalkoxy}$, $\text{Cl-C}_4\text{-alkylthio}$ and $\text{Cl-C}_4\text{-haloalkylthio}$, and preferably from hydrogen, F, Cl, Br, $\text{CH}_3$, $\text{CF}_3$, $\text{OC}_2\text{H}_5$, OCF$_2$H, OCF$_3$, SCH$_3$, SCF$_2$H, and SCF$_3$;

$R^{10a}$ and $R^{14a}$ independently from each other are selected from hydrogen, $\text{Cl-C}_6\text{-alkyl}$, $\text{Cl-C}_6\text{-haloalkyl}$, preferably from hydrogen and $\text{CH}_3$;

$R^{14b}$ is selected from hydrogen, $\text{Cl-C}_6\text{-alkyl}$, $\text{Cl-C}_6\text{-haloalkyl}$, $\text{Cl-C}_6\text{-alkenyl}$, $\text{Cl-C}_6\text{-haloalkenyl}$, $\text{Cl-C}_6\text{-alkynyl}$, $\text{Cl-C}_6\text{-haloalkynyl}$, $\text{C}_2\text{-C}_6\text{-cycloalkyl}$, $\text{C}_2\text{-C}_6\text{-halocycloalkyl}$, $\text{C}_2\text{-C}_6\text{-alkoxy}$, $\text{C}_2\text{-C}_6\text{-haloalkoxy}$, where the cycloalkyl moieties in the three last-mentioned groups may be substituted by a cyano group; $\text{Cl-C}_6\text{-alkyl}$ substituted with a cyano group, $\text{Cl-C}_6\text{-alkoxy}$, $\text{Cl-C}_6\text{-haloalkoxy}$, phenyl which is optionally substituted with 1, 2, 3 or 4, substituents each independently selected from the group consisting of halogen, cyano, nitro, $\text{Cl-C}_4\text{-alkyl}$, $\text{Cl-C}_4\text{-haloalkyl}$, $\text{Cl-C}_4\text{-alkoxy}$, $\text{Cl-C}_4\text{-haloalkoxy}$, $\text{Cl-C}_4\text{-alkylthio}$, $\text{Cl-C}_4\text{-haloalkylthio}$, $\text{C}_2\text{-C}_4\text{-cycloalkyl}$, $\text{C}_2\text{-C}_4\text{-halocycloalkyl}$, $\text{C}_2\text{-C}_6\text{-alkyl}$ and $\text{C}_2\text{-C}_6\text{-haloalkyl}$; and a heteromonocyclic ring selected from rings of formulae D-1 to D-181.
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wherein

k is 0, 1, 2 or 3;

n is 0, 1 or 2; and

each $R^{i}$ is independently selected from the group consisting of halogen, cyano, nitro, $C_{1-4}$-alkyl, $C_{1-4}$-haloalkyl, $C_{1-4}$-alkoxy, $CrC_{4}$-haloalkoxy, $CrC_{4}$-alkylthio, $C_{1-4}$-alkylsulfanyl, $CrC_{4}$-haloalkylsulfanyl, $CrC_{4}$-alkylsulfonyl, $C_{1-4}$-haloalkylsulfonyl, $C_{1-4}$-alkylcarbonyl, $C_{1-4}$-alkylaminocarbonyl, $C_{3-6}$-cycloalkyl, $C_{3-6}$-halocycloalkyl, $C_{2-4}$-alkenyl, $C_{2-4}$-haloalkenyl, $C_{2-4}$-alkynyl and $C_{2-4}$-haloalkynyl, $C_{1-4}$-alkylcarbonyl, $C_{1-4}$-alkylaminocarbonyl, or

two $R^{i}$ present on the same carbon atom of a saturated heterocyclic ring may form together =0 or =S.

[0011] Thus, the present invention relates to agrochemical oil-in-water emulsions comprising a) an isothiazoline insecticide of formula 1.1 and b) submicron particles as defined herein below.

[0012] In another form, the isothiazoline insecticide is a compound of formula 1.2:

wherein

$R^{1}$ is $C_{1-4}$-haloalkyl and is in particular $CF_{3}$;

$R^{2a}$, $R^{2b}$ and $R^{2c}$ are selected independently from one another from hydrogen, halogen and $C_{1-2}$-haloalkyl, preferably from hydrogen, F, Cl, Br and $CF_{3}$;
R^4 is selected from hydrogen, halogen, cyano, CrC4-alkyl, Ci-C4-haloalkyl, Ci-C4-alkoxy, C1-C4-haloalkoxy, CrC4-alkylthio and CrC4-haloalkylthio, and preferably from hydrogen, F, Cl, Br, CH_3, and CF_3;

R^5 is selected from hydrogen, Ci-C6-alkyl, C2-C3-alkenyl, C2-C3-alkynyl, -CH_2-CN and Ci-C6-alkoxy-methyl-, and preferably from hydrogen and Ci-C4-alkyl; and

R^6 is selected from hydrogen, Ci-C6-alkyl, Ci-C6-haloalkyl, Ci-C4-alkyl which carries one radical R^8, C2-C6-alkenyl, C2-C6-haloalkenyl, C2-C6-alkynyl, C3-C6-cycloalkyl which may be substituted by 1 to 4 substituents selected from halogen, cyano, (R^10a)R^10b, -CH=NO(R); phenyl which may be substituted with 1, 2, 3, 4, or 5 substituents R^11, and a heteromonocyclic ring selected from rings of formulae D-1 to D-181 as defined above;

R^7 is selected from hydrogen, OH, CN, Cs-Cs-cycloalkyl, C2-C6-alkenyl, C2-C6-alkynyl, wherein the three last-mentioned radicals may be partially or fully halogenated and/or may be substituted by one or more cyano group; Ci-C6-alkoxy, Ci-C6-alkylthio, CrC6-alkylsulfinyl, CrC6-alkylsulfonyl, wherein the four last-mentioned radicals may be partially or fully halogenated and/or may be substituted by one or more substituents selected from cyano, C3-C6-cycloalkyl, C2-C6-alkenyl, C_2-C_6-alkynyl; -C(=0)N(R)R^14b;
phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R^11; and a heteromonocyclic ring selected from rings of formulae D-1 to D-181 as defined above;

R^8 is selected from hydrogen, CrC6-alkyl, C3-C6-cycloalkyl, C3-C6-cycloalkylmethyl, wherein the three last-mentioned radicals may be partially or fully halogenated and/or may be substituted by one or more CN;

R^10a is selected from the group consisting of hydrogen and Ci-C6-alkyl;

R^10b is selected from the group consisting of hydrogen, C(=0)N(R)R^14b; phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R^11; and a heteromonocyclic ring selected from rings of formulae D-1 to D-181 as defined above;

each R^11 is independently selected from the group consisting of hydrogen, halogen, cyano, nitro, Ci-C4-alkyl, CrC4-haloalkyl, CrC4-alkoxy, Ci-C4-haloalkoxy, CrC4-alkylthio, CrC4-haloalkylthio, CrC4-alkylsulfinyl, CrC4-haloalkylsulfinyl, CrC4-alkylsulfonyl, CrC4-haloalkylsulfonyl, C3-C6-cycloalkyl, C3-C6-halo cycloalkyl, C2-C4-alkenyl, C2-C4-haloalkenyl, C2-C4-alkynyl and C2-C4-haloalkynyl, CrC4-alkylcarbonyl, Ci-C4-alkylaminocarbonyl; or

two R^11 present on the same carbon atom of a saturated heterocyclic ring may form together =0 or =S;
each R\textsubscript{14a} is selected from the group consisting of hydrogen and C\textsubscript{1}-C\textsubscript{6} -alkyl;

each R\textsubscript{14b} is selected from the group consisting of hydrogen, C\textsubscript{1}-C\textsubscript{6} -alkyl, C\textsubscript{1}-C\textsubscript{6} -cycloalkyl, C\textsubscript{3}-C\textsubscript{6} -cycloalkylmethyl, C\textsubscript{2}-C\textsubscript{4} -alkynyl, C\textsubscript{2}-C\textsubscript{4} -alkenyl, C\textsubscript{1}-C\textsubscript{4} -alkoxy, wherein the six last-mentioned radicals may be partially or fully halogenated and/or may be substituted with one cyano group.

Thus, the present invention relates to agrochemical oil-in-water emulsions comprising a) an isothiazoline insecticide of formula 12, and b) submicron particles as defined herein below.

In yet another form, the isothiazoline insecticide is a compound of formula 1.2a:

![Formula Image]

wherein

R\textsuperscript{1} is C\textsubscript{1}-C\textsubscript{4} -haloalkyl and is in particular C\textsubscript{F}\textsubscript{3};

R\textsuperscript{2a}, R\textsuperscript{2b} and R\textsuperscript{2c} are selected independently from one another from hydrogen, halogen and C\textsubscript{1}-C\textsubscript{2} -haloalkyl, preferably from hydrogen, F, Cl, Br and C\textsubscript{F}\textsubscript{3};

R\textsuperscript{4} is selected from hydrogen, halogen, cyano, C\textsubscript{1}-C\textsubscript{4} -alkyl, C\textsubscript{1}-C\textsubscript{4} -haloalkyl, C\textsubscript{1}-C\textsubscript{4} -alkoxy and C\textsubscript{1}-C\textsubscript{4} -alkylthio, and preferably from hydrogen, F, Cl, Br, C\textsubscript{H}\textsubscript{3}, and C\textsubscript{F}\textsubscript{3};

R\textsuperscript{5} is selected from hydrogen, C\textsubscript{1}-C\textsubscript{6} -alkyl, C\textsubscript{2}-C\textsubscript{3} -alkenyl, C\textsubscript{2}-C\textsubscript{3} -alkynyl, C\textsubscript{1}-C\textsubscript{6} -alkoxy-, and preferably from hydrogen and C\textsubscript{1}-C\textsubscript{4} -alkyl; and

R\textsuperscript{6a} is selected from -X-R\textsuperscript{6b} and -N(R\textsuperscript{5a})\textsubscript{2} R\textsuperscript{6c}; wherein

X is selected from -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -C(=O) -NR\textsuperscript{10a} -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -S(O)n-C(=O) -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -S(=O)n-C(=O) -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -S(=O)n-C(=O) -C(R\textsuperscript{a})\textsubscript{2} -, and preferably from -C(R\textsuperscript{a})\textsubscript{2} -, -C(R\textsuperscript{a})\textsubscript{2} -S(=O)n-C(=O) -C(R\textsuperscript{a})\textsubscript{2} -, and
-C(R^a)_2-C(R^a)_2-0-C(R^a)_2-, wherein
n is 0, 1 or 2, and

each R^a is independently selected from the group consisting of hydrogen, halogen, C_1-C_3 -alkyl, and
CrC_3-haloalkyl and is preferably hydrogen;

R^5a is selected from hydrogen, and C_1-C_6 -alkyl, and is preferably hydrogen;

R^6b is selected from the group consisting of C_3-C_6 -cycloalkyl, C_2-C_6 -alkenyl, C_2-C_6 -alkynyl, wherein
the three last-mentioned radicals may be partially or fully halogenated and/or may be substituted by
one or more substituents R^8;

R^{14c} is -C(=0)N(R^{14a})R^{14b}

R^8 is selected from, cyano, C_1-C_6 -alkoxy, CrC_6-haloalkoxy, C_1-C_6 -alkylthio, C_1-C_6 -haloalkylthio, Cl-
C_6-alkylsulfinyl, CrC_6-haloalkylsulfinyl, C_1-C_6 -alkylsulfanyl, C_1-C_6 -haloalkylsulfanyl, -
C(=0)N(R^{14a})R^{14b};

each R^{14a} is selected from the group consisting of hydrogen and C_1-C_6 -alkyl;

each R^{14b} is selected from the group consisting of hydrogen, C_3-C_6 -alkyl, C_3-C_6 -cycloalkylmethyl, C_2-C_4 -alkynyl, C_2-C_4 -alkenyl, C_1-C_4 -alkoxy, wherein the six last-mentioned
radicals may be partially or fully halogenated and/or may be substituted with one cyano group;

where in case that R^5 is hydrogen, R^6a is further selected from hydrogen, 1-cyanocyclopropyl, 1-
cyano-1-cyclobutyl and 1-cyanocyclopentyl.

[0015] Thus, the present invention relates to agrochemical oil-in-water emulsions comprising
a) an isothiazoline insecticide of formula 1.2a, and b) submicron particles as defined herein below.

[0016] In another form, the isothiazoline insecticide is a compound of formula 1.3:
\[ R^1 \text{is CI-C4-haloalkyl and is in particular CF}_3^3; \]

\[ R^{2a}, R^{2b} \text{and } R^{2c} \text{are selected independently from one another from hydrogen, halogen and C1-C2-haloalkyl, preferably from hydrogen, F, Cl, Br and CF}_3^3; \]

\[ R^4 \text{is selected from hydrogen, halogen, cyano, CI-C4-alkyl, CI-C4-haloalkyl, CrC4 -alkoxy, C1-C4-haloalkoxy, CrC4 -alkylthio and CI-C4-haloalkylthio, and preferably from hydrogen, F, Cl, Br, CH}_3^3, CF}_3^3, OCH}_3^3, OCF}_2^2H, OCF}_3^3, SCH}_3^3, SCF}_2^2H, \text{and SCF}_3^3; \]

\[ R^5 \text{is selected from hydrogen, CI-C4-alkyl, C2-C3-alkynyl, -CH}_2^2-CN \text{and CI-C6-alkoxy-methyl-, and preferably from hydrogen and CrC4 -alkyl;} \]

\[ R^7 \text{is hydrogen or methyl;} \]

\[ R^8 \text{is selected from the group consisting of hydrogen, d-Ce-alkyl, C1-C6 -cycloalkyl, C3-Ce-alkenyl, wherein the three last-mentioned radicals may be partially or fully halogenated and/or may be substituted by one or more substituents R}^{10}^3; C3-Ce-alkynyl, -N(R}^{10}^a)R^{10}^b.-C(=O)N(R}^{14}^a)R^{14}^b,-CH=\text{NOR}^{14}^b; \text{phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R}^{11}^3; \text{and a heterocyclic ring selected from rings of formulae D-1 to D-181 as defined above;} \]

\[ R^9 \text{is selected from hydrogen, CI-C6-alkyl, C1-C6 -cycloalkyl, C5-C6 -cycloalkylmethyl, wherein the three last-mentioned radicals may be partially or fully halogenated and/or may be substituted by one or more cyano group;} \]

\[ R^{10a} \text{is selected from the group consisting of hydrogen and CI-C6-alkyl;} \]

\[ R^{10b} \text{is selected from the group consisting of hydrogen, CI-C6-alkyl, CrC6-cycloalkyl, wherein the two last-mentioned radicals may be partially or fully halogenated and/or are optionally substituted by one cyano group; -C(=O)N(R}^{14}^a)R^{14}^b; \text{phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R}^{11}^3; \text{and a heteromonicyclic ring selected from rings of formulae D-1 to D-181 as defined above;} \]

each R}^{11}^3 \text{is independently selected from the group consisting of hydrogen, halogen, cyano, nitro, CI-C4-alkyl, CrC4 -haloalkyl, CrC4 -alkoxy, CI-C4-haloalkoxy, CI-C4-alkylthio, CrC4 -haloalkylthio, CI-C4-alkylsulfanyl, CrC4 -haloalkylsulfanyl, CI-C4-alkylsulfonyl, CI-C4-haloalkylsulfonyl, C5-C6-cycloalkyl, C5-C6 -halocycloalkyl, C2-C4 -alkenyl, C2-C4 -haloalkenyl, C2-C4 -alkynyl and C2-C4-haloalkynyl, CrC4 -alky(carbonyl, CI-C4-alkylaminocarbonyl; or}

two R}^{11} \text{present on the same carbon atom of a saturated heterocyclic ring may form together =O or =S;
R\textsuperscript{3} is selected from cyano, C\textsubscript{1}-C\textsubscript{6}-alkoxy, CrC\textsubscript{6}-haloalkoxy, CrC\textsubscript{6}-alkylthio, C\textsubscript{1}-C\textsubscript{6}-haloalkylthio, d-C\textsubscript{6}-alkylsulfinyl, CrC\textsubscript{6}-haloalkylsulfinyl, C\textsubscript{1}-C\textsubscript{6}-alkylsulfonyl, C\textsubscript{1}-C\textsubscript{6}-haloalkylsulfonyl, -(C(=0)N(R\textsuperscript{14a})R\textsuperscript{14b}), phenyl, optionally substituted with 1, 2, 3, 4 or 5 substituents R\textsuperscript{14} and a heterocyclic ring selected from rings of formulae D-1 to D-1\textsubscript{8} as defined above; and is preferably selected from d-d-alkoxy, d-d-haloalkoxy, d-d-alkylthio, d-d-haloalkylthio, d-d-alkylsulfinyl and C\textsubscript{1}-C\textsubscript{6}-haloalkylsulfonyl;

each R\textsuperscript{14a} is selected from the group consisting of hydrogen and d-d-alkyl; and each R\textsuperscript{14b} is selected from the group consisting of hydrogen, d-d-alkyl, d-d-alkynyl, d-d-alkenyl, -CH\textsubscript{2}-CN, d-d-haloalkyl, d-d-cycloalkyl, d-d-halocycloalkyl, C\textsubscript{1}-d-alkoxy and d-d-haloalkoxy, c\textsubscript{3}-C\textsubscript{6}-cycloalkylmethyl.

[0017] Thus, the present invention relates to agrochemical oil-in-water emulsions comprising a) an isothiazoline insecticide of formula 1.3, and b) submicron particles as defined herein below.

[0018] In another form, the isothiazoline insecticide is a compound of formula 1.4:

\[
\begin{array}{c}
\text{R}^1 \\
\text{R}^{2a} \quad \text{R}^{2b} \\
\text{R}^{2c} \\
\text{R} \\
\text{N} \\
\text{S} \\
\text{A} \\
\end{array}
\]

wherein

R\textsuperscript{1} is d-d-haloalkyl and is in particular CF\textsubscript{3};

R\textsuperscript{2a}, R\textsuperscript{2b} and R\textsuperscript{2c} are selected independently from one another from hydrogen, halogen and d-d-haloalkyl, preferably from hydrogen, F, Cl, Br and CF\textsubscript{3};

R\textsuperscript{4} is selected from hydrogen, halogen, cyano, d-d-alkyl, d-d-haloalkyl, d-d-alkoxy, d-d-haloalkoxy, d-d-alkylthio and d-d-haloalkylthio; and A is A\textsuperscript{4} and selected from rings of formulae D-1 to D-1\textsubscript{8} as defined above, preferably selected from D-59, D-65 and D-66 and in particular D-59.

[0019] Thus, the present invention relates to agrochemical oil-in-water emulsions comprising a) an isothiazoline insecticide of formula 1.4, and b) submicron particles as defined herein below.
In various embodiments, the oil-in-water emulsion can comprise at least 0.1% by weight, at least 20% by weight, at least 35% by weight, or at least 45% by weight of the water-insoluble pesticide or the isothiazoline insecticide. In other embodiments, the oil-in-water emulsion can comprise not more than 80% by weight, not more than 70% by weight, or not more than 60% by weight of the water-insoluble pesticide or the isothiazoline insecticide.

The submicron particles are an aqueous polymer dispersion of particles with an average particle size of less than 1000 nm said particles comprising

a) a polymer carrier prepared by heterophase oil in water radical polymerization of at least one ethylenically unsaturated monomer selected from the group consisting of C1-C18 acrylates, C1-C18 methacrylates, acrylic acid, (meth)acrylic acid, styrene, vinyltoluene, hydroxy-functional acrylates, hydroxy-functional (meth)acrylates, acrylates derived from alkoxylated alcohols, (meth)acrylates derived from alkoxylated alcohols, multifunctional acrylates and multifunctional (meth)acrylates in the presence of

b) a non-polar organic light stabilizer, wherein the non-polar organic light stabilizer has a water solubility of less than 1% by weight at room temperature and atmospheric pressure, wherein the weight ratio of non-polar organic light stabilizer to polymer carrier is greater than 100 parts of light stabilizer per 100 parts of carrier and particle content of the aqueous polymer dispersion is more than 20% by weight based on the total weight of the aqueous polymer dispersion.

The submicron particles usually have an average particle size (e.g. a D50 value) of less than 1000 nm, less than 500 nm, less than 300 nm, or less than 250 nm. The particle size may be determined by X-ray diffraction spectroscopy. The submicron particles usually comprise 1 to 40 wt%, or preferably 5 to 30 wt% of the oil-in-water emulsion.

The submicron polymeric matrix capsules containing organic light stabilizer may be prepared through a mini emulsion polymerization process. Generally, the capsules were prepared as described below:

a) dissolving, emulsifying or dispersing a non-polar organic light stabilizer in at least one ethylenically unsaturated monomer. An optimized blend of acrylic / vinylic monomers was normally used to achieve desirable glass transition temperature (Tg) and compatibility etc;

b) preparing a conventional oil-in-water emulsion of said light stabilizer dissolved, emulsified or dispersed in at least one ethylenically unsaturated monomer;

c) homogenizing the conventional emulsion to a miniemulsion wherein the droplets of the organic phase had an average diameter below 300 nm;

d) polymerizing the miniemulsion by adding a polymerization initiator;

e) The resulting polymer matrix capsules had a mean particle size less than 300 nm;
wherein the weight ratio of non-polar organic light stabilizer to polymer carrier formed from the ethylenically unsaturated monomer is greater than 50 parts of light stabilizer per 100 parts of polymer carriers (based on weight). Examples of other suitable submicron polymeric matrix capsules are described in US patent 7,687,554 B2, the entire contents of which is incorporated by reference. Many submicron polymeric matrix capsules comprising light stabilizers are available commercially under the tradename Tinuvin® (BASF SE).

[0024] Preferably the polymerization initiator is a redox initiator system or a photoinitiator, particularly a bis-azo compound, a peroxide or a hydroperoxide, more particularly a hydroperoxide. Specific preferred radical sources are 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methyl-butyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvalero-nitrile), 1,1'-azobis(1-cyclohexanecarbonitrile), 2,2'-azobis(isobutryamide) dihydrate, 2-phenylazo-2,4-dimethyl-4-methoxyvaleronitrile, dimethyl 2,2'-azobisisobutyrate, 2-(carbamoylazo)isobutryronitrile, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), 2,2'-azobis(N,N'-dimethyleisobutyramidine), free base or hydrochloride, 2,2'-azobis(2-aminopropane), free base or hydrochloride, 2,2'-azobis[2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide] or 2,2'-azobis[2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide; acetyl cyclohexane sulphonyl peroxide, diisopropyl peroxo dicarbonate, t-amyl perneodecanoate, t-buty1 perneodecanoate, t-buty1 perpivalate, t-amylperpivalate, bis(2,4-dichlorobenzoyl)peroxide, diisononanoyl peroxide, didecanoyl peroxide, dioctanoyl peroxide, dilauroyl peroxide, bis(2-methylbenzoyl) peroxide, diisuccinic acid peroxide, diacetyl peroxide, dibenzoxy peroxide, t-buty1 per 2-ethylhexanoate, bis-(4-chlorobenzoyl)-peroxide, t-buty1 perisobutyrate, t-buty1 permaleinate, 1,1-bis(t-buty1peroxy)3,5,5-trimethylcyclohexane, 1,1-bis(t-buty1peroxy)cyclohexane, t-buty1 peroxy isopropyl carbonate, t-buty1 perisononaoate, 2,5-dimethylhexane 2,5-dibenzoate, t-buty1 peracetate, t-amyl perbenzoate, t-buty1 perbenzoate, 2,2-bis (t-buty1peroxy) butane, 2,2 bis (t-buty1peroxy) propane, dicumyl peroxide, 2,5-dimethylhexane-2,5-di-t-buty1peroxide, 3-t-buty1peroxy 3-phenylphthalide, di-t-amyl peroxide, 3,5-bis (t-buty1peroxy)3,5-dimethyl 1,2-dioxolane, di-t-buty1 peroxide, 2,5-dimethylhexyne-2,5-di-t-buty1peroxide, 3,3,6,6,9-hexamethyl 1,2,4,5-tetraoxa cyclononanone, p-methane hydroperoxide, pinane hydroperoxide, diisopropylbenzene mono-alpha-hydroperoxide, cumene hydroperoxide or t-buty1 hydroperoxide, particularly preferred is t-buty1 hydroperoxide. It is also possible to use combinations of Fe-compounds or Co-compounds with peroxy salts or salts of bisulfites or hydrosulfites. These combinations are known as redox systems.

[0025] Surprisingly, a photodegradable active ingredient, such as an isothiazoline insecticide as described supra, formulated in an oil-in-water emulsion [0026] , can be photochemically stabilized when encircled by a polymer matrix formed by a film of submicron particles encapsulating the oil droplet surface, with an organic light stabilizer within the submicron particles. The aforementioned film forming polymeric matrix capsules behave as an emulsifier and a stabilizer for such an agrochemical oil-in-water emulsion in the form of an oil-in-
water emulsion. The isothiazoline insecticide usually comprises 0.1 to 70 wt%, 10 to 50 wt%, or 15 to 40 wt% of the oil-in-water emulsion.

[0027] The polymer capsules suitable for this invention should pass surface activity screening as illustrated in the Examples; preferably have a glass transition temperature (Tg) between -20 °C to 120 °C and a mean polymer particle size less than 100 nm, or preferably have a Tg between 0 °C to 105 °C, and a mean polymer particle size less than 300 nm. In an embodiment, the capsulated light stabilizers in the above polymeric matrix, can include organic UV absorbers (UVA) and/or hindered amine light stabilizers (HALS). In an embodiment, UVA stabilizers can include 2-(2-hydroxyphenyl)-benzotriazole (BTZ) and 2-hydroxyphenyl-s-triazine (HPT) derivatives. HALS, which are mainly derivatives of 2,2,6,6-tetra-methylpiperidine, act as radical scavengers and inhibit the photo-oxidative breakdown reactions.

[0028] In a particular embodiment, the non-polar organic stabilizer has the following chemical structure (formula II):

![formula II](image)

[0029] The oil phase of the agrochemical oil-in-water emulsion of the present invention may comprise a water-immiscible organic solvent. The water-immiscible organic solvent may be used to dissolve the poorly soluble pesticide for the oil-in-water emulsion of the present invention.

[0030] The solubility in water of said solvent is usually up to 10 g/l at 20 °C, preferably up to 3 g/l and in particular up to 0.5 g/l.

[0031] The agrochemical oil-in-water emulsion may comprise from 10 to 60 wt%, especially from 15 to 45 wt% of the water-immiscible organic solvent.

[0032] Examples for suitable organic solvents are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, fatty acid glycerides, aliphatic, cyclic and aromatic hydrocarbons, e.g. toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives. Mixtures of organic solvents may also be used. Preferred organic solvents are hydrocarbons.
Preferably, the oil phase of the agrochemical oil-in-water emulsion of the present invention may comprise a hydrocarbon. The hydrocarbon may be used to dissolve the poorly soluble pesticide for the oil-in-water emulsion of the present invention. Hydrocarbons can include aromatic petroleum derivatives (aromatic hydrocarbons) with a solubility in water < 0.1% (w/w) and a distillation range from 130 °C to 300 °C (commercially available under the following brand names: Solvesso™ 100, Solvesso™ 150, Solvesso™ 200, Solvesso™ 150ND, Solvesso™ 200ND, Aromatic 150, Aromatic 200, Hydrosol A 200, Hydrosol A 230/270, Caromax™ 20, Caromax™ 28, Aromat K 150, Aromat K 200, Shellsol™ A 150, Shellsol™ A 100, Fin FAS-TX 150, Fin FAS-TX 200). In an embodiment, the hydrocarbon is an aromatic hydrocarbon.

The term pesticides refer to at least one active substance selected from the group of the fungicides, insecticides, nematicides, herbicides, safeners and/or growth regulators. Pesticides include fungicides, insecticides, herbicides and growth regulators. In one embodiment, pesticides are fungicides. Mixtures of pesticides from two or more of the abovementioned classes may also be used. The skilled worker is familiar with such pesticides, which can be found, for example, in Pesticide Manual, 16th Ed. (2013), The British Crop Protection Council, London, the entire contents of which are hereby incorporated by reference. The following pesticides are suitable, by way of example (pesticides A) to K) are fungicides:

A) Respiration inhibitors

Inhibitors of complex III at Qₒ site (e.g. strobilurins): azoxystrobin, coumoxystrobin, coumoxydostrobin, dimoxystrobin, ensetrobin, fenaminstrobin, fenoxystrobin/flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, trifloxystrobin, 2-[2-(2,5-dimethyl-phenoxy)methyl]-phenyl]-3-methoxy-acrylic acid methyl ester and 2-(2-(3-[2,6-dichlorophenyl]-1-methyl-allylideneamino)-oxy-methyl)-phenyl)-2-methoxyimino-N-methyl-acetamide, pyribencarb, triclopyracarb/chlorodinacarb, famoxadone, fenamidone; inhibitors of complex III at Qₒ site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl]-2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-(acetoxymethoxy)-4-methoxy-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl]-2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarboxyloxy-4-methoxy-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl]-2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-hydroxy-4-methoxy-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl]-2-methylpropanoate; (3S,6S,7R,8R)-3-[(3-hydroxy-4-methoxy-2-pyridinyl)carbonyl]amino]-6-methyl-4,9-dioxo-8-(phenylmethyl)-1,5-dioxonan-7-yl 2-methylpropanoate; inhibitors of complex II (e.g., carboxamides): benodanil, benzovindiflupyr, bixafen, boscalid, carboxin, fenfuram, fluopyram, flutolanil, flupyradecyl, furametpyr, isopyrazam, mepronil, oxycarboxin, penflufen, penhiopyrad, sedaxane, tecloftalam, thifluzamide, N-(4′-trifluoromethylthiophenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-
dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, 3-(difluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(trifluoromethyl)-1-methyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 1,3-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(trifluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide, 3-(difluoromethyl)-1,5-dimethyl-N-(1,1,3-trimethylindan-4-yl)pyrazole-4-carboxamide; other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-am nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;

B) Sterol biosynthesis inhibitors (SBI fungicides)

[0036] C14 demethylase inhibitors (DMI fungicides): triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, paclobutrazole, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, 1-[reA(2S;3R)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-5-thiocyanato-1H-[1,2,4]triazole, 2-[reA(2S;3R)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)-oxiranylmethyl]-2H-[1,2,4]triazole-3-thiol; imidazoles: imazalil, pefurazoate, prochloraz, triflumizol; pyrimidines, pyridines and piperazines: fenarimol, nualimol, pyrifenoxy, triforine; Delta14-reductase inhibitors: aldimorph, dodemorph, dodemorph-acetate, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine; Inhibitors of 3-keto reductase: fenhexamid;

C) Nucleic acid synthesis inhibitors

[0037] phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiraxlaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl; others: hymexazole, ochthilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenoxymethoxy)pyrimidin-4-amine;

D) Inhibitors of cell division and cytoskeleton

[0038] tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine; other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, flupicilide, zoxamide, metrafenone, pyriofenone;

E) Inhibitors of amino acid and protein synthesis
methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil; protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;

F) Signal transduction inhibitors

MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fluudioxonil; G protein inhibitors: quinoxyfen;

G) Lipid and membrane synthesis inhibitors

Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane; lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole; phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyano-phenyl)-ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester; compounds affecting cell membrane permeability and fatty acids: propamocarb, propamocarb-hydrochlorid; fatty acid amide hydrolase inhibitors: oxathiapiprolin;

H) Inhibitors with Multi-Site Action

inorganic active substances: Bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulfate, sulfur; thio- and dithiocarbamates: ferbam, mancozeb, maneb, metam, metiram, propineb, thiram, zineb, ziram; organochlorine compounds (e.g. phthalimides, sulfamides, chloronitriles): anilazine, chlorothalonil, captafol, captan, folpet, dicyclomet, dichlofluanid, dichloroanil, flusulfamide, hexachlorobenzene, pentachlorphenole and its salts, phthalide, tolylfluanid, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide; guanidines and others: guanidine, dodine, dodine free base, guazatine, guazatine-acetate, iminoctadine, iminoctadine-triacetate, iminoctadine-tris(albesilate), dithianon, 2,6-dimethyl-1 H,5H-D[1,4]dithiino[2,3-c:5,6-c']dipyrrole-1 ,3,5,7(2H,6H)-tetraone;

I) Cell wall synthesis inhibitors

inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defense inducers

acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

K) Unknown mode of action
bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxathiapiprolin, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-[2-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl)-1,3-thiazol-2-yl]piperidin-1-yl]ethanone, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-[2-chloro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl)-1,3-thiazol-2-yl]piperidin-1-yl]ethanone, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-[2-fluoro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl)-1,3-thiazol-2-yl]piperidin-1-yl]ethanone, 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-[2-(3,5-bis(difluoromethyl)-1H-pyrazol-1-yl)-1,3-thiazol-2-yl]piperidin-1-yl]ethanone, oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide, N’-(6-methoxy-pyridin-3-yl)-cyclopropanecarboxylic acid amide, N-(6-methoxy-pyridin-3-yl) cyclopropane carboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzimidazole, 2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazolidin-3-yl]-pyridine, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzimidazole, 2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazolidin-5-yl]-2-prop-2-ynyloxy-acetamide;

L) Growth regulators

abscisic acid, amidochlor, ancymidol, 6-benzylaminopurine, brassinolide, butralin, chloromequat (chloromequat chloride), choline chloride, cyclanilide, daminozide, dikegulac, dimethipin, 2,6-dimethylpuridine, ethephon, flumetralin, flurprimidol, fluthiacet, forchlorfenuron, gibberellic acid, inabenfide, indole-3-acetic acid, maleic hydrazide, mefluidide, mepikuat (mepikuat chloride), napthaleneacetic acid, N-6-benzyladenine, paclobutrazol, prohexadione (prohexadione-calcium), prohydrojasmon, thidiazuron, triapenthenol, tributyl phosphorotrithioate, 2,3,5-tri-iodobenzoic acid, trinexapac-ethyl and uniconazole;

M) Herbicides

acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet, mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, pretilachlor, propachlor, thienylchlor; amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate; aryloxyphenoxypropionates: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quinclorac, quinclorac-P-teturfy; Bipyridyls: diquat, paraquat; (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate; cyclohexanediones: butroxydim, clethodim, cycloxydim, profoxydim, sethoxydim, tepraloxydim,
tralkoxydim; dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin; diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen; hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil; imidazolinones: imazamethabenz, imazamox, imazapic, imazaquin, imazapic, imazethapyr; phenoxyacetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPP, Mecoprop; pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate; pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram, picolinafen, thiazopyr; sulfonylureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyr sulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, proslufuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, triketosulfuron, triflunysulfuron, triflusulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1,2-b]pyridazin-3-yl) sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea; triazoles: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron, metribuzin, prometryn, simazine, terbutryln, triaziflam; ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, mebanthiazuron, tebuthiuron; other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, orthosulfamuron, penoxsulam, propoxycarbanzole, pyribambenz-propyl, pyribenoxim, pyrflialid, pyriminobac-methyl, pyrimisulfin, pyriothiobac, pyroxasulfone, pyroxasulfone; others: amicarbazone, aminotriazole, anilofos, biflubutamid, benazolin, bencarbazone, benfluresate, benzofenap, bentazone, benzobicyclon, bicyclopyrone, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthal, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoquat, difluflenzopyr, Drechslera monoceras, endothal, ethofumesate, etobenazid, fenoxasulfone, fentrazamide, flumiclorac-pentyl, flumioxazin, fluroxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsionic acid, naphtalam, oxadiargyl, oxadiazon, oxaziclostone, pentoxazone, pinoxaden, pyraclonil, pyraflufenesyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrone, tebutryn, thienocarbazone, topramezone, (3-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifloromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-phenoxy]-4-phenyl) acid methyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3-chloro-6-(4-chlorophenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3-chloro-6-(4-chloro-3-dimethylaminophenyl)-pyridine-2-carboxylic acid methyl ester.

P) Insecticides
[0049] organo(thio)phosphates: acephate, azamethiphos, azinphos-methyl, chlorpyrifos, chlorpyrifos-methyl, chlorsulfuron, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidophos, methidathion, methyl-parathion, mevinphos, monocrotophos, oxydemeton-methyl, paraoxon, parathion, phenthoate, phosalone, phosmet, phosphamidon, phorate, phoxim, pirimiphos-methyl, profenofos, prothiofos, sulprophos, tetrachlorvinphos, terbufos, triazophos, trichlorfon; carbamates: alany carb, aldicarb, bendiocarb, benfuracarb, carbaryl, carbofuran, carbosulfan, fenoxycarb, furathiocarb, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, thiocarb, triazamate; pyrethroids: allethrin, bifenthrin, cyfluthrin, cyhalothrin, cyfluthrin, cypermethrin, cyphenothrin, deltamethrin, esfenvalerate, etofenprox, fenpropatrin, fenvalerate, imiprothrin, lambda-cyhalothrin, permethrin, prallethrin, pyrethrin I and II, resmethrin, silafluofen, tau-fluvalinate, tebufenozide, tetramethrin, tralomethrin, transfluthrin, proflothrin, dimefluthrin; insect growth regulators: a) chitin synthesis inhibitors: benzofurazuron, cyramazin, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron; buprofezin, diofenolan, hexythiazox, etoxazole, clobenzthiazol; b) edysone antagonists: halofenozide, methoxyfenozide, tebufenozide, azadirachtin; c) juvenoids: pyriproxifen, methoprene, fenoxycarb; d) lipid biosynthesis inhibitors: spirodiclofen, spiromesifen, spirotetramat; nicotinic receptor agonists/antagonists compounds: clothianidin, dinotefuran, flupyradifuron, imidacloprid, thiamethoxam, nitenpyram, acetamiprid, thiacloprid, 1-2-chloro-thiazol-5-ymlmethy)-2-nitrimino-3,5-dimethyl-[1,3,5]triazinane; GABA antagonist compounds: endosulfan, ethiprole, fipronil, vanilliprole, pyrafluprole, pyriprole, 5-amino-1-(2,6-dichloro-4-methyl-phenyl)-4-sulfamoyl-1 H-pyrazole-3-carboxthioic acid amide; macrocyclic lactone insecticides: abamectin, emamectin, milbemectin, lepimectin, spinosad, spinetoram; mitochondrial electron transport inhibitor (METI) I acaricides: fenazaquin, pyridaben, tebufenpyrad, tolfenpyrad, flufeneter; METI II and III compounds: acequinocyl, fluacypyr, hydramethylnon; Uncouplers: chlorfenapyr; oxidative phosphorylation inhibitors: cyhexatin, diafenthiuron, fenbutatin oxide, propargite; moulting disruptor compounds: cryomazine; mixed function oxidase inhibitors: piperonyl butoxide; sodium channel blockers: indoxacarb, metaflumizone; ryanodine receptor inhibitors: chlorantraniliprole, cyantraniliprole, flubendiamide, N-[4,6-dichloro-2-(diethyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-(diethyl-lambda-4-sulfanylidene)carbamoyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-methyl-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dichloro-2-(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dichloro-2-(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4-chloro-2-(di-2-propyl-lambda-4-sulfanylidene)carbamoyl]-6-cyano-phenyl]-2-(3-chloro-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; N-[4,6-dibromo-2-(diethyl-lambda-4-
sulfanylidene)carbamoyl]-phenyl]-2-(3^-halo-2-pyridyl)-5-(trifluoromethyl)pyrazole-3-carboxamide; others: benzothiaz, bifenazate, cartap, flonicamid, pyridalyl, pymetrozine, sulfur, thiocyclam, cyenopyrafen, flupyrazofos, cyflumetofen, amidoflumet, imicyafos, bistrifluron, pyrifluquinazon and afidopyropen and the isothiazoline compounds as described herein above.

[0050] The pesticide is water-insoluble. Usually, it is soluble in water to not more than 1 g/l, preferably not more than 200 mg/l and in particular to not more than 50 mg/l at 25°C. Examples of water-insoluble pesticides include isothiazolines as described herein. Using simple preliminary experiments, the skilled worker can select a pesticide with a suitable water-solubility from the above pesticide list.

[0051] In various embodiments, the pesticide can have a melting point of more than 50°C, more than 70°C, or more than 90°C.

[0052] The pesticide can be present in the oil-in-water emulsion in dissolved form. Using simple preliminary experiments, the skilled worker can select, from the above pesticide list, a pesticide with a suitable solubility.

[0053] In various embodiments, the oil-in-water emulsion may comprise from 0.1 to 70% by weight, from 10 to 50% by weight, or from 15 to 40% by weight, of pesticide, the basis being the total of all the pesticides present in the oil-in-water emulsion.


[0055] The agrochemical compositions may be prepared in a known manner, such as described by Mollet and Grubemann, Formulation technology, Wiley VCH, Weinheim, 2001; or Knowles, New developments in crop protection product formulation, Agrow Reports DS243, T&F Informa, London, 2005.

[0056] The oil-in-water emulsion can furthermore comprise auxiliaries conventionally used for crop protection products. Suitable auxiliaries are solvents, liquid carriers, surfactants, dispersants, emulsifiers, wetters, adjuvants, solubilizers, penetrants, protective colloids, stickers, thickeners, bactericides, antifreeze agents, antifoam agents, colorants, adhesives and binders.

[0057] Suitable solvents and liquid carriers are organic solvents such as mineral oil fractions with medium to high boiling point, for example kerosene, diesel oil; oils of vegetable or animal origin; aliphatic and cyclic hydrocarbons, for example toluene, paraffin, tetrahydrofuran, alkylated naphthalenes; alcohols, for example ethanol, propanol, butanol, cyclohexanol; glycols;
ketones, for example cyclohexanone; esters, for example carbonates, fatty acid esters; fatty acids; phosphonates; amines; amides, for example N-methylpyrrolidone; and their mixtures.

[0058] Suitable surfactants are surface-active compounds, such as anionic, cationic, nonionic and amphoteric surfactants, block polymers, polyelectrolytes, and mixtures thereof. Such surfactants can be used as emulsifier, dispersant, solubilizer, wetter, penetrant, protective colloid, or auxiliary. Examples of surfactants are listed in McCutcheon’s, Vol.1: Emulsifiers & Detergents, McCutcheon’s Directories, Glen Rock, USA, 2008 (International Ed. or North American Ed.), the entire contents of which are incorporated by reference.

[0059] Suitable anionic surfactants are alkali, alkaline earth or ammonium salts of sulfonates, sulfates, phosphates, carboxylates, and mixtures thereof. Examples of sulfonates are alkylaryl sulfonates, diphenyl sulfonates, alpha-olefin sulfonates, lignine sulfonates, sulfonates of fatty acids and oils, sulfonates of ethoxylated alkylphenols, sulfonates of alkoxylated arylphenols, sulfonates of condensed naphthalenes, sulfonates of dodecyl- and tridecylbenzenes, sulfonates of naphthalenes and alkynaphthalenes, sulfosuccinates or sulfosuccinamates. Examples of sulfates are sulfates of fatty acids and oils, of ethoxylated alkylphenols, of alcohols, of ethoxylated alcohols, or of fatty acid esters. Examples of phosphates are phosphate esters. Examples of carboxylates are alkyl carboxylates, and carboxylated alcohol or alkylphenol ethoxylates. In an embodiment, anionic surfactants include sulfates and sulfonates.

[0060] Suitable nonionic surfactants are alkoxylates, N-substituted fatty acid amides, amine oxides, esters, sugar-based surfactants, polymeric surfactants, and mixtures thereof. Examples of alkoxylates are compounds such as alcohols, alkylphenols, amines, amides, alcohols, fatty acids or fatty acid esters which have been alkoxylated with 1 to 50 equivalents. Ethylene oxide and/or propylene oxide may be employed for the alkoxylatation, preferably ethylene oxide. Examples of N-substituted fatty acid amides are fatty acid glucamides or fatty acid alkanolamides. Examples of esters are fatty acid esters, glycerol esters or monoglycerides. Examples of sugar-based surfactants are sorbitans, ethoxylated sorbitans, sucrose and glucose esters or alkylpolyglucosides. Examples of polymeric surfactants are homo- or copolymers of vinylpyrrolidone, vinylalcohols, or vinylacetate. Nonionic surfactants can include alkoxylates. Nonionic surfactants such as alkoxylates may also be employed as adjuvants.

[0061] Suitable cationic surfactants are quaternary surfactants, for example quaternary ammonium compounds with one or two hydrophobic groups, or salts of long-chain primary amines. Suitable amphoteric surfactants are alkylbetains and imidazolines. Suitable block polymers are block polymers of the A-B or A-B-A type comprising blocks of polyethylene oxide and polypropylene oxide, or of the A-B-C type comprising alkanol, polyethylene oxide and polypropylene oxide. Suitable polyelectrolytes are polyacids or polybases. Examples of polyacids are alkali salts of
polyacrylic acid or polyacid comb polymers. Examples of polybases are polyvinylamines or polyethyleneamines.

[0062] Suitable adjuvants are compounds which have negligible or even no pesticidal activity themselves, and which improve the biological performance of the compound on the target. Examples are surfactants, mineral or vegetable oils, and other auxiliaries. Further examples are listed by Knowles, Adjuvants and Additives, Agrow Reports DS256, T&F Informa UK, 2006, chapter 5.

[0063] Suitable bactericides are bronopol and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones. Suitable antifreeze agents are ethylene glycol, propylene glycol, urea and glycerol. Suitable antifoam agents are silicones, long-chain alcohols, and salts of fatty acids. Suitable colorants (e.g. in red, blue, or green) are pigments which are sparingly soluble in water, and water-soluble dyes. Examples are inorganic colorants (e.g. iron oxide, titanium oxide, iron hexacyanoferrate) and organic colorants (e.g. alizarin, azo and phthaloxyazine colorants).

[0064] The oil-in-water emulsion may comprise at least one anionic surfactant. In various embodiments, the oil-in-water emulsion comprises not less than 0.5% by weight of anionic surfactants, not less than 2% by weight, or not less than 3% by weight. In other embodiments, the oil-in-water emulsion can comprise not more than 30% by weight, not more than 15% by weight, or not more than 10% by weight of anionic surfactants.

[0065] The oil-in-water emulsion preferably comprises at least one nonionic surfactant (such as alkoxylates). In various embodiments, the oil-in-water emulsion can comprise not less than 1% by weight, not less than 5% by weight, or not less than 10% by weight of nonionic surfactants. In other embodiments, the oil-in-water emulsion can comprise not more than 65% by weight, not more than 45% by weight, or not more than 35% by weight of nonionic surfactants.

[0066] The oil-in-water emulsion may optionally comprise further auxiliaries, such as 0.1-1 wt% bactericides, 5-15 wt% anti-freezing agents, 0.1-1 wt% anti-foaming agents, and 0.1-1 wt% colorants.

[0067] The invention furthermore relates to a process for the preparation of the agrochemical oil-in-water emulsion according to the invention by shear mixing the water-insoluble pesticide and submicron particles containing an organic light stabilizer. In an embodiment, the water-insoluble pesticide is an isothiazoline insecticide as described herein.

[0068] The invention furthermore relates to an oil-in-water emulsion obtainable (preferably obtained) by mixing an oil phase comprising the water-insoluble pesticide with an aqueous phase comprising water and the submicron particles described herein. The emulsion normally forms upon
shearing. The oil phase normally accounts for between about 0.1% to 70% of the total formulation by weight. In an embodiment, the oil phase accounts for between about 5% to 60% of the total formulation weight.

[0069] The invention furthermore relates to a method for controlling phytopathogenic fungi and/or undesired vegetation and/or undesired attack by insects or mites and/or for regulating the growth of plants, where the oil-in-water emulsion is allowed to act on the respective pests, their environment or on the crop plants to be protected from the respective pests, on the soil and/or on undesired plants and/or on the crop plants and/or their environment. In general, the therapeutic treatment of humans and animals is excluded from the method for controlling phytopathogenic fungi and/or undesired vegetation and/or undesired attack by insects or mites and/or for regulating the growth of plants.

[0070] When employed in crop protection, in certain embodiments, the application rates of the pesticides amount to from 0.001 to 2 kg per ha, from 0.005 to 2 kg per ha, from 0.05 to 0.9 kg per ha, or from 0.1 to 0.75 kg per ha, depending on the nature of the desired effect. In treatment of plant propagation materials such as seeds, e.g. by dusting, coating or drenching seed, amounts of active substance of from 0.1 to 1000 g, preferably from 1 to 1000 g, from 1 to 100 g, or from 5 to 100 g, per 100 kg of plant propagation material (preferably seed) are generally required. When used in the protection of materials or stored products, the amount of active substance applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are 0.001 g to 2 kg, or 0.005 g to 1 kg, of active substance per cubic meter of treated material.

[0071] Various types of oils, wetters, adjuvants, fertilizers or micronutrients may be added to the oil-in-water emulsion in the form of a premix or optionally only shortly before use (tank mix). These agents can be admixed to the oil-in-water emulsions according to the invention at a weight ratio of from 1:100 to 100:1, or from 1:10 to 10:1.

[0072] The user applies the oil-in-water emulsion according to the invention usually from a predosage device, a knapsack sprayer, a spray tank, a spray plane, or an irrigation system. Usually, the agrochemical oil-in-water emulsion is made up with water, buffer, and/or further auxiliaries to the desired application concentration and the ready-to-use spray liquor or the agrochemical oil-in-water emulsion according to the invention is thus obtained. Usually, 20 to 2000 liters, or 50 to 400 liters, of the ready-to-use spray liquor are applied per hectare of agricultural useful area.

[0073] Advantages of the present invention are, *inter alia*, that the oil-in-water emulsion is highly stable; that the pesticide does not precipitate, cream or crystallize in the oil-in-water emulsion; that the pesticide does not precipitate, cream or crystallize in the emulsion; that high pesticide concentrations in the oil-in-water emulsion can be employed; that the oil-in-water
emulsion is capable of being stored over prolonged periods (e.g. 3 months to 3 years; that adjuvants can be included in the oil-in-water emulsion formulation; that the pesticide in the oil-in-water emulsion is photostable; that the pesticide exhibits a greater effect over time. The examples which follow illustrate the invention without imposing any limitation.

EXAMPLES

[0074] The following additives were used:

Stabilizing Particles A: aqueous dispersion of a light stabilizer (red shifted hydroxy-phenyltriazine derivative) encapsulated in acrylic matrix, particle size D50 below 150 nm, stabilizer content about 20 wt%, total solid about 40 wt%, commercially available as Tinuvin® 477-DW from BASF SE.

Stabilizing Particles B: aqueous dispersion of a light stabilizer (mixture of branched and linear C7-C9 alkyl 3-[3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxyphenyl]propionates) encapsulated in acrylic matrix, particle size D50 below 150 nm, stabilizer content 20-25 wt%, total solid 40-50 wt%, commercially available as Tinuvin® 99-DW from BASF SE.

Stabilizing Particles C: aqueous dispersion of a light stabilizer (blue shifted hydroxy-phenyltriazine derivative) encapsulated in acrylic matrix, particle size D50 below 150 nm, stabilizer content 20-25 wt%, total solid 40-50 wt%, commercially available as Tinuvin® 400-DW from BASF SE.

Solvent A: Aromatic hydrocarbon solvent, initial boiling point about 230 °C; aromatic content above 99 %.

Solvent B: N,N-Dimethyl C8/C10 fatty acid amide, liquid, density about 0.88 g/cm³.

Surfactant A: Ethoxylated castor oil, melting point about 32 °C, HLB 14-15 (Griffin).

Surfactant B: Solution of calcium salt of dodecylbenzenesulfonic acid (60 wt%) in organic solvent, flash point 78 °C.

[0075] The following isothiazoline insecticide was used: 4-[5-(3,5-dichlorophenyl)-5-(trifluoromethyl)-4H-isothiazol-3-yl]-2-methyl-N-(2-pyridylmethyl)benzamide.

Example 1: Screening test to determine suitable surface activity of polymer matrix capsules

[0076] An oil-in-water emulsion A having the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Name</th>
<th>Amount (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>Solvent A</td>
<td>40</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>Stabilizing Particles A, B or C</td>
<td>2.8</td>
</tr>
<tr>
<td>Diluent</td>
<td>D.I. water</td>
<td>To 100%</td>
</tr>
</tbody>
</table>
The oil-in-water emulsions were prepared by the following procedure using Stabilizing Particles A, B or C:
1. Polymer matrix capsules were mixed with D.I. water until uniform (aqueous phase).
2. Added Solvent A (oil phase) into the above aqueous phase with agitation.
3. Homogenized the above mixture for 2 minutes at 7000 rpm using a Silverson high shear mixer.
4. Kept the sample at 21 °C for 1 day for stability observation.

The emulsion stability was determined by visual observation of sample phase separation 1 day after emulsion sample was prepared.

It was found that oil-in-water emulsions prepared from Stabilizing Particles A, B or C) were stable: no phase separation or creaming were observed after 1 day storage at 21 °C.

Example 2: 1% Isothiazoline oil-in-water emulsion stabilized by 13.8% of Stabilizing Particles A

Three isothiazoline oil-in-water emulsions (B, C, and D) having the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Name</th>
<th>Amount (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active ingredient</td>
<td>Isothiazoline</td>
<td>1.0</td>
</tr>
<tr>
<td>Solvent</td>
<td>Solvent A</td>
<td>30</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>Stabilizing Particles A (B)</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>Or Stabilizing Particles B (C)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Or Stabilizing Particles C (D)</td>
<td></td>
</tr>
<tr>
<td>Diluent</td>
<td>D.I. water</td>
<td>To 100%</td>
</tr>
</tbody>
</table>

The pesticidal oil-in-water emulsions were prepared by the following procedure:
1. Active ingredient was added to Solvent A, stirred until dissolved / uniform (oil phase).
2. Stabilizing Particles A, B or C was mixed with D.I. water until uniform (aqueous phase).
3. Added oil phase into the above aqueous phase with agitation.
4. Homogenized the above mixture for 2 minutes at 7000 rpm using a Silverson high shear mixer.

A glass plate UV stability test was used to quantify the UV degradation of the
isothiazoline. The detailed test method is described as follows:

[0083] Formulations were diluted to the same concentration using D.I. water. 5 drops of 1 x I dilution deposited on glass plate. 2 glass plates per sample per time point. After application, glass plates were put in the UV chamber. 1 and 24 hours after application, glass plates were taken out of UV chamber and washed off with 10 ml water/MEOH at ratio of 50/50. Wash off liquid was analyzed for active ingredient concentration via HLPC/MS/MS. Active ingredient recovery was calculated as percentage of active ingredient applied.

[0084] For comparison, a conventional isothiazoline emulsifiable concentrate (EC) formulation was included in the same tests with the following recipe:

<table>
<thead>
<tr>
<th>Component</th>
<th>Name</th>
<th>Amount (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active ingredient</td>
<td>Isothiazoline</td>
<td>1.0</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>Surfactant B</td>
<td>9.38</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>Surfactant A</td>
<td>6.25</td>
</tr>
<tr>
<td>Solvent</td>
<td>Solvent B</td>
<td>62.51</td>
</tr>
<tr>
<td>Solvent</td>
<td>Solvent A</td>
<td>To 100%</td>
</tr>
</tbody>
</table>

[0085] The pesticidal oil-in-water emulsion was prepared by following procedure:
1. Active ingredient is added to Solvent A and B, stir until dissolved / uniform (oil phase).
2. Surfactant A and B were added to the above mixture, agitated until uniform.

[0086] The glass plate testing result is summarized in the following table.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Isothiazoline recovery after 1 hour under UV chamber</th>
<th>Isothiazoline recovery after 24 hours under UV chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothiazoline EC</td>
<td>0.2%</td>
<td>0%</td>
</tr>
<tr>
<td>B</td>
<td>24%</td>
<td>4%</td>
</tr>
<tr>
<td>C</td>
<td>21%</td>
<td>1.1%</td>
</tr>
<tr>
<td>D</td>
<td>18.6%</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

[0087] An improved UV stabilization of isothiazoline was observed for all Tinuvin® DW samples versus no use of submicron particles with an organic light stabilizer.

Example 3: Biological Activity Testing
A UV chamber test was also performed to determine if biological activity (i.e. efficacy) was improved with Formulations B, C or D. Testing details: (isothiazoline = a.i.)

a. Treatments were applied at 50g ai/ha in the spray chamber at 300L/ha. Treated plants (Lima bean) were held in a UV chamber.

b. Plants were infested at 0, 1, 2, 5 and 7 Day After Treatment (DAT). The UV chamber was held at 26° C with a 14:10 light:dark cycle. Leaves were removed and one leaf per petri dish was infested with five 3rd instar southern armyworm. Each treatment was replicated 4 times.

c. The test was held in the holding room at 26° C with no exposure to UV light. Treatments were evaluated for mortality at 3-4 days after infest.

The results are shown in the following table:

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Mean Percentage Mortality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Infest Date</td>
</tr>
<tr>
<td></td>
<td>1 DAT</td>
</tr>
<tr>
<td>Untreated</td>
<td>0%</td>
</tr>
<tr>
<td>Isothiazoline EC</td>
<td>70%</td>
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A significant improvement in biological activity of the isothiazoline was observed using Formulation B compared to conventional isothiazoline EC formulation at each timeframe tested.
We claim:

1. An agrochemical oil-in-water emulsion comprising
   a) a water-insoluble pesticide, and
   b) submicron particles containing an organic light stabilizer.

2. The oil-in-water emulsion according to claim 1, wherein the water-insoluble pesticide is an insecticide.

3. The oil-in-water emulsion according to claims 1 or 2, wherein the water-insoluble pesticide is dissolved in the oil phase.

4. The oil-in-water emulsion according to any of claims 1 to 3, wherein the water-insoluble pesticide is an aminothiazoline.

5. The oil-in-water emulsion according to any of claims 1 to 4, wherein the submicron particles are an aqueous polymer dispersion of particles with an average particle size of less than 1000 nm said particles comprising
   a) a polymer carrier prepared by heterophase oil in water radical polymerization of at least one ethylenically unsaturated monomer selected from the group consisting of C1-C18 acrylates, C1-C18 methacrylates, acrylic acid, (meth)acrylic acid, styrene, vinlyltoluene, hydroxy-functional acrylates, hydroxy-functional (meth)acrylates, acrylates derived from alkoxylated alcohols, (meth)acrylates derived from alkoxylated alcohols, multifunctional acrylates and multifunctional (meth)acrylates in the presence of
   b) a non-polar organic light stabilizer, wherein the non-polar organic light stabilizer has a water solubility of less than 1% by weight at room temperature and atmospheric pressure, wherein the weight ratio of non-polar organic light stabilizer to polymer carrier is greater than 100 parts of light stabilizer per 100 parts of carrier and particle content of the aqueous polymer dispersion is more than 20% by weight based on the total weight of the aqueous polymer dispersion.

6. The oil-in-water emulsion according to any of claims 1 to 5, wherein the organic light stabilizer has the structure of formula II:
7. The oil-in-water emulsion according to any of claims 1 to 6, wherein the submicron particles comprise 1 to 40 wt% of the oil-in-water emulsion.

8. The oil-in-water emulsion according to any of claims 1 to 7, wherein the submicron particles are mixed with water and optionally with surfactants, thickeners, biocides, or antifoaming agents.

9. The oil-in-water emulsion according to any of claims 1 to 8 containing a hydrocarbon in the oil phase.

10. A process for the preparation of the oil-in-water emulsion according to any of claims 1 to 9 by mixing the water-insoluble pesticide in the oil phase and the submicron particles containing an organic light stabilizer in the aqueous phase.

11. A method for controlling undesired attack by insects or mites, where the oil-in-water emulsion according to any of claims 1 to 9 is allowed to act on the respective pests, their environment or on the crop plants to be protected from the respective pests.
## INTERNATIONAL SEARCH REPORT

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**Date of the actual completion of the international search**

5 June 2015

**Date of mailing of the international search report**

15/06/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Sawicki, Marcin
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