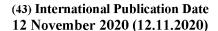
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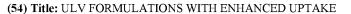
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(57) **Abstract:** The present invention relates to agrochemical compositions: their use for foliar application; their use at low spray volumes; their use by unmanned aerial systems (UAS), unmanned guided vehicles (UGV), and tractor mounted boom sprayers fitted with conventional nozzles but also pulse width modulation spray nozzles or rotating disc droplet applicators; and their application for controlling agricultural pests, 10 weeds or diseases, in particular on waxy leaves.

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## ULV formulations with enhanced uptake

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The present invention relates to agrochemical compositions: their use for foliar application; their use at low spray volumes; their use by unmanned aerial systems (UAS), unmanned guided vehicles (UGV), and tractor mounted boom sprayers fitted with conventional nozzles but also pulse width modulation spray nozzles or rotating disc droplet applicators; and their application for controlling agricultural pests, weeds or diseases, in particular on waxy leaves.

Modern agriculture faces many challenges in producing sufficient food in a safe and sustainable way.

There is therefore a need to utilise crop protection products to enhance the safety, quality and yield while minimising the impact to the environment and agricultural land. Many crop protection products, whether chemical or biological, are normally applied at relatively high spray volumes, for example in selected cases >50 L/ha, and often >150-400 L/ha. A consequence of this is that much energy must be expended to carry the high volume of spray liquid and then apply it to the crop by spray application.

This can be performed by large tractors which on account of their weight and also the weight of the spray liquid produce CO<sub>2</sub> from the mechanical work involved and also cause detrimental compaction of the soil, affecting root growth, health and yield of the plants, as well as the energy subsequently expended in remediating these effects.

There is a need for a solution that significantly reduces the high volumes of spray liquid and reduces the weight of the equipment required to apply the product.

In agriculture, low spray volume application technologies including unmanned aerial systems (UAS), unmanned guided vehicles (UGV), and tractor mounted boom sprayers fitted with pulse width modulation spray nozzles or rotating disc droplet applicators are offering farmers solutions to apply products with low spray volumes, typically down to 10 to 20 l/ha or less. These solutions have advantages including for example that they require significantly less water which is important in regions where the supply of water is limited, require less energy to transport and apply the spray liquid, are faster both from quicker filling of the spray tank and faster application, reduce the CO<sub>2</sub> generation from both the reduced volume of spray liquid to transport and from the use of smaller and lighter vehicles, reduced soil compaction damage, and enabling the use of cheaper application systems.

However, Wang et al [Field evaluation of an unmanned aerial vehicle (UAV) sprayer: effect of spray volume on deposition and the control of pests and disease in wheat. Pest Management Science 2019 doi/epdf/10.1002/ps.5321] demonstrated that as the spray volume is decreased from 450 and 225 l/ha to 28.1, 16.8 and 9.0 l/ha, the coverage (% area), number of spray deposits per area, and diameter of the spray deposits as measured on water sensitive paper all decreased (see Table 3 in Wang et al, 2019).
In parallel, the biological control efficacy for both wheat aphid control and powdery mildew control decreased at low spray volumes with the greatest decrease observed at 9.0 l/ha, followed by 16.8 l/ha (see Figures 6, 7 and 8 in Wang et al, 2019).

Separately Faers and Faers *et al* identified the importance of annulus structures in leaf spray deposits for the biodelivery of active ingredients in the presence of adjuvants, M.A. Faers [Annulus spray deposit structures and enhanced a.i. – adjuvant association with adjuvanted flowables. Proc 8th International Symposium of Adjuvants for Agrochemicals, ed. by RE Gaskin. International Society for Agrochemical Adjuvants, ISBN 978-0-473-12388-8, 2007], M.A. Faers, R. Pontzen [Factors influencing the association between active ingredient and adjuvant in the leaf deposit of adjuvanted suspo-emulsion formulations. Pest Manag. Sci. 64: 820–833, 2008], M.A. Faers, K. Tsangaris, R. Pontzen, A. Bismarck [Studies on leaf deposit microstructures through changes in colloidal and surface forces. P. Baur, M.

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Bonnet (Eds.), Proceedings 9th International Symposium on Adjuvants and Agrochemicals, pp. 309–318, ISBN 978-90-815702-1-3, International Society for Agrochemical Adjuvants, Wageningen, The Netherlands, (2010)]. Annulus spray deposit structures, also known as coffee ring structures, exhibited higher uptake of active ingredients and therefore formulation recipes and spray volumes that deliver annulus structures are preferred for improved biodelivery of active ingredients with adjuvants.

There is therefore a need to design formulation systems that overcome the reduction in the coverage and diameter of the spray deposits at low spray volumes also through high uptake.

Therefore, there is a need to provide formulations which, when sprayed at ultra-low spray volumes according to the present invention, that have a good uptake, thus, efficacy is maintained and losses of active ingredient are minimized.

The solution is provided by formulations containing specific uptake enhancers at high concentrations in the solution.

A particular advantage of the invention stemming from the low total amount of additives compared to the level required at normal higher spray volumes is lower cost of formulations and their ease of production. Further advantages include improved formulation stability and simplified manufacture, less cost of goods as well as less impact on the environment.

Formulations, also for tank mixes, known in the prior art containing additives for enhanced uptake are principally designed for much higher spray volumes and generally contain lower concentrations of additives in the spray broth. Nevertheless, due to the high spray volumes used in the prior art, the total amount of additives used and therefore in the environment is higher than according to the present invention.

Further, the concentration of the additives is an important element of the invention, since suitable properties can only be achieved with certain concentrations. However, if the spray volume now is reduced, also the amount of active ingredient is reduced. However, this leads to low volume formulations with such low concentration of additives that sufficient uptake cannot be achieved (see examples).

In this invention, we have surprisingly found that increasing the concentration of the additives indicated above as the spray volume decreases can compensate for the loss in performance (due to insufficient uptake) from the reduction in spray volume. It was surprisingly found that for every reduction of the spray volume by 50%, the concentration of surfactant should roughly be doubled.

Thus, although the absolute concentration of the additives is increased compared to formulations known in the art, the relative total amount per ha can be decreased, which is advantageous, both economically and ecologically, while uptake, rain-fastness and thus efficacy of the formulation according to the invention is improved, maintained or at least kept at an acceptable level when other benefits of the low volume applications are considered, e.g. less costs of formulation due to less cost of goods, smaller vehicles with less working costs, less compacting of soil etc.

In one aspect, the present invention is directed to the use of the compositions according to the invention for foliar application.

If not otherwise indicated, % in this application means percent by weight (%w/w).

It is understood that in case of combinations of various components, the percentages of all components of the formulations always sum up to 100.

Further, if not otherwise indicated, the reference "to volume" for water indicates that water is added to a total volume of a formulation of 1000 ml (11). For the sake of clarity it is understood that if unclear the density of the formulation is understood as to be 1 g/cm<sup>3</sup>.

In the context of the present invention aqueous based agrochemical compositions comprise at least 5% of water and include suspension concentrates, aqueous suspensions, suspo-emulsions or capsule suspensions, preferably suspension concentrates and aqueous suspensions.

Further, it is understood, that the preferred given ranges of the application volumes or application rates as well as of the respective ingredients as given in the instant specification can be freely combined and all combinations are disclosed herein, however, in a more preferred embodiment, the ingredients are preferably present in the ranges of the same degree of preference, and even more preferred the ingredients are present in the most preferred ranges.

In one aspect, the invention refers to a formulation comprising:

- a) One or more active ingredients,
- b) One or more uptake enhancer,
- 15 c) Other formulants,

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d) one or more carriers to volume (1L or 1 kg),

wherein b) is present in 5 to 250 g/l.

If not otherwise indicated in the present invention the carrier is usually used to volume the formulation. Preferably, the concentration of carrier in the formulation according to the invention is at least 5 % w/w, more preferred at least 10 % w/w such as at least 20% w/w, at least 40% w/w , at least 50% w/w, at least 50 % w/w and at least 80 % w/w or respectively at least 50 g/l, more preferred at least 100 g/l such as at least 200g/l, at least 400g/l , at least 500g/l, at least 700 g/l and at least 800 g/l .

The formulation is preferably a spray application to be used on crops.

In a preferred embodiment according to the present invention, also for the following embodiments in the specification, the carrier is water.

In a preferred embodiment the formulation of the instant invention comprises

- a) One or more active ingredients,
- b) One or more uptake enhancer,
- c1) At least one suitable non-ionic surfactant and/or suitable ionic surfactant.,
- 35 c2) Optionally, a rheological modifier,
  - c3) Optionally, a suitable antifoam substance,
  - c4) Optionally, suitable antifreeze agents,
  - c5) Optionally, suitable other formulants.
  - d) carrier to volume,
- wherein b) is present in 5 to 250 g/l, and wherein water is even more preferred as carrier.

In another embodiment at least one of c2, c3, c4 and c5 are mandatory, preferably, at least two of c2, c3, c4 and c5 are mandatory, and in yet another embodiment c2, c3, c4 and c5 are mandatory.

In a preferred embodiment component a) is preferably present in an amount from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l.

In an alternative embodiment component a) is a fungicide.

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In an alternative embodiment component a) is an insecticide.

In an alternative embodiment component a) is a herbicide.

In a preferred embodiment component b) is present in 5 to 250 g/l, preferably from 20 to 200 g/l, and most preferred from 30 to 150 g/l.

In a preferred embodiment component c) is present in 10 to 150 g/l, preferably from 25 to 150 g/l, and most preferred from 30 to 120 g/l.

In a preferred embodiment the one or more component c1) is present in 4 to 250 g/l, preferably from 8 to 120 g/l, and most preferred from 10 to 80 g/l.

In a preferred embodiment the one or more component c2) is present in 0 to 60 g/l, preferably from 1 to 20 g/l, and most preferred from 2 to 10 g/l.

In a preferred embodiment the one or more component c3) is present in 0 to 30 g/l, preferably from 0.5 to 20 g/l, and most preferred from 1 to 12 g/l.

In a preferred embodiment the one or more component c4) is present in 0 to 200 g/l, preferably from 5 to 150 g/l, and most preferred from 10 to 120 g/l.

In a preferred embodiment the one or more component c5) is present in 0 to 200 g/l, preferably from 0.1 to 120 g/l, and most preferred from 0.5 to 80 g/l.

- In one embodiment the formulation comprises the components a) to e) in the following amounts
  - a) from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l,
  - b) from 5 to 250 g/l, preferably from 20 to 200 g/l, and most preferred from 30 to 150 g/l,
  - c) from 4 to 250 g/l, preferably from 8 to 120 g/l, and most preferred from 10 to 80 g/l,
  - d) carrier to volume.

In another embodiment the formulation comprises the components a) to e) in the following amounts

- a) from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l,
- b) from 5 to 250 g/l, preferably from 20 to 200 g/l, and most preferred from 30 to 150 g/l,
- c1) from 4 to 250 g/l, preferably from 8 to 120 g/l, and most preferred from 10 to 80 g/l,
- c2) from 0 to 60 g/l, preferably from 1 to 20 g/l, and most preferred from 2 to 10 g/l,

- c3) from 0 to 30 g/l, preferably from 0.5 to 20 g/l, and most preferred from 1 to 12 g/l,
- c4) from 0 to 200 g/l, preferably from 5 to 150 g/l, and most preferred from 10 to 120 g/l,
- c5) from 0 to 200 g/l, preferably from 0.1 to 120 g/l, and most preferred from 0.5 to 80 g/l,
- d) carrier to volume.

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It is understood that in case a solid carrier is used, the above referenced amounts refer to 1 kg instead of to 1 l, i.e. g/kg.

As indicated above, component d) is always added to volume, i.e. to 11 or 1 kg.

In a further preferred embodiment of the present invention the formulation consists only of the above described ingredients a) to f) in the specified amounts and ranges.

In a preferred embodiment the herbicide is used in combination with a safener, which is preferably selected from the group comprising isoxadifen-ethyl and mefenpyr-diethyl.

The instant invention further applies to a method of application of the above referenced formulations, wherein the formulation is applied at a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha.

More preferred, the instant invention applies to a method of application of the above referenced formulations, wherein the formulation is applied at a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha, and the amount of b) is present in from 5 to 250 g/l, preferably from 20 to 200 g/l, and most preferred from 30 to 150 g/l, and most preferred from 10 to 130 g/, wherein in a further preferred embodiment a) is present f from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l.

In another aspect the instant invention applies to a method of application of the above referenced formulations,

wherein the formulation is applied at a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha, and

wherein preferably the applied amount of a) to the crop is between 2 and 150 g/ha, preferably between 5 and 120 g/ha, and more preferred between 20 and 100 g/ha.

Further, the spreading agent b) is preferably applied from 5 g/ha to 150 g/ha, more preferably from 7.5 g/ha to 100 g/ha, and most preferred from 10 g/ha to 60 g/ha.

In one embodiment, the with the above indicated method applied amount of a) to the crop is between 2 and 10 g/ha.

In another embodiment, the with the above indicated method applied amount of a) to the crop is between 40 and 110 g/ha.

In one embodiment in the applications described above, the active ingredient (ai) a) is preferably applied from 2 and 150 g/ha, preferably between 5 and 120 g/ha, and more preferred between 20 and

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100 g/ha, while correspondingly the spreading agent is preferably applied from 10 g/ha to 100 g/ha, more preferably from 20 g/ha to 80 g/ha, and most preferred from 40 g/ha to 60 g/ha.

In particular the formulations of the instant invention are useful for application with a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha on plants or crops with textured leaf surfaces, preferably on wheat, barley, rice, rapeseed, soybean (young plants) and cabbage.

Further, the instant invention refers to a method of treating crops with textured leaf surfaces, preferably wheat, barley, rice, rapeseed, soybean (young plants) and cabbage, with with a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha.

In a preferred embodiment the above described applications are applied on crops with textured leaf surfaces, preferably on wheat, barley, rice, rapeseed, soybean (young plants) and cabbage.

In one embodiment the active ingredient is a fungicide or a mixture of two fungicides or a mixture of three fungicides.

In another embodiment the active ingredient is an insecticide or a mixture of two insecticides or a mixture of three insecticides.

In yet another embodiment the active ingredient is a herbicide or a mixture of two herbicides or a mixture of three herbicides, wherein preferably in the mixtures on mixing partner is a safener.

In the context of the present invention, suitable formulation types are by definition suspension concentrates, aqueous suspensions, suspo-emulsions or capsule suspensions, emulsion concentrates, water dispersible granules, oil dispersions, emulsifiable concentrates, dispersible concentrates, wettable granules, preferably suspension concentrates, aqueous suspensions, suspo-emulsions and oil dispersions, wherein in the case of non-aqueous formulations or solid formulations the sprayable formulation are obtained by adding water.

## Active ingredients (a):

The active compounds identified here by their common names are known and are described, for example, in the pesticide handbook ("The Pesticide Manual" 16th Ed., British Crop Protection Council 2012) or can be found on the Internet (e.g. http://www.alanwood.net/pesticides). The classification is based on the current IRAC Mode of Action Classification Scheme at the time of filing of this patent application.

Examples of fungicides (a) according to the invention are:

1) Inhibitors of the ergosterol biosynthesis, for example (1.001) cyproconazole, (1.002) difenoconazole, (1.003) epoxiconazole, (1.004) fenhexamid, (1.005) fenpropidin, (1.006) fenpropimorph, (1.007) fenpyrazamine, (1.008) fluquinconazole, (1.009) flutriafol, (1.010) imazalil, (1.011) imazalil sulfate, (1.012) ipconazole, (1.013) metconazole, (1.014) myclobutanil, (1.015) paclobutrazol, (1.016) prochloraz, (1.017) propiconazole, (1.018) prothioconazole, (1.019) pyrisoxazole, (1.020) spiroxamine, (1.021) tebuconazole, (1.022) tetraconazole, (1.023) triadimenol, (1.024) tridemorph, (1.025) triticonazole, (1.026) (1R,2S,5S)-5-(4-chlorobenzyl)-2-(chloromethyl)-2-methyl-1-(1H-1,2,4-triazol-1-ylmethyl)cyclopentanol, (1.027) (1S,2R,5R)-5-(4-chlorobenzyl)-2-(chloromethyl)-2-methyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (1.029) (2R)-2-(1-chlorocyclopropyl)-4-[(1R)-2,2-dichlorocyclopropyl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (1.029) (2R)-2-(1-chlorocyclopropyl)-4-[(1S)-2,2-dichlorocyclopropyl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (1.030) (2R)-2-[4-(4-1)]

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chlorophenoxy)-2-(trifluoromethyl)phenyl]-1-(1H-1,2,4-triazol-1-yl)propan-2-ol, (1.031) (2S)-2-(1chlorocyclopropyl)-4-[(1R)-2,2-dichlorocyclopropyl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (2S)-2-(1-chloro-cyclopropyl)-4-[(1S)-2,2-dichlorocyclopropyl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (1.033) (2S)-2-[4-(4-chlorophenoxy)-2-(trifluoromethyl)phenyl]-1-(1H-1,2,4-triazol-1-yl)propan-2-ol, 5 (1.034)(R)-[3-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-1,2-oxazol-4-yl](pyridin-3-(1.035)(S)-[3-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-1,2-oxazol-4yl)methanol, yl](pyridin-3-yl)methanol, (1.036) [3-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-1,2-oxazol-4yl](pyridin-3-yl)methanol, (1.037) 1- $({(2R,4S)-2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-$ 1,3-dioxolan-2-yl}methyl)-1H-1,2,4-triazole, (1.038)1-({(2S,4S)-2-[2-chloro-4-(4-10 chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl}methyl)-1H-1,2,4-triazole, (1.039)chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2-yl]methyl}-1H-1,2,4-triazol-5-yl thiocyanate, (1.040) 1-{[rel(2R,3R)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2-yl]methyl}-1H-1,2,4-triazol-5-yl thiocyanate, (1.041) 1-{[rel(2R,3S)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2-yl]methyl}-1H-1,2,4-triazol-5-yl thiocyanate, (1.042) 2-[(2R,4R,5R)-1-(2,4-dichlorophenyl)-5-hydroxy-2,6,6trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, 15 (1.043)2-[(2R,4R,5S)-1-(2,4dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.044) 2-[(2R,4S,5R)-1-(2,4-dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.045)2-[(2R,4S,5S)-1-(2,4-dichloro-phenyl)-5-hydroxy-2,6,6trimethylheptan-4-vl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.046)2-[(2S,4R,5R)-1-(2,4dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, 20 (1.047) 2-[(2S,4R,5S)-1-(2,4-dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.048)2-[(2S,4S,5R)-1-(2,4-dichlorophenyl)-5-hydroxy-2,6,6trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.049)2-[(2S,4S,5S)-1-(2,4dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4-triazole-3-thione, 25 (1.050)2-[1-(2,4-dichlorophenyl)-5-hydroxy-2,6,6-trimethylheptan-4-yl]-2,4-dihydro-3H-1,2,4triazole-3-thione, 2-[2-chloro-4-(2,4-dichlorophenoxy)phenyl]-1-(1H-1,2,4-triazol-1vl)propan-2-ol, (1.052) 2-[2-chloro-4-(4-chlorophenoxy)phenvl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, 2-[4-(4-chlorophenoxy)-2-(trifluoromethyl)phenyl]-1-(1H-1,2,4-triazol-1-yl)butan-2-ol, (1.053)(1.054)2-[4-(4-chlorophenoxy)-2-(trifluoromethyl)phenyl]-1-(1H-1,2,4-triazol-1-yl)pentan-2-ol, 30 (1.055)mefentrifluconazole. (1.056)2-{[3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2yl]methyl}-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.057) 2-{[rel(2R,3R)-3-(2-chlorophenyl)-2-(2,4difluoro-phenyl)oxiran-2-yl]methyl}-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.058) 2-{[rel(2R,3S)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2-yl]methyl}-2,4-dihydro-3H-1,2,4-triazole-3-thione, (1.059) 5-(4-chlorobenzyl)-2-(chloromethyl)-2-methyl-1-(1H-1,2,4-triazol-1-ylmethyl)cyclopentanol, (1.060) 5-(allylsulfanyl)-1-{[3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2-yl]methyl}-1H-1,2,4-35 triazole, (1.061) 5-(allylsulfanyl)-1-{[rel(2R,3R)-3-(2-chlorophenyl)-2-(2,4-difluorophenyl)oxiran-2yl]methyl}-1H-1,2,4-triazole, (1.062)5-(allylsulfanyl)-1-{[rel(2R,3S)-3-(2-chlorophenyl)-2-(2,4difluorophenyl)oxiran-2-yl]methyl}-1H-1,2,4-triazole, (1.063)N'-(2,5-dimethyl-4-{[3-(1,1,2,2tetrafluoroethoxy)phenyl]sulfanyl}phenyl)-N-ethyl-N-methylimidoformamide, (1.064)dimethyl-4-{[3-(2,2,2-trifluoroethoxy)phenyl]sulfanyl}phenyl)-N-ethyl-N-methylimidoformamide, 40 N'-(2,5-dimethyl-4-{[3-(2,2,3,3-tetrafluoropropoxy)phenyl]sulfanyl}phenyl)-N-ethyl-Nmethylimidoformamide, (1.066) N'-(2,5-dimethyl-4-{[3-(pentafluoroethoxy)phenyl}sulfanyl}phenyl)-N-ethyl-N-methylimidoformamide, (1.067) N'-(2,5-dimethyl-4-{3-[(1,1,2,2-tetrafluoroethyl)sulfanyl]phenoxy}phenyl)-N-ethyl-N-methylimidoformamide, (1.068) N'-(2,5-dimethyl-4-{3-[(2,2,2-trifluoroethyl)sulfanyl]phenoxy}phenyl)-N-ethyl-N-methylimidoformamide, (1.069) N'-(2,5-dimethyl-4-{3-45 [(2,2,3,3-tetrafluoropropyl)sulfanyl]phenoxy}phenyl)-N-ethyl-N-methylimidoformamide, (1.070) N'-(2,5-dimethyl-4-{3-[(pentafluoroethyl)sulfanyl]phenoxy}phenyl)-N-ethyl-N-methylimidoformamide, (1.071) N'-(2,5-dimethyl-4-phenoxyphenyl)-N-ethyl-N-methylimidoformamide, (1.072) N'-(4-{[3-

(difluoromethoxy)phenyl]sulfanyl}-2,5-dimethylphenyl)-N-ethyl-N-methylimidoformamide, (1.073)

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N'-(4-{3-[(difluoromethyl)sulfanyl]phenoxy}-2,5-dimethylphenyl)-N-ethyl-N-methylimidoformamide, N'-[5-bromo-6-(2,3-dihydro-1H-inden-2-yloxy)-2-methylpyridin-3-yl]-N-ethyl-Nmethylimido-formamide, (1.075) N'-{4-[(4,5-dichloro-1,3-thiazol-2-yl)oxy]-2,5-dimethylphenyl}-Nethyl-N-methylimidoformamide, (1.076)N'-{5-bromo-6-[(1R)-1-(3,5-difluorophenyl)ethoxy]-2methylpyridin-3-yl}-N-ethyl-N-methylimidoformamide, (1.077)N'-{5-bromo-6-[(1S)-1-(3,5difluorophenyl)ethoxy]-2-methylpyridin-3-yl}-N-ethyl-N-methylimidoformamide, (1.078) N'-{5bromo-6-[(cis-4-isopropyl-cyclohexyl)oxy]-2-methylpyridin-3-yl}-N-ethyl-N-methylimidoformamide, N'-{5-bromo-6-[(trans-4-isopropylcyclohexyl)oxy]-2-methylpyridin-3-yl}-N-ethyl-Nmethylimidoformamide, (1.080) N'-{5-bromo-6-[1-(3,5-difluorophenyl)ethoxy]-2-methylpyridin-3yl}-N-ethyl-N-methylimido-formamide, (1.081) ipfentrifluconazole, (1.082) 2-[4-(4-chlorophenoxy)-2-(trifluoromethyl)phenyl]-1-(1H-1,2,4-triazol-1-yl)propan-2-ol, (1.083) 2-[6-(4-bromophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol, (1.084) 2-[6-(4-chlorophenoxy)-2-(trifluoromethyl)-3-pyridyl]-1-(1,2,4-triazol-1-yl)propan-2-ol, (1.085) 3-[2-(1-chlorocyclopropyl)-3-(3-chloro-2-fluoro-phenyl)-2-hydroxy-propyl]imidazole-4-carbonitrile, (1.086) 4-[[6-[rac-(2R)-2-(2,4difluorophenyl)-1,1-difluoro-2-hydroxy-3-(5-thioxo-4H-1,2,4-triazol-1-yl)propyl]-3pyridyl]oxy]benzonitrile, (1.087) N-isopropyl-N'-[5-methoxy-2-methyl-4-(2,2,2-trifluoro-1-hydroxy-(1.088)1-phenylethyl)phenyl]-N-methylimidoformamide, N'-{5-bromo-2-methyl-6-[(1propoxypropan-2-yl)oxy]pyridin-3-yl}-N-ethyl-N-methylimido-formamide, (1.089) hexaconazole, (1.090) penconazole, (1.091) fenbuconazole.

20 2) Inhibitors of the respiratory chain at complex I or II, for example (2.001) benzovindiflupyr, (2.002) bixafen, (2.003) boscalid, (2.004) carboxin, (2.005) fluopyram, (2.006) flutolanil, (2.007) fluxapyroxad, (2.008) furametpyr, (2.009) Isofetamid, (2.010) isopyrazam (anti-epimeric enantiomer 1R,4S,9S), (2.011) isopyrazam (anti-epimeric enantiomer 1S,4R,9R), (2.012) isopyrazam (anti-epimeric racemate 1RS,4SR,9SR), (2.013) isopyrazam (mixture of syn-epimeric racemate 1RS,4SR,9RS and anti-epimeric 25 racemate 1RS,4SR,9SR), (2.014) isopyrazam (syn-epimeric enantiomer 1R,4S,9R), (2.015) isopyrazam (syn-epimeric enantiomer 1S,4R,9S), (2.016) isopyrazam (syn-epimeric racemate 1RS,4SR,9RS), (2.017) penflufen, (2.018) penthiopyrad, (2.019) pydiflumetofen, (2.020) Pyraziflumid, (2.021) sedaxane, (2.022)1,3-dimethyl-N-(1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl)-1H-pyrazole-4carboxamide, (2.023) 1,3-dimethyl-N-[(3R)-1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl]-1H-pyrazole-30 4-carboxamide, (2.024)1,3-dimethyl-N-[(3S)-1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl]-1Hpyrazole-4-carboxamide, (2.025) 1-methyl-3-(trifluoromethyl)-N-[2'-(trifluoromethyl)biphenyl-2-yl]-1H-pyrazole-4-carboxamide, (2.026) 2-fluoro-6-(trifluoromethyl)-N-(1,1,3-trimethyl-2,3-dihydro-1Hinden-4-yl)benzamide, (2.027) 3-(difluoromethyl)-1-methyl-N-(1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl)-1H-pyrazole-4-carboxamide, (2.028) inpyrfluxam, (2.029) 3-(difluoromethyl)-1-methyl-N-[(3S)-1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl]-1H-pyrazole-4-carboxamide, (2.030) fluindapyr, (2.031) 35 3-(difluoromethyl)-N-[(3R)-7-fluoro-1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl]-1-methyl-1Hpyrazole-4-carboxamide, (2.032) 3-(difluoromethyl)-N-[(3S)-7-fluoro-1,1,3-trimethyl-2,3-dihydro-1H-inden-4-yl]-1-methyl-1H-pyrazole-4-carboxamide, (2.033) 5,8-difluoro-N-[2-(2-fluoro-4-{[4-(trifluoromethyl)-pyridin-2-ylloxy\phenyl)ethyllquinazolin-4-amine, (2.034) N-(2-cyclopentyl-5fluorobenzyl)-N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4-carboxamide, 40 N-(2-tert-butyl-5-methylbenzyl)-N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-1H-(2.035)pyrazole-4-carboxamide, (2.036) N-(2-tert-butylbenzyl)-N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-

methyl-1H-pyrazole-4-carboxamide, (2.037) N-(5-chloro-2-ethylbenzyl)-N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.038) isoflucypram, (2.039) N-[(1R,4S)-9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, (2.040) N-[(1S,4R)-9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, (2.041) N-[1-(2,4-dichlorophenyl)-1-methoxypropan-2-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, (2.042) N-[2-chloro-6-(trifluoromethyl)benzyl]-N-cyclopropyl-3-(difluoromethyl)-5-

fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.043)N-[3-chloro-2-fluoro-6-(trifluoromethyl)benzyl]-N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4carboxamide, (2.044) N-[5-chloro-2-(trifluoromethyl)benzyl]-N-cyclopropyl-3-(difluoromethyl)-5fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.045) N-cyclopropyl-3-(difluoromethyl)-5-fluoro-1methyl-N-[5-methyl-2-(trifluoromethyl)benzyl]-1H-pyrazole-4-carboxamide, (2.046) N-cyclopropyl-3-(difluoromethyl)-5-fluoro-N-(2-fluoro-6-isopropylbenzyl)-1-methyl-1H-pyrazole-4-carboxamide, N-cyclopropyl-3-(difluoromethyl)-5-fluoro-N-(2-isopropyl-5-methylbenzyl)-1-methyl-1Hpyrazole-4-carboxamide, (2.048) N-cyclopropyl-3-(difluoromethyl)-5-fluoro-N-(2-isopropylbenzyl)-1-methyl-1H-pyrazole-4-carbothioamide, (2.049) N-cyclopropyl-3-(difluoromethyl)-5-fluoro-N-(2isopropylbenzyl)-1-methyl-1H-pyrazole-4-carboxamide, (2.050) N-cyclopropyl-3-(difluoromethyl)-5fluoro-N-(5-fluoro-2-isopropylbenzyl)-1-methyl-1H-pyrazole-4-carboxamide, (2.051) N-cyclopropyl-3-(difluoromethyl)-N-(2-ethyl-4,5-dimethylbenzyl)-5-fluoro-1-methyl-1H-pyrazole-4-carboxamide, N-cyclopropyl-3-(difluoromethyl)-N-(2-ethyl-5-fluorobenzyl)-5-fluoro-1-methyl-1Hpyrazole-4-carboxamide, (2.053) N-cyclopropyl-3-(difluoromethyl)-N-(2-ethyl-5-methylbenzyl)-5fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.054)N-cyclopropyl-N-(2-cyclopropyl-5fluorobenzyl)-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.055)cyclopropyl-N-(2-cyclopropyl-5-methylbenzyl)-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4carboxamide, (2.056) N-cyclopropyl-N-(2-cyclopropylbenzyl)-3-(difluoromethyl)-5-fluoro-1-methyl-1H-pyrazole-4-carboxamide, (2.057)pyrapropovne, (2.058)N-[rac-(1S,2S)-2-(2,4dichlorophenyl)cyclobutyl]-2-(trifluoromethyl)-nicotinamide, (2.059)N-[(1S,2S)-2-(2,4dichlorophenyl)cyclobutyl]-2-(trifluoromethyl)nicotinamide.

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- 3) Inhibitors of the respiratory chain at complex III, for example (3.001) ametoctradin, (3.002) amisulbrom, (3.003) azoxystrobin, (3.004) coumethoxystrobin, (3.005) coumoxystrobin, (3.006) cyazofamid, (3.007) dimoxystrobin, (3.008) enoxastrobin, (3.009) famoxadone, (3.010) fenamidone, (3.011) flufenoxystrobin, (3.012) fluoxastrobin, (3.013) kresoxim-methyl, (3.014) metominostrobin, (3.015) orysastrobin, (3.016) picoxystrobin, (3.017) pyraclostrobin, (3.018) pyrametostrobin, (3.019) (2E)-2-{2-[({[(1E)-1-(3-{[(E)-1-fluoro-2pyraoxystrobin, (3.020)trifloxystrobin, (3.021)phenylvinyl]oxy}phenyl)ethylidene]amino}oxy)methyl]phenyl}-2-(methoxyimino)-Nmethylacetamide, (3.022) (2E,3Z)-5-{[1-(4-chlorophenyl)-1H-pyrazol-3-yl]oxy}-2-(methoxyimino)-N,3-dimethylpent-3-enamide, (3.023) (2R)-2-{2-[(2,5-dimethylphenoxy)methyl]phenyl}-2-methoxy-N-methylacetamide. (3.024)(2S)-2-{2-[(2,5-dimethylphenoxy)methyl]phenyl}-2-methoxy-Nmethylacetamide, (3.025)fenpicoxamid, (3.026) mandestrobin, (3.027) N-(3-ethyl-3,5,5trimethylcyclohexyl)-3-formamido-2-hydroxybenzamide, (3.028) $(2E,3Z)-5-\{[1-(4-chloro-2$ fluorophenyl)-1H-pyrazol-3-yl]oxy}-2-(methoxyimino)-N,3-dimethylpent-3-enamide, (3.029) methyl {5-[3-(2,4-dimethylphenyl)-1H-pyrazol-1-yl]-2-methylbenzyl}carbamate, (3.030) metyltetraprole, (3.031) florylpicoxamid.
- 4) Inhibitors of the mitosis and cell division, for example (4.001) carbendazim, (4.002) diethofencarb, (4.003) ethaboxam, (4.004) fluopicolide, (4.005) pencycuron, (4.006) thiabendazole, (4.007) thiophanate-methyl, (4.008) zoxamide, (4.009) pyridachlometyl, (4.010) 3-chloro-5-(4-chlorophenyl)-4-(2,6-difluorophenyl)-6-methylpyridazine, (4.011) 3-chloro-5-(6-chloropyridin-3-yl)-6-methyl-4-40 (2,4,6-trifluorophenyl)pyridazine, (4.012) 4-(2-bromo-4-fluorophenyl)-N-(2,6-difluorophenyl)-1,3dimethyl-1H-pyrazol-5-amine, (4.013) 4-(2-bromo-4-fluorophenyl)-N-(2-bromo-6-fluorophenyl)-1,3dimethyl-1H-pyrazol-5-amine, (4.014) 4-(2-bromo-4-fluorophenyl)-N-(2-bromophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.015) 4-(2-bromo-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1,3-dimethyl-45 1H-pyrazol-5-amine, (4.016)4-(2-bromo-4-fluorophenyl)-N-(2-chlorophenyl)-1,3-dimethyl-1Hpyrazol-5-amine, (4.017) 4-(2-bromo-4-fluorophenyl)-N-(2-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5amine, (4.018) 4-(2-chloro-4-fluorophenyl)-N-(2.6-difluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.019) 4-(2-chloro-4-fluorophenyl)-N-(2-chloro-6-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine,

- (4.020) 4-(2-chloro-4-fluorophenyl)-N-(2-chlorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.021) 4-(2-chloro-4-fluorophenyl)-N-(2-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.022) 4-(4-chlorophenyl)-5-(2,6-difluorophenyl)-3,6-dimethylpyridazine, (4.023) N-(2-bromo-6-fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.024) N-(2-bromophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.025) N-(4-chloro-2,6-difluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.026) fluorophenyl)-4-(2-chloro-4-fluorophenyl)-1,3-dimethyl-1H-pyrazol-5-amine, (4.026) fluorophenyl
- 5) Compounds capable to have a multisite action, for example (5.001) bordeaux mixture, (5.002) captafol, (5.003) captan, (5.004) chlorothalonil, (5.005) copper hydroxide, (5.006) copper naphthenate, (5.007) copper oxide, (5.008) copper oxychloride, (5.009) copper(2+) sulfate, (5.010) dithianon, (5.011) dodine, (5.012) folpet, (5.013) mancozeb, (5.014) maneb, (5.015) metiram, (5.016) metiram zinc, (5.017) oxine-copper, (5.018) propineb, (5.019) sulfur and sulfur preparations including calcium polysulfide, (5.020) thiram, (5.021) zineb, (5.022) ziram, (5.023) 6-ethyl-5,7-dioxo-6,7-dihydro-5H-pyrrolo[3',4':5,6][1,4]dithiino[2,3-c][1,2]thiazole-3-carbonitrile.
- 6) Compounds capable to induce a host defence, for example (6.001) acibenzolar-S-methyl, (6.002) isotianil, (6.003) probenazole, (6.004) tiadinil.
  - 7) Inhibitors of the amino acid and/or protein biosynthesis, for example (7.001) cyprodinil, (7.002) kasugamycin, (7.003) kasugamycin hydrochloride hydrate, (7.004) oxytetracycline, (7.005) pyrimethanil, (7.006) 3-(5-fluoro-3,3,4,4-tetramethyl-3,4-dihydroisoquinolin-1-yl)quinoline.
  - 8) Inhibitors of the ATP production, for example (8.001) silthiofam.

- 9) Inhibitors of the cell wall synthesis, for example (9.001) benthiavalicarb, (9.002) dimethomorph, (9.003) flumorph, (9.004) iprovalicarb, (9.005) mandipropamid, (9.006) pyrimorph, (9.007) valifenalate, (9.008) (2E)-3-(4-tert-butylphenyl)-3-(2-chloropyridin-4-yl)-1-(morpholin-4-yl)prop-2-en-1-one, (9.009) (2Z)-3-(4-tert-butylphenyl)-3-(2-chloropyridin-4-yl)-1-(morpholin-4-yl)prop-2-en-1-one.
- 25 10) Inhibitors of the lipid and membrane synthesis, for example (10.001) propamocarb, (10.002) propamocarb hydrochloride, (10.003) tolclofos-methyl.
  - 11) Inhibitors of the melanin biosynthesis, for example (11.001) tricyclazole, (11.002) tolprocarb.
  - 12) Inhibitors of the nucleic acid synthesis, for example (12.001) benalaxyl, (12.002) benalaxyl-M (kiralaxyl), (12.003) metalaxyl, (12.004) metalaxyl-M (mefenoxam).
- 30 13) Inhibitors of the signal transduction, for example (13.001) fludioxonil, (13.002) iprodione, (13.003) procymidone, (13.004) proquinazid, (13.005) quinoxyfen, (13.006) vinclozolin.
  - 14) Compounds capable to act as an uncoupler, for example (14.001) fluazinam, (14.002) meptyldinocap.
- 15) Further fungicides selected from the group consisting of (15.001) abscisic acid, (15.002) benthiazole, (15.003) bethoxazin, (15.004) capsimycin, (15.005) carvone, (15.006) chinomethionat, (15.007) cufraneb, (15.008) cyflufenamid, (15.009) cymoxanil, (15.010) cyprosulfamide, (15.011) flutianil, (15.012) fosetyl-aluminium, (15.013) fosetyl-calcium, (15.014) fosetyl-sodium, (15.015) methyl isothiocyanate, (15.016) metrafenone, (15.017) mildiomycin, (15.018) natamycin, (15.019) nickel dimethyldithiocarbamate, (15.020) nitrothal-isopropyl, (15.021) oxamocarb, (15.022) oxathiapiprolin, (15.023) oxyfenthiin, (15.024) pentachlorophenol and salts, (15.025) phosphorous acid and its salts, (15.026) propamocarb-fosetylate, (15.027) pyriofenone (chlazafenone), (15.028) tebufloquin, (15.029) tecloftalam, (15.030) tolnifanide, (15.031) 1-(4-{4-[(5R)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl}piperidin-1-yl)-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-

yl]ethanone, (15.032) 1-(4-{4-[(5S)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl]-1,3-thiazol-2-yl}piperidin-1-yl)-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone, benzylpyridin-2-yl)quinazoline, (15.034) dipymetitrone, (15.035) 2-[3,5-bis(difluoromethyl)-1Hpvrazol-1-yl]-1-[4-(4-{5-[2-(prop-2-vn-1-yloxy)phenyl]-4.5-dihydro-1,2-oxazol-3-yl}-1,3-thiazol-2-5 yl)piperidin-1-yl]ethanone, (15.036)2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[2chloro-6-(prop-2-yn-1-yloxy)phenyl]-4,5-dihydro-1,2-oxazol-3-yl}-1,3-thiazol-2-yl)piperidin-1yl]ethanone, (15.037) 2-[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]-1-[4-(4-{5-[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, (15.038) 2-[6-(3-fluoro-4-methoxyphenyl)-5-methylpyridin-2-yl]quinazoline, (15.039) 2-{(5R)-3-[2-(1-{[3,5-10 bis(difluoro-methyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl $\}$ -3-chlorophenyl methanesulfonate, (15.040) 2- $\{(5S)$ -3- $[2-(1-\{[3,5-bis(difluoromethyl)-1H-bis)]$ pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}-3-chlorophenyl methanesulfonate, (15.041) ipflufenoquin, (15.042) 2-{2-fluoro-6-[(8-fluoro-2-methylquinolin-3yl)oxy|phenyl}propan-2-ol, (15.043) fluoxapiprolin, (15.044) 2-{3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-4,5-dihydro-1,2-oxazol-5-yl}phenyl 15 methanesulfonate, (15.045) 2-phenylphenol and salts, (15.046) 3-(4,4,5-trifluoro-3,3-dimethyl-3,4dihydroisoquinolin-1-yl)quinoline, (15.047) quinofumelin, (15.048) 4-amino-5-fluoropyrimidin-2-ol (15.049)(tautomeric 4-amino-5-fluoropyrimidin-2(1H)-one), phenylethyl)aminolbutanoic acid, (15.050) 5-amino-1,3,4-thiadiazole-2-thiol, (15.051) 5-chloro-N'phenyl-N'-(prop-2-yn-1-yl)thiophene-2-sulfonohydrazide, (15.052) 5-fluoro-2-[(4-fluorobenzyl)oxy]-20 pyrimidin-4-amine, (15.053) 5-fluoro-2-[(4-methylbenzyl)oxy]pyrimidin-4-amine, (15.054) 9-fluoro-2,2-dimethyl-5-(quinolin-3-yl)-2,3-dihydro-1,4-benzoxazepine, (15.055) but-3-yn-1-yl {6-[({[(Z)-(1-2)methyl-1H-tetrazol-5-yl)(phenyl)methylene]amino}oxy)methyl]pyridin-2-yl}carbamate, ethyl (2Z)-3-amino-2-cyano-3-phenylacrylate, (15.057) phenazine-1-carboxylic acid, (15.058) propyl 3,4,5-trihydroxybenzoate, (15.059) quinolin-8-ol, (15.060) quinolin-8-ol sulfate (2:1), (15.061) tert-25 {6-[({[(1-methyl-1H-tetrazol-5-yl)(phenyl)methylene|amino}oxy)methyl]pvridin-2vl}carbamate, (15.062)5-fluoro-4-imino-3-methyl-1-[(4-methylphenyl)sulfonyl]-3,4dihydropyrimidin-2(1H)-one, (15.063) aminopyrifen, (15.064) (N'-[2-chloro-4-(2-fluorophenoxy)-5methylphenyl]-N-ethyl-N-methylimido-formamide), (15.065)(N'-(2-chloro-5-methyl-4-30 phenoxyphenyl)-N-ethyl-N-methylimidoformamide), (15.066) (2-{2-[(7,8-difluoro-2-methylquinolin-3-yl)oxyl-6-fluorophenyl}propan-2-ol), (15.067)(5-bromo-1-(5,6-dimethylpyridin-3-yl)-3,3-(15.068)dimethyl-3,4-dihydroisoquinoline), (3-(4,4-difluoro-5,5-dimethyl-4,5-dihydrothieno[2,3c]pyridin-7-yl)quinoline), (15.069)(1-(4,5-dimethyl-1H-benzimidazol-1-yl)-4,4-difluoro-3,3dimethyl-3,4-dihydroisoguinoline), (15.070)8-fluoro-3-(5-fluoro-3,3-dimethyl-3,4-35 dihydroisoquinolin-1-yl)quinolone, (15.071)8-fluoro-3-(5-fluoro-3,3,4,4-tetramethyl-3,4dihydroisoquinolin-1-yl)quinolone, (15.072) 3-(4,4-difluoro-3,3-dimethyl-3,4-dihydroisoquinolin-1yl)-8-fluoroquinoline, (15.073)(N-methyl-N-phenyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3vllbenzamide), (15.074) methyl {4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl}carbamate, (15.075) (N-{4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzyl}cyclopropanecarboxamide), (15.076) N-methyl-4-(5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.077) N-[(E)-methoxyimino-40 methyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.078)N-[(Z)methoxyiminomethyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.079)N-[4-[5-(15.080)(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]cyclopropanecarboxamide, N-(2fluorophenyl)-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.081)2,2-difluoro-Nmethyl-2-[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]acetamide, (15.082) N-allyl-N-[[4-[5-45 (trifluoromethyl)-1,2,4-oxadiazol-3-yl)phenyl]methyl]acetamide, (15.083)N-[(E)-N-methoxy-Cmethyl-carbonimidoyl]-4-(5-(trifluoro-methyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.084) N-[(Z)-Nmethoxy-C-methyl-carbonimidoyl]-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.085)

N-allyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide, (15.086) 4,4-

dimethyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]pyrrolidin-2-one, (15.087) Nmethyl-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzenecarbothioamide, (15.088) 5-methyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]pyrrolidin-2-one, (15.089) N-((2,3-difluoro-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-vl]phenyl]methyl]-3,3,3-trifluoro-propanamide, (15.090) 1-5 methoxy-1-methyl-3-[[4-[5-(trifluoro-methyl]-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, (15.091) 1,1diethyl-3-[[4-[5-(trifluoromethyl]-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, (15.092)(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phen-yl]methyl]propanamide, (15.093) N-methoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]-methyl]cyclopropanecarboxamide, (15.094)methoxy-3-methyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]urea, (15.095) N-10 methoxy-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl)cyclopropanecarboxamide, (15.096) N,2-dimethoxy-N-[[4-[5-(trifluoromethyl]-1,2,4-oxadiazol-3-yl]phenyl]methyl]propanamide, (15.097)N-ethyl-2-methyl-N-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-1-methoxy-3-methyl-1-[[4-[5-(trifluoro-methyl)-1,2,4yl)phenyl]methyl]propanamide, (15.098)oxadiazol-3-yl]phenyl]methyl]urea, (15.099)1,3-dimethoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-(15.100) 3-ethyl-1-methoxy-1-[[4-[5-(trifluoromethyl)-1,2,4-15 oxadiazol-3-yl]phenyl]methyl]urea, oxadiazol-3-yl]phenyl]methyl]urea, (15.101) 1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]piperidin-2-one, (15.102)4,4-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3yl]phenyl]-methyl]isooxazolidin-3-one, (15.103)5,5-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one, (15.104) 3,3-dimethyl-1-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]piperidin-2-one, (15.105) 1-[[3-fluoro-4-(5-(trifluoromethyl)-20 1,2,4-oxadiazol-3-yl]-phenyl]methyl]azepan-2-one, (15.106) 4,4-dimethyl-2-[[4-(5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]-phenyl]methyl]isoxazolidin-3-one, (15.107)5,5-dimethyl-2-[[4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl]methyl]isoxazolidin-3-one, (15.108) ethyl 1-{4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzyl}-1H-pyrazole-4-carboxylate, (15.109) N,N-dimethyl-1-25 {4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzyl}-1H-1,2,4-triazol-3-amine, (15.110) $N-\{2,3$ difluoro-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzyl}butanamide, (15.111)N-(1methylcyclopropyl)-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.112)N-(2,4difluorophenyl)-4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]benzamide, (15.113)1-(5,6dimethylpyridin-3-yl)-4,4-difluoro-3,3-dimethyl-3,4-dihydroisoquinoline, (15.114)1-(6-30 (difluoromethyl)-5-methyl-pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-3,4-dihydro-isoquinoline, (15.115) 1-(5-(fluoromethyl)-6-methyl-pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-3,4-dihydroisoquinoline, (15.116)1-(6-(difluoromethyl)-5-methoxy-pyridin-3-yl)-4,4-difluoro-3,3-dimethyl-3,4dihydroisoquinoline, (15.117) 4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl dimethyl-carbamate, (15.118) N-{4-[5-(trifluoromethyl)-1,2,4-oxadiazol-3-yl]phenyl}propanamide, (15.119) 3-[2-(1-{[5methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-1,5-dihydro-2,4-35 benzodioxepin-6-yl methanesulfonate, (15.120) 9-fluoro-3-[2-(1-{[5-methyl-3-(trifluoromethyl)-1Hpyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-1,5-dihydro-2,4-benzodioxepin-6-yl methanesulfonate, (15.121) 3-[2-(1-{[3,5-bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-1,5-dihydro-2,4-benzodioxepin-6-yl methanesulfonate, (15.122) 3-[2-(1-{[3,5bis(difluoromethyl)-1H-pyrazol-1-yl]acetyl}piperidin-4-yl)-1,3-thiazol-4-yl]-9-fluoro-1,5-dihydro-40 2,4-benzodioxepin-6-yl methanesulfonate, (15.123) 1-(6,7-dimethylpyrazolo[1,5-a]pyridin-3-yl)-4,4difluoro-3,3-dimethyl-3,4-dihydroisoguinoline, (15.124)8-fluoro-N-(4,4,4-trifluoro-2-methyl-1phenylbutan-2-yl)quinoline-3-carboxamide, (15.125) 8-fluoro-N-[(2S)-4,4,4-trifluoro-2-methyl-1phenylbutan-2-yl]quinoline-3-carboxamide, (15.126)N-(2,4-dimethyl-1-phenylpentan-2-yl)-8-45 fluoroquinoline-3-carboxamide and (15.127)N-[(2S)-2,4-dimethyl-1-phenylpentan-2-yl]-8fluoroquinoline-3-carboxamide.

Examples of insecticides (a) according to the invention are:

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(1) Acetylcholinesterase(AChE)-inhibitors, e.g. Carbamates Alanycarb, Aldicarb, Bendiocarb, Benfuracarb, Butocarboxim, Butoxycarboxim, Carbaryl, Carbofuran, Carbosulfan, Ethiofencarb, Fenobucarb, Formetanate, Furathiocarb, Isoprocarb, Methiocarb, Methomyl, Metolcarb, Oxamyl, Pirimicarb, Propoxur, Thiodicarb, Thiofanox, Triazamate, Trimethacarb, XMC and an Xylylcarb, or organophosphates, e.g. Acephat, Azamethiphos, Azinphos-ethyl, Azinphos-methyl, Cadusafos, Chlorethoxyfos, Chlorfenvinphos, Chlormephos, Chlorpyrifos-methyl, Coumaphos, Cyanophos, Demeton-S-methyl, Diazinon, Dichlorvos/DDVP, Dicrotophos, Dimethoat, Dimethylvinphos, Disulfoton, EPN, Ethion, Ethoprophos, Famphur, Fenamiphos, Fenitrothion, Fenthion, Fosthiazat, Isopropyl-O-(methoxyaminothio-phosphoryl)salicylat, Heptenophos, Imicvafos, Isofenphos. Isoxathion, Malathion, Mecarbam, Methamidophos, Methidathion, Mevinphos, Monocrotophos, Naled, Omethoate, Oxydemeton-methyl, Parathion-methyl, Phenthoat, Phorat, Phosalon, Phosmet, Phosphamidon, Phoxim, Pirimiphos-methyl, Profenofos, Propetamphos, Prothiofos, Pyraclofos, Pyridaphenthion, Quinalphos, Sulfotep, Tebupirimfos, Temephos, Terbufos, Tetrachlorvinphos, Thiometon, Triazophos, Triclorfon and and Vamidothion.

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- 15 (2) GABA-gated chloride channel antagonists, preferably Cyclodien-organochlorine selected from the group of Chlordan and Endosulfan, or Phenylpyrazole (Fiprole) selected from Ethiprol and Fipronil.
  - (3) Sodium channel modulators / voltage-dependent sodium channel blockers, for example pyrethroids, e.g. Acrinathrin, Allethrin, d-cis-trans Allethrin, d-trans Allethrin, Bifenthrin, Bioallethrin, Bioallethrin S-cyclopentenyl isomer, Bioresmethrin, Cycloprothrin, Cyfluthrin, beta-Cyfluthrin, Cyhalothrin, lambda-Cyhalothrin, gamma-Cyhalothrin, Cypermethrin, alpha-Cypermethrin, beta-Cypermethrin, theta-Cypermethrin, zeta-Cypermethrin, Cyphenothrin [(1R)-trans isomers], Deltamethrin, Empenthrin [(EZ)-(1R) isomers), Esfenvalerate, Etofenprox, Fenpropathrin, Fenvalerate, Flucythrinate, Flumethrin, tau-Fluvalinate, Halfenprox, Imiprothrin, Kadethrin, Momfluorothrin, Permethrin, Phenothrin [(1R)-trans isomer), Prallethrin, Pyrethrine (pyrethrum), Resmethrin, Silafluofen, Tefluthrin, Tetramethrin, Tetramethrin [(1R) isomers)], Tralomethrin and Transfluthrin or DDT or Methoxychlor.
    - (4) Nicotinic acetylcholine receptor (nAChR) competitive activators, preferably Neonicotinoids selected from Acetamiprid, Clothianidin, Dinotefuran, Imidaeloprid, Nitenpyram, Thiaeloprid and Thiamethoxam, or Nicotin, or Sulfoximine selected from Sulfoxaflor, or Butenolide selected from Flupyradifurone, or Mesoionics selected from Triflumezopyrim.
- 30 (5) Nicotinic acetylcholine receptor (nAChR) allosteric activators, preferably Spinosynes selected from Spinetoram and Spinosad.
  - (6) Allosteric modulators of the glutamate-dependent chloride channel (GluCl), preferablyAvermectine/Milbemycine selected from Abamectin, Emamectin-benzoate, Lepimectin and Milbemectin.
- 35 (7) Juvenile hormone mimetics, preferably Juvenile hormon-analogs selected from Hydropren, Kinopren and Methopren, or Fenoxycarb or Pyriproxyfen.
  - (8) Various non-specific (multi-site) inhibitors, preferably Alkylhalogenides selected from Methylbromide and other Alkylhalogenides, or Chloropicrin or Sulfurylfluorid or Borax or Tartar emetic or Methylisocyanate generators selected from Diazomet and Metam.
- 40 (9) TRPV channel modulators of chordotonal organs selected from Pymetrozin and Pyrifluquinazon.
  - (10) Mite growth inhibitors selected from Clofentezin, Hexythiazox, Diflovidazin and Etoxazol.
  - (11) Microbial disruptors of the insect intestinal membrane selected from Bacillus thuringiensis Subspezies israelensis, Bacillus sphaericus, Bacillus thuringiensis Subspezies aizawai, Bacillus thuringiensis Subspezies kurstaki, Bacillus thuringiensis subspecies tenebrionis and B.t.-plant proteins

- selected from Cry1Ab, Cry1Ac, Cry1Fa, Cry1A.105, Cry2Ab, VIP3A, mCry3A, Cry3Ab, Cry3Bb and Cry34Ab1/35Ab1.
- (12) Mitochondrial ATP synthase inhibitors, preferably ATP-disruptors selected from Diafenthiuron, or Organo-tin-compounds selected from Azocyclotin, Cyhexatin and Fenbutatin-oxid, or Propargit or Tetradifon.
- (13) Decoupler of oxidative phosphorylation by disturbance of the proton gradient selected from Chlorfenapyr, DNOC and Sulfluramid.
- (14) Nicotinic acetylcholine receptor channel blocker selected from Bensultap, Cartap-hydrochlorid, Thiocyclam and Thiosultap-Sodium.
- 10 (15) Inhibitors of chitin biosynthesis, Typ 0, selected from Bistrifluron, Chlorfluazuron, Diflubenzuron, Flucycloxuron, Flufenoxuron, Hexaflumuron, Lufenuron, Novaluron, Noviflumuron, Teflubenzuron and Triflumuron.
  - (16) Inhibitors of chitin biosynthesis, Typ 1 selected from Buprofezin.
  - (17) Molting disruptor (especially dipteras, i.e. two-winged insects) selected from Cyromazin.
- 15 (18) Ecdyson receptor agonists selected from Chromafenozid, Halofenozid, Methoxyfenozid and Tebufenozid.
  - (19) Octopamin-receptor-agonists selected from Amitraz.

- (20) Mitochondrial complex III electron transport inhibitors selected from Hydramethylnon, Acequinocyl and Fluacrypyrim.
- 20 (21) Mitochondrial complex I electron transport inhibitors, preferably so-called METI-acaricides selected from Fenazaquin, Fenpyroximat, Pyrimidifen, Pyridaben, Tebufenpyrad and Tolfenpyrad, or Rotenon (Derris).
  - (22) Blocker of the voltage-dependent sodium channel selected from Indoxacarb and Metaflumizone.
- (23) Inhibitors of acetyl-CoA carboxylase, preferably tetronic and tetramic acid derivatives selected from Spirodiclofen, Spiromesifen, Spirotetramat and Spidoxamate (IUPAC Name: 11-(4-chloro-2,6-xylyl)-12-hydroxy-1,4-dioxa-9-azadispiro[4.2.4.2]tetradec-11-en-10-one).
  - (24) Mitochondrial complex IV electron transport inhibitors, preferably Phosphines selected from Aluminiumphosphid, Calciumphosphid, Phosphin and Zinkphosphid, or Cyanides selected from Calciumcyanid, Potassiumcyanid and Sodiumcyanid.
- 30 (25) Mitochondrial complex II electron transport inhibitors, preferablybeta-Ketonitrilderivate selected from Cyenopyrafen and Cyflumetofen, or Carboxanilide selected from Pyflubumid.
  - (28) Ryanodinreceptor-modulators, preferably Diamide selected from Chlorantraniliprol, Cyantraniliprol and Flubendiamid.
  - (29) Modulators of chordotonal organs (with undefined target structure) selected from Flonicamid.
- 35 (30) other active ingredients selected from Acynonapyr, Afidopyropen, Afoxolaner, Azadirachtin, Benclothiaz, Benzoximat, Benzpyrimoxan, Bifenazat, Broflanilid, Bromopropylat, Chinomethionat, Chloroprallethrin, Cryolit, Cyclaniliprol, Cycloxaprid, Cyhalodiamid, Dicloromezotiaz, Dicofol, Dimpropyridaz, epsilon-Metofluthrin, epsilon-Momfluthrin, Flometoquin, Fluazaindolizin, Fluensulfon, Flufenerim, Flufenoxystrobin, Flufiprol, Fluhexafon, Fluopyram, Flupyrimin, Fluralaner,

Fluxametamid, Fufenozid, Guadipyr, Heptafluthrin, Imidaclothiz, Iprodione, Isocycloseram, kappa-Bifenthrin, kappa-Tefluthrin, Lotilaner, Meperfluthrin, Oxazosulfyl, Paichongding, Pyridalyl, Pyrifluquinazon, Pyriminostrobin, Spirobudiclofen, Spiropidion, Tetramethylfluthrin, Tetraniliprol, Tetrachlorantraniliprol, Tigolaner, Tioxazafen, Thiofluoximat and Iodmethan; products from Bacillus 5 firmus (I-1582, BioNeem, Votivo), as well as following compounds: 1-{2-Fluor-4-methyl-5-[(2,2,2trifluorethyl)sulfinyl|phenyl}-3-(trifluormethyl)-1H-1,2,4-triazol-5-amin (known from WO2006/043635) (CAS 885026-50-6), {1'-[(2E)-3-(4-Chlorphenyl)prop-2-en-1-yl]-5fluorspiro[indol-3,4'-piperidin]-1(2H)-yl}(2-chlorpyridin-4-yl)methanon (known from 637360-23-7), 2-Chlor-N-[2-{1-[(2E)-3-(4-chlorphenyl)prop-2-en-1-WO2003/106457) (CAS yl|piperidin-4-yl}-4-(trifluormethyl)phenyl|isonicotinamid (known from WO2006/003494) (CAS 10 872999-66-1), 3-(4-Chlor-2,6-dimethylphenyl)-4-hydroxy-8-methoxy-1,8-diazaspiro[4.5]dec-3-en-2on (known from WO 2010052161) (CAS 1225292-17-0), 3-(4-Chlor-2, 6-dimethylphenyl)-8-methoxy-2-oxo-1,8-diazaspiro[4.5]dec-3-en-4-yl-ethylcarbonat EP (known from (CAS-1440516-42-6), 4-(But-2-in-1-yloxy)-6-(3,5-dimethylpiperidin-1-yl)-5-fluorpyrimidin (known from WO2004/099160) (CAS 792914-58-0), PF1364 (known from JP2010/018586) (CAS-Reg.No. 15 1204776-60-2), (3E)-3-[1-[(6-Chlor-3-pyridyl)methyl]-2-pyridyliden]-1,1,1-trifluorpropan-2-on (known from WO2013/144213) (CAS 1461743-15-6), N-[3-(Benzylcarbamoyl)-4-chlorphenyl]-1methyl-3-(pentafluorethyl)-4-(trifluormethyl)-1H-pyrazol-5-carboxamid WO2010/051926) (CAS 1226889-14-0), 5-Brom-4-chlor-N-[4-chlor-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chlor-2-pyridyl)pyrazol-3-carboxamid (known from CN103232431) 20 1449220-44-3), 4-[5-(3,5-Dichlorphenyl)-4,5-dihydro-5-(trifluormethyl)-3-isoxazolyl]-2-(CAS methyl-N-(cis-1-oxido-3-thietanyl)benzamid, 4-[5-(3,5-Dichlorphenyl)-4,5-dihydro-5-(trifluormethyl)-3-isoxazolyl]-2-methyl-N-(trans-1-oxido-3-thietanyl)benzamid and 4-[(5S)-5-(3,5-Dichlorphenyl)-4,5-dihydro-5-(trifluormethyl)-3-isoxazolyl]-2-methyl-N-(cis-1-oxido-3-

thietanyl)benzamid (known from WO 2013/050317 A1) (CAS 1332628-83-7), N-[3-Chlor-1-(3-pyridinyl)-1H-pyrazol-4-yl]-N-ethyl-3-[(3,3,3-trifluorpropyl)sulfinyl]propanamid, (+)-N-[3-Chlor-1-(3-pyridinyl)-1H-pyrazol-4-yl]-N-ethyl-3-[(3,3,3-trifluorpropyl)sulfinyl]propanamid and (-)-N-[3-Chlor-1-(3-pyridinyl)-1H-pyrazol-4-yl]-N-ethyl-3-[(3,3,3-trifluorpropyl)sulfinyl]propanamid (known from WO 2013/162715 A2, WO 2013/162716 A2, US 2014/0213448 A1) (CAS 1477923-37-7), 5-[(2E)-3-Chlor-2-propen-1-yl]amino]-1-[2,6-dichlor-4-(trifluormethyl)phenyl]-4-

[(trifluormethyl)sulfinyl]-1H-pyrazol-3-carbonitrile (known from CN 101337937 A) (CAS 1105672-77-2), 3-Brom-N-[4-chlor-2-methyl-6-[(methylamino)thioxomethyl]phenyl]-1-(3-chlor-2-pyridinyl)-1H-pyrazol-5-carboxamid, (Liudaibenjiaxuanan, known from CN 103109816 A) (CAS 1232543-85-9); N-[4-Chlor-2-[[(1,1-dimethylethyl)amino]carbonyl]-6-methylphenyl]-1-(3-chlor-2-pyridinyl)-3-

(fluormethoxy)-1H-pyrazol-5-carboxamid (known from WO 2012/034403 A1) (CAS 1268277-22-0), N-[2-(5-Amino-1,3,4-thiadiazol-2-yl)-4-chlor-6-methylphenyl]-3-brom-1-(3-chlor-2-pyridinyl)-1H-pyrazol-5-carboxamid (known from WO 2011/085575 A1) (CAS 1233882-22-8), 4-[3-[2,6-Dichlor-4-[(3,3-dichlor-2-propen-1-yl)oxy]phenoxy]propoxy]-2-methoxy-6-(trifluormethyl)pyrimidin (known from CN 101337940 A) (CAS 1108184-52-6); (2E)- and 2(Z)-2-[2-(4-Cyanophenyl)-1-[3-

40 (trifluormethyl)phenyl]ethyliden]-N-[4-(difluormethoxy)phenyl]hydrazincarboxamid (known from CN 101715774 A) (CAS 1232543-85-9); Cyclopropancarbonsäure-3-(2,2-dichlorethenyl)-2,2-dimethyl-4-(1H-benzimidazol-2-yl)phenylester (known from CN 103524422 A) (CAS 1542271-46-4); (4aS)-7-Chlor-2,5-dihydro-2-[[(methoxycarbonyl)[4-

[(trifluormethyl)thio]phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazin-4a(3H)-

carbonsäuremethylester (known from CN 102391261 A) (CAS 1370358-69-2); 6-Desoxy-3-O-ethyl-2,4-di-O-methyl-1-[N-[4-[1-[4-(1,1,2,2,2-pentafluorethoxy)phenyl]-1H-1,2,4-triazol-3-yl]phenyl]carbamat]-α-L-mannopyranose (known from US 2014/0275503 A1) (CAS 1181213-14-8); 8-(2-Cyclopropylmethoxy-4-trifluormethylphenoxy)-3-(6-trifluormethylpyridazin-3-yl)-3-azabicyclo[3.2.1]octan (CAS 1253850-56-4), (8-anti)-8-(2-Cyclopropylmethoxy-4-trifluormethylphenoxy-4-trifluor

trifluormethylphenoxy)-3-(6-trifluormethylpyridazin-3-yl)-3-azabicyclo[3.2.1]octan (CAS 933798-27-7), (8-syn)-8-(2-Cyclopropylmethoxy-4-trifluormethylphenoxy)-3-(6-trifluormethylpyridazin-3-yl)-3-azabicyclo[3.2.1]octan (CAS 933798-27-7), (8-syn)-8-(2-Cyclopropylmethoxy-4-trifluormethylphenoxy)-3-(6-trifluormethylphenoxy-4-trifluorme

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azabicyclo[3.2.1]octan (known from WO 2007040280 A1, WO 2007040282 A1) (CAS 934001-66-8), N-[3-Chlor-1-(3-pyridinyl)-1H-pyrazol-4-yl]-N-ethyl-3-[(3,3,3-trifluorpropyl)thio]-propanamid (known from WO 2015/058021 A1, WO 2015/058028 A1) (CAS 1477919-27-9) and N-[4-

- (known from WO 2015/058021 A1, WO 2015/058028 A1) (CAS 1477919-27-9) and N-[4-(Aminothioxomethyl)-2-methyl-6-[(methylamino)carbonyl]phenyl]-3-bromo-1-(3-chloro-2-pyridinyl) 1H-pyrazol-5-carboxamid (known from CN 103265527 A) (CAS 1452877-50-7), 5-(1,3-Dioxan-2-yl)-4-[[4-(trifluormethyl)phenyl]methoxy]-pyrimidin (known from WO 2013/115391 A1) (CAS 1449021-97-9), 3-(4-Chlor-2,6-dimethylphenyl)-8-methoxy-1-methyl-1,8-diazaspiro[4.5]decane-2,4-dion (known from WO 2014/187846 A1) (CAS 1638765-58-8), 3-(4-Chlor-2,6-dimethylphenyl)-8-methoxy-1-methyl-2-oxo-1,8-diazaspiro[4.5]dec-3-en-4-yl-carbonsäureethylester (known from WO 2010/066780 A1, WO 2011151146 A1) (CAS 1229023-00-0), 4-[(5S)-5-(3,5-Dichlor-4-fluorophenyl)-4,5-dihydro-5-(trifluoromethyl)-3-isoxazolyl]-N-[(4R)-2-ethyl-3-oxo-4-isoxazolidinyl]-2-methyl-benzamid (known from WO 2011/067272, WO2013/050302) (CAS 1309959-62-3).
- Examples of herbicides a) according to the invention are:

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Acetochlor, acifluorfen, acifluorfen-sodium, aclonifen, alachlor, allidochlor, alloxydim, alloxydim sodium, ametryn, amicarbazone, amidochlor, amidosulfuron, 4-amino-3-chloro-5-fluoro-6-(7-fluoro-1H-indol-6-yl)pyridine-2-carboxylic acid, aminocyclopyrachlor, aminocyclopyrachlor-potassium, aminocyclopyrachlor-methyl, aminopyralid, amitrole, ammoniumsulfamate, anilofos, asulam, atrazine, azafenidin, azimsulfuron, beflubutamid, benazolin, benazolin-ethyl, benfluralin, benfuresate, bensulfuron, bensulfuron-methyl, bensulide, bentazone, benzobicyclon, benzofenap, bicyclopyron, bifenox, bilanafos, bilanafos-sodium, bispyribac, bispyribac-sodium, bixlozone, bromacil, bromobutide, bromofenoxim, bromoxynil, bromoxynil-butyrate, -potassium, -heptanoate, and -octanoate, busoxinone, butachlor, butafenacil, butamifos, butenachlor, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone, carfentrazone-ethyl, chloramben, chlorbromuron, 1-{2-chloro-3-[(3-cyclopropyl-5hydroxy-1-methyl-1H-pyrazol-4-yl)carbonyl]-6-(trifluormethyl)phenyl}piperidin-2-on, 4-{2-chloro-3-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-4-(methylsulfonyl)benzoyl}-1,3-dimethyl-1H-pyrazol-5-yl-1,3-dimethyl-1H-pyrazol-4-carboxylat, chlorfenac, chlorfenac-sodium, chlorfenprop, chlorflurenol, chlorflurenol-methyl, chloridazon, chlorimuron, chlorimuron-ethyl, 2-[2-chloro-4-(methylsulfonyl)-3-(morpholin-4-ylmethyl)benzoyl]-3-hydroxycyclohex-2-en-1-on, 4-{2-chloro-4-(methylsulfonyl)-3-[(2,2,2-

trifluorethoxy)methyl]benzoyl}-1-ethyl-1H-pyrazol-5-yl-1,3-dimethyl-1H-pyrazol-4-carboxylat, chlorophthalim, chlorotoluron, chlorthal-dimethyl, 3-[5-chloro-4-(trifluormethyl)pyridine-2-yl]-4hydroxy-1-methylimidazolidine-2-on, chlorsulfuron, cinidon, cinidon-ethyl, cinmethylin, cinosulfuron, clacyfos, clethodim, clodinafop, clodinafop-propargyl, clomazone, clomeprop, clopyralid, cloransulam, cloransulam-methyl, cumyluron, cyanamide, cyanazine, cycloate, cyclopyranil, cyclopyrimorate, cyclosulfamuron, cycloxydim, cyhalofop, cyhalofop-butyl, cyprazine, 2,4-D, 2,4-D-butotyl, -butyl, dimethylammonium, -diolamin, -ethyl, -2-ethylhexyl, -isobutyl, -isooctyl, -isopropylammonium, potassium, -triisopropanolammonium, and -trolamine, 2,4-DB, 2,4-DB-butyl, -dimethylammonium, isooctyl, -potassium, and -sodium, daimuron (dymron), dalapon, dazomet, n-decanol, desmedipham, detosyl-pyrazolate (DTP), dicamba, dichlobenil, dichlorprop, dichlorprop-P, diclofop, diclofop-methyl, diclofop-P-methyl, diclosulam, difenzoquat, diflufenican, diflufenzopyr, diflufenzopyr-sodium, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimethenamid-P, 3-(2,6dimethylphenyl)-6-[(2-hydroxy-6-oxocyclohex-1-en-1-yl)carbonyl]-1-methylchinazolin-2,4(1H,3H)-1,3-dimethyl-4-[2-(methylsulfonyl)-4-(trifluormethyl)benzoyl]-1H-pyrazol-5-yl-1,3-dimethyl-1H-pyrazol-4-carboxylat, dimetrasulfuron, dinitramine, dinoterb, diphenamid, diquat, diquat-dibromid, dithiopyr, diuron, DMPA, DNOC, endothal, EPTC, esprocarb, ethalfluralin, ethametsulfuron, ethametsulfuron-methyl, ethiozin, ethofumesate, ethoxyfen, ethoxyfen-ethyl, ethoxysulfuron,

etobenzanid, ethyl-[(3-{2-chloro-4-fluoro-5-[3-methyl-2,6-dioxo-4-(trifluormethyl)-3,6dihydropyrimidin-1(2H)-yl]phenoxy}pyridin-2-yl)oxy|acetat, F-9960, F-5231, i.e. N-{2-chloro-4fluoro-5-[4-(3-fluoropropyl)-5-oxo-4,5-dihydro-1H-tetrazol-1-yl]phenyl}ethanesulfonamide, F-7967, i. 3-[7-chloro-5-fluoro-2-(trifluoromethyl)-1H-benzimidazol-4-vl]-1-methyl-6-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione, fenoxaprop, fenoxaprop-P, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenoxasulfone, fenquinotrione, fentrazamide, flamprop, flamprop-M-isopropyl, flamprop-M-methyl, flazasulfuron, florasulam, fluazifop, fluazifop-P, fluazifop-butyl, fluazifop-Pbutyl, flucarbazone, flucarbazone-sodium, flucetosulfuron, fluchloralin, flufenacet, flufenpyr, flufenpyr-ethyl, flumetsulam, flumiclorac, flumiclorac-pentyl, flumioxazin, fluometuron, flurenol, flurenol-butyl, -dimethylammonium and -methyl, fluoroglycofen, fluoroglycofen-ethyl, flupropanate, flupyrsulfuron, flupyrsulfuron-methyl-sodium, fluridone, fluro-chloridone, fluroxypyr, fluroxypyrmeptyl, flurtamone, fluthiacet, fluthiacet-methyl, fomesafen, fomesafen-sodium, foramsulfuron, fosamine, glufosinate, glufosinate-ammonium, glufosinate-P-sodium, glufosinate-P-ammonium, glufosinate-P-sodium, glyphosate, glyphosate-ammonium, -isopropylammonium, -diammonium, dimethylammonium, -potassium, -sodium, and -trimesium, H-9201, i.e. O-(2,4-dimethyl-6nitrophenyl) O-ethyl isopropylphosphoramidothioate, halauxifen, halauxifen-methyl ,halosafen, halosulfuron, halosulfuron-methyl, haloxyfop, haloxyfop-P, haloxyfop-ethoxyethyl, haloxyfop-Pethoxyethyl, haloxyfop-methyl, haloxyfop-P-methyl, hexazinone, HW-02, (dimethoxyphosphoryl) ethyl-(2,4-dichlorophenoxy)acetate, 4-hydroxy-1-methoxy-5-methyl-3-[4-(trifluormethyl)pyridine-2-yl]imidazolidine-2-on, 4-hydroxy-1-methyl-3-[4-

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(trifluormethyl)pyridine-2-yl]imidazolidine-2-on, (5-hydroxy-1-methyl-1H-pyrazol-4-yl)(3,3,4trimethyl-1,1-dioxido-2,3-dihydro-1-benzothiophen-5-yl)methanon, 6-[(2-hydroxy-6-oxocyclohex-1en-1-yl)carbonyl]-1,5-dimethyl-3-(2-methylphenyl)chinazolin-2,4(1H,3H)-dion, imazamethabenz, imazamox, imazamox-ammonium, imazamethabenz-methyl, imazapic, imazapic-ammonium, imazapyr, imazapyr-isopropylammonium, imazaquin, imazaquin-ammonium, imazethapyr, imazethapyr-immonium, imazosulfuron, indanofan, indaziflam, iodosulfuron, iodosulfuron-methylsodium, ioxynil, ioxynil-octanoate, -potassium and -sodium, ipfencarbazone, isoproturon, isouron, isoxaben, isoxaflutole, karbutilate, KUH-043, i.e. 3-({[5-(difluoromethyl)-1-methyl-3-(trifluoromethyl)-1H-pyrazol-4-yl]methyl}sulfonyl)-5,5-dimethyl-4,5-dihydro-1,2-oxazole, spiradox, lactofen, lenacil, linuron, MCPA, MCPA-butotyl, -dimethylammonium, -2-ethylhexyl, isopropylammonium, -potassium, and -sodium, MCPB, MCPB-methyl, -ethy,l and -sodium, mecoprop, mecoprop-sodium, and -butotyl, mecoprop-P, mecoprop-P-butotyl, -dimethylammonium, ethylhexyl, and -potassium, mefenacet, mefluidide, mesosulfuron, mesosulfuron-methyl, mesotrione, metazosulfuron, methabenzthiazuron, metam, metamifop, metamitron, metazachlor, methabenzthiazuron, methiopyrsulfuron, methiozolin, 2-({2-[(2-methoxyethoxy)methyl]-6-(trifluormethyl)pyridin-3-yl}carbonyl)cyclohexan-1,3-dion, methyl isothiocyanate, [(3,3,4-trimethyl-1,1-dioxido-2,3-dihydro-1-benzothiophen-5-yl)carbonyl]-1H-pyrazol-5-ylpropan-1sulfonat, metobromuron, metolachlor, S-metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, metsulfuron-methyl, molinat, monolinuron, monosulfuron, monosulfuron-ester, MT-5950, i.e. N-(3chloro-4-isopropylphenyl)-2-methylpentan amide, NGGC-011, napropamide, NC-310, i.e. [5-(benzyloxy)-1-methyl-1H-pyrazol-4-yl](2,4-dichlorophenyl)-methanone, neburon, nicosulfuron, nonanoic acid (pelargonic acid), norflurazon, oleic acid (fatty acids), orbencarb, orthosulfamuron, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxaziclomefon, oxyfluorfen, paraquat, paraquat dichloride, pebulate, pendimethalin, penoxsulam, pentachlorphenol, pentoxazone, pethoxamid, petroleum oils, phenmedipham, picloram, picolinafen, pinoxaden, piperophos, pretilachlor, primisulfuron, primisulfuron-methyl, prodiamine, profoxydim, prometon, prometryn, propachlor, propanil, propaquizafop, propazine, propham, propisochlor, propoxy-carbazone, propoxycarbazonesodium, propyrisulfuron, propyzamide, prosulfocarb, prosulfuron, pyraclonil, pyraflufen, pyraflufenethyl, pyrasulfotole, pyrazolynate (pyrazolate), pyrazosulfuron, pyrazosulfuron-ethyl, pyrazoxyfen,

pyribambenz, pyribambenz-isopropyl, pyribambenz-propyl, pyribenzoxim, pyributicarb, pyridafol, pyridate, pyriftalid, pyriminobac, pyriminobac-methyl, pyrimi-sulfan, pyrithiobac, pyrithiobac-sodium, pyroxasulfone, pyroxsulam, quinclorac, quinmerac, quino-clamine, quizalofop, quizalofop-ethyl, quizalofop-P-tefuryl, QYM-201, QYR-301, rimsulfuron, saflufenacil, sethoxydim, siduron, simazine, simetryn, SL-261, sulcotrion, sulfentrazone, sulfometuron, sulfometuron-methyl, sulfosulfuron, SYN-523, SYP-249, i.e. 1-ethoxy-3-methyl-1-oxobut-3-en-2-yl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate, SYP-300, i.e. 1-[7-fluoro-3-oxo-4-(prop-2-yn-1-yl)-3,4-dihydro-2H-1,4-benzoxazin-6-yl]-3-propyl-2- thioxoimidazolidine-4,5-dione, 2,3,6-TBA, TCA (trichloroacetic acid), TCA-sodium, tebuthiuron, tefuryltrione, tembotrione, tepraloxydim, terbacil, terbucarb, terbumeton, terbuthylazin, terbutryn, tetflupyrolimet, thenylchlor, thiazopyr, thiencarbazone, thiencarbazone-methyl, thifensulfuron, thifensulfuron-methyl, thiobencarb, tiafenacil, tolpyralate, topramezone, tralkoxydim, triafamone, tri-allate, triasulfuron, triaziflam, tribenuron, tribenuron-methyl, triclopyr, trietazine, trifloxysulfuron, trifloxysulfuron-sodium, trifludimoxazin, trifluralin, triflusulfuron, triflusulfuron-methyl, tritosulfuron, urea sulfate, vernolate, ZJ-0862, i.e. 3,4-dichloro-N-{2-[(4,6-dimethoxypyrimidin-2-yl)oxy]benzyl}aniline.

The at least one active ingredient is preferably selected from the group comprising fungicides selected from the group comprising classes as described here above (1) Inhibitors of the respiratory chain at complex, in particular azoles, (2) Inhibitors of the respiratory chain at complex I or II, (3) Inhibitors of the respiratory chain at complex, (4) Inhibitors of the mitosis and cell division, (6) Compounds capable to induce a host defence, (10) Inhibitors of the lipid and membrane synthesis, and (15).

Further preferred, the at least one active ingredient a) as fungicide is selected from the group comprising bixafen, fluoxapiprolin, inpyrfluxam, isoflucypram, prothioconazole, tebuconazole, trifloxystrobin

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The at least one insecticide is preferably selected from the group comprising insecticides selected from the group comprising classes as described here above (2 GABA-gated chloride channel antagonists, (3) Sodium channel modulators / voltage-dependent sodium channel blockers (4) (4) Nicotinic acetylcholine receptor (nAChR) competitive activators, (23) Inhibitors of acetyl-CoA carboxylase, (28) Ryanodinreceptor-modulators, (30) other active ingredients.

also further preferred, the at least one active ingredient a) as insecticide is selected from the group comprising ethiprole, imidacloprid, spidoxamat, spirotetramat, tetraniliprole.

Lastly further preferred, the at least one active ingredient a) as herbicide is selected from the group comprising thiencarbazone-methyl, triafamone, isoxadifen-ethyl and mefenpyr-diethyl.

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Even more preferred, the at least one active ingredient is selected from the group comprising bixafen, fluoxapiprolin, inpyrfluxam, isoflucypram, prothioconazole, tebuconazole, trifloxystrobin, ethiprole, imidacloprid, spidoxamat, spirotetramat, tetraniliprole, thiencarbazone-methyl, triafamone, isoxadifen-ethyl and mefenpyr-diethyl.

All named active ingredients as described here above can be present in the form of the free compound or, if their functional groups enable this, an agrochemically active salt thereof.

Furthermore, mesomeric forms as well as stereoisomeres or enantiomeres, where applicable, shall be enclosed, as these modifications are well known to the skilled artisan, as well as polymorphic modifications.

If not otherwise specified, in the present invention solid, agrochemical active compounds a) are to be understood as meaning all substances customary for plant treatment, whose melting point is above 20°C.

### **Uptake enhancers (b)**

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- 10 Oils that function as penetration promoters, suitable oils are all substances of this type which can customarily be employed in agrochemical agents. Preferably, oils of vegetable, mineral and animal origin and alkyl esters of these oils. Examples are:
  - sunflower oil, rapeseed oil, corn oil, soybean oil, rice bran oil, olive oil;
- ethylhexyl oleate, ethylhexyl palmitate, ethylhexyl myristate/laurate, ethylhexyl laurate, ethylhexyl caprylate/caprate, iso-propyl myristate, iso-propyl palmitate, methyl oleate, methyl 15 palmitate, ethyl oleate, rape seed oil methyl ester, soybean oil methyl ester, rice bran oil methyl ester,
  - Mineral oils, e.g. Exxsol® D100, Solvesso® 200ND, and white oil.
  - tris-alkyl-phosphate esters, preferably tris (2-ethylhexyl) phosphate, e.g. Disflamoll® TOF;

The uptake enhancer may also be selected from the following group of compounds:

- 20 i. ethoxylated branched alcohols (e.g. Genapol<sup>®</sup> X-type) with 2-20 EO units;
  - methyl end-capped, ethoxylated branched alcohols (e.g. Genapol® XM-type) comprising 2-20 ii.
  - ethoxylated coconut alcohols (e.g. Genapol® C-types) comprising 2-20 EO units: iii.
  - ethoxylated C12/15 alcohols (e.g. Synperonic® A-types) comprising 2-20 EO units; iv.
- propoxy-ethoxylated alcohols, branched or linear, e.g. Antarox® B/848, Atlas® G5000, 25 v. Lucramul® HOT 5902;
  - propoxy-ethoxylated fatty acids, Me end-capped, e.g. Leofat® OC0503M; vi.
  - alkyl ether citrate surfactants (e.g. Adsee® CE range, Akzo Nobel); vii.
  - ethoxylated mono- or diesters of glycerine comprising fatty acids with 8-18 carbon atoms and viii. an average of 10-40 EO units (e.g. Crovol® range);
    - castor oil ethoxylates comprising an average of 5-40 EO units (e.g. Berol® range, Emulsogen® ix. EL range).
    - ethoxylated oleic acid (e.g. Alkamuls® A and AP) comprising 2-20 EO units; X.
- ethoxylated sorbitan fatty acid esters comprising fatty acids with 8-18 carbon atoms and an xi. average of 10-50 EO units (e.g. Arlatone® T, Tween range). 35

Preferred uptake enhancers according to the present invention are tris (2-ethylhexyl) phosphate, rapeseed oil methyl esters, ethoxylated branched alcohols, ethoxylated coconut alcohols, propoxyethoxylated alcohols and mineral oils.

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## Other formulants (c) are

- c1 Suitable non-ionic surfactants or dispersing aids c1) are all substances of this type which can customarily be employed in agrochemical agents. Preferably, polyethylene oxide-polypropylene oxide block copolymers, preferably having a molecular weight of more than 6,000 g/mol or a polyethylene oxide content of more than 45%, more preferably having a molecular weight of more than 6,000 g/mol and a polyethylene oxide content of more than 45%, polyethylene glycol ethers of branched or linear alcohols, reaction products of fatty acids or fatty acid alcohols with ethylene oxide and/or propylene oxide, furthermore polyvinyl alcohol, polyoxyalkylenamine derivatives, polyvinylpyrrolidone, copolymers of polyvinyl alcohol and polyvinylpyrrolidone, and copolymers of
- polyvinylpyrrolidone, copolymers of polyvinyl alcohol and polyvinylpyrrolidone, and copolymers of (meth)acrylic acid and (meth)acrylic acid esters, furthermore branched or linear alkyl ethoxylates and alkylaryl ethoxylates, where polyethylene oxide-sorbitan fatty acid esters may be mentioned by way of example. Out of the examples mentioned above selected classes can be optionally phosphated, sulphonated or sulphated and neutralized with bases.
- Possible anionic surfactants c1) are all substances of this type which can customarily be employed in agrochemical agents. Alkali metal, alkaline earth metal and ammonium salts of alkylsulphonic or alkylphospohric acids as well as alkylarylsulphonic or alkylarylphosphoric acids are preferred. A further preferred group of anionic surfactants or dispersing aids are alkali metal, alkaline earth metal and ammonium salts of polystyrenesulphonic acids, salts of polyvinylsulphonic acids, salts of alkylnaphthalene sulphonic acids, salts of naphthalene-sulphonic acid-formaldehyde condensation products, salts of condensation products of naphthalenesulphonic acid, phenolsulphonic acid and formaldehyde, and salts of lignosulphonic acid.
  - **c2** A rheological modifier is an additive that when added to the recipe at a concentration that reduces the gravitational separation of the dispersed active ingredient during storage results in a substantial increase in the viscosity at low shear rates. Low shear rates are defined as 0.1 s<sup>-1</sup> and below and a substantial increase as greater than x2 for the purpose of this invention. The viscosity can be measured by a rotational shear rheometer.

Suitable rheological modifiers c4) by way of example are:

- Polysaccharides including xanthan gum, guar gum and hydroxyethyl cellulose. Examples are Kelzan<sup>®</sup>, Rhodopol<sup>®</sup> G and 23, Satiaxane<sup>®</sup> CX911 and Natrosol<sup>®</sup> 250 range.
- Clays including montmorillonite, bentonite, sepeolite, attapulgite, laponite, hectorite. Examples are Veegum<sup>®</sup> R, Van Gel<sup>®</sup> B, Bentone<sup>®</sup> CT, HC, EW, 34, 38 Pangel<sup>®</sup> M100, M200, M300, S, M, W, Attagel<sup>®</sup> 50, Laponite<sup>®</sup> RD,
- Fumed and precipitated silica, examples are Aerosil® 200, Siponat® 22.
- 40 Preferred are xanthan gum, montmorillonite clays, bentonite clays and fumed silica.

- c3 Suitable antifoam substances c3) are all substances which can customarily be employed in agrochemical agents for this purpose. Silicone oils, silicone oil preparations are preferred. Examples are Silcolapse<sup>®</sup> 426 and 432 from Bluestar Silicones, Silfoam<sup>®</sup> SRE and SC132 from Wacker, SAF-184<sup>®</sup> fron Silchem, Foam-Clear ArraPro-S<sup>®</sup> from Basildon Chemical Company Ltd, SAG<sup>®</sup> 1572 and SAG<sup>®</sup> 30 from Momentive [Dimethyl siloxanes and silicones, CAS No. 63148-62-9]. Preferred is SAG<sup>®</sup> 1572.
- **c4** Suitable antifreeze substances are all substances which can customarily be employed in agrochemical agents for this purpose. Suitable examples are propylene glycol, ethylene glycol, urea and glycerine.
- c5 Suitable other formulants c5) are selected from biocides, antifreeze, colourants, pH adjusters, buffers, stabilisers, antioxidants, inert filling materials, humectants, crystal growth inhibitors, micronutirients by way of example are:
- Possible preservatives are all substances which can customarily be employed in agrochemical agents for this purpose. Suitable examples for preservatives are preparations containing 5-chloro-2-methyl-4-isothiazolin-3-one [CAS-No. 26172-55-4], 2-methyl-4-isothiazolin-3-one [CAS-No. 2682-20-4] or 1.2-benzisothiazol-3(2H)-one [CAS-No. 2634-33-5]. Examples which may be mentioned are Preventol® D7 (Lanxess), Kathon® CG/ICP (Dow), Acticide® SPX (Thor GmbH) and Proxel® GXL (Arch Chemicals).
- Possible colourants are all substances which can customarily be employed in agrochemical agents for this purpose. Titanium dioxide, carbon black, zinc oxide, blue pigments, Brilliant Blue FCF, red pigments and Permanent Red FGR may be mentioned by way of example.
  - Possible pH adjusters and buffers are all substances which can customarily be employed in agrochemical agents for this purpose. Citric acid, sulfuric acid, hydrochloric acid, sodium hydroxide, sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>), sodium dihydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>), potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>), potassium hydrogen phosphate (K<sub>2</sub>HPO<sub>4</sub>), may be mentioned by way of example.
  - Suitable stabilisers and antioxidants are all substances which can customarily be employed in agrochemical agents for this purpose. Butylhydroxytoluene [3.5-Di-tert-butyl-4-hydroxytoluol, CAS-No. 128-37-0] is preferred.

#### 30 Carriers d)

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Carriers are those which can customarily be used for this purpose in agrochemical formulations.

<u>A carrier</u> is a solid or liquid, natural or synthetic, organic or inorganic substance that is generally inert, and which may be used as a solvent. The carrier generally improves the application of the compounds, for instance, to plants, plants parts or seeds. Examples of suitable

- solid carriers include, but are not limited to, ammonium salts, in particular ammonium sulfates, ammonium phosphates and ammonium nitrates, natural rock flours, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite and diatomaceous earth, silica gel and synthetic rock flours, such as finely divided silica, alumina and silicates. Examples of typically useful solid carriers for preparing granules include, but are not limited to crushed and fractionated natural rocks such as calcite, marble,
   pumice, sepiolite and dolomite, synthetic granules of inorganic and organic flours and granules of organic material such as paper, sawdust, coconut shells, maize cobs and tobacco stalks.
  - Preferred solid carriers are selected from clays, talc and silica.

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Examples of suitable *liquid carriers* include, but are not limited to, water, organic solvents and combinations thereof. Examples of suitable *solvents* include polar and nonpolar organic chemical liquids, for example from the classes of

- alcohols and polyols (which may optionally also be substituted, etherified and/or esterified, such as ethanol, propanol, butanol, benzylalcohol, cyclohexanol or glycol, 2-ethyl hexanol),
- ethers such as dioctyl ether, tetrahydrofuran, dimethyl isosorbide, solketal, cyclopentyl methyl ether, solvents offered by Dow under the Dowanol Product Range e.g. Dowanol DPM, anisole, phenetole, different molecular weight grades of dimethyl polyethylene glycol, different molecular weight grades of dimethyl polypropylene glycol, dibenzyl ether
- ketones (such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, cyclohexanone, acetophenone, propiophenone).
  - lactate esters, such as methyl lactate, ethyl lactate, propyl lactate, butyl lactate, 2-ethyl hexyl lactate
  - (poly)ethers such as different molecular weight grades of polyethylene glycol, different molecular weight grades of polypropylene glycol
- unsubstituted and substituted amines
  - amides (such as dimethylformamide, or N,N-dimethyl lactamide, or N-formyl morpholine, or fatty acid amides such N,N-dimethyl decanamide or N,N-dimethyl dec-9-en-amide) and esters thereof
  - lactams (such as 2-pyrrolidone, or N-alkylpyrrolidones, such as N-methylpyrrolidone, or N-butylpyrrolidone, or N-octylpyrrolidone, or N-dodecylpyrrolidone or N-methyl caprolactam, N-alkyl caprolactam)
  - lactones (such as gamma-butyrolactone, gamma-valerolactone, delta-valerolactone, or alphamethyl gamma-butyrolactone
  - sulfones and sulfoxides (such as dimethyl sulfoxide),
  - nitriles, such as linear or cyclic alkyl nitriles, in particular acetonitrile, cyclohexane carbonitrile, octanonitrile, dodecanonitrile).
  - linear and cyclic carbonates, such as diethyl carbonate, dipropyl carbonate, dibutyl carbonate, dioctyl carbonate, or ethylene carbonate, propylene carbonate, butylene carbonate, glycerine carbonate
- 30 As liquid carrier water is most preferred.

These spray liquids are applied by customary methods, i.e., for example, by spraying, pouring or injecting, in particular by spraying, and most particular by spraying by UAV.

The application rate of the formulations according to the invention can be varied within a relatively wide range. It is guided by the particular active agrochemicals and by their amount in the formulations.

With the aid of the formulations according to the invention it is possible to deliver active agrochemical to plants and/or their habitat in a particularly advantageous way.

The present invention is also directed to the use of agrochemical compositions according to the invention for the application of the agrochemical active compounds contained to plants and/or their habitat.

With the formulations of the invention it is possible to treat all plants and plant parts. By plants here are meant all plants and plant populations, such as desirable and unwanted wild plants or crop plants (including naturally occurring crop plants). Crop plants may be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and gene-technological methods or combinations of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by varietal property rights. By plant parts are to be meant all above-ground and below-ground parts and organs of the plants, such as shoot, leaf, flower and root, an exemplary listing embracing leaves, needles, stems, trunks, flowers, fruit bodies, fruits and seeds and also roots, tubers and rhizomes. The plant parts also include harvested material and also vegetative and generative propagation material.

What may be emphasized in this context is the particularly advantageous effect of the formulations according to the invention with regard to their use in cereal plants such as, for example, wheat, oats, barley, spelt, triticale and rye, but also in maize, sorghum and millet, rice, sugar cane, soya beans, sunflowers, potatoes, cotton, oilseed rape, canola, tobacco, sugar beet, fodder beet, asparagus, hops and fruit plants (comprising pome fruit such as, for example, apples and pears, stone fruit such as, for example, peaches, nectarines, cherries, plums and apricots, citrus fruits such as, for example, oranges, grapefruits, limes, lemons, kumquats, tangerines and satsumas, nuts such as, for example, pistachios, almonds, walnuts and pecan nuts, tropical fruits such as, for example, mango, papaya, pineapple, dates and bananas, and grapes) and vegetables (comprising leaf vegetables such as, for example, endives, corn salad, Florence fennel, lettuce, cos lettuce, Swiss chard, spinach and chicory for salad use, cabbages such as, for example, cauliflower, broccoli, Chinese leaves, Brassica oleracea (L.) convar. acephala var. sabellica L. (curly kale, feathered cabbage), kohlrabi, Brussels sprouts, red cabbage, white cabbage and Savoy cabbage, fruit vegetables such as, for example, aubergines, cucumbers, capsicums, table pumpkins, tomatoes, courgettes and sweetcorn, root vegetables such as, for example celeriac, wild turnips, carrots, including yellow cultivars, Raphanus sativus var. niger and var. radicula, beetroot, scorzonera and celery, legumes such as, for example, peas and beans, and vegetables from the Allium family such as, for example, leeks and onions.

The treatment of the plants and plant parts in accordance with the invention with the inventive formulations is carried out directly or by action on their environment, habitat or storage area in accordance with the customary treatment methods, for example by dipping, spraying, vaporizing, atomizing, broadcasting or painting on and, in the case of propagation material, especially seeds, additionally by single or multiple coating.

The active agrochemicals comprised develop a better biological activity than when applied in the form of the corresponding conventional formulations.

#### Leaf surfaces

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In Tables 1a and 1b the contact angle of water on leaf surfaces for textured and non-textured is shown.

Table 1a Plants with textured leaves

Plant	Species	Contact angle of water °
		(adaxial)
barley	Hordeum vulgare (var. Montoya)	143°
corn, BBCH-11	Zea mays	150°
corn, BBCH-12	Zea mays	149°
corn, BBCH-13/14	Zea mays	148°
soybean, BBCH-12	Glycine max	149°
soybean, BBCH-13	Glycine max	144°
rice	Oryza sativa	180°
wheat, BBCH-12	Triticum aestivum	148°
fat-hen	Chenopodium album	137°
purple crabgrass	Digitaria sanguinalis	144°

<u>Table 1b</u> Plants with non-textured leaves

Plant	Species	Contact angle of water °
		(adaxial)
apple	Malus domestica	104°
tomato	Solanum lycopersicum	106°
corn, BBCH-15/16	Zea mays	108°
corn, BBCH-17	Zea mays	107°
corn, BBCH-18	Zea mays	96°
corn, BBCH-19	Zea mays	87°
velvetleaf	Abutilon theophrasti	103°
redroot pigweed	Amaranthus retroflexus	not measured

Examples of non-textured crops and plants include tomatoes, peppers, potatoes, carrot, celery, sugar beet, beetroot, spinach, lettuce, beans, peas, clover, apple, pear, peach, apricot, plum, mango, avocado, olive, citrus, orange, lemon, lime, grape, fig, cucumber, melon, water melon, strawberry, raspberry, blueberry, sunflower, pumpkin, soybean (> BBCH XX), corn (> BBCH15), cotton.

Examples of textured crops and plants include garlic, onions, leeks, soybean (< BBCH-XX), oats, wheat, barley, rice, sugarcane, pineapple, banana, linseed, lilies, orchids, corn (< BBCH15), cabbage, brussels sprouts, broccoli, Cauliflower, rye, rapeseed, tulips and peanut.

Examples of non-textured weeds include Abutilon theophrasti, Capsella bursa-pastoris, Datura stramonium, Galium aparine, Ipomoea purpurea, Polygonum lapathifolium, Portulaca oleracea, Senecio vulgaris, Sida spinosa, Sinapis arvensis, Solanum nigrum, Stellaria media, Xanthium orientale, Cyperus rotundus, and Amaranthus retroflexus.

Examples of textured weeds include Cassia obtusifolia, Chenopodium album, Agropyron repens, Alopecurus myosuroides, Apera spica-venti, Avena fatua, Brachiaria plantaginea, Bromus secalinus, Cynodon dactylon, Digitaria sanguinalis, Echinochloa crus-galli, Panicum dichotomiflorum, Poa annua, Setaria faberi and Sorghum halepense.

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The invention is illustrated by the following examples.

#### **Examples**

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### Method 1: SC preparation

The method of the preparation of suspension concentrate formulations are known in the art and can be produced by known methods familiar to those skilled in the art. A 2% gel of the xanthan (c) in water and the biocides (c) was prepared with low shear stirring. The active ingredient (a), non-ionic and anionic dispersants (c), antifoam (c) and other formulants (c) were mixed with water to form a slurry, first mixed with a high shear rotor-stator mixer (Ultra-Turrax®) to reduce the particle size D(v,0.9) to approximately 50 microns, then passed through one or more bead mills (Eiger® 250 Mini Motormill) to achieve a particles size D(v,0.9) typically 1 to 15 microns. Then the additives (b), (c) and (d) and xanthan gel prepared above were added and mixed in with low shear stirring until homogeneous. Finally, the pH is adjusted if needed with acid or base (e).

### Method 2: WG preparation

The methods of the preparation water dispersible granule formulations are known in the art and can be produced by known methods familiar to those skilled in the art.

For example, to produce a fluid bed granule first a water-based technical concentrate has to be prepared. With low shear stirring all ingredients (a, b and c) like e.g. the active ingredient, surfactants, dispersants, binder, antifoam, spreader, and filler are mixed in water and finally pre-milled in a high shear rotor-stator mixer (Ultra-Turrax $^{\text{(B)}}$ ) to reduce the particle size D(v,0.9) to approximately 50 microns, afterwards passed through one or more bead mills (KDL, Bachofen, Dynomill, Bühler, Drais, Lehmann) to achieve a particles size D(v,0.9) typically 1 to 15 microns. This water-based technical concentrate is then spray-dried in a fluid-bed granulation process to form the wettable granules (WG).

The particle size is determined according to CIPAC (CIPAC = Collaborative International Pesticides Analytical Council; <a href="www.cipac.org">www.cipac.org</a>) method MT 187. The particle size distribution is determined by means of laser diffraction. A representative amount of sample is dispersed in degassed water at ambient temperature (self-saturation of the sample), treated with ultrasound (usually 60 s) and then measured in a device from the Malvern Mastersizer series (Malvern Panalytical). The scattered light is measured at various angles using a multi-element detector and the associated numerical values are recorded. With the help of the Fraunhofer model, the proportion of certain size classes is calculated from the scatter data and from this a volume-weighted particle size distribution is calculated. Usually the d50 or d90 value = active ingredient particle size (50 or 90% of all volume particles) is given. The average particle size denotes the d50 value.

Likewise, any other spraying process, like e.g. classical spray drying can be used as granulation method.

A further technique to produce water dispersible granules is for example low pressure extrusion. The ingredients of the formulation are mixed in dry from and are subsequently milled, e.g. using air-jet milling to reduce the particle size. Subsequently this dry powder is stirred while water is added to the mixture (approximately 10 – 30 wt%, dependent on the composition of the formulation). In a further step the mixture is pushed through an extruder (like a dome extruder, double dome extruder, basket extruder, sieve mill, or similar device) with a die size of usually between 0.8 and 1.2 mm to form the extrudates. In a last step the extrudates are post-dried, e.g. in a fluidized bed dryer to reduce the water content of the powder, commonly to a level of 1-3 wt% of residual water.

### **Method 3: EC preparation**

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The method of the preparation of EC formulations are known in the art and can be produced by known methods familiar to those skilled in the art. In general, EC formulations are obtained by mixing the active ingredient (a) with the rest of the formulation components, which include, amongst others, surfactants (c), spreader (b), a carrier (d) in a vessel equipped with a stirring device. In some cases the dissolving or mixing was facilitated by raising the temperature slightly (not exceeding 60°C). Stirring is continued until a homogeneous mixture has been obtained.

#### Method 4: OD preparation

Formulation components (c), carrier (d) active ingredient (a), spreader (b) are weighed in, homogenized with a high-shear device (e.g. Ultraturrax or colloidal mill) and subsequently milled in a bead mill (e.g. Dispermat SL50, 80% filling, 1.0-1.25 mm glass beads, 4000 rpm, circulation grinding) until a particle size of <10μ is achieved. Alternatively, formulation components are mixed in a bottle followed by addition of approx. 25vol.-% of 1.0-1.25 mm glass beads. The bottle is then closed, clamped in an agitator apparatus (e.g. Retsch MM301) and treated at 30 Hz for several minutes until a particle size of <10μ is achieved.</li>

### **Method 5**: Coverage

Greenhouse plants in the development stage as indicated in Tables 1a&1b were used for these experiments. Single leaves were cut just before the spraying experiment, placed into petri dishes and attached by tape at both tips at 0° (horizontally) or at 60° (so that 50% of leaf area can be sprayed). The leaves were carried with caution to avoid damage of the wax surface. These horizontally orientated leaves were either a) placed into a spay chamber where the spray liquid was applied via a hydraulic nozzle or b) a 4 µl drop of spray liquid was pipetted on top without touching the leaf surface.

A small amount of UV dye was added to the spray liquid to visualize the spray deposits under UV light. The concentration of the dye has been chosen such that it does not influence the surface properties of the spray liquid and does not contribute to spreading itself. Tinopal OB as a colloidal suspension was used for all flowable and solid formulation such as WG, SC, OD and SE. Tinopal CBS-X or Blankophor SOL were used for formulations where active ingredient is dissolved such as EC, EW and SL. The Tinopal CBS-X was dissolved in the aqueous phase and the Blankophor SOL dissolved in the oil phase.

After evaporation of the spray liquid, the leaves were placed into a Camag, Reprostar 3 UV chamber where pictures of spray deposits were taken under visual light and under UV light at 366 nm. A Canon EOS 700D digital camera was attached to the UV chamber and used to acquire images the leaves. Pictures taken under visual light were used to subtract the leaf shape from the background. ImageJ software was used to calculate either a) the percentage coverage of the applied spray for sprayed leaves or b) spread area for pipetted drops in mm<sup>2</sup>.

## **Method 6: Insecticide greenhouse tests**

Selected crops were grown under greenhouse conditions in plastic pots containing "peat soil T". At appropriate crop stage, plants were prepared for the treatments, e.g. by infestation with target pest approximately 2 days prior to treatment (s. table below).

Spray solutions were prepared with different doses of active ingredient directly by dilution of formulations with tap water and addition of appropriate amount of additives in tank mix, where required.

The application was conducted with a tracksprayer onto the upperside of leaves with 300 l/ha or 10 l/ha application volume. Nozzles used: Lechler's TeeJet TP8003E (for 300 l/ha) and Lechler's 652.246 together with a pulse-width-module (PWM) (for 10 l/ha). For each single dose applied, usually 2 to 5 replicates were simultaneously treated.

After treatment, plants were artificially infested, if needed, and kept during test duration in a greenhouse or climate chamber. The efficacy of the treatments was rated after evaluation of mortality (in general, given in %) and/or plant protection (calculated e.g. from feeding damage in comparison to corresponding controls) at different points of time. Only mean values are reported.

Table M1:	Pests	and	crops	used	in	the	tests.
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crop	ı <del>-</del>	infestation	pest	English name	pest life stage	test objective
	stage					
soybean	BBCH12,	after	Nezara	green stink bug	10x nymphs N2-	contact and oral
	5 plants	treatment	viridula		N3	uptake
	in pot					
cabbage	BBCH12,	prior to	Myzus	green peach	mixed	translaminar
	1-leaf	treatment	persicae	aphid	population	activity

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Selected crops were grown under greenhouse conditions in plastic pots containing "peat soil T". At appropriate crop stage, plants were prepared for the treatments, e.g. by infestation with target pest approximately 2 days prior to treatment (table M1).

Spray solutions were prepared with different doses of active ingredient directly by dilution of formulations with tap water and addition of appropriate amount of additives in tank mix, where required.

The application was conducted with tracksprayer onto upperside of leaves with 300 l/ha or 10 l/ha application volume. Nozzles used: Lechler's TeeJet TP8003E (for 300 l/ha) and Lechler's 652.246 together with a pulse-width-module (PWM) (for 10 l/ha). For each single dose applied, usually 2 to 5 replicates were simultaneously treated.

After treatment, plants were artificially infested, if needed, and kept during test duration in a greenhouse or climate chamber. The efficacy of the treatments was rated after evaluation of mortality (in general, given in %) and/or plant protection (calculated e.g. from feeding damage in comparison to corresponding controls) at different points of time. Only mean values are reported.

### Method 7 : Cuticle wash-off

A disc from an apple cuticle was fixed with the outside surface facing upwards to a glass microscope slide with a thin layer of medium viscosity silicone oil. To this 0.9 µl drops of the different formulations diluted at the spray dilution in deionised water containing 5% CIPAC C water were applied with a micropipette and left to dry for 1 hour. Each deposit was examined in an optical transmission microscope fitted with crossed polarising filters and an image recorded. The slide containing the cuticle with the dried droplets of the formulations was held under gently running deionised water (flow rate

approximately 300ml/minute at a height 10cm below the tap outlet) for 15s. The glass slide was allowed to dry and the deposits were re-examined in the microscope and compared to the original images. The amount of active ingredient washed off was visually estimated and recorded in steps of 10%. Three replicates were measured and the mean value recorded.

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#### Method 8: Leaf wash-off

Apple or corn leaf sections were attached to a glass microscope slide. To this 0.9 µl drops of the different formulations diluted at the spray dilution in deionised water containing 5% CIPAC C water and a small amount of fluorescent tracer (Tinopal OB as a micron sized aqueous suspension) were applied with a micropipette and left to dry for 1 hour. Under UV illumination (365nm) the leaf deposits were imaged by a digital camera. The leaf sections were then held under gently running deionised water (flow rate approximately 300ml/minute at a height 10cm below the tap outlet) for 15s. The leaf sections were allowed to dry and the deposits were re-imaged and compared to the original images. The amount of active ingredient washed off was visually estimated between 5 with most remaining and 1 with most removed. Three or more replicates were measured and the mean value recorded.

### Method 9: Suspo-emulsion preparation

The method of the preparation of suspo-emulsion formulations are known in the art and can be produced by known methods familiar to those skilled in the art. A 2% gel of the xanthan in water and the biocides (e) was prepared with low shear stirring. The active ingredient spiroxamine (a), oils (b/c) and antioxidant (e) were mixed and added to an aqueous dispersion comprising a portion of the non-ionic dispersants (c) under high shear mixing with a rotor-stator mixer until an oil in water emulsion was formed with a droplet size D(v,0.9) typically 1 to 5 microns. The active ingredient (a), the remaining non-ionic and anionic dispersants (c/e) and other remaining formulants (c/e) were mixed with the remaining water to form a slurry, first mixed with a high shear rotor-stator mixer to reduce the particle size D(v,0.9) to approximately 50 microns, then passed through one or more bead mills to achieve a particles size D(v,0.9) typically 1 to 15 microns as required for the biological performance of the active ingredient(s). Those skilled in the art will appreciate that this can vary for different active ingredients. The oil in water emulsion, polymer dispersion (c/d) and xanthan gel were added and mixed in with low shear stirring until homogeneous.

## Method 10: Description for Herbicide Greenhouse tests

Seeds of crops and monocotyledonous and dicotyledonous harmful plants are laid out in sandy loam in plastic pots, covered with soil and cultivated in a greenhouse under optimum growth conditions. Two to three weeks after sowing, the test plants are treated at the one- to two-leaf stage. The test herbicide formulations are prepared with different concentrations and sprayed onto the surface of the green parts of the plants using different water application rates: 200 I/ha as a standard conventional rate and 10 I/ha as an ultra-low-volume (ULV) application rate. The nozzle type used for all applications is TeeJet DG 95015 EVS. The ULV application rate is achieved by using a pulse-width-modulation (PWM) –system that gets attached to the nozzle and the track sprayer device. After application, the test plants were left to stand in the greenhouse for 3 to 4 weeks under optimum growth conditions. Then, the activity of the herbicide formulation is scored visually (for example: 100% activity = the whole plant material is dead, 0% activity = plants are similar to the non-treated control plants).

Table M2: Plant species used in the tests.

Plant species	Abbreviation/EPPO Code	Crop Variety
Setaria viridis	SETVI	
Echinochloa crus-galli	ECHCG	
Alopecurus myosuroides	ALOMY	
Hordeum murinum	HORMU	
Avena fatua	AVEFA	
Lolium rigidum	LOLRI	
Matricaria inodora	MATIN	
Veronica persica	VERPE	
Abutilon theophrasti	ABUTH	
Pharbitis purpurea	PHBPU	
Polygonum convolvulus	POLCO	
Amaranthus retroflexus	AMARE	
Stellaria media	STEME	
Zea mays	ZEAMA	Aventura
Triticum aestivum	TRZAS	Triso
Brassica napus	BRSNW	Fontan

## **Method 11: Description for Fungicide Greenhouse tests**

- Seeds were laid out in "peat soil T" in plastic pots, covered with soil and cultivated in a greenhouse under optimum growth conditions. Two to three weeks after sowing, the test plants were treated at the one- to two-leaf stage. The test fungicide formulations were prepared with different concentrations and sprayed onto the surface of the plants using different water application rates: 200 I/ha as a standard conventional rate and 10 I/ha as an ultra-low-volume (ULV) application rate. The nozzle type used for all applications was TeeJet TP 8003E, used with 0,7 1,5 bar and 500 600 mm height above plant level. Cereal were put in an 45° angle as this reflected best the spray conditions in the field for cereals. The ULV application rate was achieved by using a pulse-width-modulation (PWM) system attached to the nozzle and the track sprayer device at 30Hz, opening 8% 100% (10 I/ha 200 I/ha spray volume).
- In a protective treatment the test plants were inoculated 1 day after the spray application with the respective disease and left to stand in the greenhouse for 1 to 2 weeks under optimum growth conditions. Then, the activity of the fungicide formulation was assessed visually.
  - In curative conditions plants were first inoculated with the disease and treated 2 days later with the fungicide formulations. Visual assessment of the disease was done 5 days after application of formulations.
- 20 The practices for inoculation are well known to those skilled in the art.

Table M3: Diseases and crops used in the tests.

Plant species	Crop Variety	Disease	English Name	Abbreviation / EPPO Code disease
Soybean	Merlin	Phakopsora pachyrhizi	Soybean rust	PHAKPA
Wheat	Monopol	Puccinia triticina	Brown rust	PUCCRT
Barley	Gaulois	Pyrenophora teres	Net blotch	PYRNTE
Barley	Villa	Blumeria graminis	Powdery mildew	ERYSGH

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Tomato	Rentita	Phytophtora	Late blight	PHYTIN
		infestans		

## Method 12: Cuticle penetration test

The cuticle penetration test is a further developed and adapted version of the test method SOFU (simulation of foliar uptake) originally described by Schönherr and Baur (Schönherr, J., Baur, P. (1996), Effects of temperature, surfactants and other adjuvants on rates of uptake of organic compounds. In: The plant cuticle - an integrated functional approach, 134-155. Kerstiens, G. (ed.), BIOS Scientific publisher, Oxford); it is well suited for systematic and mechanistic studies on the effects of formulations, adjuvants and solvents on the penetration of agrochemicals.

Apple leaf cuticles were isolated from leaves taken from trees growing in an orchard as described by Schönherr and Riederer (Schönherr, J., Riederer, M. (1986), Plant cuticles sorb lipophilic compounds during enzymatic isolation. Plant Cell Environ. 9, 459-466). Only the astomatous cuticular membranes of the upper leaf surface lacking stomatal pores were obtained. Discs having diameters of 18 mm were punched out of the leaves and infiltrated with an enzymatic solution of pectinase and cellulase. The cuticular membranes were separated from the digested leaf cell broth, cleaned by gently washing with water and dried. After storage for about four weeks the permeability of the cuticles reaches a constant level and the cuticular membranes are ready for the use in the penetration test.

The cuticular membranes were applied to diffusion vessels. The correct orientation is important: the inner surface of the cuticle should face to the inner side of the diffusion vessel. A spray was applied in a spray chamber to the outer surface of the cuticle. The diffusion vessel was turned around and carefully filled with acceptor solution. Aqueous mixture buffered to pH 5.5 was used as acceptor medium to simulate the apoplast as natural desorption medium at the inner surface of the cuticle.

The diffusion vessels filled with acceptor and stirrer were transferred to a temperature-controlled stainless steel block which ensures not only a well-defined temperature but also a constant humidity at the cuticle surface with the spray deposit. The temperature at the beginning of experiments was 25°C or 30°C and changes to 35° 24h after application at constantly 60% relative humidity.

An autosampler took aliquots of the acceptor in regular intervals and the content of active ingredient is determined by HPLC (DAD or MS). All data points were finally processed to obtain a penetration kinetic. As the variation in the penetration barrier of the cuticles is high, five to ten repetitions of each penetration kinetic were made.

#### Materials

Table MAT1: Exemplified trade names and CAS-No's of preferred super-spreading compounds (b)

Product	Chemical name	Cas No.	Supplier
Geropon® DOS- PG	Dioctylsulfosuccinate sodium salt (65-70% in propylene glycol)	577-11-7	Rhodia
Synergen® W 10	Dioctylsulfosuccinate sodium salt (65-70% in propylene glycol)	577-11-7	Clariant

Aerosol® OT 70 PG	Dioctylsulfosuccinate sodium salt (65-70% in propylene glycol)	577-11-7	Cytec
Lankropol KPH70	Dioctylsulfosuccinate sodium salt (65-70% in propylene glycol)	577-11-7	Nouryon
Enviomet EM 5669	Dioctylsulfosuccinate sodium salt (65-70% in propylene glycol)	577-11-7	Innospec
Surfynol® S420	2,4,7,9-Tetramethyl-5-Decyne- 4,7-Diol ethoxylate (1 mole)	9014-85-1	Evonik
Surfynol® S440	2,4,7,9-Tetramethyl-5-Decyne- 4,7-Diol ethoxylate (3.5 moles)	9014-85-1	Evonik
Surfynol® S465	2,4,7,9-Tetramethyl-5-Decyne- 4,7-Diol ethoxylate (10 moles)	9014-85-1	Evonik
Surfynol® S485	2,4,7,9-Tetramethyl-5-Decyne- 4,7-Diol ethoxylate (30 moles)	9014-85-1	Evonik
Break-Thru® Vibrant	Not disclosed		Evonik
Genapol® EP	C10-12 alcohol alkoxylate		Clariant
0244	(PO+EO)		Ciariant
Synergen® W06	C11 alcohol alkoxylate (PO+EO)		Clariant
Genapol® EP 2584	C12-15 alcohol alkoxylate (PO+EO)		Clariant
Agnique® PG8107	Oligomeric D-glucopyranose decyl octyl glycosides	68515-73-1	BASF
Silwet® L77	3-(2-methoxyethoxy)propyl- methyl- bis(trimethylsilyloxy)silane	27306-78-1	Momentive
Silwet® 408	2-[3- [[dimethyl(trimethylsilyloxy)sil yl]oxy-methyl- trimethylsilyloxysilyl]propoxy]e thanol	67674-67-3	Momentive
Silwet® 806	3-[methyl-bis(trimethylsilyloxy)silyl]propa n-1-ol;2-methyloxirane;oxirane	134180-76-0	Momentive
Break-thru® S240	3-[methyl- bis(trimethylsilyloxy)silyl]propa n-1-ol;2-methyloxirane;oxirane	134180-76-0	Evonik
Break-thru® S278	3-(2-methoxyethoxy)propyl- methyl- bis(trimethylsilyloxy)silane	27306-78-1	Evonik
Silwet® HS 312			
Silwet® HS 604			
BreakThru® OE 444	Siloxanes and Silicones, cetyl Me, di-Me	191044-49-2	Evonik

Table MAT2: Exemplified trade names and CAS-No's of preferred uptake enhancing compounds (b)

Product	Chemical name	Cas No.	Supplier
Emulsogen® EL 400	Ethoxylated Castor Oil with 40 EO	61791-12-6	Clariant
ETOCAS® 10	Ethoxylated Castor Oil with 10 EO	61791-12-6	Croda
Crovol® CR70G	fats and glyceridic oils, vegetable, ethoxylated	70377-91-2	Croda
Synperonic® A3	alcohol ethoxylate (C12/C15-EO3)	68131-39-5	Croda
Synperonic® A7	alcohol ethoxylate (C12/C15-E07)	68131-39-5	Croda
Genapol® X060	alcohol ethoxylate (iso-C13-EO6)	9043-30-5	Clariant
Alkamuls® A	Oleic acid, ethoxylated	9004-96-0	Solvay
Lucramul® HOT 5902	alcohol ethoxylate-propoxylate (C8-PO8/EO6)	64366-70-7	Levaco
Antarox B/848	Butyl alcohol propoxylate/ethoxylate	9038-95-3	Solvay
Tween® 80	Sorbitan monooleate, ethoxylated (20EO)	9005-65-6	Croda
Tween® 85	Sorbitan trioleate, ethoxylated (20EO)	9005-70-3	Croda
Tween® 20	Sorbitan monolaurate, ethoxylated (20EO)	9005-64-5	Croda
Sunflower oil	Triglycerides from different C14-C18 fatty acids, predominantly unsaturated	8001-21-6	
Rapeseed oil	Triglycerides from different C14-C18 fatty acids, predominantly unsaturated	8002-13-9	
Corn oil	Triglycerides from different C14-C18 fatty acids, predominantly unsaturated	8001-30-7	
Soybean oil	Triglycerides from different C14-C18 fatty acids, predominantly unsaturated	8001-22-7	
Rice bran oil	Triglycerides from different C14-C18 fatty acids, predominantly unsaturated	68553-81-1	
Radia® 7129 Crodamol® OP	ethylhexyl palmitate	29806-73-3	Oleon NV, BE Croda, UK
Radia® 7331	ethylhexyl oleate	26399-02-0	Oleon NV, BE
Radia® 7128	ethylhexyl myristate/laurate C12/C14	29806-75-5	Oleon NV, BE
Radia® 7127	ethylhexyl laurate	20292-08-4	Oleon NV, BE
Radia® 7126	ethylhexyl caprylate/caprate C8/10	63321-70-0	Oleon NV, BE
Estol® 1514	iso-propyl myristate	110-27-0	Croda
Radia® 7104	Caprylic, capric triglycerides, neutral vegetable oil	73398-61-5. 65381-09-1	Oleon NV, BE

	T	T	T
Radia® 7732	iso-propyl palmitate	142-91-6	Oleon NV, BE
Crodamol® IPM			Croda, UK
Radia® 7060	methyl oleate	112-62-9	Oleon NV, BE
Radia® 7120	methyl palmitate	112-39-0	Oleon NV, BE
Crodamol® EO	ethyl oleate	111-62-6	Croda
AGNIQUE ME® 18	Rape seed oil methyl ester	67762-38-3.	Clariant
RD-F, Edenor®		85586-25-0	
MESU			BASF
Miglyol 812 N	Glycerides, mixed decanoyl and	65381-09-1	
	octanoly	73398-61-5	
Exxsol® D100	Hydrotreated light distillates	64742-47-8	Exxon Mobil
	(petroleum)		
Solvesso® 200ND	Solvent naphtha (petroleum),	64742-94-5	ExxonMobil
	heavy aromatic, naphthalene		
	depleted		
Kristol® M14	White mineral oil (petroleum),	8042-47-5	Carless
Marcol® 82	C14-C30 branched and linear		ExxonMobil
Ondina® 917			Shell
Exxsol®D130	White mineral oil (petroleum)	64742-46-7	ExxonMobil
Banole® 50			Total
Genera®-12	White mineral oil (petroleum)	72623-86-0	Total
Genera®-9	White mineral oil (petroleum)	97862-82-3	Total

Table MAT3: Exemplified trade names of preferred wash-off reducing materials (d)

Product	Chemical name	Tg	MFFT	Supplier
Atplus® FA	Aqueous styrene acrylic co-	<30°C		Croda
	polymer emulsion dispersion			
Acronal® V215	aqueous acrylate co-polymer	- 43°C		BASF
Acronal® V115	dispersion containing carboxylic	- 58°C		
Acronal® A245	groups.	- 45°C		
Acronal® A240		- 30°C		
Acronal® A225		- 45°C		
Acronal® A145		- 45°C		
Acronal® 500 D	aqueous acrylic co-polymer	- 13°C		BASF
Acronal® S 201	dispersion	- 25°C		
Acronal® DS 3618	aqueous acrylic ester co-	- 40°C		BASF
Acronal® 3612	polymer dispersion	+ 12°C		
Acronal® V 212		- 40°C		
Acronal® DS 3502		+ 4°C		
Acronal® S 400		- 8°C		
Licomer® ADH205	aqueous acrylic ester co-	<30°C		Michelman
Licomer® ADH203	polymer dispersion containing			
	carboxylic groups.			
Primal® CM-160	Aqueous acrylic copolymer			DOW
Primal® CM-330	emulsion polymer			

Axilat® UltraGreen	Aqueous acrylic emulsion	- 15°C	0°C	Synthomer
5500	polymer			
Povol® 26/88	Polyvinyl alcohol			Kuraray

Table MAT4: Exemplified trade names and CAS-No's of preferred compounds (e)

Table I1 Exemplified trade names and CAS-No's of preferred compounds (e) for Insecticide Examples

Product Chemical name Cas No. Supplier  Lucramul PS 29 Poly(oxy-1,2-ethanediyl),. alpha phenylomegahydroxy-, styrenated  Atlox® 4913 methyl methacrylate graft copolymer with polyethylene glycol  Morwet IP Naphthalenesulfonic acid, bis(1- methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate formaldehyde condensate  Cas No. Supplier  Levaco  Levaco  Akzo Croda  Croda  Croda  Synperonic® p003-11-6  Croda  Synperonic® p1-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2-2	Nobel,
phenylomegahydroxy-, styrenated  Atlox® 4913 methyl methacrylate graft copolymer with polyethylene glycol  Morwet IP Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
phenylomegahydroxy-, styrenated  Atlox® 4913 methyl methacrylate graft copolymer with polyethylene glycol  Morwet IP Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pe/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
Atlox® 4913 methyl methacrylate graft copolymer with polyethylene glycol  Morwet IP Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene perfect oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9  Croda  Croda  Croda  Akzo Nobel  Akzo Nobel  Sodium salts  Synperonic® block-copolymer of polyethylene oxide  Synperonic® oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9	Nobel
copolymer with polyethylene glycol  Morwet IP Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pe/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
glycol  Morwet IP  Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene perfect oxide and polypropylene oxide  Morwet D425  Sodium naphthalene sulphonate 577773-56-9  Akzo  Akzo  Akzo  Akzo  Akzo  Akzo	Nobel
Morwet IP  Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pe/F127  Naphthalenesulfonic acid, bis(1-methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene oxide  PE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9  Akzo	Nobel
methylethyl)-, Me derivs., sodium salts  Synperonic® block-copolymer of polyethylene pE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
salts  Synperonic® block-copolymer of polyethylene PE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
Synperonic® block-copolymer of polyethylene 9003-11-6 Croda PE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
PE/F127 oxide and polypropylene oxide  Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
Morwet D425 Sodium naphthalene sulphonate 577773-56-9 Akzo	Nobel
	Nobel
formaldehyde condensate   68425-94-5   Nourvon	1,0001,
9008-63-3	
ATLAS® G Oxirane, methyl-, polymer with 9038-95-3 Croda	
5000 oxirane, monobutyl ether	
Glycerin 56-81-5	
Propylene 1,2-Propylene glycol 57-55-6	
Glycol	
RHODOPOL® Polysaccharide 11138-66-2 Solvay	
23	
Sipernat 22 S synthetic amorphous silica 112926-00-8 Evonik	
(silicon dioxide) 7631-86-9	
Veegum R   Smectite-group minerals   12199-37-0	
SILCOLAPSE® Polydimethylsiloxanes and silica 9016-00-6 BLUESTAR	
426R SILICONES	
SAG® 1572 Dimethyl siloxanes and silicones 63148-62-9 Momentive	
Citric Acid 77-92-9 (anhydrous);	
5949-29-1	
(Monohydrate)	
Proxel® GXL1.2-benzisothiazol-3(2H)-one2634-33-5Arch ChemicKathon®5-chloro-2-methyl-4-isothiazolin-26172-55-4 plusDow	als
CG/ICP 3-one plus 2-methyl-4-	
isothiazolin-3-one 2682-20-4	

Table MAT5: Exemplified trade names and CAS-No's of preferred compounds (e)

Product Chemical name Cas No. Supplier	Product	Chemical name	Cas No.	Supplier
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Morwet® D425	Naphthalene sulphonate formaldehyde condensate Na salt	9008-63-3	New XX
Synperonic® PE/F127	block-copolymer of polyethylene oxide and polypropylene oxide	9003-11-6	Croda
Synperonic® A7	alcohol ethoxylate (C12/C15-EO7)	68131-39-5	Croda
Xanthan	Polysaccharide	11138-66-2	
Proxel® GXL	1.2-benzisothiazol-3(2H)-one	2634-33-5	Arch Chemicals
Kathon® CG/ICP	5-chloro-2-methyl-4-isothiazolin-3- one plus 2-methyl-4-isothiazolin-3- one	26172-55-4 plus 2682-20-4	Dow
Propylene glycol	1,2-Propylene glycol	57-55-6	
SAG® 1572	Dimethyl siloxanes and silicones	63148-62-9	Momentive
Atlox® 4913	methyl methacrylate graft copolymer with polyethylene glycol	119724-54-8	Croda
ATLAS® G 5000	Oxirane, methyl-, polymer with oxirane, monobutyl ether	9038-95-3	Croda
SILCOLAPSE® 454	Polydimethylsiloxanes and silica	9016-00-6	BLUESTAR SILICONES
RHODOPOL® 23	Polysaccharide	11138-66-2	Solvay
ACTICIDE® MBS	Mixture of 2-methyl-4-isothiazolin-3-one (MIT) and 1,2-benzisothiazolin-3-one (BIT) in water	2682-20-4 2634-33-5	Thor GmbH
Sokalan® K 30	Polyvinylpyrrolidone	9003-39-8	BASF
Supragil® WP	Sodium diisopropyl naphthalene sulfonate	1322-93-6	Solvay
Morwet® D-425	Sodium naphthalene sulphonate formaldehyde condensate	577773-56-9 68425-94-5 9008-63-3	Akzo Nobel, Nouryon
Soprophor® 4 D 384	Tristyrylphenol ethoxylate sulfate (16 EO) ammonium salt	119432-41-6	Solvay
Rhodorsil® Antim EP 6703	absorbed polydimethyl siloxane antifoam	unknown	Solvay
Kaolin Tec 1	Aluminiumhydrosilicate	1318-74-7 1332-58-7	Ziegler & Co. GmbH
Sipernat® 22 S	synthetic amorphous silica (silicon dioxide)	112926-00-8 7631-86-9	Evonik
RHODACAL® 60 BE	Calcium- dodecylbenzenesulphonate in 2- Ethylhexanol	26264-06-2 104-76-7	Solvay
Emulsogen® EL 400	Ethoxylated Castor Oil with 40 EO	61791-12-6	Clariant
Solvesso® 200ND	Mixture of aromatic hydrocarbons (C9-C11), naphtalene depleted	64742-94-5	ExxonMobil

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# **FUNGICIDES EXAMPLES**

**Example FN1:** Isoflucypram SC

Table FN1: Recipes FN1, FN2 and FN3.

Component (g/l)		Recipe FN1 reference	Recipe FN2 according to the invention	Recipe FN3 according to the invention
Isoflucypram	(a)	50.0	50.0	50.0
Morwet® D425	(c)	5.0	5.0	5.0
Synperonic® PE/F127	(c)	12.0	12.0	12.0
Etocas® 10-LQ	(b)	0.0	50.0	0.0
Lucramol® HOT5902	(b)	0.0	0.0	50.0
Xanthan	(c)	3.0	3.0	3.0
Proxel® GXL	(c)	1.8	1.8	1.8
Kathon® CG/ICP	(c)	0.8	0.8	0.8
Propylene glycol	(c)	80.0	80.0	80.0
SAG® 1572	(c)	6.0	6.0	6.0
Water (add to 1 litre)	(c)	To volume (~862)	To volume (~812)	To volume (~812)

The method of preparation used was according to Method 1.

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# **Cuticle penetration**

The penetration through apple leaf cuticles was determined according to cuticle penetration test method 12.

Table FN2: Cuticle penetration for isoflucypram SC formulations.

Recipe	Penetration %	Penetration %	Uptake	Uptake
	24h	61h	enhancing	enhancing
			surfactant dose	

			g/ha	surfactant dose in spray liquid %w/v
Recipe FN1 not according to the invention – 10 l/ha	3.1	33.2	0	0
Recipe FN1 not according to the invention – 200 l/ha	4.4	29.6	0	0
Recipe FN2 according to the invention – 10 l/ha	6.8	80.8	50	0.5
Recipe FN2 according to the invention – 200 l/ha	10.3	90.5	50	0.025
Recipe FN3 according to the invention – 10 l/ha	7.9	70.9	50	0.5
Recipe FN3 according to the invention – 200 l/ha	7.3	56.6	50	0.025

Formulations tested at 1.0 l/ha.

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The recipe FN3 illustrative of the invention shows higher penetration of the active ingredient at 10 l/h than at 200 l/ha. The recipe FN2 illustrative of the invention shows high penetration at both 10 l/ha and 200 l/ha, with 200 l/ha a little greater. Both FN3 and FN2 show significantly greater penetration than the reference FN1 at both 10 l/ha and 200 l/ha.

**Example FN2:** Isoflucypram SC

Table FN3: Recipes FN4 and FN5.

Component (g/l)		Recipe FN4 reference	Recipe FN5 according to the invention
Isoflucypram	(a)	50.0	50.0
Morwet® D425	(c)	1.0	1.0
Synperonic® PE/F127	(c)	5.0	5.0
Crovol® CR70G	(b)	0.0	100.0
Xanthan	(c)	3.6	3.6
Proxel® GXL	(c)	1.8	1.8
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60.0	60.0
SAG® 1572	(c)	6.0	6.0
Water (add to 1 litre)	(c)	To volume (~917)	To volume (~817)

The method of preparation used was according to Method 1.

## Greenhouse

Efficacy data

Table FN4: Biological efficacy on PYRNTE

Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN4 reference Efficacy [%]	Recipe FN5 according to the invention Efficacy [%]
200	0.5	25	97	100
200	0.1	5	43	100
200	0.05	2,5	29	97
10	0.5	25	93	100
10	0.1	5	71	100
10	0.05	2,5	71	100

5 Method 11: wheat, protective 1 day before inoculation, evaluation 10 DAT

The results show that recipe FN5 shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN4 without the uptake enhancing additive (b).

## 10 Example FN3: Tebuconazole 20 SC

Table FN5: Recipes FN6 and FN7.

Component (g/l)		Recipe FN6 reference	Recipe FN7 according to the invention
Tebuconazole	(a)	20.0	20.0
Morwet® D425	(c)	2.0	2.0
Synperonic® PE/F127	(c)	5.0	5.0
Crovol® CR70G	(b)	0.0	100
Xanthan	(c)	3.0	3.0
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60.0	60.0
SAG® 1572	(c)	2.0	2.0
Na <sub>2</sub> HPO <sub>4</sub> (Buffer solution pH = 7)	(c)	1.5	1.5
NaH <sub>2</sub> PO <sub>4</sub> (Buffer solution pH = 7)	(c)	0.8	0.8

Water (add to 1 litre)	(c)	To volume (~913)	To volume (~773)
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The method of preparation used was according to Method 1.

#### 5 Greenhouse

Efficacy data

Table FN6: Biological efficacy on PHAKPA

Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN6 reference Efficacy [%]	Recipe FN7 according to the invention Efficacy [%]
200	0.25	5	99	100
200	0.05	1	53	79
200	0.025	0.5	25	19
10	0.25	5	100	100
10	0.05	1	86	100
10	0.025	0.5	55	81

Method 11: soybean, 1 day protective, evaluation 7 dat

The results show that recipe FN7 illustrative of the invention shows higher efficacy at 10 l/ha spray volume than 200 l/ha. Furthermore, recipe Y shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN6 without the uptake enhancing additive (b).

#### Greenhouse

Table FN7: Biological efficacy on PHAKPA

Spray volume I/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN6 reference Efficacy [%]	Recipe FN7 according to the invention Efficacy [%]
200	0.5	10	100	100
200	0.1	5	62	100
200	0.05	1	35	63
10	0.5	10	96	100
10	0.1	5	69	100
10	0.05	1	46	77

Method 11: soybean, 1 day protective, evaluation 7 dat

The results show that recipe FN7 illustrative of the invention shows higher efficacy at 10 l/ha spray volume than 200 l/ha. Furthermore, recipe FN7 shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN6 without the uptake enhancing additive (b).

# Example FN4: Bixafen 20 SC

Table FN8: Recipes FN8 and FN9.

Component (g/l)		Recipe FN8 reference	Recipe FN9 according to the invention
Bixafen	(a)	20.0	20.0
Morwet® D425	(c)	2.0	2.0
Synperonic® PE/F127	(c)	5.0	5.0
Crovol® CR70G	(b)	0.0	140
Xanthan	(c)	3.0	3.0
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60.0	60.0
SAG® 1572	(c)	2.0	2.0
Na <sub>2</sub> HPO <sub>4</sub> (Buffer solution pH = 7)	(c)	1.5	1.5
NaH <sub>2</sub> PO <sub>4</sub> (Buffer solution pH = 7)	(c)	0.8	0.8
Water (add to 1 litre)	(c)	To volume (~913)	To volume (~773)

<sup>5</sup> The method of preparation used was according to Method 1.

## Greenhouse

Table FN9: Biological efficacy on ERYSGH

Spray volume I/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN8 reference Efficacy [%]	Recipe FN9 according to the inventio Efficacy [%]
200	5	100	50	100
200	2.5	50	17	100
200	1.25	25	0	100
200	0.5	10	17	33
10	5	100	17	67
10	2.5	50	0	67

10	1.25	25	0	67
10	0.5	10	0	50

Method 11: barley, 1 day protective, evaluation 7 dat

The results show that recipe FN9 illustrative of the invention shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN8 without the uptake enhancing additive (b).

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# Example FN5: Prothioconazole 20 SC

Table FN10: Recipes FN10 and FN11.

Component (g/l)		Recipe FN10 reference	Recipe FN11 according to the invention
Prothioconazole	(a)	20.0	20.0
Morwet® D425	(c)	2.0	2.0
Synperonic® PE/F127	(c)	5.0	5.0
Crovol® CR70G	(b)	0.0	100
Xanthan	(c)	3.0	3.0
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60.0	60.0
SAG® 1572	(c)	2.0	2.0
Na <sub>2</sub> HPO <sub>4</sub> (Buffer solution pH = 7)	(c)	1.5	1.5
NaH <sub>2</sub> PO <sub>4</sub> (Buffer solution pH = 7)	(c)	0.8	0.8
Water (add to 1 litre)	(c)	To volume (~913)	To volume (~813)

The method of preparation used was according to Method 1.

#### 10 Greenhouse

Table FN11: Biological efficacy on PUCCRT

Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	reference	Recipe FN11 according to the invention Efficacy [%]
200	5	100	78	100

200	2.5	50	33	89
200	1.25	25	22	78
10	5	100	94	100
10	2.5	50	67	100
10	1.25	25	22	94

Method 11: wheat, 1 day protective, evaluation 9 DAT

The results show that recipe FN11 illustrative of the invention shows higher efficacy at 10 l/ha spray volume than 200 l/ha. Furthermore, recipe FN11 shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN10 without the uptake enhancing additive (b).

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Table FN12: Biological efficacy on PHAKPA

Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN10 reference	Recipe FN11 according to
				the invention Efficacy [%]
			Efficacy [%]	Efficacy [70]
200	0.25	5	98	100
200	0.05	1	94	99
200	0.025	0.5	95	95
200	0.005	0.1	58	73
10	0.25	5	100	100
10	0.05	1	98	100
10	0.025	0.5	89	98
10	0.005	0.1	46	92

Method 11: soybean, 2days curative, evaluation 7 days after infestation

The results show that recipe FN11 illustrative of the invention shows higher efficacy at 10 l/ha spray volume than 200 l/ha. Furthermore, recipe FN11 shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN10 without the uptake enhancing additive (b).

# Example FN6: Fluoxapiprolin 5 SC

<u>Table FN13:</u> Recipes FN12 and FN13.

Component (g/l)		Recipe FN12 reference	Recipe FN13 according to the invention
Fluoxapiprolin	(a)	5.0	5.0
Morwet® D425	(c)	1.0	1.0
Synperonic® PE/F127	(c)	5.0	5.0
Crovol® CR70G	(b)	0.0	100.0

Xanthan	(c)	3.6	3.6
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	50.0	50.0
SAG® 1572	(c)	4.0	4.0
Water (add to 1 litre)	(c)	To volume (~930)	To volume (~830)

The method of preparation used was according to Method 1.

#### Greenhouse

Table FN14: Biological efficacy on PHYTIN

Spray volume I/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN12 reference	Recipe FN13 according to the invention Efficacy [%]
200	0.5	2,5	83	96
200	0.2	1	59	95
200	0.1	0.5	61	91
10	0.5	2,5	54	81
10	0.2	1	37	69
10	0.1	0.5	24	53

Method 11: tomato, 1 day preventive, evaluation 7 days after infestation

Recipe FN13 shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN12 without the uptake enhancing additive (b).

# 10 Example FN7: Trifloxystrobin 20 SC

Table FN15: Recipes X and Y.

Component (g/l)		Recipe FN14 reference	Recipe FN15 according to the invention
Trifloxystrobin	(a)	20	20
Morwet® D425	(c)	2	2
Synperonic® PE/F127	(c)	5	5
Crovol® CR70G	(b)		140

Xanthan	(c)	3.0	3.0
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60	60
SAG® 1572	(c)	2	2
Na <sub>2</sub> HPO <sub>4</sub> (Buffer solution pH = 7)	(c)	1.5	1.5
NaH <sub>2</sub> PO <sub>4</sub> (Buffer solution pH = 7)	(c)	0.8	0.8
Water (add to 1 litre)	(c)	To volume (~913)	To volume (~773)

The method of preparation used was according to Method 1.

## Greenhouse

Table FN17: Biological efficacy on PHAKPA

Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Recipe FN14 reference Efficacy [%]	Recipe FN15 according to the invention Efficacy [%]
200	0.5	10	71	94
200	0.1	5	27	84
200	0.05	1	10	56
10	0.5	10	79	98
10	0.1	5	38	83
10	0.05	1	25	73

5 Method 11: soybean, 1 day protective, evaluation 7 dat

The results show that recipe FN15 illustrative of the invention shows higher efficacy at both 200 l/ha and 10 l/ha spray volumes than the reference recipe FN14 without the uptake enhancing additive (b).

# **Example FN8:** Inpyrfluxam 100 SC

## 10 <u>Table FN18:</u> Recipes FN16 and FN17.

Component (g/l)		Recipe FN16 reference	Recipe FN17 according to the invention
Inpyrfluxam	(a)	100.0	100.0
Morwet® D425	(c)	5.0	5.0

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Atlox® 4913	(c)	10.0	10.0
Synperonic® PE/F127	(c)	5.0	5.0
Alkamuls® A	(b)	0.0	80.0
Xanthan	(c)	3.6	3.6
Proxel® GXL	(c)	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8
Propylene glycol	(c)	60.0	60.0
SAG® 1572	(c)	6.0	6.0
Na <sub>2</sub> HPO <sub>4</sub> (Buffer solution pH = 7)	(c)	1.5	1.5
NaH <sub>2</sub> PO <sub>4</sub> (Buffer solution pH = 7)	(c)	0.8	0.8
Water (add to 1 litre)	(c)	To volume (~866)	To volume (~765)

5 The method of preparation used was according to Method 1.

#### **Penetration tests**

The penetration through apple leaf cuticles was determined according to cuticle penetration test method

10 Table FN19: Cuticle penetration for inpyrfluxam SC formulations.

Recipe	Penetration 24h	Penetration 48h	Uptake enhancing surfactant dose g/ha	Uptake enhancing surfactant dose in spray liquid %w/v
Recipe FN16 not according to the invention – 10 l/ha	17.0	46.9	0	0
Recipe FN16 not according to the invention – 200 l/ha	24.0	50.7	0	0
Recipe FN17 according to the invention – 10 l/ha	73.7	97.3	40	0.4
Recipe FN17 according to the invention – 200 l/ha	36.6	57.8	40	0.02

Formulations tested at 0.5 l/ha.

The results show that recipe FN17 illustrative of the invention has a higher cuticle penetration at 10 l/ha than at 200 l/ha, and also greater than the reference recipe FN16 at both 10 l/ha and 200 l/ha.

**Example FN9:** Fungicide Isoflucypram 50 SC

Table FN20: Recipes FN18, FN19, FN20 and FN21.

Component (g/l)		Recipe FN18 reference	Recipe FN19 according to the invention	Recipe FN20 reference	Recipe FN21 according to the invention
Isoflucypram	(a)	50.0	50.0	50.0	50.0
Morwet® D425	(c)	5.0	5.0	5.0	5.0
Synperonic® PE/F127	(c)	12.0	12.0	17.0	17.0
Crodamol® OP	(b)	0.0	50	0.0	0.0
Crodamol® PC DAB	(b)	0.0	0.0	50	0.0
Exxsol® D80	(b)	0.0	0.0	0.0	50
Xanthan	(c)	3.0	3.0	3.0	3.0
Proxel® GXL	(c)	1.5	1.5	1.5	1.5
Kathon® CG/ICP	(c)	0.8	0.8	0.8	0.8
Propylene glycol	(c)	80.0	80.0	80.0	80.0
SAG® 1572	(c)	6.0	6.0	6.0	6.0
Water (add to 1 litre)	(c)	To volume (~862)	To volume (~807)	To volume (~806)	To volume (~806)

The method of preparation used was according to Method 1.

## 5 Penetration tests

The penetration through apple leaf cuticles was determined according to method 12.

Table FN21: Cuticle penetration for isoflucypram SC formulations.

Recipe	Penetration 24h	Penetration 61h	Uptake enhancing surfactant dose g/ha	Uptake enhancing surfactant dose in spray liquid %w/v
Recipe FN18 not according to the invention – 10 l/ha	3.1	33.2	0	0
Recipe FN18 not according to the invention – 200 l/ha	4.4	29.6	0	0
Recipe FN19 according to the invention – 10 l/ha	6.8	61.8	50	0.5
Recipe FN19 according to the invention – 200 l/ha	10.3	44.0	50	0.025

Recipe FN20 according to the	7.9	59.4	50	0.5
invention – 10 l/ha				
Recipe FN20 according to the	7.3	33.4	50	0.025
invention – 200 l/ha				
Recipe FN21 according to the	3.9	50.0	50	0.5
invention – 10 l/ha				
Recipe FN21 according to the	4.3	30.8	50	0.025
invention – 200 l/ha				

The results show that recipes FN19, FN20 and FN21 illustrative of the invention shows greater uptake of the a.i. at 10 L/ha spray volume than at 200 L/ha and also compared to the reference recipe FN18.

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# **INSECTICIDE EXAMPLES**

All formulations/recipes were prepared/tested according to the methods described above.

Example I1 Spirotetramat SC Formulations

Table I2 Recipes Spirotetramat SC Formulations

Component (g/l)	Recipe I1 reference	Recipe I2 according to the invention	Recipe I3 according to the invention	Recipe I4 according to the invention	Recipe 125 according to the invention
Spirotetramat	75	75	75	75	75
Lucramul PS 29	40	40	40	40	40
Glycerin	100	100	100	100	100
Rhodopol 23	3	3	3	3	3
Preventol D7	0.8	0.8	0.8	0.8	0.8
Proxel GXL 20%	1.2	1.2	1.2	1.2	1.2
Silcolapse 426R	1	1	1	1	1
Citric Acid	1	1	1	1	1
Crovol CR 70	-	50	-	-	-
Genapol X060	-	-	50	-	-
Antarox B848	-	-	-	50	-

RME EW 500	-	-	-	-	100
Water (add to 1	fill	fill	Fill	fill	fill
litre)					

## **Cuticle penetration**

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The penetration through apple leaf cuticles was determined according to method 12.

Table I3 Cuticle penetration spirotetramat SC Formulations

Table 13 Cuticle penetration spirotetramat SC Formulations				
Recipe	% cuticular	%	Uptake	Uptake
	penetration	cuticular	enhancing	enhancing
	24h after	penetration	surfactant	surfactant
	application	48h after	dose	dose
		application	g/ha	$\%\mathrm{W/V}$
				(g/100 mL)
Recipe I1 not	3.8	6.3	0	0
according to				
the invention –				
10 l/ha				
Recipe II not	1.6	3.7	0	0
according to				
the invention –				
300 l/ha				
Recipe I2	11.1	17.9	50	0.5
according to				
the invention –				
10 l/ha				
Recipe I2	6.9	12.5	50	0.016
according to				
the invention –				
300 l/ha				

Formulations applied at 1 l/ha.

The results show that recipe I2 illustrative of the invention shows greater penetration of the a.i. at 10 L/ha spray volume than at 200 L/ha and also compared to the reference recipe I1.

Table I4 Cuticle penetration spirotetramat SC Formulations

Tuole 11 Cuticle penetration spirotetramat SC 1 of matations					
Recipe	% cuticular	%	Uptake	Uptake	
	penetration	cuticular	enhancing	enhancing	
	24h after	penetration	surfactant	surfactant	
	application	48h after	dose	dose	
		application	g/ha	$\%_{ m W/V}$	
				(g/100 mL)	
Recipe I1 not	11.4	20.8	0	0	
according to					
the invention –					
10 l/ha					
Recipe I1 not	9.5	23.6	0	0	
according to					

the invention – 200 l/ha				
Recipe I3 according to the invention –		28.0	50	0.5
10 l/ha				
Recipe I3		30.2	50	0.025
according to				
the invention –				
200 l/ha				
Recipe I4	20.5	35.8	50	0.5
according to				
the invention –				
10 l/ha				
Recipe I4	15.8	28.6	50	0.025
according to				
the invention –				
200 l/ha				

Formulations applied at 1 l/ha.

The results show that recipe I3 illustrative of the invention shows greater penetration compared to the reference recipe I1.

The results show that recipe I4 illustrative of the invention shows greater penetration of the a.i. at 10 L/ha spray volume than at 200 L/ha and also compared to the reference recipe I1.

Table I5 Cuticle penetration spirotetramat SC Formulations

Recipe	% cuticular penetration 24h after application	% cuticular penetration 48h after application	Uptake enhancing surfactant dose g/ha	Uptake enhancing surfactant dose in spray liquid g/100 mL
Recipe II not according to the invention – 10 l/ha	3.8	6.3	0	0
Recipe I1 not according to the invention – 300 l/ha	1.6	3.7	0	0
Recipe I25 according to the invention – 10 l/ha	7.2	12.5	50	0.5
Recipe I25 according to the invention – 300 l/ha	2.6	5.5	50	0.025

Formulations applied at 1 l/ha.

The results show that recipe I25 illustrative of the invention shows greater penetration of the a.i. at 10 L/ha spray volume than at 200 L/ha. Also, recipe I25 illustrative of the invention shows greater penetration of the a.i @ 10 L/ha than the standard recipe I1.

# 5 Example I2 /Spidoxamat OD Formulations

Table I6 Recipes /Spidoxamat OD Formulations

Component (g/l) Recipe I5 Recipe I6 Recipe I7 Recipe I8					
Recipe I5	Recipe I6	Recipe I7	Recipe I8		
reference	according	according	according		
	to the	to the	to the		
	invention	invention	invention		
12	12	12	12		
150	150	150	150		
40	40	40	40		
20	20	20	20		
20	20	20	50		
20	20	20	30		
_	50	_	_		
_	_	50	_		
To volume	To volume	To volume	To volume		
	12 150 40 20	Recipe I5 reference         Recipe I6 according to the invention           12         12           150         40           40         40           20         20           -         50           -         -	Recipe I5 reference         Recipe I6 according to the invention         Recipe I7 according to the invention           12         12         12         12           150         150         150         40           40         40         40         40           20         20         20         20           -         50         -           -         50         -		

## **Cuticle penetration**

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The penetration through apple leaf cuticles was determined according to method 12.

Table I7 Cuticle penetration /Spidoxamat OD Formulations

Table 17 Cuticite penetration 75 prodoxamat OB 1 officiations				
Recipe	% cuticular	%	Uptake	Uptake
	penetration	cuticular	enhancing	enhancing
	24h after	penetration	surfactant	surfactant
	application	48h after	dose	dose in
		application	g/ha	spray liquid
			_	$\%\mathrm{W/V}$
				(g/100 mL)
Recipe I5 not	14.0	16.0	0	0
according to				
the invention –				
10 l/ha				
Recipe I5 not	17.4	35.1	0	0
according to				
the invention –				
200 l/ha				

Recipe according the inventio 10 l/ha	I6 to n –	60.8	81.7	50	0.5
Recipe according the inventio 200 l/ha	I6 to n –	58.0	74.7	50	0.025
Recipe according the inventio 10 l/ha	I8 to n –	66.6	80.6	50	0.5
Recipe according the inventio 200 l/ha	I8 to n –	71.7	96.1	50	0.025

Formulations applied at 1 l/ha.

The results show that recipes I6 and I8 illustrative of the invention shows greater penetration compared to the reference recipe I5.

# 5 Example I3 Spirotetramat OD Formulations

Table I8 Recipes Spirotetramat OD Formulations

Component (g/l)	Recipe I9 reference	Recipe I10 according to the invention	Recipe I11 according to the invention
Spirotetramate	75	75	75
Morwet D425	5	5	5
Rhodacal 60/B	5	5	5
Atlox 4914	20	20	20
Soprophor TS/10	50	50	50
Leofat OC-0503M	ı	100	-
Lucramul HOT 5902	-	-	100
SILFOAM SC 1132	0.5	0.5	0.5
Citric Acid	2	2	2
Miglyol 812 N (add to 1 litre)	To volume	To volume	To volume

Example I4 Tetraniliprole SC Formulations

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Table I9 Recipes Tetraniliprole SC Formulations

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Component (g/l)	Recipe I12 reference	Recipe I13	Recipe I14	Recipe I15	Recipe I24
	reference	according to the invention	according to the invention	according to the invention	according to the invention
Tetraniliprole	40.0	40.0	40.0	40.0	40.0
Atlox 4913	40.0	40.0	40.0	40.0	40.0
Morwet IP	10.0	10.0	10.0	10.0	10.0
Synperonic PE/F127	15.0	15.0	15.0	15.0	15.0
Lucramul PS 54	_	-	-	_	_
Atlox 4913	-	-	-	-	-
Citric Acid	1.0	1.0	1.0	1.0	1.0
Rhodopol 23	3.0	3.0	3.0	3.0	3.0
Sipernat 22 S	7.5	7.5	7.5	7.5	7.5
Crovol CR 70	-	50	-	_	_
Genapol X060	-	-	50	_	_
Antarox B848	-	-	-	50	-
RME EW 500	-	-	-	-	100
Kathon CG/ICP	0.8	0.8	0.8	0.8	0.8
Proxel GXL	1.2	1.2	1.2	1.2	1.2
Glycerin	100.0	100.0	100.0	100.0	100.0
SAG1572	1.5	1.5	1.5	1.5	1.5
Water (add to 1 litre)	fill	fill	fill	fill	fill

Example I5 Tetraniliprole OD Formulations

Table I10 Recipes Tetraniliprole OD Formulations

Component (g/l)	Recipe I16 reference	Recipe I17 according to the invention	Recipe I18 according to the invention
Tetraniliprole	40	40	40
Morwet D425	5	5	5
Rhodacal 60/B	60	60	60
Soprophor BSU	40	40	40

Antarox B848	-	100	-
Lucramul HOT 5902	-	-	100
SILFOAM SC 1132	0.5	0.5	0.5
Citric Acid	2	2	2
Crodamol DA (add to 1 litre)	To volume	To volume	To volume

Example I6 Ethiprole + Imidacloprid SC Formulations
Table I11 Recipes Ethiprole + Imidacloprid SC Formulations

Component (g/l)	Recipe I19 reference	Recipe I20 according to the invention	Recipe 121 according to the invention	Recipe 122 according to the invention	Recipe 123 according to the invention
Ethiprole	100	100	100	100	100
Imidacloprid	100	100	100	100	100
Morwet D425	11	11	11	11	11
Atlox 4913	69	69	69	69	69
Atlas G 5000	22	22	22	22	22
Citric Acid	2	2	2	2	2
Rhodopol 23	4	4	4	4	4
Veegum R	6	6	6	6	6
Crovol CR 70	-	50	-	-	-
Genapol X060	-	-	50	-	-
Antarox B848	-	-	-	50	-
RME EW 500	-	-	-	-	100
Kathon CG/ICP	0.8	0.8	0.8	0.8	0.8
Proxel GXL	1.2	1.2	1.2	1.2	1.2
Propylene Glycol	110	110	110	110	110

Silcolapse 426R	3	3	3	3	3
Water (add to 1 litre)	fill	fill	fill	fill	fill

## **Cuticle penetration**

The penetration through apple leaf cuticles was determined according to method 12.

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Table I12 Cuticle penetration of imidacloprid from Ethiprole + Imidacloprid SC Formulations

Recipe	% cuticular penetration 24h after application	% cuticular penetration 48h after application	Uptake enhancing surfactant dose g/ha	Uptake enhancing surfactant dose in spray liquid %w/v (g/100 mL)
Recipe I19 not according to the invention – 10 l/ha	16.0	32.8	0	0
Recipe I19 not according to the invention – 200 l/ha	54.2	72.8	0	0
Recipe I21 according to the invention – 10 l/ha	33.0	58.2	50	0.5
Recipe I21 according to the invention – 200 l/ha	64.4	77.6	50	0.025
Recipe I22 according to the invention – 10 l/ha	45.8	69.1	50	0.5
Recipe I22 according to the invention – 200 l/ha	97.0	106.1	50	0.25

Formulations applied at 1 l/ha.

The results show that recipe I21 illustrative of the invention shows greater penetration of Imidacloprid 48h after application compared to the reference recipe I19.

The results show that recipe I22 illustrative of the invention shows greater penetration of Imidacloprid at comparable water volume use rates than the reference recipe I19.

Table I13 Cuticle penetration of ehtiprole from Ethiprole + Imidacloprid SC Formulations

	o/ · · · · · ·		•	
Recipe	% cuticular	%	Uptake	Uptake
	penetration	cuticular	enhancing	enhancing
	24h after	penetration	surfactant	surfactant
	application	48h after	dose	dose in
		application	g/ha	spray liquid
				%w/v
				(g/100 mL)
Recipe I19 not	2.7	6.9	0	0
according to				
the invention –				
10 l/ha				
Recipe I19 not	1.9	4.6	0	0
according to				
the invention –				
200 l/ha				
Recipe I21	5.7	12.8	50	0.5
according to				
the invention –				
10 l/ha				
Recipe I21	3.1	7.0	50	0.025
according to				
the invention –				
200 l/ha				
Recipe I22	8.2	15.5	50	0.5
according to				
the invention –				
10 l/ha				
Recipe I22	6.3	13.2	50	0.025
according to				
the invention –				
200 l/ha				
	11 1 . 4 1/1			

Formulations applied at 1 l/ha.

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The results show that recipes I21 and I22 illustrative of the invention show greater penetration of Ethiprole at 10 L/ha than at 200 L/ha water volume use rates, and also than the reference recipe I19.

## Example I7 Greenhouse Testing TETRANILIPROLE SC formulations

Test methodology: application onto upperside of pre-infested 1-leaf cabbage plants, BBCH12, for translaminar activity, 2 replicates. Tracksprayer settings: 10 l/ha applied using Lechler's PWM together with nozzle 652.246; 300 l/ha applied using nozzle TeeJet TP8003E.

Table I14 Biological efficacy (in % mortality) against mixed population of *Myzus persicae* on pre-infested cabbage, evaluation 7 days after application

Spray volume I/ha	Rate of a.i. g/ha	Recipe I12 reference	ı <del>-</del>	Recipe I24 according to the invention
300	100	0	30	0
300	20	0	0	0

300	4	0	0	0
10	100	85	100	100
10	20	0	65	50
10	4	0	0	0

The results show that the recipes according to the invention have higher efficacy at 10 l/ha water volume than at 300 l/ha. Additionally, the recipes according to the invention are slightly more efficacious than the recipes not according to the invention.

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Example I8 Greenhouse Testing Imidacloprid + Ethiprole SC200 formulation

Test methodology: application onto upperside of soybeans, BBCH12, for contact and oral uptake, 2 replicates; artificial infestation with 10 Southern green stink bugs nymphs. Tracksprayer settings: 10 l/ha applied using Lechler's PWM together with nozzle 652.246; 300 l/ha applied using nozzle TeeJet TP8003E.

Table I15 Biological efficacy (in % mortality) against mixed population of *Nezara viridula* (N2 nymphs) on soybean, evaluation 3 days after application

Spray volume l/ha	Rate of a.i. g/ha (delivered as recipe I19 not according to the invention)	Rate of adjuvant g/ha	% Mortality
300	20	0	70
300	4	0	20
300	0.8	0	5
10	20	0	80
10	4	0	15
10	0.8	0	5

Spray volume l/ha	Rate of a.i. g/ha (delivered as recipe I19 not according to the invention)	Rate of adjuvant Crovol CR70G g/ha	% Mortality (tank mix adjuvanted SC200 formulation)	Concentration of adjuvant in spray solution (g/l)
300	20	30	100	0.1
300	4	30	30	0.1
300	0.8	30	0	0.1
10	20	30	95	3
10	4	30	85	3
10	0.8	30	30	3

The results show that the addition of Crovol CR70G improves the biological efficacy of the active ingredients, particularly at 10 l/ha water spray volume

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## **HERBICIDE EXAMPLES**

# 10 Example HB1: WG

Table HB1: Recipes HB1, HB2 and HB3.

Component (g/kg)	Recipe HB1 reference	Recipe HB2 according to the invention	Recipe HB3 according to the invention
Triafamone (a)	200	200	200
Supragil WP (c)	50	50	50
Morwet D 425 (c)	200	200	200
Sokalan K 30 (c)	20	20	20
Crovol 70 G (b)	0	150	0
Genapol X 60 (b)	0	0	150
Rhodorsil Antim EP 6703 (c)	40	40	40
Sipernat 50 S (c)	100	100	100
Kaolin Tec 1	390	240	240

Dose rate: 0.25 kg/ha

The method of preparation used was according to Method 2.

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## **Cuticle penetration**

The penetration through apple leaf cuticles was determined according to method 12.

**Table HB2:** Cuticle penetration for HB1, HB2 and HB3.

Recipe	%	%	Uptake	Uptake
	cuticular	cuticular	enhancing	enhancing

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	penetration 24h after application	penetration 48h after application	surfactant dose g/ha	surfactant dose in spray liquid %w/v
Recipe HB1 not according to the invention – 10 l/ha	0.2	0.8	0	0
Recipe HB1 not according to the invention - 200 l/ha	1.3	4,9	0	0
Recipe HB2 according to the invention – 10 l/ha	2.1	12.7	37.5	0.4
Recipe HB2 according to the invention – 200 l/ha	4.4	12.8	37.5	0.02
Recipe HB 3according to the invention – 10 l/ha	2.3	5.8	37.5	0.4
Recipe HB3 according to the invention – 200 l/ha	5.1	12.4	37.5	0.02

Formulations applied at 0.25 kg/ha.

The results show that recipe HB2 illustrative of the invention shows greater penetration of the a.i.

Triafamone at 10 L/ha spray volume than at 200 L/ha and also compared to the reference recipe HB1. Also recipe HB3 shows better penetration at low spray volume compared to the reference recipe HB1 at low spray volume.

**BOP – CUPET "Uptake" tests** 

The penetration through apple leaf cuticles was determined according to method described as cuticle penetration test.

Example HB2a: SC

5 **Table HB3:** Recipes HB4, HB5 and HB6.

Component (g/kg)	Recipe HB4 reference	Recipe HB5 according to the invention	Recipe HB6 according to the invention
TEMBOTRIONE (a)	100.00	100.00	100.00
ISOXADIFEN-ETHYL (a)	50.00	50.00	50.00
ATLOX G 5000 (c)	12.20	12.20	12.20
SYNPERONIC A7 (c)	12.20	12.20	12.20
ATLOX 4913 (c)	36.60	36.60	36.60
Synperonic PE/F 127 (c)	16.00	16.00	16.00
1,2-PROPYLENE GLYCOL (c)	61.00	61.00	61.00
SILICOLAPSE 454 (c)	2.44	2.44	2.44
ACTICIDE MBS (c)	2.44	2.44	2.44
Genapol X0 60 (b)	0.00	100.00	0.00
Tween 80 (b)	0.00	0.00	100.00
RHODOPOL 23 (c)	2.20	2.20	2.20
WATER (add to 1 litre)	to volume	to volume	to volume

The method of preparation used was according to Method 1.

Example HB2b: SC

Table HB4: Recipes HB7, HB8 and HB9.

Component (g/kg)	Recipe HB7 according to the invention	Recipe HB8 according to the invention	Recipe HB9 according to the invention
TEMBOTRIONE (a)	100.00	100.00	100.00
ISOXADIFEN-ETHYL (a)	50.00	50.00	50.00
ATLOX G 5000 (c)	12.20	12.20	12.20
SYNPERONIC A7 (c)	12.20	12.20	12.20
ATLOX 4913 (c)	36.60	36.60	36.60
Synperonic PE/F 127 (c)	16.00	16.00	16.00
1,2-PROPYLENE GLYCOL (c)	61.00	61.00	61.00

SILICOLAPSE 454 (c)	2.44	2.44	2.44
ACTICIDE MBS (c)	2.44	2.44	2.44
Triton CG-50 (b)	100,00	0,00	0,00
Sophorphor 796/P (b)	0,00	100,00	0,00
Disflamoll TOF (b)	0,00	0,00	140,00
RHODOPOL 23 (c)	2.20	2.20	2.20
WATER (add to 1 litre)	to volume	to volume	to volume

The method of preparation used was according to Method 1.

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Table HB5: Cuticle penetration for HB4-HB9 (Tembotrione)

Recipe	% cuticular penetration 20h after application	% cuticular penetration 53h after application	Uptake enhancing surfactant dose g/ha	Uptake enhancing surfactant dose in spray liquid %w/v
Recipe HB4 not according to the invention – 10 l/ha	4.7	10.0	0	0
Recipe HB4 not according to the invention – 200 l/ha	3.3	6.4	0	0
Recipe HB5 according to the invention – 10 l/ha	11.8	23.6	100	1
Recipe HB5 according to the invention – 200 l/ha	2.1	6.2	100	0,05
Recipe HB6 according to the invention – 10 l/ha	26.8	59.8	100	1
Recipe HB6 according to the invention – 200 l/ha	5.0	8.0	100	00,5
Recipe HB7 according to the invention –	14.6	32.7	100	1

10 l/ha				
Recipe HB7 according to the invention – 200 l/ha	8.3	19.3	100	0,05
Recipe HB8 according to the invention – 10 l/ha	15.0	29.7	100	1
Recipe HB8 according to the invention – 200 l/ha	6.9	16.2	100	0,05
Recipe HB9 according to the invention – 10 l/ha	14.7	28.4	140	1,4
Recipe HB9 according to the invention – 200 l/ha	8.4	13.4	140	0,07

Formulations applied at 1 L/ha.

The results show that recipes HB5-HB9 illustrative of the invention show greater penetration of the Tembotrione at 10 L/ha spray volume compared to the reference recipe HB4 and greater than at 200 L/ha.

# Greenhouse

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Efficacy data

**Table HB6a:** Additive dose g/ha for each treatment.

HB4 reference				
Spray volume l/ha	Rate of SC applied l/ha	Rate of a.i. g/ha	Additive dose g/ha	Additive dose %w/v
200	1	50 +100	100	0
10	1	50+100	100	0

Table HB6b: Additive dose g/ha for each treatment

HB5, HB6		
and HB7		

Spray volume l/ha	Rate of SC applied l/ha	Rate of a.i. g/ha	Additive dose g/ha	Additive dose %w/v
200	1	50 +100	100	0,05
10	1	50+100	100	1

# 5 **Table HB7a:** Biological efficacy on *Echinochloa crus-galli (ECHCG)*.

ECHCG	HB4	HB5	НВ6	HB7
2001/ha	96	96	96	97
10 l/ha	80	93	97	96

**Table HB7b:** Biological efficacy on *Alopecurus myosuroides (ALOMY)*.

ALOMY	HB4	HB5	HB6	HB7
200l/ha	60	78	88	20
10 l/ha	8	73	90	90

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**Table HB7c:** Biological efficacy on *Amaranthus retroflexus (AMARE)*.

AMARE	HB4	HB5	НВ6	HB7
2001/ha	98	100	100	98
10 l/ha	48	100	100	100

Table HB7d: Biological efficacy on Abutilon theophrasti (ABUTH).

ABUTH	HB4	HB5	НВ6	HB7
200l/ha	88	96	90	90
10 l/ha	60	98	90	88

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The results in **table HB7a-d** show that recipes **HB5**, **HB6** and **HB7** illustrative of the invention show greater or same efficacy at 10 L/ha spray volume as at 200 L/ha on different weeds and also compared to the reference recipe **HB4**.

20 Example HB3: OD

Table HB8: Recipes HB10, HB11, HB12 and HB13.

Component (g/kg)	Recipe HB10 reference	Recipe HB11 according to the invention	Recipe HB12 according to the invention	Recipe HB13 according to the invention
THIENCARBAZONE- METHYL (a)	10	10	10	10
MEFENPYR-DIETHYL (a)	60	60	60	60
RAPESEED OIL METHYL ESTER (b)	0	200	0	0
GENAPOL X 090 (b)	0	0	200	0
DISFLAMOLL TOF (b)	0	0	0	200
BENTONE 34 (c)	20	20	20	20
CALSOGEN AR 100 ND (c)	80	80	80	80
EMULSOGEN EL400 (c)	60	60	60	60
PROPYLENE CARBONATE (c)	2	2	2	2
SILICOLAPSE 482	1,5	1,5	1,5	1,5
SODIUM CARBONATE (c)	2	2	2	2
SOLVESSO 200ND (add to 1 litre)	to volume	to volume	to volume	to volume

The method of preparation used was according to Method 4.

# 5 **Table HB9a:** Additive dose g/ha for each treatment

HB10 reference				
Spray volume l/ha	Rate of SC applied I/ha	Rate of a.i. g/ha	Additive dose g/ha	Additive dose In spray liquid %w/v
200	1,5	15+90	0	0
10	1,5	15+90	0	0
200	0,75	7,5+45	0	0
10	0,75	7,5+45	0	0

Table HB9b: Additive dose g/ha for each treatment

HB11, HB12 and HB13				
Spray volume l/ha	Rate of OD applied I/ha	Rate of a.i. g/ha	Additive dose g/ha	Additive dose In spray liquid %w/v
200	1,5	15+90	300	0.15
10	1,5	15+90	300	3
200	0,75	7,5+45	150	0,075
10	0,75	7,5+45	150	1,5

## Table HB10a: Biological efficacy on Setaria viridis (SETVI) @7,5g TCM

SETVI	HB10	HB11	HB12	HB13
200 l/ha	90	95	90	90
10 l/ha	80	90	90	90

# Table HB10b: Biological efficacy on Avena fatua (AVEFA) @7,5g TCM

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AVEFA	HB10	HB11	HB12	HB13
200 l/ha	20	80	50	40
10 l/ha	40	80	80	60

#### Table HB10c: Biological efficacy on Hordeum murinum (HORMU) @7,5g TCM

HORMU	HB10	HB11	HB12	HB13
200 l/ha	20	70	20	30
10 l/ha	40	80	80	60

# 10 Table HB10d: Biological efficacy on Pharbitis purpurea (PHBPU) @15g TCM

PHBPU	HB10	HB11	HB12	HB13
200 l/ha	90	90	90	60
10 l/ha	70	90	90	90

Table HB10e: Biological efficacy on Abutilon theophrasti (ABUTH) @15g TCM

ABUTH	HB10	HB11	HB12	HB13
200 l/ha	90	80	90	60
10 l/ha	40	90	80	85

The results in table **HB10a-e** show that recipes **HB11**, **HB12** and **HB13** illustrative of the invention show greater or same efficacy at 10 L/ha spray volume as at 200 L/ha on different weeds and also compared to the reference recipe **HB10**.

#### Patent claims

- 1. Agrochemical formulation comprising
- a) One or more active ingredients.
  - b) One or more uptake enhancer,
  - c) Other formulants,
  - d) one or more carriers to volume,
- wherein b) is present in 5 to 200 g/l.
  - 2. Agrochemical formulation according to claim 1, wherein b) is selected from the group comprising
  - sunflower oil, rapeseed oil, corn oil, soybean oil, rice bran oil, olive oil;
- ethylhexyl oleate, ethylhexyl palmitate, ethylhexyl myristate/laurate, ethylhexyl laurate, ethylhexyl caprylate/caprate, iso-propyl myristate, iso-propyl palmitate, methyl oleate, methyl palmitate, ethyl oleate, rape seed oil methyl ester, soybean oil methyl ester, rice bran oil methyl ester,
  - Mineral oils and white oil.
  - tris-alkyl-phosphate esters, preferably tris (2-ethylhexyl) phosphate,
- 20 The uptake enhancer may also be selected from the following group of compounds:
  - i. ethoxylated branched alcohols with 2-20 EO units;
  - ii. methyl end-capped, ethoxylated branched alcohols comprising 2-20 EO units;
  - iii. ethoxylated coconut alcohols comprising 2-20 EO units;
  - iv. ethoxylated C12/15 alcohols comprising 2-20 EO units;
- v. propoxy-ethoxylated alcohols, branched or linear,
  - vi. propoxy-ethoxylated fatty acids, Me end-capped,
  - vii. alkyl ether citrate surfactants
  - viii. ethoxylated mono- or diesters of glycerine comprising fatty acids with 8-18 carbon atoms and an average of 10-40 EO units;
- ix. castor oil ethoxylates comprising an average of 5-40 EO units,
  - x. ethoxylated oleic acid comprising 2-20 EO units;
  - xi. ethoxylated sorbitan fatty acid esters comprising fatty acids with 8-18 carbon atoms and an average of 10-50 EO units.
- 35 3. Agrochemical formulation according to claim 1 or 2, wherein b) selected selected from the group comprising tris (2-ethylhexyl) phosphate, rapeseed oil methyl esters, ethoxylated coconut

alcohols, ethoxylated branched alcohols, propoxy-ethoxylated alcohols, ethoxylated mono- or diesters of glycerine comprising fatty acids with 8-18 carbon atoms and an average of 10-40 EO units, ethoxylated oleic acid and mineral oils.

- 4. Agrochemical formulation according to one or more of claims 1 to 3, wherein a) is present in an amount from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l.
  - 5. Agrochemical formulation according to one or more of claims 1 to 4, wherein b) is present in 5 to 200 g/l, preferably from 10 to 150 g/l, and most preferred from 10 to 130 g/l.
- Agrochemical formulation according to one or more of claims 1 to 5, wherein c) is present in 4 to 250 g/l, preferably from 8 to 120 g/l, and most preferred from 10 to 80 g/l.
  - 7. Agrochemical formulation according to one or more of claims 1 to 6, wherein the active ingredient is selected from the group consisting of bixafen, fluoxapiprolin, inpyrfluxam, isoflucypram, prothioconazole, tebuconazole, trifloxystrobin, ethiprole, imidacloprid, spidoxamat, spirotetramat, tetraniliprole, thiencarbazone-methyl, triafamone, isoxadifen-ethyl and mefenpyr-diethyl.
  - 8. Agrochemical formulation according to one or more of claims 1 to 7, wherein component c) comprises at least one non-ionic surfactant and / or ionic surfactant (c1), one rheological modifier (c2), and one antifoam substance (c3) and at least one antifreeze agent (c4).
  - 9. Agrochemical formulation according to claim any one of claims 1 to 8, comprising the components a) to e) in the following amounts
    - b) from 5 to 300 g/l, preferably from 10 to 280 g/l, and most preferred from 10 to 250 g/l,
    - b) from 5 to 250 g/l, preferably from 20 to 200 g/l, and most preferred from 30 to 150 g/l,
    - c1) from 4 to 250 g/l, preferably from 8 to 120 g/l, and most preferred from 10 to 80 g/l,
    - c2) from 0 to 60 g/l, preferably from 1 to 20 g/l, and most preferred from 2 to 10 g/l,
    - c3) from 0 to 30 g/l, preferably from 0.5 to 20 g/l, and most preferred from 1 to 12 g/l,
    - c4) from 0 to 200 g/l, preferably from 5 to 150 g/l, and most preferred from 10 to 120 g/l,
    - c5) from 0 to 200 g/l, preferably from 0.1 to 120 g/l, and most preferred from 0.5 to 80 g/l,
- d) carrier to volume.

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10. Agrochemical composition according to one or more claims 1 to 9, wherein the formulation is applied at a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, more preferably 5 and 15 l/ha.

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- 11. Method of applying an agrochemical composition according to one or more claims 1 to 10 onto crops, wherein wherein the formulation is applied at a spray volume of between 1 and 20 l/ha, preferably 2 and 15 l/ha, and more preferably 5 and 15 l/ha.
- 5 12. Method according to claim 11, wherein the applied amount of a) to the crop is between 2 and 150 g/ha, preferably between 5 and 120 g/ha, and more preferred between 20 and 200 g/ha.
  - 13. Method according to claim 11 or 12, wherein the uptake enhancer b) is preferably applied from 5 g/ha to 150 g/ha, more preferably from 7.5 g/ha to 100 g/ha, and most preferred from 10 g/ha to 60 g/ha.

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- 14. Method according to one or more of claims 11 to 13, wherein the formulation is applied on plants or crops with textured leaf surfaces.
- 15. Use of an agrochemical composition according to one or more of the claims 1 to 10 in application of the agrochemical compounds for controlling harmful organisms, wherein the composition is applied by a UAV, UGV, PWM.
- 16. Method of controlling harmful organisms, comprising the contacting of the harmful organisms, their habitat, their hosts, such as plants and seed, and the soil, the area and the environment in which they grow or could grow, but also of materials, plants, seeds, soil, surfaces or spaces which are to be protected from attack or infestation by organisms that are harmful to plants, with an effective amount of the formulations according to one or more of Claims 1 to 10, characterized in that the composition is applied by a UAV, UGV, PWM.

#### INTERNATIONAL SEARCH REPORT

International application No PCT/EP2020/062918

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

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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

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

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X Further documents are listed in the continuation of Box C.	X See patent family annex.
* Special categories of cited documents:  "A" document defining the general state of the art which is not considered to be of particular relevance  "E" earlier application or patent but published on or after the international filing date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means  "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  "&" document member of the same patent family
Date of the actual completion of the international search  16 July 2020	Date of mailing of the international search report $29/07/2020$
Name and mailing address of the ISA/  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040,  Fax: (+31-70) 340-3016	Authorized officer  Galley, Carl

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