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(54) **Titre : SUSPENSIONS HUILEUSES DE SULFONYLUREES ET DE COMBINAISONS AGROCHIMIQUES**
(54) **Title: OIL SUSPENSIONS OF SULPHONYLUREAS AND AGROCHEMICAL COMBINATIONS**

(57) **Abrégé/Abstract:**

An agrochemical formulation in the form of an oil suspension characterised in that it contains as essential elements of the formulation (percentages by weight related to the total weight of the formulation) at least; a herbicide of the sulphonylurea type at a concentration of 0.5-50%, preferably 2-30%, a paraffin mineral oil at a concentration of 10-75%, preferably without the existence of any other type of mineral or vegetable oil in the formulation and the concentration of mineral oil being 40-60%, an organomodified silane compound at a concentration of 5-40%, preferably 10-25%, with the existence of other coformulants until reaching 100% by weight of the formulation.



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(54) Title: OIL SUSPENSIONS OF SULPHONYLUREAS AND AGROCHEMICAL COMBINATIONS

Figure 1



(57) Abstract: An agrochemical formulation in the form of an oil suspension characterised in that it contains as essential elements of the formulation (percentages by weight related to the total weight of the formulation) at least; a herbicide of the sulphonylurea type at a concentration of 0.5-50%, preferably 2-30%, a paraffin mineral oil at a concentration of 10-75%, preferably without the existence of any other type of mineral or vegetable oil in the formulation and the concentration of mineral oil being 40-60%, an organomodified silane compound at a concentration of 5-40%, preferably 10-25%, with the existence of other coformulants until reaching 100% by weight of the formulation.

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5 It is understood that throughout this patent, the term sulphonylureas also includes the so-called sulphonamides. These two terms are occasionally used interchangeably or even confused: we would like to note that we always refer to both types with the term "sulphonylureas".

10 Non-restrictive examples of sulphonylureas object of the invention, are: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron, ethoxysulfuron, flazasulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron; as well as active
15 herbicide derivatives (such as methyl, ethyl or alkyl ethers or esters) and salts thereof.

They are easily degradable, especially in aqueous mediums.

It is known that SUs can be formulated in oil medium in order to improve their stability.

Since it is a very important requirement of the agrochemical sector, there are numerous patents and articles relating to the same problem indicated in this invention, but they solve it by
20 other means.

Some documents demonstrate that their formulation as oil suspensions improves SU stability, particularly when used in combination with urea. However, the stability of said formulations is far from optimal.

Our formulations, even without urea, show adequate stability. None of the tests
25 performed with different products in the market have provided any formulation as stable as those proposed (e.g. Examples 1, A and B) since, despite the fact that adequate product stability and homogeneity can be obtained in laboratory conditions and with skilled handling, it is true that the products mentioned must be handled, amongst others, by farmers in their own facilities, and real usage conditions may therefore be very different from the conditions in which
30 the laboratory tests were performed, causing a great reduction in product stability/homogeneity, and therefore a great reduction in product qualities: this relates essentially to the need of strong stirring and the necessary industrial application of the formulation (i.e. coformulant availability at the industrial level, their price realistically allowing industrial use).

Take as an example the photograph in Figure 1, that shows a sample of the leading
35 formulation of sulphonylurea nicosulfuron that in the market Motivell® (BASF), where there is an evident separation of the phases when left to settle for some days (15 days at room temperature and 8 at 54°C).

Errors and omissions excepted, neither the applicant or the inventors know any commercially viable product that offers a stability such as the one proposed, neither, in fact,
40 have they found anything at the commercial level or published in scientific articles or registered with stability characteristics such as those obtained by the product object of the present invention.

Some patents that describe different solutions to the aforementioned problem are:

5 WO2007/042152 (Vermeer et al., Bayer), wherein an SU is combined with pyrethroids, with the use of cyclohexanone (which is very inflammable and is not used in this invention).

DE10258216 (anonymous, Bayer), wherein a sulphosuccinate is necessarily used (we do not use sulphosuccinates in our invention).

10 US2006/0276337 (Sterne et al, Bayer) where it is shown in [0415] that the preferred embodiment required the use of a sulphosuccinate, as demonstrated in the examples and deduced from the description (we do not use sulphosuccinates in our invention)

WO2007/028517 (Bailo-Schleier-Macher et al., Bayer) where an oil suspension is used to fight against the eggs and nymphs of the white fly, being applicable only in neonicotinoids (not sulphonylureas)

15 WO2007/042138 (Schnable et al., Bayer) where polycation salts of certain solubility in water are used (not used in our invention)

EP554015 (Kanbayashi et al., ISK), where the use of sulphonylureas in oil suspensions is protected when combining an emulsifier, an oil and urea.

20 There are other patents dealing essentially with the type of oil used in the suspension, but none of them shows the preferred use of a paraffin oil with an organomodified silane derivative. For a better embodiment, we recommend the preferred use only of paraffin oils -or at least mixtures containing at least 10% of these-, since these paraffin oils in combination with the organomodified silane derivatives show greater stability than the rest when used according to our invention.

25

Description of the invention

The invention propose refers essentially to the use of organic derivatives of silane (or siloxane), such as trisiloxane polyethers represented by several types of Break-Thru®
30 compounds (e.g. those with CAS No. [67674-67-3], [134180-76-0], [27306-78-1]) in oil suspensions of sulphonylureas. The preferred concentrations with 5-40% or even better with 10-25%.

The amount of AI (alone or combined AIs) must not be less than a minimum amount for herbicide efficacy (estimated at 0.5%) and not more than 50% in order to avoid problems of
35 formulation stability, although logic dictates that we should tend as much as possible not to approach the upper limit, since the handling of these formulations is difficult due to their great viscosity and density, it being preferable not to use more than 30% in AI or a mixture of AIs in suspended solid form.

40 The presence of a paraffin mineral oil is essential for our invention, at an estimated minimum of 10%.

The paraffin oil may be mixed with other mineral oils such as those mentioned above (e.g. naphtha) or with vegetable oils, although the use of only paraffin oil is preferred, in a concentration of not more than 75%, in order to include in the formulation the necessary coformulants to aid emulsification, crystal dispersion, modification of viscosity, etc. It is very

5 convenient that no coformulants negatively affect the degradation of the sulphonylureas in the formulation. This is easily verified by performing the formulation at a certain concentration, leaving it in an oven at 35°C for two weeks and verifying how much sulphonylurea has degraded. A value above 10% is completely unacceptable.

10 The most adequate concentrations of oil base are 40-60%, in order to make adequate room for the coformulants and AIs.

Sulphonylureas (or sulphonamides) may be used in our formulations alone or combined with other sulphonylureas. One or several sulphonylureas can be used at the same time, and they can also be mixed with other agrochemical agents in the general sense (such as insecticides, other herbicides, fungicides, plant hormones, etc.), the latter alone or in
15 combination and also dispersed in the oil phase or dissolved (totally or partially). The invention contemplates the case that the sulphonylureas are partially dissolved in the oil or even totally dissolved in the case of a second sulphonylurea combined with another that is in suspension.

It is possible, and occasionally convenient, that the AIs that are not sulphonylureas are soluble (or partially soluble) in the oil phase, in which case we can have superemulsions.

20 We can also have ZC formulations (suspension of capsules + suspension concentrate), by means of the combination of microcapsule formulations.

The preferred combinations are of different herbicides with different modes of action, herbicide/insecticide, herbicide/fungicide.

The following combinations are especially preferred:

25 - At least two sulphonylureas, preferably: metsulfuron with tribenuron, metsulfuron with thifensulfuron, nicosulfuron with rimsulfuron;

- Any sulphonylurea with one of the following agrochemicals: fluroxypyr, diflufenican, lactofen, mesotrione, sulcotrione, flurochloridone, metazachlor, clomazone (or a mixture of clomazone with metazachlor), pyrethroids (preferably alpha-cypermethrin, lambda-cyhalothrin, permethrin, resmethrin, allethrin), triazole fungicides (preferably tebuconazole, propiconazole,
30 triadimenol), glyphosate (in salt form or more preferably as an acid); gluphosinate (in salt form or more preferably as an acid)

- Mixtures of sulphonylureas according to 3 a. combined with agrochemicals according to 3 b.

35 It is perfectly possible to perform these combinations by grinding the insoluble AIs in the oil phase at the same time as grinding the sulphonylurea(s), or solubilising said AIs in the oil phase, if applicable.

Brief description of the drawings

40

Figure 1 shows a sample of Motivell® (BASF), the leading sulphonylurea nicosulfuron formulation in the market, which shows evident separation of phases when left to rest for a few days versus a sample of the formulation proposed by the applicant and object of the present

- 5 invention, which maintained in the same conditions as the reference sample, shows optimal product homogeneity.

Description of a preferred embodiment of the invention

- 10 The state of the art shows that oil suspensions of sulphonylureas are performed preferably in vegetable oils (e.g., coconut oil, sunflower oil) or in aromatic mineral oils (of the Solvesso[®], light or heavy naphtha type).

Since commercial products with said oil composition do not result in adequate stability, the inventors have tried another type of oil: Isopar[®] and Marcol[®], that is, paraffin oil.

- 15 The amount of oil to be used will depend on the active ingredient content -it is understood that the AI can be one or a combination of different sulphonylureas or even combinations of sulphonylureas with other AIs, preferably with herbicidal action, wither an insecticide or fungicide or mixtures thereof, the use of AIs with herbicidal activity being preferred.

- 20 Since it is more difficult to formulate a composition with a high AI concentration, the examples refer to this situation, since applying the invention to lower concentrations can be achieved simply by proportionally substituting the rest of coformulants for the difference in the amount of AI used with respect to the examples.

- 25 The oil phase must be formed by a paraffin oil in an amount of 40-60% (we always refer to % by weight/weight related to the total weight of the formulation).

For example, for an oil suspension with a 4% AI content (or total IA content), a suitable percentage of oil is approximately 43-67%, for about 20% of AI(s) a suitable oil content is 38-63%.

- 30 The commercial products corresponding to this oil are representatively designated by those of Exxon, that is, any of the Isopar[®] brand (comprising several paraffin petroleum fractions with different boiling points).

Both Isopar[®] M, and "V" or "L" or "K" provide good results, Isopar[®] M being extraordinarily adequate, as well as those with greater boiling points commercialised with the brand Marcol[®].

- 35 The invention proposed works with other oils, both vegetable and mineral, as long as there is 10% of paraffin oil.

- 40 The properties of product and formulation and emulsion stability (not expected according to the state of the art for a formulation lacking sulphosuccinates) together with acceptable biological activity as well as the ease of the milling step is not achieved with the (combined) use of other non-paraffin oils, but still solves partial problems mentioned in this invention.

That is, the best embodiment of the invention is with paraffin oils, but a person skilled in the art may still achieve better formulations than those of the state of the art with non-paraffin

5 oils and without mixing them with paraffin oils, but we insist, far from the extraordinary properties gained with the use of paraffin oils claimed herein.

However, we have not achieved formulations with acceptable stability without the use of organosilane derivatives of the Break-Thru[®] type (mainly trisiloxane polyethers with or without adjuvants) using this trade name since for a person skilled in the art it is clear what derivatives
10 we refer to by naming a commercial product that representative of them all (much clearer for a person skilled in the art than a confusing name that may lead to not finding the product to be used in catalogues).

Vegetable oils that may be used are the usual ones in agriculture (castor oil, sunflower oil, coconut oil, corn, rape oil, etc), and mineral oils that can be used are all those offered by
15 Exxon[®] for use in agriculture, particularly naphtha oils ((Solvesso[®] 100, 150, 200, etc –ND ("naphthalene depleted") or not) and pentanes, heptanes, etc.

It is also particularly surprising that mixtures in which paraffin oil is present in at least
20 20% (with respect to total solvent oil) with other oils (particularly of the Solvesso[®] type or vegetable oils –and mixtures thereof) also show stability above that of oil suspensions in the state of the art.

A compound we have observed as very interesting in preventing phase separation in the formulation and the emulsion are organomodified siloxanes, of the commercial type Break-
25 Thru[®] (e.g. S 240, S 278).

It is especially surprising that these compounds are not described as dispersing or emulsifying agents (which is the function they perform in our invention before being applied in the field), but as wetting agents (that is, so that the drops of water extend over the leaves and fruits - or insects- treated). The recommendations of the manufacturer of these organomodified
30 silanes prevents a person skilled in the art from thinking of using them to produce a formulation with improved stability properties (no oil separation), but exactly the opposite: a person skilled in the art would avoid using it for any purpose other than increasing the wetting effect.

Preferred silanes do not have to be restricted exclusively to the trisiloxane ether type: A person skilled in the art knows that modifications without excessively affecting said structure are
35 very probably also suitable for use according to the present invention. This principle of chemical equivalents is applicable to the other coformulants.

A minimum content in silanes (siloxanes) according to our invention is of 5%, and it is recommended that it is present at 5-40%, preferably at 10-25%.

With the use of organomodified silanes we do not only achieve the main result sought
40 by this invention (formulation stability) but also other important problems such as biological activity and AI stability.

We can understand that biological activity is improved due to the large amount of an agent that reduces the surface tension of water, however, why organomodified silanes prove to be products in which the stability of sulphonylureas is higher is a matter that we can only think

5 to be due to the high hydrophobic environment they produce, because for some unknown reason they prevent sulphonylurea hydrolysis by means of some chemical process.

We have found that formulations with organomodified silanes exhibit similar stability to that obtained with known stabilisers such as urea. However, nothing prevents the combination of products of the Break-Thru[®] chemical type with urea in order to simultaneously obtain an
10 unexpected double effect an increase in suspension and emulsion stability; and also in AI by double effect. (It is understood throughout this document that AI may refer to mixtures of different active ingredients, nevertheless it is understood that the improvement in chemical stability of the AI refers exclusively to sulphonylurea(s), which is precisely the labile type of AI).

Another compound that facilitates product stability is a viscosity modifier of the
15 bentonite type.

Although in principle any viscosity modifier may be used, specifically all chemical equivalents of bentonite (bentone) [that is, clays, sepiolites, attapulgites, zeolites, talcs, silicates, aluminium silicates, etc. and mixtures thereof], we have observed that those with the chemical structure of the product "Bentone[®]" (and its different versions) are the ones that work
20 best (effectively increasing viscosity with results in emulsion stability and especially in suspension stability) the product with the best results within the range being Bentone[®] SD-1.

Its use in our invention is aimed at increasing viscosity.

The amount used will depend on the viscosity (high, adequate or low) of the formulation according to the other coformulants chosen according to the invention.

25 It should be within the range of 0-20%, preferably 0-5%.

Bentonite has been described in suspensions of sulphonylureas; but with emulsifiers/dispersing agents other than those of this invention, and to modify viscosity in a completely different medium (different oil and coformulants).

Since the effect depends on the medium in which the viscosity modifier is used, it is not
30 in the least evident or predictable that bentonite would have a beneficial effect in preventing the oil from separating in our formulation and moreover, to aid towards a good suspension and emulsion.

It is even less obvious that the use of bentonite is suitable in paraffin oils and with the expected effect.

35 Nevertheless, the main effect for the non-separation and stability of the AI is given by the organosilane derivative in the paraffin medium.

On the other hand, we have seen that a greater amount of AI does not necessarily imply that the amount of bentonite must be increased, in contrast to what a person skilled in the art may think. Moreover, we have verified that bentonite amounts of 2-5% are sufficient to
40 maintain suitable viscosity for AI concentrations of 2-50%.

Greater amounts of AI (>50%) do not result in formulation properties –positive results in FAO tests- as good as those object of this invention (not more than 50% AI content, or preferably not more than 30%).

The best results for suspension and emulsion stability are found when the AI is <50%.

5 Our formulation necessarily contains nonionic surfactants (emulsifiers or dispersing agents) -these three concepts are used interchangeably.

Ionic emulsifiers may optionally and preferably be used, such as those described in emulsifier, dispersing agent or wetting agent catalogues for agriculture.

10 The ionic emulsifier is preferably of the salt of (mono-, di- or tri-) alkylbenzene sulphonate type, e.g. sodium (or calcium, or ammonium or ethanolamine) sulphonate and mixtures thereof.

A representative trade name for the ionic agent is Calsogen[®] 4814. The content in ionic agent is 0-20%, preferably 1-15%, and more preferably 5-10%.

15 Nonionic dispersing agents/emulsifiers must be present in an amount of 2-40%, depending on whether the ionic agent mentioned in the previous paragraph is used or not (if ionic agents are used, then the amount of nonionic dispersing agent is less). We differentiate between two groups of nonionic emulsifiers/dispersing agents (NIO-1 and NIO-2).

NIO-1 Group

20 Sulphonylureas contain a very small (but technically significant) percentage of crystallisation water.

When they are applied in the field, or even beforehand, if the medium they are formulated in favours the loss of said water, the sulphonylurea crystals have a great tendency to agglomerate, and this is another problem in the state of the art. Similarly, the milling process is industrially difficult using dispersing agents of the sulphosuccinate type (as described in patents
25 regarding oil suspensions).

At least, we find great difficulty for the product, once ground, not to finish up as agglomerated crystals.

30 In order to solve this partial problem, part of the general problem of formulating sulphonylureas in oil, we have seen that the combination of two types of certain dispersing agents (NIO-1.A and NIO-1.B) have a surprising effect. This combination of special and surprising activity in sulphonylurea oil suspensions concerns two different types of polymers:

35 NIO-1.A: Dispersing agents the hydrophobic part of which is formed by poly-12-hydroxystearic acid (APHS/EO), and a hydrophilic part of which is formed by polyethylene oxide (the representative of which is the commercial product Atlox[®] 4914 or Hypermer B261 by Uniquema). Atlox 4912 is a nonionic A-B-A block copolymer dispersing agent of 12-hydroxystearic acid and polyethylene glycol.

Specifically, nonionic polymeric dispersing agents with an HLB of between 4-8, preferably 5-7.

40 Although the dispersing agents of the type mentioned are without a doubt the best, other similar types can be used, specifically those corresponding to the structures of commercial dispersing agents Hypermer A 109, A394, A409, 4914 or oligomeric Hypermer E475, E476, E488, all by Uniquema (ICI).

NIO-1.B: Dispersing agents of the condensed fatty acid type (the representative of which is commercial product Atlox[®] LP-1, or LP-5, or LP-6 by Uniquema).

5 These dispersing agents (preferably used in combination NIO-1.A:NIO-1.B of 5:1 to 1:5 and at a total concentration in the formulation of 0.1-10%, preferably between 0.1-2%) allow the milling process to be performed without obstructions in the ball mills, and the ground product to be stable for several days (a least 3 days) without any large crystals forming. This represents a logistic advantage, since the milling process (and the ground product) may be accomplished
10 days before the final formulation.

 In the tests, substitution of these dispersing agents (at 2%) for sulphosuccinates at the same concentration -and in the same isoparaffinic oil medium- shows that they are essential for good milling (obtaining and maintaining the desired crystal size).

NIO-2 Group

15 The use of emulsifiers in an amount of more than 10% is necessary for a good embodiment of this invention.

 We have found that ethoxylated (and/or propoxylated) fatty acids (represented by Alkamul® VO/2003) have very good emulsifying properties when performing the final emulsion of the oil in water (which will be performed by the farmer).

20 Other typical emulsifiers used in agriculture can also be used (ethoxylated/propoxylated fatty alcohols, ethoxylated/propoxylated block copolymers, ethoxylated/propoxylated tristirilphenols, ethoxylated castor oil, etc.)

 Please note that in order to obtain a good emulsion –solves a partial problem of the invention- emulsifiers can be used that are not ethoxylated alcohols.

25 However, we have verified that biological activity is greater if ethoxylated fatty acids are used. It is also possible to combined several types of nonionic emulsifiers.

 Preferable concentrations of nonionic emulsifiers are 5-20%, preferably 5-15%.

 If no other emulsifier is used (that is not a dispersing agent) other than the ethoxylated acid fatty, the recommended proportions are of 2-25%, preferably 5-20%.

30 Suitable ratios of combinations of ionic and nonionic emulsifiers (e.g., Calsogen® 4814 and Alkamul VO/2003 – NIO-2) are from 1:9 to 9:1, preferably 2:8 to 7:3.

 Optionally, and in order to attend the requirements imposed by Guideline 91/414 in Appendix VI (i.e., FAO specifications regarding agrochemical formulations), it is convenient to
35 use an antifoaming agent.

 Any type of approved antifoaming agent for agrochemicals is suitable, whether it is a silane derivative or not, at a concentration of 0.05-5%, preferably from 0.5-1.5%.

 The best antifoaming agent we have found for these formulations is of the type represented by the chemical structure of commercial product Amersil WS 930. There are no
40 great differences with the use of other antifoaming agents.

 Other coformulants may be added if required, this task is obvious for a person skilled in the art.

 For example, an AI that is sensitive to light may be protected with UV blockers or absorbers; as well as additives to improve penetration (e.g., alkyl lactams, ethyl lactate, tributyl

5 citrate), colorants, compounds that reduce phototoxicity ("safeners"), pH regulators –e.g., acetic acid, citrus acid, buffers, antimicrobial agents, etc. (according to the special requirements of each AI).

We have observed that these types of coformulants do not have negative affects upon formulation properties, therefore any coformulant of this type, unless there are obvious chemical
10 reasons not to use it (e.g., it hydrolyses sulphonylureas with total safety, causes undesirable precipitation), especially used below 5% (as a guideline), it must not be prevented by the formulation expert.

A coformulant that seems to be useful is the biuret, which has been observed to facilitate sulphonylurea stability, which has nothing to do with the incorporation of neat urea as
15 claimed in several patents.

In order to facilitate comprehension of the invention and the use of chemical equivalents different to those specifically mentioned herein, we enclose as an integral part of the invention the product catalogues for use in agrochemical formulations of Exxon, Uniquema and Clariant that are current in June 2007 (or surviving companies), with which the person skilled in the art
20 will not experience any problems in reproducing the invention, if necessary, with other dispersing agents, surfactants, emulsifiers, oils, etc.

Similarly, the oil suspension described in the present invention may be used to be combined with microcapsule formulations, specifically those described by the same inventors in the applications for European patents EP 6024299, EP 6006748 and PCT/EP07/002809.
25

The manner of incorporating microcapsules to the oil suspensions described herein is simple: Simply by mixing them in the desired concentration with gentle stirring in a reactor (anchor type stirrer).

If it were necessary to combine several phases, the use of emulsifiers is recommended,
30 as explained in PCT/EP07/002809.

Preferably the microcapsule formulation will have a continuous water phase and the necessary emulsifiers to emulsify the water phase in the oil (those typically used in agriculture).

If this is a reverse phase microcapsule formulation (e.g., micro-encapsulated glyphosate), the mixing is then more simple, it being highly recommended that both oil phases
35 (the microcapsule formulation phase and that of the present invention) are miscible, or at least that they are miscible in the presence of suitable emulsifiers.

Example 1

We have tried to summarise some of the experiments in the long series of combinations
40 we have tested in the following table, where we indicate the ingredients as well as the results both for the stability properties of the suspension, the emulsion performed by technical farmer, AI stability and biological activity.

Discussion of the results, and conclusions derived from said results have been mentioned above in the description.

5 The type of compound is indicated on each line.

The examples were performed with the preferred products named above, specifically paraffin oil Isopar[®] M, dispersing agents Calsogen CA (calcium phenylsulphonate, ionic emulsifier) Atlox[®] 4912 (derivative of 12-hydroxystearic acid, NIO-A.1 emulsifier), Silanos Break-Thru[®] S240 (organomodified silane) Alkamul VO/2003 (ethoxylated fatty acid, NIO-A.2 emulsifier), Amersil[®] (antifoaming agent), Bentone[®] (viscosity modifier) in powder and Isopar[®] M (base oil).

One possible process (the most preferred) consists in mixing the ingredients except the viscosity modifier and grinding them altogether, dispersing the viscosity modifier at the end of the grinding process.

15 It is worth highlighting that for an adequate grinding process the presence of nonionic dispersing agents NIO-A.1 and NIO-A.2 is very highly recommended to avoid agglomeration of the crystals (we see that the combination of modified 12-hydroxystearic acid dispersing agents, together with organomodified silanes is surprisingly effective to prevent primary agglomeration problems during grinding and also long-term).

20 Nevertheless, the AI (or AIs) may be ground in the presence of the base oil (or a mixture of base oils) and dispersing agents and/or emulsifiers (e.g., Atlox[®] 4912 and Alkamul[®] VO/2003); and adding the remaining coformulants to the rest of the formulation after grinding.

The grinding should preferably produce crystals smaller than 5 µm. We have observed that the best stability is observed with crystals with a size of 1-3 µm, preferably when the mean is approximately 2 µm. This is easily achieved by using all the coformulants of the invention together, and almost impossible industrially (without increasing temperature and AI degradation) according to the state of the art processes.

30

Active ingredient stability refers to the decomposition of the active ingredient in a test in an oven at 35° for 15 days with respect to the initial content of the freshly prepared formulation.

Biological activity refers to the herbicidal activity according to basic tests for each sulphonylurea.

Sorgum halepense seeds were used for herbicidal activity in comparison with Zea mais seeds, having performed the treatment when at least the 3 first leaves had formed.

40 In a greenhouse environment, 200 m² were used with each species, and they were treated with each product at its minimum recommended dose according to the e-Pesticide Manual of the BCPC –e.g., in the case of nicosulfuron at 35 g/Ha-) with Table 1 showing the comparative results (in formulation stability: suspension without oil separation after 15 days +++

5 ; 0.2-0.5 mL ++; 0.5-1 mL as + and > 1 mL as -; in emulsion stability the results are following 24 hours).

Table 1.

	A	B	C	D	E	F	G	H	I	J	K
Nicosulfuron	4.82	21.90	4.80	4.80	4.80	21.90	-	4.82	4.82	21.90	-
Tribenuron	-	-	-	-	-	-	10.90	-	-	-	-
Metsulfuron	-	-	-	-	-	-	11.00	-	-	-	3.30
Fluroxipir	-	-	-	-	-	-	-	-	-	-	30.00
Lambda-cyhalothrin	-	-	-	-	-	-	-	-	10.00	-	-
Tebuconazole	-	-	-	-	-	-	-	10.00	5.00	-	-
Ethoxylated hydroxystearic acid	0.12	0.57	0.12	0.12	0.12	0.57	0.57	2.50	2.50	0.57	0.00
Condensed fatty acid	0.35	1.67	0.35	0.35	0.35	1.67	1.67	7.33	7.33	1.67	0.00
Trisiloxane polyether	19.58	14.20	19.58	19.58	19.58	-	14.20	10.00	10.00	-	19.00
Dodecylbenzenesulphonate salt	4.00	7.00	4.00	4.00	4.00	7.00	7.00	0.00	0.00	7.00	10.00
Ethoxylated 18C fatty alcohol	10.00	7.00	10.00	10.00	10.00	7.00	7.00	35.00	35.00	7.00	10.00
Silicone anti-foaming agent	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.05	0.05	0.38	0.00
Bentonite in powder	3.70	3.08	3.70	3.70	3.70	3.08	3.08	0.30	0.30	3.08	1.00
Paraffin oil	57.05	44.20	55.00	55.00	25.00	-	44.20	10.00	10.00	44.20	26.70
Diocetyl sulphosuccinate	-	-	-	-	-	12.13	-	-	-	14.20	-
Solvesso 200	-	-	-	-	-	44.20	-	10.00	5.00	-	-
Sunflower oil	-	-	-	-	30.00	-	-	10.00	5.00	-	-
Urea	-	-	-	2.07	2.07	2.07	-	-	-	-	-
Biuret	-	-	2.07	-	-	-	-	-	5.00	-	-
Formulation stability	+++	+++	+++	+++	+	-	+++	++	+	-	++
Emulsion stability	+++	+++	+++	+++	++	-	+++	++	+	-	+
AI stability (% degraded)	2.8	1.7	1.4	1.6	2.0	4.9	3.4/2.9	1.3	0.7	4.9	3.4
Herbicidal biological activity	96	97	99	99	96	78	99	94	99	73	100

10 Figure 1 shows the lack of phase separation in formulation B of Example 1 (GAT) versus phase separation in commercial formulation Motivell® (nicosulfuron in oil suspension) marketed by BASF (Batch 161106-113 bought in Germany in June 2007) after 15 days standing and for 8 days at 54°C. This indicates a high percentage of the packages of this formulation, which is very representative of the state of the art, have phase separation before being used by
15 the farmer, thus requiring strong stirring for its correct manipulation, as indicated on the label by "vor Gebrauch heftig schütteln" (stir well before use).

In order to perfectly understand the claims regarding the specified sulphonylureas, you must understand that the common name of one of them includes any herbicidal derivatives thereof, especially alkyl ethers or esters (usually "ethyl" or "methyl") and salts thereof. For

- 5 example, when claiming tribenuron, the reader must understand that "tribenuron-methyl" is also being claimed. It is worth highlighting that in many documents sulphonylureas are referred to by their "incomplete" name(metsulfuron for metsulfuron-methyl).

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An agrochemical formulation in the form of an oil suspension, comprising, by percentages by weight related to the total weight of the formulation:
 - a) At least one herbicide of the sulphonylurea type at a concentration of 0.5-50%;
 - b) At least one paraffin mineral oil at a concentration of 10-75%; and
 - c) At least one organomodified silane compound at a concentration of 5-40%;with the existence of other conformulants until reaching 100% by weight of the formulation.
2. An agrochemical formulation according to claim 1 wherein the concentration of the at least one herbicide of sulphonylurea type is 2-30%.
3. An agrochemical formulation according to claim 1 or 2 wherein the at least one paraffin mineral oil is presented without the existence of any other mineral or vegetable oil in the formulation and the paraffin mineral oil concentration is between 40-60%.
4. An agrochemical formulation according to any one of claims 1 to 3 wherein the concentrate of the at least one organomodified silane compound is 10-25%.
5. An agrochemical formulation according to any one of the claims 1 to 4, wherein that the herbicide or herbicides referred to in claim 1 a) are (is) chosen from: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron, ethoxysulfuron, flazasulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron; and active herbicidal derivatives and salts thereof.
6. An agrochemical formulation according to any one of claims 1 to 5, wherein there is at least one agrochemical active ingredient in addition to the sulphonylurea, or mixture of

sulphonylureas, said agrochemical being chosen from the group of herbicides, insecticides, fungicides, planned hormones, semiochemicals and antibiotics.

7. The agrochemical formulation according to claim 5, wherein it combines:

a) at least two sulphonylureas; or

b) any sulphonylurea with one of the following agrochemicals: fluoroxyppr, diflufenican, lactofen, mesotrione, sulcotrione, fluorchloridone, metazachlor, clomazone, or a mixture of clomazone with metazachlor, pyrethroids, triazole fungicides, glyphosate, or gluphosinate.

8. An agrochemical formulation according to any one of claims 1 to 7, wherein that the silane organomodified derivative is a trisiloxane polyether, optionally combined with sodium tetraborate.

9. An agrochemical formulation according to claim 1, wherein that a nonionic dispersing agent chosen as one of the coformulants is an A-B-A block copolymer of 12-hydroxystearic acid and polyethylene glycol at a concentration of 0.1-10%.

10. An agrochemical formulation according to claim 1, wherein that a nonionic dispersing agent chosen as one of the coformulants is an A-B-A block copolymer of 12-hydroxystearic acid and polyethylene glycol at a concentration of 0.1-2%.

11. An agrochemical formulation according to claim 1, wherein that a nonionic dispersing agent chosen as one of the coformulants is of the condensed fatty acid type at a concentration of 0.1-10%.

12. An agrochemical formulation according to claim 1, wherein that a nonionic dispersing agent chosen as one of the coformulants is of the condensed fatty acid type at a concentration of 0.1-2%.

13. An agrochemical formulation according to claim 1 wherein that it has two types of nonionic dispersing agents, one of the nonionic A-B-A block copolymer of 12- hydroxyl stearic acid with polyethylene glycol type, and another dispersing agent of the condensed fatty acid type, at a total concentration of both types of dispersing agents of 0.1-10%.
14. An agrochemical formulation according to claim 1 wherein that one of the coformulants is chosen as an ionic emulsifier of the alkylbenzene sulphonate type, either from calcium, sodium, ethanolamine or other possible salts, at a concentration of 2-15%.
15. An agrochemical formulation according to claim 1 wherein that one of the coformulants is chosen as an ionic emulsifier of the alkylbenzene sulphonate type, either from calcium, sodium, ethanolamine or other possible salts, at a concentration of 3-8%.
16. An agrochemical formulation according to claim 1, wherein that a nonionic emulsifier chosen as one of the coformulants is of the ethoxylated fatty acid type at a concentration of 2-25%.
17. An agrochemical formulation according to claim 1, wherein that a nonionic emulsifier chosen as one of the coformulants is of the ethoxylated fatty acid type at a concentration of 5-20%.
18. An agrochemical formulation according to claim 1, wherein that a viscosity modifier is chosen as one of the coformulants is of the bentonite group, at a concentration of 0.1-20%.
19. An agrochemical formulation according to claim 1, wherein that a viscosity modifier is chosen as one of the coformulants is of the bentonite group, at a concentration of 0.1-5%.
20. An agrochemical formulation according to claim 1, wherein that it contains:
 - a) a herbicide or a mixture of active ingredients at 0.5-50%;
 - b) Paraffin mineral oil at 30-75%;

- c) Trisiloxane polyether at 5-40%;
- d) Nonionic dispersing agents of the A-B-A block copolymer type of 12-hydroxystearic acid with polyethylene glycol at 0.1-10%;
- e) Nonionic dispersing of the condensed fatty acid type at 0.1-10%;
- f) Nonionic emulsifier of the ethoxylated fatty alcohol type at 2-25%;
- g) Ionic emulsifier of the alkylbenzene sulphonate type, at 2-15%;
- h) Viscosity modifier of the bentonite type at 0.1-20%;
- i) Optionally Biuret at a concentration of 0.1-5%;
- j) Optionally other coformulants in order to control pH, protect from light, antimicrobial agents, penetrants, phytotoxicity reducers, markers, colorants and other functions recommended for said specific formulation.

21. An agrochemical formulation according to claim 20, wherein that it contains:

- a) a herbicide or a mixture of active ingredients at 0.5-30%;
- b) Paraffin mineral oil at 40-60%;
- c) Trisiloxane polyether at 10-25%;
- d) Nonionic dispersing agents of the A-B-A block copolymer type of 12-hydroxystearic acid with polyethylene glycol at 0.1-2%;
- e) Nonionic dispersing of the condensed fatty acid type at 0.1-2%;
- f) Nonionic emulsifier of the ethoxylated fatty alcohol type at 5-20%;
- g) Ionic emulsifier of the alkylbenzene sulphonate type, at 3-8%;
- h) Viscosity modifier of the bentonite type at 0.1-5%;
- i) Optionally Biuret at a concentration of 0.1-5%;
- j) Optionally other coformulants in order to control pH, protect from light, antimicrobial agents, penetrants, phytotoxicity reducers, markers, colorants and other functions recommended for said specific formulation.

22. An agrochemical formulation according to claim 1 or 20, wherein that it contains a mixture of base oils formed by at least:

- i) 10% paraffin mineral oil;

ii) 0-60% aromatic mineral oil;

iii) 0-60% of vegetable oil;

the concentration of ii) and iii) not being able to be simultaneously 0%;

and moreover where the total amount of base oils forms about 30-75%.

23. An agrochemical formulation according to claim 1 or 20, wherein that it contains a mixture of base oils formed by at least:

i) 10% paraffin mineral oil;

ii) 0-60% aromatic mineral oil;

iii) 0-60% of vegetable oil;

the concentration of ii) and iii) not being able to be simultaneously 0%;

and moreover where the total amount of base oils forms about 40-60%.

24. An agrochemical formulation according to claim 1 or 20, wherein that it further contains at least one micro-encapsulated agrochemical active ingredient, whether sulphonylurea or not.

25. A formulation production procedure for formulating the formulation according to claim 20, wherein it comprises the steps of:

i) Mixing the paraffin mineral oil together with the active ingredient or ingredients and with the dispersing agents as well as the organomodified silane;

ii) Milling up to particle size $<5\ \mu\text{m}$;

iii) Additional stirring of the remaining types of compounds mentioned in claim 20, if necessary.

26. A formulation production procedure for formulating the formulation according to claim 21, wherein that it comprises the steps of:

i) Mixing the combination of base oils together with the active ingredient or ingredients and with the dispersing agents as well as the organomodified silane;

ii) Milling up to particle size $<5\ \mu\text{m}$;

iii) Additional stirring of the remaining types of compounds mentioned in claim 21, if necessary.

27. The use of a formulation according to claim 1 or 20 to control pests or diseases or to increase crop yield in agricultural activities.

28. An agrochemical formulation according to claim 13 wherein the total concentration of both types of dispersing agents is 0.1-2%.

29. An agrochemical formulation according to claim 20 or claim 21 wherein the ionic emulsifier of the alkylbenzene sulphonate type is calcium or sodium or ethanolamine dodecylbenzenesulphonate.

30. An agrochemical formulation according to claim 22 wherein the vegetable oil is linen, corn, coconut, rape, sunflower, or any other industrial vegetable oil.

31. An agrochemical formulation according to claim 23, wherein the mineral oil is of the naphtha type and the vegetable oil is linen, corn, coconut, rape, sunflower, or any other industrial vegetable oil.

32. A formulation production procedure of claim 25 or 26 wherein the milled particle size is $<2\ \mu\text{m}$.

Figure 1

