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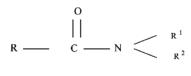
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(54) Title: AGROCHEMICAL COMPOSITION AND METHOD FOR PREPARING AND USING THE SAME



**(I)** 

(57) Abstract: An agrochemical composition comprises an azole active ingredient and an N,N-dialkyl long chain alkylamide. The N,N-dialkyl long chain alkylamide is present in sufficient amount to prevent or inhibit the crystallization of the azole derivative during the application of the composition to a locus. Preferred N, N-Dialkyl long chain alkylamide(s) comprised in the composition during the application of the composition to a locus. Preferred N, N-Dialkyl long chain alkylamide(s) comprised in the composition is/are selected from the group consisting of compounds of the formula (I): in which (a) R and R are independently normal alkyl radicals having 2 carbon atoms, and R represents an alkyl group having from 10 to 30 carbon atoms; or (b) R and R are independently normal alkyl radicals having 3 carbon atoms, and R represents an alkyl group having from 9 to 30 carbon atoms; or 20 (c) R and R are independently normal alkyl radicals having from 4 to 20 carbon atoms and R represents an alkyl group having from 6 to 30 carbon atoms. The composition is particularly advantageous when formulated with a fungicide, in particular one or more of tebuconazole, cyproconazole, difienconazole, diniconazole, triticonazole, hexaconazole, triflumiazole, metconazole, flusilazole, flutriafol, and myclobutanil.

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# AGROCHEMICAL COMPOSITION AND METHOD FOR PREPARING AND USING THE SAME

#### FIELD OF THE INVENTION

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The present invention relates to an agrochemical composition The invention is especially concerned with such compositions comprising one or more compounds active as a fungicide. The present invention further relates to a method of preparing the aforementioned compositions and their use in crop protection. The present invention is particularly concerned with the inhibition of crystal growth in aqueous spray liquors based on azole pesticidal compounds and to compositions exhibiting reduced crystal growth.

#### BACKGROUND OF THE INVENTION

Perhaps the most prevalent practice for applying pesticides to plants is by spraying aqueous liquors onto the plants to be treated. The spray equipment customarily used for the application of aqueous formulations of plant treatment agents is well known in the art and generally comprises one or more filters and/or nozzles. Some technical difficulties are associated with spraying practice when predominantly aqueous compositions of pesticides which are essentially water insoluble, are employed. In such cases, often the filters and nozzles are clogged as a result of crystal growth of the water insoluble active ingredients. Certain pesticidally active azole derivates show a particular tendency to crystallize in such situations.

A particular method for overcoming this problem is by inhibiting or preventing the crystal growth of the pesticide in the sprayer parts by employing a crystal growth inhibitor in the pesticidal composition. Thus, US Patent No. 5,206,225 describes the use of certain alkyl carboxylic acid dimethylamides as crystallization inhibitors of azole fungicides. Further, US Patent No. 5,369,118 describes the use of alkyl lactam as a crystal growth inhibitor of azole fungicides.

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The crystal growth inhibitors disclosed in the prior publications do not offer a solution for all needs, practices and conditions employed in agriculture. Thus, there is an ongoing need to develop further crystal growth inhibitors applied in agriculture which overcome the shortcoming of the prior art and to provide formulations comprising such inhibitors.

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#### DETAILED DESCRIPTION OF THE INVENTION

In the present invention it is surprisingly found that certain N, N-dialkyl long chain alkylamides are useful for preventing the crystallization during the application of aqueous spray liquors having azole derivatives as the active agrochemical ingredient.

US Patent No. 5,206,225 discloses the use of varieties of alkylcarboxylic acid dimethylamide of the formula R-CO-N(CH<sub>3</sub>)<sub>2</sub> as crystallization inhibitors of azole fungicides. Although US 5,206,225 describes the R group may represent alkyl having 5 to 19 carbon atoms, the amide group is exclusively dimethylamide. Thus, US 5,206,225 teaches away from developing other dialkylamide derivatives for using as a crystallization inhibitor in agrochemical composition comprising azole derivatives as active ingredients.

DE 4,341,986 is concerned with the use of carboxylic acid amides having the general formula R-CO-N( $R_1R_2$ ) as crystallization inhibitors, in particular for fungicidally active compounds. DE 4,341,986 discloses a very wide range of compounds having the aforementioned formula and suggests that compounds of the aforementioned formula in which R is hydrogen, alkyl having from 1 to 16 carbon atoms, hydroxy alkyl having from 1 to 10 carbon atoms, alkenyl having from 2 to 16 carbon atoms, cycloalkyl having from 5 to 7 carbon atoms, cycloalkyl having from 5 to 7 carbon atoms, aralkyl having from 6 to 10 carbon atoms in the aryl group and from 1 to 4 carbon atoms in the alkyl chain, aralkenyl having from 6 to 10 carbon atoms in the alkyl group and from 2 to 4 carbon atoms in the alkenyl chain, phenoxyalkyl having from 1 to 4 carbon atoms in the alkyl or a wide range of amide groups, and in which  $R^1$  is

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hydrogen, alkyl having from 1 to 12 carbon atoms, hydroxyalkyl having from 1 to 8 carbon atoms, alkenyl having from 2 to 12 carbon atoms, optionally substituted cycloalkyl having from 5 to 7 carbon atoms, phenyl, benzyl or phenethyl, and R<sup>2</sup> is alkyl having from 2 to 12 carbon atoms, hydroxyalkyl having from 1 to 8 carbon atoms, alkenyl having from 2 to 12 carbon atoms, optionally substituted cycloalkyl having from 5 to 7 carbon atoms, phenyl, benzyl or phenethyl may inhibit the crystallization of a wide range of azole derivatives.

DE 4,341,986 indicates a very large number of carboxylic acid amides and prefers to have R,  $R_1$  and  $R_2$  different classes of groups, in particular mixing saturated groups, such as alkyl and cycloalkyl, with unsaturated group, such as alkenyl, phenyl-containing groups, and amide groups. DE 4,341,986 discloses within the very broad range of carboxylic acid amides indicated a range of alkyl amides. However, DE 4,341,986 favours the use of carboxylic acid amides in which lower alkyl groups are present, that is in which the length of the alkyl chain and/or the total number of alkyl carbon atoms is low. In particular, of the alkyl amides specifically exemplified in table 2 of DE 4,341,986, representing a minority of the carboxylic amides exemplified in table 2 of 986', R is an alkyl group having 11 carbon atoms or fewer, with an emphasis being placed on R being a lower alkyl group. Further, of the alkyl amides specifically exemplified, the total number of carbon atoms in the alkyl groups of R,  $R_1$  and  $R_2$  does not exceed 16.

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In the present invention, the surprising finding is that alkyl amides of the general formula of DE 4,341,986 in which R is a higher alkyl group, in particular, depending upon the nature of  $R_1$  and  $R_2$  in the formula having at least 6 carbon atoms, and/or the total number of carbon atoms in the alkyl groups of R,  $R_1$  and  $R_2$  exceeds 16, exhibit a markedly superior activity to inhibiting crystallization of a specific class of azole derivatives.

Based on the above surprising finding, the present invention relates to a use of certain N, N-dialkyl long chain alkylamides for preventing the crystallization during the application of

aqueous spray liquors having azole derivatives as the active agrochemical ingredient. It has been found that such N, N-Dialkyl long chain alkylamides are particularly effective as crystal growth inhibitor in spray liquors comprising azole derivatives as active ingredients.

Accordingly, in a first aspect, the present invention provides an agrochemical composition comprising an azole active ingredient and a N, N-dialkyl long chain alkylamide.

More particularly, in the first aspect, the present invention provides an agrochemical composition comprising an N,N-dialkyl long chain alkylamide of the formula (I)

in which:

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- 15 (a) R<sup>1</sup> and R<sup>2</sup> are independently normal alkyl radicals having 2 carbon atoms, and R represents an alkyl group having from 10 to 30 carbon atoms; or
  - (b) R<sup>1</sup> and R<sup>2</sup> are independently normal alkyl radicals having 3 carbon atoms, and R represents an alkyl group having from 9 to 30 carbon atoms; or
- (c) R<sup>1</sup> and R<sup>2</sup> are independently normal alkyl radicals having from 4 to 20 carbon atoms and R represents an alkyl group having from 6 to 30 carbon atoms;
  - and at least one azole active ingredient having the general formula (II)

$$R_{1} - C - R_{2}$$

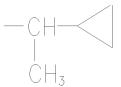
$$CH_{2}$$

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(II)

in which R<sub>1</sub> represents phenyl, 4-chlorophenyl, 4-chlorophenylethyl, 4-fluorophenyl, 2,4-dicholorophenyl, or 4-chlorophenyloxy;

R<sub>2</sub> represents n-butyl, tert-butyl, phenyl, 2-fluorophenyl or a group of the general formula (III):



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(III)

and

R<sub>3</sub> represents hydroxyl, oxygen or cyano,

and optionally at least one member selected from the group consisting of a surface-active agent, organic diluent and low temperature stabilizer.

The azole active ingredients are water insoluble compounds and such compounds are prone to crystallizing in aqueous compositions. However, the compositions are generally applied in the form of an aqueous liquor, prepared by the dilution of a concentrate with water. The N, N-dialkyl long chain alkylamide is present in the composition in an amount sufficient to reduce and/or inhibit crystal growth formation of the azole active ingredient. It has been found that the N, N-dialkyl long chain alkylamides are effective in reducing and/or inhibiting crystal growth of azole active compounds. Thus, the inclusion of one or more N, N-dialkyl long chain alkylamides in the aqueous composition prevents the spray equipment and the like from being blocked and makes the spray liquor free of any crystals. This in turn maintains the composition in a more homogeneous condition. In addition, it has been found that the use of the N, N-dialkyl long chain alkylamides to prevent crystal formation and growth improves the efficiency and efficacy of the active ingredient.

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The N, N-dialkyl long chain alkylamides are present in an amount sufficient to reduce and/or inhibit crystal growth of the azole compounds. The amount of the N, N-dialkyl long chain alkylamide present may depend upon the concentration of the azole active ingredient and may be determined by routine experimentation. The N, N-dialkyl long chain alkylamides are preferably present in an amount such as to give a weight ratio of the azole active ingredient to the N, N-dialkyl long chain alkylamide of from 1:0.1 to 1:5, more preferably from 1:1 to 1:4.

The composition may comprise a single N, N-dialkyl long chain alkylamide or a combination of two or more N, N-dialkyl long chain alkylamides.

The N, N-Dialkyl long chain alkylamide(s) comprised in the composition of the present invention is/are selected from the group consisting of compounds of the formula I:

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(l)

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in which,

- (a) R<sup>1</sup> and R<sup>2</sup> are normal alkyl radicals having 2 carbon atoms, and R represents an alkyl group having 10 to 30 carbon atoms, more preferably from 11 to 18 carbon atoms;
- (b) R<sup>1</sup> and R<sup>2</sup> are normal alkyl radicals having 3 carbon atoms, then R represents an alkyl group having 9 to 30 carbon atoms, more preferably from 9 to 18 carbon atoms; and
- (c) R<sup>1</sup> and R<sup>2</sup> are normal alkyl radicals having 4 to 20 carbon atoms, more preferably from 4 to 8 carbon atoms, R represents an alkyl group having 6 to 30 carbon atoms, more preferably from 6 to 18 carbon atoms.

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Alkyl groups present as R in the compounds of formula (I) may be straight chain or branched.

In one embodiment of the present invention, it is preferred that the alkyl groups R, R<sup>1</sup> and R<sup>2</sup> contain, in total, greater than 16 carbon atoms, more preferably greater than 18 carbon atoms, especially greater than 20 carbon atoms.

According to a preferred embodiment of the present invention, the preferred N,

N-dialkyl long chain alkylamides are selected from the group consisting of
diethyldodecanamide, diethyltridecanamide,
N,N-diethyltetradecanamide,
N,N-diethylhexadecanamide,
N,N-diethylhexadecanamide,
N,N-diethylnonadecanamide,
N,N-dipropyldecanamide,
N,N-dipropyltridecanamide,
N,N-dipropyltetradecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,
N,N-dipropylhexadecanamide,

- N,N-dipropylnonadecanamide, N,N-dibutylheptamide,
  - N,N-dibutyloctanamide,N,N-dibutylnonamide, N,N-dibutyldecanamide,
  - N,N-dibutyldodecanamide, N,N-dibutyltridecanamide,
  - N,N-dibutyltetradecanamide,N,N-dibutylhexadecanamide,N,N-dibutylheptadecanamide,
- 20 N,N-dibutyloctadecanamide,N,N-dibutylnonadecanamide,
  - N,N-dipentyloctanamide,N,N-dipentyldecanamide,
  - N,N-dipentyldodecanamide,N,N-dipentyltetradecanamide, N,N-dipentylhexadecanamide, N,N-dipentyloctadecanamide,or any mixture thereof.
- The composition of the present invention may be a concentrate, which is diluted with water prior to application on the plants to be treated. In this case, the one or more N, N-dialkyl long chain alkylamides are preferably present in an amount of from 5% to 80% by weight, more preferably from 20% to 60% by weight.

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As noted above, it has been found that N, N-dialkyl long chain alkylamides are effective in reducing or inhibiting the crystal formation of certain azole derivatives active as agrochemicals, in particular pesticides. The composition may comprise one or more azole derivative active ingredients.

The N, N-dialkyl long chain alkylamides are particularly effective in preventing the crystallization of azole derivatives that are active as fungicides. In particular, the N, N-dialkyl long chain alkylamides have been found to be effective as inhibiting crystal growth in aqueous formulations of azole derivatives of the general formula (II):

$$R_{1} - C - R_{2}$$

$$C + C$$

20 in which R<sub>1</sub>

represents phenyl,

4-chlorophenyl, 4-chlorophenylethyl, 4-fluorophenyl, 2,4-dicholorophenyl, or 4-chlorophenyloxy;

R<sub>2</sub> represents n-butyl, tert-butyl, phenyl, 2-fluorophenyl or a group of the general formula (III):

(III)

and

R<sub>3</sub> represents hydroxyl, oxygen or cyano.

Preferred compounds of the general formula (II) are those in which  $R_1$  represents 4-chlorophenyl. Compounds of the general formula (II) in which  $R_2$  represents tert-butyl are also preferred. In addition, compounds in which  $R_3$  is a hydroxyl group are also preferred.

A particularly preferred compound for use in the composition of the present invention is tebuconazole, which is the compound of general formula (II) in which  $R_1$  is 4-chlorophenyl,  $R_2$  is tert-butyl and  $R_3$  is hydroxyl. The concentrate of the present invention has been found to be particularly stable when used to formulate tebuconazole, without any reduction in the fungicidal activity of the compound when applied to a locus. Tebuconazole is a well known compound in the art and is available commercially.

A further preferred compound for use in the composition of the present invention is hexaconazole, which is the compound of general formula (II) in which  $R_1$  is 2,4-dichlorophenyl,  $R_2$  is n-butyl and  $R_3$  is hydroxyl. The concentrate of the present invention has been found to be particularly stable when used to formulate hexaconazole, without any reduction in the fungicidal activity of the compound when applied to a locus. Again, hexaconazole is a well known compound in the art and is available commercially.

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A further preferred compound for use in the composition of the present invention is cyproconazole, that is the compound of general formula (II) in which  $R_1$  is 4-chlorophenyl,  $R_2$  is a group of general formula (III) and  $R_3$  is hydroxyl. The concentrate of the present invention has been found to be particularly stable when used to formulate cyproconazole, without any reduction in the fungicidal activity of the compound when applied to a locus. Cyproconazole is a well known compound in the art and is available commercially.

A further preferred compound for use in the composition of the present invention is

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myclobutanil, that is the compound of general formula (II) in which  $R_1$  is 4-chlorophenyl,  $R_2$  is n-butyl and  $R_3$  is cyano. The concentrate of the present invention has been found to be particularly stable when used to formulate myclobutanil, without any reduction in the fungicidal activity of the compound when applied to a locus. Myclobutanil is a well known compound in the art and is available commercially.

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A further preferred compound for use in the composition of the present invention is flutriafol, that is the compound of general formula (II) in which R<sub>1</sub> is 4-fluorophenyl, R<sub>2</sub> is 2-fluorophenyl and R<sub>3</sub> is hydroxyl. The concentrate of the present invention has been found to be particularly stable when used to formulate flutriafol, without any reduction in the fungicidal activity of the compound when applied to a locus. Flutriafol is a well known compound in the art and is available commercially.

The compositions of the present invention have also been found to be effective in preventing the crystallization of triadimefon, that is a compound of general formula (II) in which R<sup>1</sup> is 4-chlorophenyloxy, R<sup>2</sup> is tert-butyl and R<sup>3</sup> is oxygen. Triadimefon is a commercially available fungicide.

In other embodiments, the composition of the present invention comprises one or more of difenoconazole, diniconazole, propiconazole, tricyclazole, triticonazole, triflumizole, flusilazole, metconazole.

In one embodiment, the formulation contains azole derivatives as active ingredients selected from the group consisting of tebuconazole, cyproconazole, difenoconazole, diniconazole, triticonazole, hexaconazole, triflumiazole, metconazole, tricylazole, flusilazole, flutriafol, myclobutanil and mixtures thereof.

The composition to be applied to the plants to be treated, in particular by spraying, may

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contain the active azole derivative in any suitable concentration. As noted above, the spray liquors are typically prepared by the dilution with water of a concentrate. Typically, the spray liquor contains azole active ingredients from 0.0001 to 3%, more preferably 0.002 to 2%, by weight.

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In addition to one or more N, N-dialkyl long chain alkylamides and one or more azole derivative active ingredients, the compositions of the present invention may comprise other components, including one or more of organic diluents or solvents, water and emulsifiers. Suitable components are known in the art.

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Organic diluents or solvents that may be included in the composition include both polar and non-polar organic solvents, for example ketones, amides, such as dimethyl formamide, and aromatic hydrocarbons, such as xylene. Other suitable solvents will be known to the person skilled in the art.

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Suitable emulsifiers comprised in the compositions of the present invention are also known in the art and commercially available. Suitable emulsifiers include both ionic and non-ionic emulsifiers, such as fatty acid esters, fatty alcohol esters, ethers, alkyl sulphonates and aryl sulphonates. Other suitable surface active components will also be known to the person skilled in the art.

Further components comprised in the composition are well known in the art and include, for example stabilizers and thickeners. Such components are commercially available and their use will be recognized and understood by the person skilled in the art.

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In a further aspect, the present invention provides an aqueous spray composition comprising an azole active ingredient and an N, N-dialkyl long chain alkylamide, as hereinbefore defined, and water.

Other components that may be included in the aqueous spray composition are as hereinbefore described. Details of the components of the aqueous spray composition are as given hereinbefore.

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In a further aspect, the present invention provides the use of N, N-dialkyl long chain alkylamides, in particular the N, N-dialkyl long chain alkylamides as hereinbefore defined, to inhibit the crystal growth of pesticidally active azole derivatives.

The compositions of the present invention may be prepared using techniques known in the art. A particularly preferred method of preparing the composition is as follows:

Each component is added according to the weight fraction required in the final composition. First, the solvent, and one or more N, N-dialkyl long chain alkylamide crystallization inhibitors are charged to a suitable mixing vessel, for example a blending tank equipped with a hot water circulation. The resulting mixture is agitated. The one or more azole derivatives are added to the mixture and the agitation continued until all azole derivatives are dissolved completely in the solvent. An agitation time of about 30 minutes is typical. Thereafter, further components, such as emulsifiers, if present, are added and the mixture further agitated to ensure homogeneity. A further agitation time of about 1 hour is typical.

When the composition is to be sprayed, the formulation is diluted with water to the desired concentration of active ingredient, for example by adding the concentrated formulation to water in a vessel with stirring.

In a further aspect, the present invention comprises a method of preventing crystallization of pesticidal liquid formulations comprising azole derivatives during

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application, the method comprising adding a N, N-dialkyl long chain alkylamide as hereinbefore defined to the formulation in an amount sufficient to reduce crystallization of the azole derivative.

In still a further aspect, the present invention provides a method of treating pests at a locus comprising applying to the locus a composition as hereinbefore described. The composition is preferably applied in the form of a diluted aqueous formulation. The method is particularly suitable for the application of fungicides to treat fungal infestations of plants in the locus.

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Embodiments of the present invention will now be described, by way of example only.

#### **EXAMPLES**

In each of the following examples, a composition was prepared according to the following general methodology:

Charge every component based on the recipe composition into a vessel in the following manner. First, add the solvent and crystallization inhibitor to a blending tank equipped with a hot water circulation; agitate the solution; add one or more azole active ingredients into the blending tank; continue agitating for 30 minutes until all azole active ingredients are dissolved completely; add the emulsifiers to the tank; continue agitating for one hour until the mixture is uniform; stop agitating.

25 Samples of each composition prepared were taken from the tank and analysed in accordance with the international testing methods CIPAC (Collaborative International Pesticides Analytical Council).

To test the crystallization properties, in each case 20 L of an aqueous spray liquor, prepared by dilution of the composition prepared with water to a concentrate content of 0.5% by weight, were pumped in circulation through a fine-meshed sieve for 1 hour in a flow-through apparatus with the aid of a pump. The solution after preparation was analyzed in a chromatograph to measure the concentration of the azole derivative active ingredient in PPM. The gauge pressure of the liquid being circulated was recorded every one hour. An increase in the pressure is an indication the nozzles and the fine-meshed sieve are being blocked by crystals. Every hour, a sample of the circulating liquid was taken and analyzed in the chromatograph to determine the concentration of the azole derivative active ingredient.

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The preparation and the crystallization behavior of various spray liquors according to the present invention, prepared and tested as described above, are described in the following examples, taken in conjunction with comparative test results given in the respective table.

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#### Example 1

The liquid formulation described in Table 1 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole and N, N-dialkyl long chain alkylamides was approx 1:1.8. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 1 contained N,N-dialkyl long chain alkylamides in an amount of 45% wt. Table 1 describes the liquid formulation of Example 1 and the comparison formulation, Comparison A.

Table 1.

	EXAMPLE 1: Tebuconazole EC (with COMPARISON A: Tebuconazole EC Crystallization inhibitors) (without Crystallization inhibitors)			Remark
Component	Composition	Component	Composition	
Tebuconazole tech	250kg( as	Tebuconazole tech	250kg (as	Active
	pure)		pure)	ingredient
Calcium	100kg	Calcium	100kg	Emulsifier
dodecylphenylsulfonate		dodecylphenylsulfonate		
	; ;			
TWEEN 80	100kg	TWEEN 80	100kg	Emulsifier
Sorbitan monooleate		Sorbitan monooleate		
ethoxylate		ethoxylate		
Cyclohexanone	100kg	Cyclohexanone	550kg	Solvent
N,N-diethyl	450kg			Crystallization
dodecanamide		6 6 6		inhibitor
Total	1000kg	Total	1000kg	

 $\label{thm:continuous} \mbox{Use Example} \quad \mbox{I}$  The experimental results are set forth in the following table.

	Example I			Comparison A		
	Press.	Tebuconazole	Tebuconazole	Press.	Tebuconazole	
	(PSI)	(ppm)	decrease %	(PSI)	(ppm)	Tebuconazole
	200			200		decrease%
	mesh			mesh		
Initial	40	1059	0	38	1141	0
solution						
After	40	1043	-1.51	Nozzles		

1h				100 %
				blocked
After	40	1028	-2.93	Nozzles
2h				100 %
				blocked
After	41	1002	-5.38	
3h				
After	41	988	-6.70	
4h				

#### Example 2

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The liquid formulation was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of diniconazole and N, N-dialkyl long chain alkylamides was approx 1:5. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 2 contained N,N-dialkyl long chain alkylamides in an amount of 80% wt. Table 2 describes the liquid formulation of Example 2 and the comparison formulation, Comparison B.

Table 2.

EXAMPLE 2: Dinicon	azole EC (with	COMPARISON B: Diniconazole EC		Remark
Crystallization inhibitor	s)	(without Crystallization inhibitors)		
Component	Composition	Component	Composition	
Diniconazole tech	160kg (as	Diniconazole tech	160kg (as	Active
	pure)		pure)	ingredient

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Rhodocal 70	10kg	Rhodocal 70	10kg	Emulsifier
Calcium		Calcium		
dodecylphenylsulpho		dodecylphenylsulphonate		
nate				
Tween 80	10kg	Tween 80	10kg	Emulsifier
Sorbitan monooleate		Sorbitan monooleate		
ethoxylate		ethoxylate		
N-methyl pyrrolidone	20kg	N-methyl pyrrolidone	820kg	Solvent
N,N-diethylnonadeca	800kg			Crystalliza
namide				tion
				inhibitors
Total	1000kg	Total	1000kg	

# Use Example II

The experimental results are set forth in the following table.

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		Example 2		Comparison B		
	Pressure Diniconazole Dinicona		Diniconazole	Pressure	Diniconazole	Diniconazole
	(PSI)	(ppm)	decrease %	(PSI)	(ppm)	decrease%
	200			200		
	mesh			mesh		
Initial	39	755	0	38	780	0
solution						
After 1h	39	746	-1.19	40	532	-31.75
After 2h	39	732	-3.05	42	440	-43.70

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After 3h	40	728	-3.58	46	369	-52.74
After 4h	40	699	-7.42	49	335	-57.12

## Example 3

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The liquid formulation was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of different and N, N-dialkyl long chain alkylamides was approx 1:3.33. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 3 contained N,N-dialkyl long chain alkylamides in an amount of 50% wt. Table 3 describes the liquid formulation of Example 3 and the comparison formulation, Comparison C.

Table 3.

EXAMPLE 3: Difeno	conazole EC	COMPARISON C: Dife	Remark			
(with Crystallization inhibitors)		EC (without Crystalliza	ation inhibitors)			
Component	Composition	Component	Composition			
Difenoconazole	150kg (as	Difenoconazole tech	150kg (as	Active		
tech	pure)		pure)	ingredient		
Rhodocal 70	100kg	Rhodocal 70	100kg	Emulsifier		
Sodium		Sodium				
dodecylphenylsulp		dodecylphenylsulph				
honate		onate				
IGEPAL BC/9	100kg	IGEPAL BC/9	100kg	Emulsifier		

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Nonylphenol		Nonylphenol		
ethoxylate		ethoxylate		
Dimethyl	150kg	Dimethyl formamide	650kg	Solvent
formamide				
N,N-dipropyldecan	200kg			Crystallization
amide				inhibitor
N, N-diethyl-	300kg			Crystallization
dodecanamide				inhibitor
Total	1000kg	Total	1000kg	

Use Example III

The experimental results are set forth in the following table.

	Example 3			Comparison C		
	Press.	Difenoco	Difenoconazole	Press.	Difenocona	Difenocon
	(PSI)	nazole	decrease %	(PSI) 200	zole	azole
	200	(ppm)		mesh	(ppm)	decrease
	mesh					%
Initial	40	660	0	38	664	0
solution						
After	40	655	-0.70	40	459	-30.97
1h						
After	40	647	-1.84	42	373	-43.81
2h						
After	40	643	-2.54	44	313	-52.82
3h						
After	41	611	-7.44	44	282	-57.55

	4h			
١				

## Example 4

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The formulation of Example 4 was prepared with a combination of tebuconazole and triadimefon. The liquid formulation was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole and triadimefon to N, N-dialkyl long chain alkylamides was approximately 1:0.1. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 4 contained N,N-dialkyl long chain alkylamides in an amount of 5% wt. Table 4 describes the liquid formulation of Example 4 and the comparison formulation, Comparison D.

Table 4.

EXAMPLE 4:		COMPARISON D:		Remark
Tebuconazole-Ti	riadimefon EC	Tebuconazole <sup>.</sup> T	riadimefon EC	
(Containing Crys	stallization	(Not containing	Crystallization	
inhibitor)		inhibitor)		
Component	Composition	Component	Composition	
Tebuconazole	100kg(as pure)	Tebuconazole	100kg (as	Active
tech		tech	pure)	ingredient
Triadimefon	400kg(as pure)	Triadimefon	400kg (as	Active
tech		tech	pure)	ingredient
Rhodocal 70	100kg	Rhodocal 70	100kg	Emulsifier
Calcium		Calcium		
dodecylphenyl		dodecylphenyl		
sulphonate		sulphonate		

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Emulsogen		Emulsogen		Emulsifier
EL 540	100kg	EL 540	100kg	
Castor oil		Castor oil		
ethoxylate		ethoxylate		
Dimethyl	250kg	Dimethyl	300kg	Solvent
formamide		formamide		
N, N-dipropyl-	25kg			Crystallization
nonadecan-				inhibitor
amide				
N, N-dipropyl-	25kg			Crystallization
decanamide				inhibitor
Total	1000kg	Total	1000kg	

Use Example  $\ensuremath{\mathrm{IV}}$  The experimental results are set forth in the following table.

	Example 4				Comparison D					
	Press. (PSI) 200 mesh	Tebuc- onazo- le (TB) (ppm)	Triadi m-efon (TRI) (ppm)	TB decre ase %	TRI Decre ase %	Press. (PSI) 200 mesh	Tebu- cona- zole (TB)	Tria- dime- fon (TRI) (ppm)	TB decr eas e %	TRI decr ease %
							(ppm)		_	_
Initial Solu- tion	40	448	1765	0	0	38	445	1760	0	0
After	40	432	1756	-3.57	-0.51	Nozz-				
1h						les				

						100 %		
						blocke		
						d		
After	40	426	1743	-4.91	-1.25	Nozz-		
2h						les		
						100 %		
						blocke		
						d		
After	41	410	173	-8.48	-1.70			
3h			5					
After	42	402	1720	-10.2	-2.55			
4h				6				

# Example 5

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The liquid formulation was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of propiconazole and N, N-dialkyl long chain alkylamides was approx 1:2. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

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The formulation of Example 5 contained N,N-dialkyl long chain alkylamides in an amount of 40% wt. Table 5 describes the liquid formulation of Example 5 and the comparison formulation, Comparison E.

#### 15 Table 5.

EXAMPLE 5: Propiconazole EC COMPARISON E: Remark
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(Containing Crystalliz	ation inhibitor)	Propiconazole E	EC (Not	
		Containing Crys		
		inhibitor)		
Component	Composition	Component	composition	
Propiconazole tech	200kg (as	Propiconazole	200kg (as	Active
	pure)	tech	pure)	ingredient
Agnique ABS 70 C	100kg	Agnique ABS	100kg	Emulsifier
Calcium		70 C		
dodecylphenyl		Calcium		
sulphonate		dodecylphenyl		
		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulsifier
EL 540		EL 540		
Castor oil ethoxylate		Castor oil		
		ethoxylate		
Dimethyl formamide	200kg	Dimethyl	600kg	Solvent
		formamide		
N, N-diethyl	300kg	*		Crystallization
dodecanamide		# # # #		inhibitor
N,N-dibutylheptamide	100kg	6 6 6 6		Crystallization
		# # # #		inhibitor
Total	1000kg	Total	1000kg	

# Use Example $\,V\,$

The experimental results are set forth in the following table.

Example 5	Comparison E

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	Pressur	Propicona	Propiconazole	Pressure	Propico	
	e (PSI)	zole (ppm)	decrease %	(PSI) 200	nazole	Propicon
	200			mesh	(ppm)	azole
	mesh					decrease
						%
Initial	39	878	0	38	884	0
solution						
After 1h	39	862	-1.82	40	624	-29.41
After 2h	39	850	-3.19	Nozzles 100		
				% blocked		
After 3h	40	838	-4.56	Nozzles 100		
				% blocked		
After 4h	40	820	-6.61			

## Example 6

The formulation of Example 6 was prepared with a combination of hexaconazole and myclobutanil as active ingredients. The liquid formulation was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of hexaconazole and myclobutanil to N, N-dialkyl long chain alkylamides was approx 1:1.8. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

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The formulation of Example 6 contained N,N-dialkyl long chain alkylamides in an amount of 45% wt. Table 6 describes the liquid formulation of Example 6 and the comparison formulation, Comparison F.

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Table 6.

		*		
EXAMPLE 6:	:	COMPARISON	Remark	
Hexaconazioe-M	/lyclobutanil EC	Hexaconazloe·M		
(Containing Cr	ystallization	(without Crysta	allization	
inhibitor)		inhibitor)		
Component	Composition	Component	Composition	
Hexaconazole	100kg (as pure)	Hexaconazole	100kg (as	Active
tech		tech	pure)	ingredient
Myclobutanil	150kg (as pure)	Myclobutanil	150kg (as	Active
tech		tech	pure)	ingredient
Agnique ABS	100kg	Agnique ABS	100kg	Emulsifier
70 C		70 C		
Calcium		Calcium		
dodecylphenyl		dodecylphenyl		
sulphonate		sulphonate		
		0 0 0 0		
Alkamuls	100kg	Alkamuls	100kg	Emulsifier
OR/36		OR/36		
Castor oil		Castor oil		
ethoxylate		ethoxylate		
Dimethyl	100kg	Dimethyl	550kg	Solvent
formamide		formamide		
N, N-diethyl	450kg	X X X X		Crystallization
dodecanamide		X X X X		inhibitor
Total	1000kg	Total	1000kg	

Use Example  $\ensuremath{\mathrm{VI}}$  The experimental results are set forth in the following table.

		E	xample 6			Comparison F				
	Press (PSI)	Hexa- con- azole	Myclo- butanil (MYC) (ppm)	HEX decr ease	MYC decrea se%	Press.(P SI)200 mesh	Hex- acon- azole	Myclo butan il (MYC	HEX decr ease	MYC Decre ase
	200 mesh	(HEX)		%			(HEX)	(ppm)	%	%
Initial soluti on	40	450	657	0	0	38	445	664	0	0
After 1h	40	438	648	2.67	-1.37	Nozzles 100 % blocked				
After 2h	40	430	633	4.44	-3.65	Nozzles 100% blocked				
After 3h	41	422	625	6.22	-4.88					
After 4h	42	408	614	9.33	-6.55					

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# Example 7

The formulation of Example 7 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole to N, N-dialkyl long chain alkylamides

was approx 1:1. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 7 contained N,N-dialkyl long chain alkylamides in an amount of 30% wt. Table 7 describes the liquid formulation of Example 7 and the comparison formulation, Comparison G.

Table 7.

EXAMPLE 7: Tebuconazole E	EC ( with	COMPARISON	G:	Remark
Crystallization inhibitor)		Tebuconazole E		
		Crystallization i	nhibitor)	
Component	Composition	Component	Composition	
Tebuconazole tech	300kg (as	Tebuconazole	300kg (as	Active
	pure)	tech	pure)	ingredient
Agnique ABS 70 C	100kg	Agnique ABS	100kg	Emulsifier
Calcium dodecylphenyl		70 C		
sulphonate		Calcium		
		dodecylphenyl		
		sulphonate		
Alkamuls OR/36	100kg	Alkamuls	100kg	Emulsifier
Castor oil ethoxylate		OR/36		
		Castor oil		
		ethoxylate		
Butanole	200kg	Butanole	500kg	Solvent
N,N-dibutylnonadecanamide	150kg			Crystallization
				inhibitor

N, N-dibutyldecanamide	150kg			Crystallization
				inhibitor
Total	1000kg	Total	1000kg	

Use Example VII

The experimental results are set forth in the following table.

		Example	e 7	Comparison G			
	Pressure	Tebucon	Tebuconazole	Pressure	Tebucon	Tebuconazole	
	(PSI) 200	azole	decrease %	(PSI) 200	azole	decrease%	
	mesh	(ppm)		mesh	(ppm)		
Initial	40	1400	0	38	13	0	
solution					98		
After 1h	40	1380	-1.43	39	685	-51.0	
After 2h	40	1300	-7.14	Nozzles 100			
				% blocked			
After 3h	40	1280	-8.57	Nozzles 100			
				% blocked			
After 4h	42	1200	-14.3				

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# Example 8

The formulation of Example 8 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of Myclobutanil to N, N-dialkyl long chain alkylamides was approx 1:0.5. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 8 contained N,N-dialkyl long chain alkylamides in an amount of 20% wt. Table 8 describes the liquid formulation of Example 8 and the comparison formulation, Comparison H.

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Table 8.

EXAMPLE 8: Myclobutanil	COMPARISON	Remark			
Crystallization inhibitors)		Myclobutanil E0			
	Crystallization i	Crystallization inhibitors)			
Component	Composition	Component			
Myclobutanil tech	400kg (as	Myclobutanil	400kg (as	Active	
	pure)	tech	pure)	ingredient	
Agnique ABS 60C	100kg	Agnique ABS	100kg	Emulsifier	
Calcium dodecylphenyl		60C			
sulphonate		Calcium	Calcium		
		dodecylphenyl			
		sulphonate			
Alkamuls OR/36	100kg	Alkamuls	100kg	Emulsifier	
Castor oil ethoxylate		OR/36			
		Castor oil			
		ethoxylate			
Methanol	200kg	Methanol	400kg	Solvent	
N,N-dipentyloctanamide	100kg			Crystallization	
				inhibitor	
N,N-diethyldodecanamide	100kg			Crystallization	
				inhibitor	
Total	1000kg	Total	1000kg		

Use Example VIII

The experimental results are set forth in the following table.

	Example 8			Comparison H		
	Pressure	Myclobu	Myclobutanil	Pressure	Myclobutanil	Myclobutanil
	(PSI) 200	tanil	decrease %	(PSI) 200	(ppm)	decrease%
	mesh	(ppm)		mesh		
Initial	40	1700	0	38	1660	0
solution						
After 1h	40	1657	-2.53	Nozzles 100		
				% blocked		
After 2h	40	1605	-5.59	Nozzles 100		
				% blocked		
After 3h	40	1574	-7.41			
After 4h	42	1526	-10.23			

# Example 9

The formulation of Example 9 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of diniconazole to N, N-dialkyl long chain alkylamides was approx 1:3. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

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The formulation of Example 9 contained N,N-dialkyl long chain alkylamides in an amount of 30% wt. Table 9 describes the liquid formulation of Example 9 and the comparison formulation, Comparison I.

# 5 Table 9.

EXAMPLE 9: Diniconazole	COMPARISON	Remark		
Crystallization inhibitor)	Diniconazole E			
	Crystallization i			
Component	Composition	Component	composition	
Diniconazole tech	100kg (as	Diniconazole	100kg (as	Active
	pure)	tech	part)	ingredient
Agnique ABS 60C	100kg	Agnique ABS	100kg	Emulsifier
Calcium dodecylphenyl	Calcium dodecylphenyl			
sulphonate		Calcium		
		dodecylphenyl		
		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulsifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil		
		ethoxylate		
Dimethyl formamide	400kg	Dimethyl	700kg	Solvent
		formamide		
N,N-dipentyldecanamide	300kg			Crystallization
				inhibitor
Total	1000kg	Total	1000kg	

Use Example  $\, \mathrm{I\!X} \,$ 

The experimental results are set forth in the following table.

	Example 9			Comparison I			
	Press.	Diniconazol	Diniconazole	Press.	Diniconazol	Diniconazole	
	(PSI)	e (ppm)	decrease %	(PSI)	e (ppm)	decrease%	
	200			200			
	mesh			mesh			
Initial	40	435	0	38	443	0	
solutio							
n							
After	40	430	-1.15	38	346	-21.89	
1h							
After	40	421	-2.07	39	270	-39.06	
2h							
After	40	417	-4.14	40	184	-58.47	
3h							
After	42	410	-5.75	40	107	-75.85	
4h							

# 5 Example 10

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The formulation of Example 10 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole to N, N-dialkyl long chain alkylamides was approx 1:4. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 10 contained N,N-dialkyl long chain alkylamides in an amount of 40% wt. Table 10 describes the liquid formulation of Example 10 and the comparison formulation, Comparison J.

# 5 Table 10.

EXAMPLE 10: Tebuconazole EC (with		COMPARISON J:		Remark
Crystallization inhibitor)	Tebuconazole E			
	Crystallization i			
Component Composition		Component	Composition	
Tebuconazole tech	100kg (as	Tebuconazole	100kg (as	Active
	pure)	tech	pure)	ingredient
Agnique ABS 60C	100kg	Agnique ABS	100kg	Emulsifier
Calcium dodecylphenyl		60C		
sulphonate		Calcium		
		dodecylphenyl		
		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulsifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil		
		ethoxylate		
Xylene	300kg	Xylene	700kg	Solvent
N,N-dipentyloctadecanamide 400kg				Crystallizat
				ion
				inhibitor
Total	1000kg	Total	1000kg	

Use Example  $\, X \,$ 

The experimental results are set forth in the following table.

	Example 10			Comparison J		
	Pressure	Tebucona	Tebuconazole	Pressure	Tebucona	Tebuconazo
	(PSI) 200	zole (ppm)	decrease %	(PSI)	zole	le
	mesh			200	(ppm)	decrease%
				mesh		
Initial	40	438	0	38	447	0
solution						
After 1h	40	430	-1.83	38	300	-32.89
After 2h	40	414	-5.48	41	143	-68.00
After 3h	39	408	-6.85	Nozzles		
				100 %		
				blocked		
After 4h	42	400	-8.68	Nozzles		
				100 %		
				blocked		

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# Example 11

The formulation of Example 11 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tricyclazole to N, N-dialkyl long chain alkylamides was approx 1:2.2. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

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The formulation of Example 11 contained N,N-dialkyl long chain alkylamides in an amount of 55% wt. Table 11 describes the liquid formulation of Example 11 and the comparison formulation, Comparison K.

# 5 **Table 11**.

EXAMPLE 11: Tricyclazole EC		COMPARISON K:		Remark
(Containing Crystallization inhibitors)		Tricyclazole EC (Not		
		containing Crystallization		
		inhibitors)		
Component	Composition	Component	Composition	
Tricyclazole tech	250kg (as	Tricyclazole	250kg (as	Active
	pure)	tech	pure)	ingredient
Agnique ABS 70 C	80kg	Agnique ABS	80kg	Emulisifier
Calcium dodecylphenyl		70 C		
sulphonate		Calcium		
		dodecylphenyl		
		sulphonate		
Emulsogen	120kg	Emulsogen	120kg	Emulsifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil		
		ethoxylate		
Dimethyl formamide		Dimethyl	550kg	Solvent
		formamide		
N,N-dipropyldodecanamide	350kg			Crystalliztion
				inhibitor
N,N-dibutyldecanamide	200kg			Crystalliztion
				inhibitor

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Total 1	1000kg To	otal 1000kg	
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Use Example  $\ensuremath{\mathrm{XI}}$  The experimental results are set forth in the following table.

	Example 11			Comparison K		
	Pressure	Tricycl	Tricyclazole	Pressure	Tricyclazole	Tricyclazole
	(PSI) 200	azole	decrease %	(PSI) 200	(ppm)	decrease%
	mesh	(ppm)		mesh		
Initial	40	1250	0	40	1262	0
solution						
After 1h	40	1197	-4.24	40	863	-31.62
After 2h	40	1138	-8.96	41	654	-48.18
After 3h	39	1106	-11.52	Nozzles 100		
				% blocked		
After 4h	42	1097	-12.24	Nozzles 100		
				% blocked		

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## Example 12

The formulation of Example 12 was prepared containing flutriafol as the active ingredient and N, N-dialkyl long chain alkylamides, wherein the weight ratio of flutriafol to N, N-dialkyl long chain alkylamides was approx 1:1.6. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but without any crystallization inhibitors.

The formulation of Example 12 contained N,N-dialkyl long chain alkylamides in an

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amount of 40% wt. Table 12 describes the liquid formulation of Example 12 and the comparison formulation, Comparison L.

Table 12.

EXAMPLE 12: Flutriafol E	COMPARISON	Remark		
Crystallization inhibitors)	EC (Not contair			
	Crystallization i	nhibitors)		
Component	Composition	Component	Composition	
Flutriafol tech	250kg (as	Flutriafol tech	250kg (as	Active
	pure)		pure)	ingredient
Agnique ABS 70 C	80kg	Agnique ABS	80kg	Emulisifier
Calcium dodecylphenyl		70 C		
sulphonate		Calcium		
		dodecylphenyl		
		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulisifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil		
		ethoxylate		
Dimethyl formamide	170kg	Dimethyl	570kg	Solvent
		formamide		
N, N-dipropyl-	300kg	**************************************		Crystallization
dodecanamide		8 8 8		inhibitor
N,N-dipentyloctanamide	100kg	*		Crystallization
		* * * *		inhibitor
Total	1000kg	Total	1000kg	

Use Example  $\mbox{ XII}$  The experimental results are set forth in the following table.

	Example 12			Comparison L		
	Pressure	Flutriafol	Flutriafol	Pressure	Flutriafol	Flutriafol
	(PSI) 200	(ppm)	decrease %	(PSI)	(ppm)	decrease
	mesh			200		%
				mesh		
Initial	40	1133	0	40	1253	0
solution						
After 1h	40	1106	-2.38	42	690	-44.96
After 2h	40	1059	-8.96	Nozzles		
				100 %		
				blocked		
After 3h	39	1022	-9.79	Nozzles		
				100 %		
				blocked		
After 4h	42	998	-11.92			

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## Example 13

The formulation of Example 13 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole to N, N-dialkyl long chain alkylamides was approx 1:1.2. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but containing an alkylamide with a lower alkyl constituent group.

The formulation of Example 13 contained N,N-dialkyl long chain alkylamides in an amount of 30% wt. Table 13 describes the liquid formulation of Example 13 and the comparison formulation, Comparison M, in which the lower alkyl alkylamide was used.

# 5 Table 13.

EXAMPLE 13: Tebuconazole EC (with		COMPARISON M: Te	Remark	
long chain alkylamide)		EC (with lower chain a		
Component	Composition	Component	Composition	
Tebuconazole tech	250kg (as	Tebuconazole tech	250kg (as	Active
	pure)		pure)	ingredient
Agnique ABS 60C	100kg	Agnique ABS 60C	100kg	Emulsifier
Calcium dodecylphenyl		Calcium		
sulphonate		dodecylphenyl		
		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulsifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil ethoxylate		
Xylene	250kg	Xylene	250kg	Solvent
N,N-diethyldodecanamid	300kg	N,N-diethyloctanami	300kg	Crystallizati
е		de		on inhibitor
Total	1000kg	Total	1000kg	

# Use Example XIII

The experimental results are set forth in the following table.

Example 13	Comparison M

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	Press.	Tebucona	Tebucona	Press.	Tebuconazole	Tebuconazole
	(PSI)	zole	zole	(PSI)	(ppm)	decrease%
	200	(ppm)	decrease	200		
	mesh		%	mesh		
Initial	40	1133	0	40	1253	0
solution						
After 1h	40	1106	-2.38	40	1054	-15.88
After 2h	40	1059	-8.96	41	906	-27.66
After 3h	39	1022	-9.79	41	579.4	-53.76
After 4h	42	998	-11.92	40	504.3	-59.75

## Example 14

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The formulation of Example 14 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole to N, N-dialkyl long chain alkylamides was approx 1:1.2. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but containing an alkylamide with lower alkyl constituent groups.

The formulation of Example 14 contained N,N-dialkyl long chain alkylamides in an amount of 30% wt. Table 14 describes the liquid formulation of Example 14 and the comparison formulation, Comparison N.

Table 14.

EXAMPLE 14: Tebuconazole EC		COMPARISON N: Tebuconazole EC		Remark
(with long chain alkylamide)		(with lower chain alkylamide)		
Component	Composition	Component	Composition	

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Tebuconazole tech	250kg (as	Tebuconazole tech	250kg (as	Active
	pure)		pure)	ingredient
Agnique ABS 60C	100kg	Agnique ABS 60C	100kg	Emulsifier
Calcium		Calcium dodecylphenyl		
dodecylphenyl		sulphonate		
sulphonate				
Emulsogen	100kg	Emulsogen	100kg	Emulsifier
EL 360		EL 360		
Castor oil ethoxylate		Castor oil ethoxylate		
Xylene	250kg	Xylene	250kg	Solvent
N,N-dipropyldodeca	300kg	N,N-dipropylnonamide	300kg	Crystallizati
namide				on inhibitor
Total	1000kg	Total	1000kg	

# Use Example XIV

The experimental results are set forth in the following table.

	Example 14			Comparison N		
	Press.	Tebucona	Tebuconazole	Press.	Tebucona	Tebucona
	(PSI)	zole (ppm)	decrease %	(PSI)	zole	zole
	200			200	(ppm)	decrease
	mesh			mesh		%
Initial	40	1098	0	40	1148	0
solution						

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After 1h	40	1057	-3.73	40	712	-37.98
After 2h	40	1044	-4.92	42	564	-50.87
After 3h	39	1026	-6.56	46	484	-57.88
After 4h	42	994	-9.47	46	402	-65.03

#### Example 15

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The formulation of Example 15 was prepared containing N, N-dialkyl long chain alkylamides, wherein the weight ratio of tebuconazole to N, N-dialkyl long chain alkylamides was approx 1:1.2. Crystal formation of this formulation was compared with a second liquid formulation, which was prepared from identical components in an identical manner, but containing an alkylamide with lower alkyl groups.

The formulation of Example 15 contained N,N-dialkyl long chain alkylamides in an amount of 30% wt. Table 15 describes the liquid formulation of Example 15 and the comparison formulation, Comparison O

EXAMPLE 15: Tebuconazole EC		COMPARISON O: Tebuconazole		Remark
(with long chain alkylam	nide)	EC (with lower chain a	alkylamide)	
Component	Composition	Component	Composition	
Tebuconazole tech	250kg (as	Tebuconazole tech	250kg (as	Active
	pure)		pure)	ingredient
Agnique ABS 60C	100kg	Agnique ABS 60C	100kg	Emulsifier
Calcium		Calcium		
dodecylphenyl		dodecylphenyl		
sulphonate		sulphonate		
Emulsogen	100kg	Emulsogen	100kg	Emulsifier

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EL 360		EL 360		
Castor oil ethoxylate		Castor oil ethoxylate		
Xylene	250kg	Xylene	250kg	Solvent
N,N-dibutyloctanamide	300kg	N,N-dibutylhexamide	300kg	Crystallizati
				on inhibitor
Total	1000kg	Total	1000kg	

Use Example No. XV

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The experimental results of the test for crystal formation are set out in the table which follows.

	Example 15		Comparison O			
	Press.	Tebuco	Tebuconazole	Press.	Tebuconaz	Tebuconazole
	(PSI)	nazole	decrease %	(PSI)	ole (ppm)	decrease%
	200	(ppm)		200		
	mesh			mesh		
Initial	40	1243	0	40	1234	0
solution						
After	40	1195	-3.86	40	743	-39.79
1h						
After	40	1154	-7.16	Nozzles		
2h				100%		
				blocked		
After	39	1138	-8.45	Nozzles		
3h				100%		

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				blocked	
After	41	1102	-11.3		
4h					

From the experimental data set out above, it can be seen that the long chain alkyl amides of Formula I above exhibit significant performance in inhibiting the crystallization of the pesticidally active azole derivatives. In particular, the long chain alkyl amides perform significantly better than the corresponding lower alkyl compounds and exhibit a markedly higher activity in preventing crystallization of the azole derivatives.

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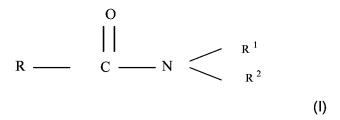
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The foregoing written specification is considered to be sufficient to enable one skilled in the art to practice the invention. The present invention is not to be limited in scope by examples provided, since the examples are intended as a single illustration of one aspect of the invention and other functionally equivalent embodiments are within the scope of the invention. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art form the foregoing description and fall within the scope of the appended calims. The advantages and objects of the invention are not necessarily encompassed by each embodiment of the invention.

#### **CLAIMS**

 An agrochemical composition comprising an N,N-dialkyl long chain alkylamide of the formula (I)



in which:

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- (a) R<sup>1</sup> and R<sup>2</sup> are each independently normal alkyl radicals having 2 carbon atoms, and R represents an alkyl group having from 10 to 30 carbon atoms; or
- (b) R<sup>1</sup> and R<sup>2</sup> are each independently normal alkyl radicals having 3 carbon atoms, and R represents an alkyl group having from 9 to 30 carbon atoms; or
- (c) R<sup>1</sup> and R<sup>2</sup> are each independently normal alkyl radicals having from 4 to 20 carbon atoms and R represents an alkyl group having from 6 to 30 carbon atoms; and at least one azole active ingredient having the general formula (II)

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$$R_{1} - C - R_{2}$$

$$CH_{2}$$

25 (II)

in which R<sub>1</sub> represents phenyl, 4-chlorophenyl, 4-chlorophenylethyl, 4-fluorophenyl, 2,4-dicholorophenyl, or 4-chlorophenyloxy;

R<sub>2</sub> represents n-butyl, tert-butyl, phenyl, 2-fluorophenyl or a group of the general

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formula (III):

(III)

and

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R<sub>3</sub> represents hydroxyl, oxygen or cyano,

and optionally at least one member selected from the group consisting of a surface-active agent, organic diluent and low temperature stabilizer.

- 2. The composition according to claim 1, wherein in case (a), R represents an alkyl group having from 10 to 25 carbon atoms, more preferably from 11 to 18 carbon atoms.
- 15 3. The composition according to claim 1, wherein in case (b), R represents an alkyl group having from 9 to 25 carbon atoms, more preferably from 9 to 18 carbon atoms.
  - 4. The composition according to claim 1, wherein in case (c), R represents an alkyl group having from 6 to 25 carbon atoms, more preferably from 6 to 18 carbon atoms.
  - 5. The composition according to either of claims 1 or 4, wherein in case (c), R<sup>1</sup> and R<sup>2</sup> each represent an alkyl group having from 4 to 12 carbon atoms, more preferably from 4 to 8 carbon atoms.
- 25 6. The composition according to any preceding claim, wherein R is a normal alkyl group.
  - 7. The composition according to any preceding claim, wherein the total number of carbon atoms in R, R<sup>1</sup> and R<sup>2</sup> is greater than 16, preferably greater than 18, more preferably

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greater than 20.

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- 8. The composition according to any preceding claim, wherein the ratio of azole active ingredient and N, N-dialkyl long chain alkylamide is from 1:0.1 to 1:5, more preferably from 1:1 to 1:4.
- 9. The composition according to any preceding claim, wherein two or more N, N-dialkyl long chain alkylamides are present.
- 10. The composition according to any preceding claim, wherein two or more azole active ingredients are present.
  - 11. The composition according to any preceding claim, wherein the N, N-dialkyl long chain alkylamide is selected from the group consisting of diethyldodecanamide,
- diethyltridecanamide, N,N-diethyltetradecanamide, N,N-diethylhexadecanamide, N,N-diethylheptadecanamide, N,N-diethyloctadecanamide, N,N-diethylnonadecanamide, N,N-dipropyldecanamide, N,N-dipropyldecanamide, N,N-dipropyltetradecanamide, N,N-diethylhexadecanamide, N,N-dipropylheptadecanamide, N,N-dipropyl octadecanamide, N,N-dipropylnonadecanamide, N,N-dibutylheptamide,
- 20 N,N-dibutyloctanamide,N,N-dibutylnonamide, N,N-dibutyldecanamide,
  - N,N-dibutyldodecanamide, N,N-dibutyltridecanamide,
  - N, N-dibuty I tetra decanamide, N, N-dibuty I hexadecanamide, N, N-dibuty I hepta decanamide, N, N-dibuty I hepta decanamide
  - N,N-dibutyloctadecanamide,N,N-dibutylnonadecanamide,
  - N,N-dipentyloctanamide,N,N-dipentyldecanamide,
- N,N-dipentyldodecanamide, N,N-dipentyltetradecanamide, N,N-dipentylhexadecanamide, N,N-dipentyloctadecanamide, or any mixture thereof.
  - The composition according to any preceding claim, wherein the N, N-dialkyl long chain

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alkylamide is present in an amount of from 5% to 80% by weight, more preferably from 20% to 60% by weight.

- 13. The composition according to any preceding claim, wherein the azole derivative is
   5 selected from tebuconazole, cyproconazole, triticonazole, hexaconazole, flutriafol,
   myclobutanil and mixtures thereof.
  - 14. The composition according to any of claims 1 to 12, wherein the azole derivative is selected from difenoconazole, diniconazole, propiconazole, tricyclazole, triticonazole, triflumizole, flusilazole, metconazole.

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- 15. The composition according to any preceding claim, further comprising a solvent or diluent.
- 16. The composition according to claim 15, wherein the solvent or diluent is dimethyl formamide or xylene.
  - 17. The composition according to any preceding claim, further comprising an emulsifier.
- 20 18. An aqueous spray composition comprising a composition according to any preceding claim and water.
  - 19. The composition according to claim 18, wherein the azole derivative is present in an amount of from 0.0001% to 3% by weight, more preferably from 0.002% to 2% by weight.
  - 20. A use of N, N-dialkyl long chain alkylamides as defined in any preceding claim to inhibit and/or prevent the crystal growth of pesticidally active azole derivatives.

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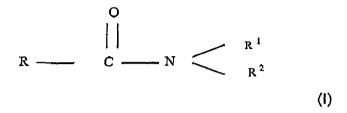
21. A method of preventing crystallization of pesticidal liquid formulations comprising azole derivatives during application, the method comprising adding a N, N-dialkyl long chain alkylamide to the formulation in an amount sufficient to reduce crystallization of the azole derivative.

- 22. A method of treating pests at a locus comprising applying to the locus a composition according to any of claims 1 to 19.
- 23. The method according to claim 22, wherein the composition is applied in the form of a diluted aqueous formulation.
  - 24. The method according to any one of claims 21 to 23, wherein the composition comprises a fungicidally active compound and treats fungal infestations of plants in the locus.

#### **AMENDED CLAIMS**

# received by the International Bureau on 27 October 2008(27.10.2008)

 An agrochemical composition comprising an N,N-dialkyl long chain alkylamide of the formula (I)



in which:

- (a) R<sup>1</sup> and R<sup>2</sup> are each normal alkyl radicals having 2 carbon atoms, and R represents an alkyl group having from 10 to 30 carbon atoms; or
- (b) R<sup>1</sup> and R<sup>2</sup> are each normal alkyl radicals having 3 carbon atoms, and R represents an alkyl group having from 9 to 30 carbon atoms; or
- (c) R<sup>1</sup> and R<sup>2</sup> are each normal alkyl radicals having from 4 to 20 carbon atoms and R represents an alkyl group having from 6 to 30 carbon atoms; and at least one azole active ingredient having the general formula (II)

(11)

in which R<sub>1</sub> represents phenyl, 4-chlorophenyl, 4-chlorophenylethyl,
4-fluorophenyl, 2,4-dicholorophenyl, or 4-chlorophenyloxy;
R<sub>2</sub> represents n-butyl, tert-butyl, phenyl, 2-fluorophenyl or a group of the general

formula (III):

(111)

and

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R<sub>3</sub> represents hydroxyl, oxygen or cyano, and optionally at least one member selected from the group consisting of a surface-active agent, organic diluent and low temperature stabilizer.

- 2. The composition according to claim 1, wherein in case (a), R represents an alkyl group having from 10 to 25 carbon atoms, more preferably from 11 to 18 carbon atoms.
- 15 3. The composition according to claim 1, wherein in case (b), R represents an alkyl group having from 9 to 25 carbon atoms, more preferably from 9 to 18 carbon atoms.
  - 4. The composition according to claim 1, wherein in case (c), R represents an alkyl group having from 6 to 25 carbon atoms, more preferably from 6 to 18 carbon atoms.
  - 5. The composition according to either of claims 1 or 4, wherein in case (c), R<sup>1</sup> and R<sup>2</sup> each represent an alkyl group having from 4 to 12 carbon atoms, more preferably from 4 to 8 carbon atoms.
- 25 6. The composition according to any preceding claim, wherein R is a normal alkyl group.
  - 7. The composition according to any preceding claim, wherein the total number of carbon atoms in R, R<sup>1</sup> and R<sup>2</sup> is greater than 16, preferably greater than 18, more preferably

greater than 20.

- 8. The composition according to any preceding claim, wherein the ratio of azole active ingredient and N, N-dialkyl long chain alkylamide is from 1:0.1 to 1:5, more preferably from 1:1 to 1:4.
- 9. The composition according to any preceding claim, wherein two or more N, N-dialkyl long chain alkylamides are present.
- 10 10. The composition according to any preceding claim, wherein two or more azole active ingredients are present.
  - 11. The composition according to any preceding claim, wherein the N, N-dialkyl long chain alkylamide is selected from the group consisting of diethyldodecanamide,
- diethyltridecanamide, N,N-diethyltetradecanamide, N,N-diethylhexadecanamide, N,N-diethylheptadecanamide, N,N-diethyloctadecanamide, N,N-diethylnonadecanamide, N,N-dipropyldecanamide, N,N-dipropyldecanamide, N,N-dipropyltetradecanamide, N,N-diethylhexadecanamide, N,N-dipropylheptadecanamide, N,N-dipropyl octadecanamide, N,N-dipropylnonadecanamide, N,N-dibutylheptamide,
- 20 N,N-dibutyloctanamide,N,N-dibutylnonamide, N,N-dibutyldecanamide,
  - N.N-dibutyldodecanamide, N,N-dibutyltridecanamide,
  - N,N-dibutyltetradecanamide,N,N-dibutylhexadecanamide,N,N-dibutylheptadecanamide,
  - N,N-dibutyloctadecanamide,N,N-dibutylnonadecanamide,
  - N,N-dipentyloctanamide,N,N-dipentyldecanamide,
- N,N-dipentyldodecanamide, N,N-dipentyltetradecanamide, N,N-dipentylhexadecanamide, N,N-dipentyloctadecanamide, or any mixture thereof.
  - 12. The composition according to any preceding claim, wherein the N, N-dialkyl long chain

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alkylamide is present in an amount of from 5% to 80% by weight, more preferably from 20% to 60% by weight,

- 13. The composition according to any preceding claim, wherein the azole derivative is selected from tebuconazole, cyproconazole, triticonazole, hexaconazole, flutriafol, myclobutanil and mixtures thereof.
- 14. The composition according to any of claims 1 to 12, wherein the azole derivative is selected from difference azole, diniconazole, propiconazole, tricyclazole, triticonazole, triflumizole, flusilazole, metconazole.
- 15. The composition according to any preceding claim, further comprising a solvent or diluent.
- 16. The composition according to claim 15, wherein the solvent or diluent is dimethyl formamide or xylene.
  - 17. The composition according to any preceding claim, further comprising an emulsifier.
- 18. An aqueous spray composition comprising a composition according to any preceding claim and water.
  - 19. The composition according to claim 18, wherein the azole derivative is present in an amount of from 0.0001% to 3% by weight, more preferably from 0.002% to 2% by weight.
  - 20. A use of N, N-dialkyl long chain alkylamides as defined in any preceding claim to inhibit and/or prevent the crystal growth of pesticidally active azole derivatives.

21. A method of preventing crystallization of pesticidal liquid formulations comprising azole derivatives during application, the method comprising adding a N, N-dialkyl long chain alkylamide to the formulation in an amount sufficient to reduce crystallization of the azole derivative.

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- 22. A method of treating pests at a locus comprising applying to the locus a composition according to any of claims 1 to 19.
- 23. The method according to claim 22, wherein the composition is applied in the form of adiluted aqueous formulation.
  - 24. The method according to any one of claims 21 to 23, wherein the composition comprises a fungicidally active compound and treats fungal infestations of plants in the locus.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2008/071116

#### A. CLASSIFICATION OF SUBJECT MATTER See extra sheet According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED В. Minimum documentation searched (classification system followed by classification symbols) IPC: A01N25, A01N43, A01P3, A01N37, C07C233 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) WPI, EPODOC, PAJ, CAPLUS, REG, CNPAT, CNKI, +azole?, +conazole?, flutriafol?, myclobutanil?, tricyclazole?, triflumizole?, flusiazole?, amide?, alklyamid??, carboxamid??, acylamide?, acidamide? C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Category\* 1-24 Х WO 9515685 A1 (BAYER AG.) 15 June 1995 (15.06.1995), claim 1 and example 1, table 2 1-24 X US 5206225 A (BAYER AG.) 27 April 1993 (27.04.1993), claim 1 and examples See patent family annex. Further documents are listed in the continuation of Box C. later document published after the international filing date "T" Special categories of cited documents: or priority date and not in conflict with the application but document defining the general state of the art which is not cited to understand the principle or theory underlying the considered to be of particular relevance invention "X" document of particular relevance; the claimed invention earlier application or patent but published on or after the cannot be considered novel or cannot be considered to involve international filing date an inventive step when the document is taken alone document which may throw doubts on priority claim (S) or document of particular relevance; the claimed invention which is cited to establish the publication date of another cannot be considered to involve an inventive step when the citation or other special reason (as specified) document is combined with one or more other such documents, such combination being obvious to a person document referring to an oral disclosure, use, exhibition or skilled in the art other means "&"document member of the same patent family document published prior to the international filing date but later than the priority date claimed Date of mailing of the international search report Date of the actual completion of the international search 04 Sep. 2008 (04.09.2008) 08 Aug. 2008 (08.08.2008) Name and mailing address of the ISA/CN Authorized officer The State Intellectual Property Office, the P.R.China Changxiaoyu 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Telephone No. (86-10)62084403

Form PCT/ISA/210 (second sheet) (April 2007)

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2008/071116

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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		EP 0453899 A1	1991-10-30
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2008/071116

# Continue of A. CLASSIFICATION OF SUBJECT MATTER

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

A01N 25/22 (2006.01)i

A01N 43/653 (2006.01)I

A01N 37/18 (2006.01)i

C07C 233/00 (2006.01)i

A01P 3/00 (2006.01)n

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