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PATENT SPECIFICATION

NO DRAWINGS

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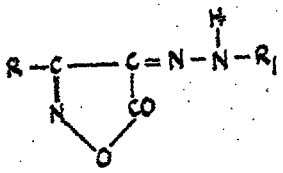
COMPLETE SPECIFICATION

2-Isoxazolin-5-ones and Fungicidal Compositions containing them

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the use as fungicides of 2-isoxazolin-5-ones, to new 2-isoxazolin-5-ones and to processes for their preparation.

The invention provides fungicidal compositions comprising as active ingredient a 2-isoxazolin-5-one of the formula:—



where R is a carboxymethyl or carboxyethyl radical, an alkoxycarbonylalkyl radical or an alkyl radical of 1—6 carbon atoms optionally having a substituent hydroxy or cyano group or a halogen atom and R_1 is a substituted or unsubstituted phenyl or naphthyl radical, and a carrier for the active ingredient said carrier comprising a solid inert diluent, or a liquid diluent containing a surface active agent.

Where the group R_1 is a substituted phenyl or naphthyl radical the substituents can be, for example, one or more of the following:— alkyl and alkoxy radicals of from 1 to 12 and especially from 1 to 4 carbon atoms, *cyclo*alkyl, aryl, (or substituted aryl), arylazo (or substituted arylazo), aryloxy, halogen, carboxy, alkoxycarbonyl, carboamino, cyano, nitro, hydroxyl, trifluoromethyl, amino, N-alkylamino N,N-di-alkylamino, sulphonic acid, sulphonamido, aminosulphonyl or thiocyanate radicals.

It has been found that compounds where the group R_1 is a chloro-substituted phenyl radical or a lower alkyl-substituted phenyl radical possess useful fungicidal properties as is shown in the Examples. Examples of di-substituted phenyl radicals are those in which the substituents are two alkyl or two alkoxy radicals, two atoms of any of the halogens, alkyl and alkoxy, alkyl and nitro, alkoxy and nitro, alkyl and halogen or alkoxy and halogen.

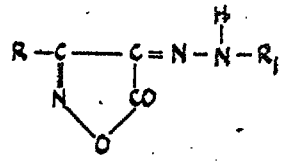
The compound used as active ingredient can if desired be in the form of one of its salts, for example its sodium or potassium salt.

Some of the compounds of the invention have been found to be very effective when applied as foliage fungicides, some when applied as seed-dressings and some as soil fungicides; and the exact form of the fungicidal composition depends to a

large extent upon the use to which the composition is to be put and the pathogen which it is wished to control. For example, the compositions can be powders, solutions, dispersions or pastes. Where they are powders they can be ones in which the active ingredient is in admixture with a powder diluent. Where the composition is liquid it can be one in which the active ingredient is dissolved or suspended in a suitable liquid, for example water or a suitably non-phytotoxic liquid. The ingredients used with the active ingredient in any of the fungicidal compositions of this invention can be substances known to the art as being suitable in the formulation of fungicidal compositions, for example surface active substances such as wetting and dispersing agents, binders, stickers, corrosion inhibitors and stabilising agents.

Fungicidal compositions of the invention which have been found to be useful as liquid seed dressings are solutions of the sodium salt of 3-methyl-4-phenylhydrazono-2-isoxazolin-5-one in β-ethoxyethanol, diacetonyl alcohol or ethylene glycol, and in particular solutions in which the sodium salt is present in a proportion of about 25% w/v.

The invention also consists in the new 2-isoxazolin-5-ones of the general formula:—



where R is an alkyl radical of 2—6 (especially 2—4) carbon atoms, a carboxyalkyl or alkoxycarbonylalkyl radical of not more than 4 carbon atoms, and R_1 is a substituted or unsubstituted phenyl or naphthyl radical; or where R is an alkyl radical of 1—6 (especially 1—4) carbon atoms or a carboxyalkyl or alkoxycarbonylalkyl radical of not more than 4 carbon atoms and R_1 is a chloro-substituted phenyl radical; and their salts.

The 2-isoxazolin-5-ones useful as active ingredients in the fungicidal compositions of this invention can be obtained, for example, by a process in which there is reacted together a keto-ester of the formula:—

$$R—CO—CH_2—COOR_3$$

where R is an alkyl radical of 1—6 (especially 1—4) carbon atoms or a carboxyalkyl or an alkoxycarbonylalkyl radical of not more than 4 carbon atoms and R_3 is an alkyl radical of 1—4 carbon atoms, the appropriate substituted or unsubstituted phenyl or naphthyl diazonium salt and hydroxylamine or a salt of hydroxylamine. The process is conveniently performed with the reactants dissolved or dispersed in water or in a mixture of water and ethanol. The diazonium salt can be conveniently produced *in situ* by the reaction of the appropriate amine and nitrous acid as is illustrated in the Examples of this specification.

A second process for the preparation of the 2-isoxazolin-5-ones is one in which an azo compound of the formula:—

$$R—CO—\underset{\displaystyle COOR_3}{\underset{|}{CH}}—N=N—R_1$$

where R and R_3 have the meanings given to them in connection with the first process described above and R_1 is a substituted or unsubstituted phenyl or naphthyl radical, is reacted with hydroxylamine or a salt thereof. This process is conveniently carried out in mildly alkaline conditions, for example with the reactants dissolved or dispersed in water or in a mixture of water and ethanol and in the presence of caustic alkali or sodium acetate, or in pyridine. Since reaction at room temperature is generally slow the process is preferably carried out at an elevated temperature, for example at a temperature in the range 60—115°C. The azo compound used in this second process can conveniently be obtained *in situ* by the reaction of a keto-ester of formula:—

$$R—CO—CH_2—COOR_3$$

and the appropriate diazonium salt.

In the preparation of compounds of this invention where the group R is a methyl group satisfactory results have been obtained using diketene instead of ethyl acetoacetate.

The invention also consists in a method of combating plant pathogens, in which the foliage of a plant susceptible to such pathogens, seed from which the plant can be grown or soil in which the plant is to be grown, is treated with a compound or fungicidal composition as herein-described.

The invention is illustrated by the following Examples:—

EXAMPLE 1.

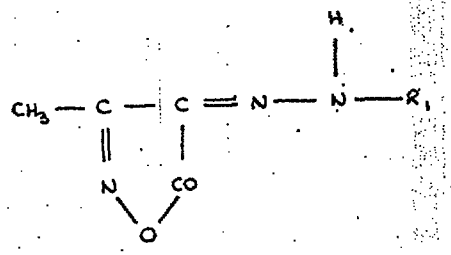
Ethyl acetoacetate (6.6 g.), hydroxylamine hydrochloride (3.5 g.), *m*-toluidine (5.4 g.) and concentrated aqueous hydrochloric acid (10 ml.) were mixed with water (25 ml.) and the mixture was cooled to about 5°C. A cold aqueous solution of sodium nitrite (4.0 g.) in water (10 ml.) was added slowly to the mixture with stirring, care being taken that the temperature did not rise above 10°C. The mixture was then stirred for 6 hours, the temperature being allowed during this time to rise slowly to about 20°C., and filtered. The solid residue which was obtained on the filter was washed with water and crystallised from a mixture of ethanol and benzene. The product thus obtained was *3-methyl-4-(3¹-methylphenyl-hydrazono)-2-isoxazolin-5-one*, as yellow crystals, m.p. 172°C.

EXAMPLE 2.

3-Chloro-4-methylaniline (7.1 g.) was suspended in water (60 ml.) and the mixture acidified with concentrated aqueous hydrochloric acid (18 ml.). After cooling to 5°C. the mixture was diazotised with a solution of sodium nitrite (4.0 g.) in water (15 ml.). The solution so obtained was then added slowly with stirring to a cold (5°C.) mixture of ethyl acetoacetate (6.6 g.) in ethanol (170 ml.) and water (45 ml.) to which had been added anhydrous sodium acetate, (24 g.). The mixture was allowed to stand at about 20°C. for 15 hours, filtered and the solid residue obtained on the filter washed with water. The residue was dissolved in boiling ethanol (100 ml.) and to this solution there was added slowly a hot solution of hydroxylamine hydrochloride (3.5 g.) in water (100 ml.) to which had been added anhydrous sodium acetate (8.2 g.). The mixture so obtained was heated under reflux for 15 minutes, allowed to stand for 15 hours at about 20°C. and filtered. The solid residue which was obtained on the filter was washed with water and crystallised from ethanol. The product thus obtained was *3-methyl-4-(3¹-chloro-4-methylphenylhydrazono)-2-isoxazolin-5-one* as yellow crystals, m.p. 192°C.

EXAMPLES 3—33.

A number of other 2-isoxazolin-5-ones have been prepared by the general methods described above in Examples 1 and 2, but using the appropriate amine in each instance instead of *m*-toluidine and 3-chloro-4-methylaniline used respectively in those Examples. These other 2-isoxazolin-5-ones are set out in the table below as Examples 3—33. The products of Examples 3—15 were obtained by the process of Example 1 while those of Examples 16—33 were obtained by the process of Example 2. The products of Examples 3—33 are believed to all have the general formula:—



where R_1 is a substituted benzene ring and the products are identified in each Example by the meaning given to R_1 in the column having that heading. For the sake of convenience the double bonds have been omitted from all the benzene rings shown. The melting point shown against each product is that obtained using a sample of the product which had been purified by recrystallisation.

TABLE I

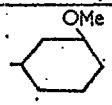
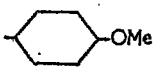
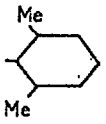
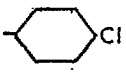
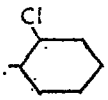
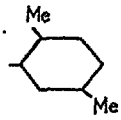
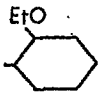
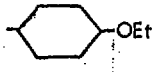
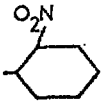
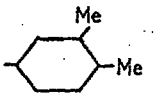
Example No.	Product		
	R_1	m.p. (°C)	Appearance
3		193	yellow crystals
4		208	orange crystals
5		150	orange crystals
6		192	yellow crystals
7		168	orange crystals
8		142	orange crystals
9		140	orange crystals
10		150	orange crystals
11		214	yellow crystals
12		199	yellow crystals

TABLE I (*continued*)

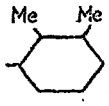
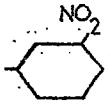
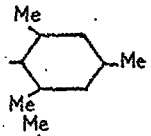
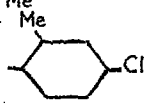
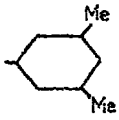
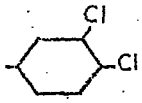
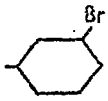
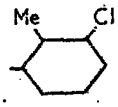
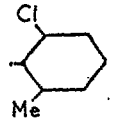
Example No.	Product		
	R_1	m.p.(°C)	Appearance
13		136	orange crystals
14		205	brown crystals
15		128	orange crystals
16		148	orange crystals
17		171	orange crystals
18		193	yellow crystals
19		163	brown crystals
20		194	yellow crystals
21		148	yellow crystals

TABLE I (*continued*)

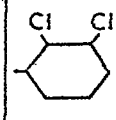
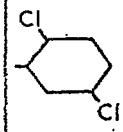
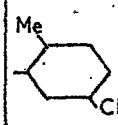
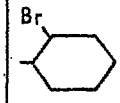
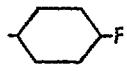
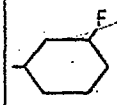
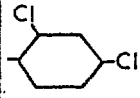
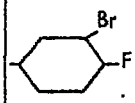
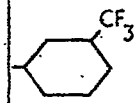
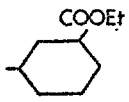
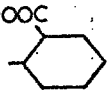
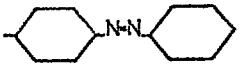
Example No.	Product		
	R_1	m.p. (°C)	Appearance
22		170	yellow crystals
23		182	yellow crystals
24		168	yellow crystals
25		145	yellow crystals
26		165	orange crystals
27		200	yellow crystals
28		160	yellow crystals
29		182	red crystals
30		198	orange crystals

TABLE I (*continued*)

Example No.	Product		
	R_1	m.p.(°C)	Appearance
31		96	yellow crystals
32		120	yellow crystals
33		208	brick-red crystals

EXAMPLE 34.

Ethylacetoacetate (6.6 g.), hydroxylamine hydrochloride (3.5 g.), *m*-chloroaniline (6.4 g.) and concentrated aqueous hydrochloric acid (10 ml.) were added to ethanol (10 ml.) and the mixture cooled to about 5°C. A cold aqueous solution of sodium nitrite (4.0 g.) in water (10 ml.) was added slowly to the mixture with stirring so that the temperature did not exceed 10°C. The mixture was then stirred for a further 6 hours, the temperature being allowed during this time to rise slowly to about 20°C., and filtered. The solid residue which was obtained on the filter was washed with water and crystallised from a mixture of ethanol and benzene. The product thus obtained was *3-methyl-4-(3¹-chlorophenylhydrazono)-2-isoxazolin-5-one* as brown crystals, m.p. 162°C.

EXAMPLE 35.

p-Ethylaniline (6.1 g.) was suspended in water (60 ml.) and the mixture acidified with concentrated aqueous hydrochloric acid (18 ml.). After cooling to 5°C. the mixture was diazotised with a solution of sodium nitrite (4.0 g.) in water (15 ml.). The resulting solution was added slowly with stirring to a cold (5°C.) mixture of ethyl acetoacetate (6.6 g.) in ethanol (170 ml.) and water (45 ml.) to which had been added anhydrous sodium acetate (24 g.). The mixture was allowed to stand at about 20°C. for 15 hours and the heavy oil which was obtained was separated from the aqueous layer and washed with water. The washed oil was dissolved in boiling ethanol (100 ml.) and to this solution there was added slowly a hot solution of hydroxylamine hydrochloride (3.5 g.) in water (100 ml.) to which had been added anhydrous sodium acetate (8.2 g.). The mixture so obtained was heated under reflux for 15 minutes, allowed to stand for 15 hours at about 20°C. and filtered. The solid residue which was obtained on the filter was washed with water and crystallised from ethanol. The product thus obtained was *3-methyl-4-(4¹-ethylphenylhydrazono)-2-isoxazolin-5-one* as yellow crystals, m.p. 154°C.

EXAMPLE 36.

The process described in Example 35 was repeated except that the *p*-ethylaniline (6.1 g.) was replaced by *o*-ethylaniline (6.1 g.). The product when crystallised from ethanol was *3-methyl-4-(2¹-ethylphenylhydrazono)-2-isoxazolin-5-one* as orange crystals, m.p. 122°C.

Examples 37, 38 and 39 describe the preparation of various salts of 2-isoxazolin-5-ones.

EXAMPLE 37.

3-Methyl-4-(3¹-methylphenylhydrazono)-2-isoxazolin-5-one (3 g. of the compound obtained as the product of Example 1 above) was suspended in 10% aqueous sodium hydroxide solution (30 ml.) and ethanol (30 ml.) was added. The mixture was heated at about 80°C. for 2 minutes and the resultant solution was filtered. On cooling the resulting filtrate, a crystalline solid precipitated which was removed by filtration and was washed with ether. The product thus obtained was the *sesquihydrate of the sodium salt of 3-methyl-4-(3¹methylphenylhydrazono)-2-isoxazolin-5-one* as

yellow needles which slowly decomposed on heating but were not completely fused at 300°C.

EXAMPLE 38.

The process described in Example 37 was repeated except that the 3-methyl-4-(3¹-methylphenylhydrazono)-2-isoxazolin-5-one (3 g.) was replaced by 3-methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one (3 g. of the compound obtained as product of Example 6 above). The product was the *trihydrate of the sodium salt of 3-methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one* as yellow crystals, m.p. 170°C. with decomposition.

EXAMPLE 39.

The process described in Example 37 was repeated except that the 3-methyl-4-(3¹-methylphenylhydrazono)-2-isoxazolin-5-one (3 g.) was replaced by 3-methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one (3 g. of the compound obtained as product of Example 6 above) and the 10% aqueous sodium hydroxide (30 ml.) by 10% aqueous potassium hydroxide (30 ml.). The product was the *sesquihydrate of the potassium salt of 3-methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one* as yellow crystals which decomposed at 170—180°C.

EXAMPLE 40.

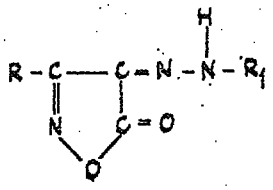
This Examples describes the preparation of 3-methyl-4-(2¹:4¹:5¹-trichlorophenylhydrazono)-2-isoxazolin-5-one by a process which is a modification of the general process described in Example 2 above. The modification consists essentially of the use of pyridine, in place of ethanol, in the process's third stage where the product of the diazonium salt and the keto-ester is reacted with hydroxylamine hydrochloride.

The wet, crude intermediate (23 g.) obtained by reacting ethyl aceto-acetate (6.5 g.) with 2:4:5-trichlorophenyl-diazonium chloride by the general method of Example 2 was mixed with hydroxylamine hydrochloride (3.5 g.) and pyridine (75 ml.) and the mixture was refluxed for 1 hour. The product obtained was then poured into iced water containing hydrochloric acid and the solid which precipitated was removed by filtration and recrystallised from ethanol yielding *3-methyl-4-(2¹:4¹:5¹-trichlorophenylhydrazono) - 2 - isoxazolin - 5 - one* as a reddish - brown solid, m.p. 151°C.

EXAMPLES 41—78.

A number of other 2-isoxazolin-5-ones have been prepared by the general method described in Examples 1, 2 or 40 above, but using various keto-esters and the appropriate amine in each instance. These 2-isoxazolin-5-ones are set out in Table II below as Examples 41—78.

The products of Examples 41—78 were obtained by processes involving a keto-ester of the formula: R—CO—CH_2—COOEt and a diazonium chloride of formula: Cl—N=N—R_1 and are believed to all have a structure corresponding to the general formula:



where R is an alkyl or alkoxycarbonylalkyl radical and R_1 is a substituted benzene ring.

In Table II the product of each Example is identified by reference to the nature of the groups R and R_1, and for the sake of convenience the double bonds have been omitted from all the benzene rings depicted.

With the exceptions of Examples 52, 67, 68, 72, 73, 75 and 76, the compounds of all the Examples in Table II were obtained using the general process described in Example 2 above, but using the appropriate keto-ester and amine in each instance. With regard to the exceptions, the compounds of Examples 67 and 68 were obtained by the general process of Example 1 above; and the compounds of Examples 52, 72, 73, 75 and 76 by the general process of Example 40, using the appropriate keto-ester and amine in each instance.

TABLE II

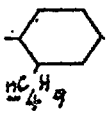
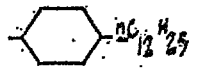
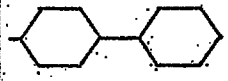
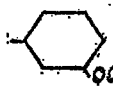
Example No.	Product		
	R	R_1	m.p. (°C).
41	CH_3		48
42	"		92
43	"		91
44	"		202
45	"		162

TABLE II (*continued*)

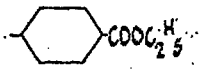
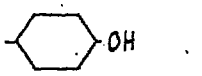
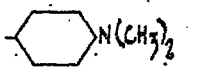
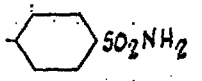
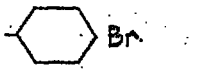
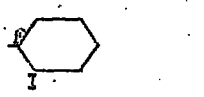
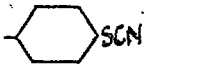
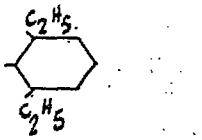
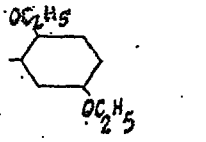
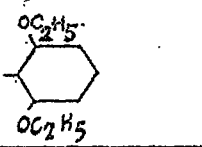
Example No.	Product		
	R	R_1	m.p. (°C.)
46	CH_3		204
47	"		227
48	"		170
49	"		226
50	"		194
51	"		199
52	"		174
53	"		60
54	"		151
55	"		176

TABLE II (*continued*)

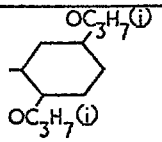
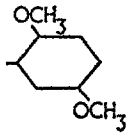
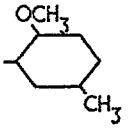
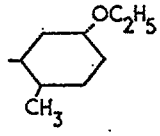
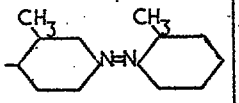
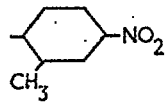
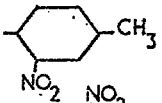
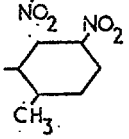
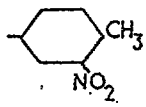
Example No.	Product		
	R	R_1	m.p.(°C)
56	CH_3		124
57	"		187
58	"		146
59	"		151
60	"		127
61	"		190
62	"		177
63	"		175
64	"		199

TABLE II (continued)

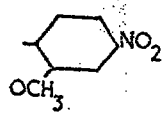
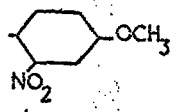
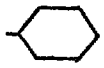
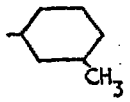
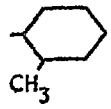
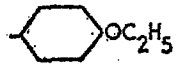
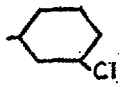
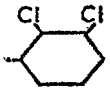
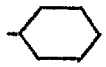
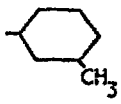
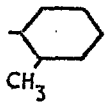
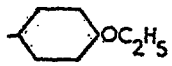
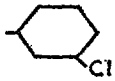
Example No.	Product		
	R	R_1	m.p. (°C).
65	CH_3		208
66	"		184
67	C_2H_5		118
68	"		134
69	"		135
70	"		145
71	"		160
72	"		150
73	nC_4H_9		83

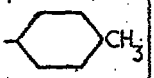
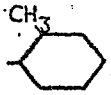
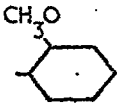
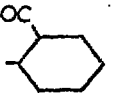
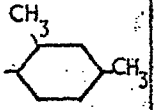
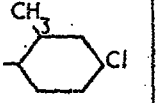
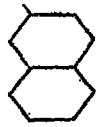
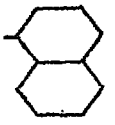
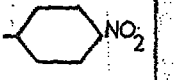
TABLE II (continued)

Example No.	Product		
	R	R_1	m.p. (°C.)
74	C_2H_5—OOC—CH_2—		126
75	"		115
76	"		113
77	"		127
78	"		220

EXAMPLES 79—88.

Table III below includes as Examples 79—88 a number of further 2-isoxazolin-5-ones which have been formulated as fungicidal compositions. The various compounds are identified in Table III, as in Tables I and II, by reference to the nature of the groups R and R_1. The double bonds have, for convenience, been omitted from all the structures depicted.

TABLE III

Example No.	R	R_1	m.p. (°C.)
79	CH_3		190
80	"		204
81	"		160
82	"		178
83	"		228 (with decomposition)
84	"		126
85	"		148
86	"		208
87	"		168
88	"		176

Good results have been obtained using fungicidal compositions of this invention as seed dressings, and in Table IV below there is shown compounds which have been found to be active against a number of economically important fungus and bacterial diseases. Similarly, Table V shows compounds found to be active against various foliage fungus diseases. The active ingredients of the compositions tested have been referred to below, for simplicity, by the number of the Examples in Tables I, II or III in which they appear.

Seed Dressings

TABLE IV

Disease	Crop	Active Ingredient — the product of Example Nos.
Pythium ultimum	Peas	5, 11, 16, 17, 79 and 81
Fusarium culmorum	„	6, 7, 10, 26 and 81
Xanthomonas malvacearum	Cotton	22
Tilletia caries	Wheat	6, 82 and 84

Foliage Fungicides

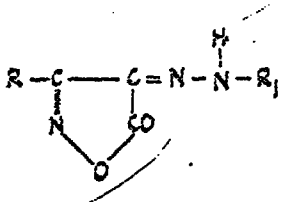
TABLE V

Disease	Crop	Active Ingredient — the product of Example Nos.
Piricularia oryzae	Rice	6, 7, 20, 36 and 85
Plasmopara viticola	Vines	7
Erysiphe cichoracearum	Cucumbers	1, 7, 10, 81 and 84
Venturia inaequalis	Apples	7, 19 and 81
Alternaria solani	Tomatoes	34 and 79
Erysiphe graminis	Oats	4 and 7
Botrytis fabae	Broad Beans	19 26, 39 and 79

The compounds of Examples 5, 6, 11, 16, 26, 81, 82 and 84 have been found to be active against the soil-borne disease *Rhizoctonia solani*.

WHAT WE CLAIM IS:—

1. A fungicidal composition comprising as active ingredient a 2-isoxazolin-5-one of the formula:—



Good results have been obtained using fungicidal compositions of this invention as seed dressings, and in Table IV below there is shown compounds which have been found to be active against a number of economically important fungus and bacterial diseases. Similarly, Table V shows compounds found to be active against various foliage fungus diseases. The active ingredients of the compositions tested have been referred to below, for simplicity, by the number of the Examples in Tables I, II or III in which they appear.

Seed Dressings

TABLE IV

Disease	Crop	Active Ingredient — the product of Example Nos.
Pythium ultimum	Peas	5, 11, 16, 17, 79 and 81
Fusarium culmorum	„	6, 7, 10, 26 and 81
Xanthomonas malvacearum	Cotton	22
Tilletia caries	Wheat	6, 82 and 84

Foliage Fungicides

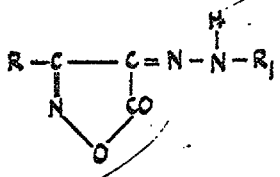
TABLE V

Disease	Crop	Active Ingredient — the product of Example Nos.
Piricularia oryzae	Rice	6, 7, 20, 36 and 85
Plasmopara viticola	Vines	7
Erysiphe cichoracearum	Cucumbers	1, 7, 10, 81 and 84
Venturia inaequalis	Apples	7, 19 and 81
Alternaria solani	Tomatoes	34 and 79
Erysiphe graminis	Oats	4 and 7
Botrytis fabae	Broad Beans	19 26, 39 and 79

The compounds of Examples 5, 6, 11, 16, 26, 81, 82 and 84 have been found to be active against the soil-borne disease *Rhizoctonia solani.*

WHAT WE CLAIM IS:—

1. A fungicidal composition comprising as active ingredient a 2-isoxazolin-5-one of the formula:—



* C L M S *

where R is a carboxymethyl or carboxyethyl radical, an alkoxycarbonyl alkyl radical or an alkyl radical of 1—6 carbon atoms optionally having a substituent hydroxy or cyano group or a halogen atom and R_1 is a substituted or unsubstituted phenyl or naphthyl radical, and a carrier for the active ingredient, said carrier comprising a solid inert diluent, or a liquid diluent containing a surface active agent.

2. A composition according to Claim 1 where the active ingredient is a compound in which the group R is a methyl radical.

3. A composition according to Claims 1 or 2 where the active ingredient is a compound in which the group R_1 is a chloro-substituted phenyl radical.

4. A composition according to Claims 1 or 2 where the active ingredient is a compound in which the group R_1 is a lower alkyl-substituted phenyl radical.

5. A fungicidal composition containing as active ingredient 3-methyl-4-phenylhydrazono-2-isoxazolin-5-one.

6. A fungicidal composition containing as active ingredient 3-methyl-4-(2¹-methylphenylhydrazono)-2-isoxazolin-5-one.

7. A fungicidal composition containing as active ingredient 3-methyl-4-(2¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

8. A fungicidal composition containing as active ingredient 3-methyl-4-(3¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

9. A fungicidal composition containing as active ingredient 3-methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

10. A fungicidal composition containing an active ingredient 3-methyl-4-(2¹-methyl-4¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

11. A fungicidal composition containing as active ingredient a salt of a 2-isoxazolin-5-one referred to in any one of the preceding claims.

12. A fungicidal composition according to Claim 11 in which the salt is a sodium or potassium salt.

13. A composition according to any one of Claims 1 to 12 in which the carrier is a solid inert diluent which is in powdered form.

14. A composition according to any one of Claims 1 to 12 in which the carrier is a suitably non-phytotoxic liquid.

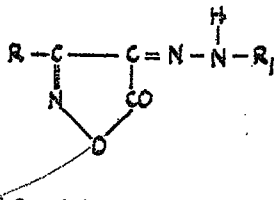
15. A composition according to Claim 13 wherein said composition comprises a surface active agent.

16. A composition according to any one of Claims 1 to 15 which contains a corrosion inhibitor.

17. A fungicidal seed-dressing composition comprising a solution of the sodium or potassium salt of 3-methyl-4-phenylhydrazono-2-isoxazolin-5-one in a suitably non-phytotoxic solvent.

18. A fungicidal composition according to Claim 17 in which the sodium salt is present in a proportion of about 25% w/v.

19. A 2-isoxazolin-5-one of the general formula:—



where R is an alkyl radical of 2—6 (especially 2—4) carbon atoms, or a carboxyalkyl or alkoxycarbonylalkyl radical of not more than 4 carbon atoms, and R_1 is a substituted or unsubstituted phenyl or naphthyl radical.

20. A 2-isoxazolin-5-one of the formula shown in Claim 19 where R is an alkyl radical of 1—6 (especially 1—4) carbon atoms, or a carboxyalkyl or alkoxycarbonylalkyl radical of not more than 4 carbon atoms, and R_1 is a chloro-substituted phenyl radical.

21. 3-Methyl-4-(2¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

22. 3-Methyl-4-(3¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

23. 3-Methyl-4-(4¹-chlorophenylhydrazono)-2-isoxazolin-5-one.

24. A salt of a 2-isoxazolin-5-one claimed in any one of Claims 19 to 23.

25. A process for the preparation of the 2-isoxazolin-5-ones claimed in Claims 19 or 20 in which there is reacted together a keto-ester of the formula:—

* C L M S *

$$R—CO—CH_2—COOR_3$$

where R has the meaning given to it in Claim 20 and R_3 is an alkyl radical of 1—4 carbon atoms, the appropriate substituted or unsubstituted phenyl or naphthyl diazonium salt and hydroxylamine or a salt of hydroxylamine.

26. A process for the preparation of the 2-isoxazolin-5-ones, claimed in Claims 19 or 20, in which an azo compound of the formula: —

$$R—CO—\underset{\displaystyle COOR_3}{\underset{|}{CH}}—N=N—R_1$$

where R and R_3 have the meanings given to them in Claim 25, R_1 is a substituted or unsubstituted phenyl or naphthyl radical, is reacted with hydroxylamine or a salt thereof.

27. A modification of the process claimed in Claim 25 in which diketene is used instead of ethyl acetoacetate.

28. A process for the preparation of a 2-isoxazolin-5-one substantially as described in Examples 1, 2, 34, 35 or 40.

29. A 2-isoxazolin-5-one which has been obtained by the process of any one of Claims 25 to 28.

30. A fungicidal composition containing as active ingredient the compound obtained as product of any of Examples 1 to 39.

31. A fungicidal composition containing as active ingredient the compound obtained as product of any one of Examples 40 to 78.

32. A fungicidal composition containing as active ingredient the compound of any one of Examples 79 to 88.

33. A method of combating plant pathogens, in which the foliage of a plant susceptible to such pathogens, seed from which the plant can be grown or soil in which the plant is to be grown, is treated with a compound or a fungicidal composition substantially as herein-before described with particular reference to the examples.

WALTER SCOTT,
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ERRATUM

SPECIFICATION No. 999,097
Amendment No. 1

Page 16, line 1, *for* "alkoxycarbonyl alkyl"
read "alkoxycarbonylalkyl"

THE PATENT OFFICE
27th August 1965

