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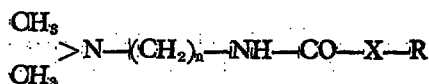


(54) SALTS OF CARBAMIC ACID ESTERS AND
 THIOCARBAMIC ACID ESTERS HAVING A
 FUNGICIDAL AND FUNGISTATIC ACTION

(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, 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:—

The present invention is concerned with new salts of N-(dialkylaminoalkyl)- carbamic acid esters and N-(dialkylaminoalkyl)-thiocarbamic acid esters having a fungicidal and fungistatic action, and with their manufacture and use.

The present invention provides a salt of a compound of the general formula I



I

in which

- 20 R represents an aliphatic hydrocarbon group preferably containing 2 to 4 carbon atoms,
 X represents an oxygen or sulphur atom and
 n represents 2, 3 or 4,
 25 with any inorganic or organic acid.

It is found that these new compounds exhibit a fungicidal as well as a fungistatic action and are, therefore, especially suitable for combatting phytopathogenic fungi.

- 30 In the general formula I, the symbol R may represent, for example, a straight-chain or branched, saturated or unsaturated, aliphatic hydrocarbon group, for example an ethyl, propyl, butyl, isopropyl, tert.-butyl or allyl group.
 35

As acids from which the salts of the present invention are derived, there may be mentioned any desired inorganic or organic acids, for example mineral acids, monocarboxylic or polycarboxylic acids and sulphonic acids, amongst which the following may be mentioned by way of example: hydrochloric acid, sulphuric acid, formic acid, propionic acid, valeric acid, oxalic acid, malonic acid, succinic acid, cyanoacetic acid, chloroacetic acid, dihaloroacetic acid, trifluoroacetic acid, benzoic acid, furan-2-carboxylic acid, *p*-toluenesulphonic acid, methanesulphonic acid, thioglycollic acid and citric acid.

The salts of the present invention exhibit an outstanding fungicidal and fungistatic action and in this respect surprisingly surpass the compounds best-known for having the same type of action. In particular, germination stimulants such as *Pythium ultimum* can be combatted. A further advantage is their excellent toleration by plants. Furthermore, their good solubility in water as well as their suitability for the manufacture of dry preparations should be emphasised, since some of the salts are crystalline substances and others are highly viscous oils.

They may, therefore, be used in agriculture or in horticulture, predominantly for general soil treatment, as disinfectants for seed treatment or as co-drilling agents for the treatment of seed furrows.

Accordingly the present invention also provides a fungicidal preparation which comprises a salt of a compound of the general formula I with an inorganic acid or an organic acid, in admixture or conjunction with a suitable carrier.

The present invention further provides a method of treating a seed, wherein a seed is

treated with one or more of the new salts of the present invention.

The present invention furthermore provides a method of treating a crop area, wherein a crop area is treated with one or more of the new salts of the present invention.

In addition, the present invention provides a method of protecting a living plant against phytopathogenic fungi, wherein a living plant is treated with one or more of the new salts of the present invention. The salts according to the present invention may in each case be employed alone or as mixtures with one another and/or with other plant protection agents or pesticides, for example with insecticides or nematocides, if the simultaneous control of these or other pests is desired, or with other fungicides in order to widen the action spectrum. The fungicidal preparations may be in the form of, for example, dusting agents, granulates, solutions, emulsions or suspensions and may contain solid and/or liquid diluents or carriers and, if desired, adhesives, wetting agents, emulsifiers and/or dispersing agents. It is also possible to use the new salts in the form of their aqueous solutions.

As liquid carriers, there may be mentioned water, mineral oils or other organic solvents, for example xylene, chlorobenzene, cyclohexanol, cyclohexanone, dioxan, acetonitrile, ethyl acetate, dimethylformamide and dimethylsulphoxide.

As solid carriers there may be mentioned, for example, lime, attaclay and other clays, kaolin, chalk, talc as well as natural or synthetic silica.

As surface-active substances, there may be mentioned, for example, salts of ligninsulphonic acids, salts of alkylated benzenesulphonic acids, sulphonated acid amides and their salts, polyethoxylated amines and alcohols.

When the active substances are intended to be used for the disinfection of seeds, it is also possible to admix them with dyestuffs, for example New Fuchsine, in order to distinguish seeds that have been treated with the active substances by a clearly visible colouration.

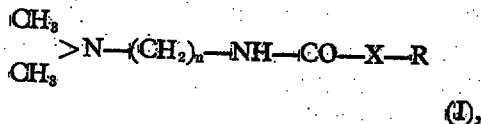
The manufacture of the various forms of fungicidal preparations is effected in a manner known *per se*, for example by a grinding or mixing process.

In order to promote the germination of seeds, the materials are either directly applied to the seed, in a manner which is known *per se* before sowing, or are introduced into the seed furrow (so-called co-drilling) during sowing. When the soil itself is treated, the materials are preferably introduced into the upper soil layers, up to a depth of about 20 cm, for example by milling-in.

Examples 9 to 11 below illustrate the action and use, of salts of the present invention.

The new salts of the present invention may be manufactured by methods that are known *per se*, for example by

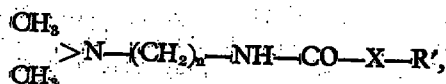
a) neutralising, in a known manner, a compound of the general formula I



in which R represents an aliphatic hydrocarbon group preferably containing 2 to 4 carbon atoms, X represents an oxygen or sulphur atom and n represents 2, 3 or 4, with an inorganic or organic acid, or

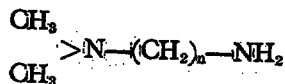
b) replacing, in a known manner, the acid residue of a salt of a compound of the general formula I, in which R, X and n have the meanings given above, by another acid residue by double decomposition of two salts, or

c) replacing, in a known manner, the ester group R' of a salt of a compound of the general formula



in which R' represents an aliphatic hydrocarbon group and X and n have the meanings given above, by an ester group R, R having the meaning given above, by trans-esterification, or

d) reacting, in a known manner, a compound of the general formula

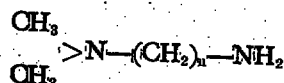


in which n has the meaning given above, or a salt thereof with a hydrohalic acid, with a chloroformic acid ester or thioester of the general formula

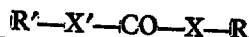


in which R and X have the meanings given above, and, if desired, replacing, in a known manner, the acid residue in the resulting chloride by another acid residue by double decomposition of two salts, or

e) reacting, in a known manner, a compound of the general formula



in which n has the meaning given above, or a salt thereof with a hydrohalic acid, with a carbonic acid ester, thioester or dithioester of the general formula



in which R' represents an aliphatic hydrocarbon group, X' represents an oxygen or sul-

phur atom and R and X have the meanings given above, and neutralising, in a known manner, the resulting compound of the general formula I with an inorganic or organic acid.

- 5 The reactions (a), (b) and (d) are preferably carried out in a solvent such as water or an organic solvent, for example an ether, alcohol, hydrocarbon or halogenated hydrocarbon. For reaction (c), the alcohol having the desired ester group is used in excess.

10 Reactions (a) and (d) may, however, also be carried out without the use of solvents.

The reaction temperatures may be chosen as desired and depend on the nature of the

reagents. They lie approximately within the range of from -20 to 100°C . The isolation of the resulting salts is also effected according to methods that are known *per se*, for example by filtering off the resulting crystals with suction, by decantation of the supernatant solutions from the precipitated oils or by concentrating the solutions to dryness.

Examples 1 to 8 below illustrate some manufacturing processes used for preparing compounds of the present invention.

Some salts according to the present invention are listed in the following Table:

Name of Compound	Physical constant
N-(3-Dimethylaminopropyl)-carbamic acid ethyl ester chloride	$n_D^{20}=1.4915$
N-(3-Dimethylaminopropyl)-carbamic acid ethyl ester benzoate	$n_D^{20}=1.5080$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester chloride	$n_D^{20}=1.4865$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester formate	$n_D^{20}=1.4600$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester propionate	$n_D^{20}=1.4390$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester valerate	$n_D^{20}=1.4440$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester hydrogen oxalate	melting point: $112-115^{\circ}\text{C}$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester malonate	$n_D^{20}=1.4675$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester succinate	$n_D^{20}=1.4700$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester cyanoacetate	$n_D^{20}=1.4662$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester chloroacetate	$n_D^{20}=1.4740$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester dichloroacetate	$n_D^{20}=1.4675$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester trifluoroacetate	$n_D^{20}=1.4245$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester furan-2-carboxylate	$n_D^{20}=1.4860$
N-(3-Dimethylaminopropyl)-carbamic acid propyl ester <i>p</i> -toluenesulphonate	$n_D^{20}=1.5000$
N-(3-Dimethylaminopropyl)-carbamic acid butyl ester chloride	$n_D^{20}=1.4729$
N-(3-Dimethylaminopropyl)-thiocarbamic acid S-propyl ester chloride	$n_D^{20}=1.5210$

The compounds are mostly crystalline substances or highly viscous oils. They possess a good to very good solubility in water, methanol and ethanol, and other solvents.

- 5 The starting materials for the manufacture of the salts according to the present invention can also be manufactured by methods that are known *per se*, for example by reaction of a dimethylalkylamine with an appropriate chloroformic acid ester or thioester in a suitable solvent, if desired in the presence of an acid-binding agent. Inert organic liquids, for example ethers or hydrocarbons, may be used as solvents for this purpose. Suitable acid-binding agents are, for example, tertiary organic amines, for example triethylamine or

pyridine, inorganic bases, for example alkali metal hydroxides or alkali metal carbonates, or also the amine required for the reaction, which is then used in an appropriately larger amount. The reaction takes place smoothly within a temperature range of from about 0° to 100°C but can also be effected at higher or lower temperatures. The reaction can be carried out as a single-phase or two-phase reaction, the latter whilst using non-miscible liquids, for example water and an organic solvent.

The following are some of the starting materials used to prepare salts of the present invention:

N-(γ-Dimethylaminopropyl)-thiocarbamic acid S-ethyl ester

undistillable oil
 $n_D^{20}=1.4965$

N-(γ-Dimethylaminopropyl)-carbamic acid ethyl ester

boiling point (16 mm):
121—124°C
 $n_D^{20}=1.4478$

N-(γ-Dimethylaminopropyl)-carbamic acid propyl ester

boiling point (18 mm):
139—141°C
 $n_D^{20}=1.4490$

N-(γ-Dimethylaminopropyl)-carbamic acid butyl ester

boiling point (18 mm):
146—148°C
 $n_D^{20}=1.4505$

The following Examples illustrate the invention:

EXAMPLE 1.

- 35 N-(3-Dimethylaminopropyl)-thiocarbamic acid S-ethyl ester chloride
14.25 g (0.075 mol) of N-(3-dimethylaminopropyl)-thiocarbamic acid S-ethyl ester were dissolved in 250 ml of absolute ether. Dry hydrogen chloride gas was introduced whilst stirring and cooling. After 1 hour the product was filtered with suction. 14.1 g of product (83.4% of the theoretical yield) of melting point 87—94°C were obtained. After reprecipitation from isopropanol/ether a product of melting point 93—94°C was obtained.

EXAMPLE 2.

- 50 N-(3-Dimethylaminopropyl)-carbamic acid propyl ester hydrogen sulphate
11.0 g (0.0585 mol) of N-(3-dimethylaminopropyl)-carbamic acid propyl ester were dissolved in 200 ml of ether. 3.2 ml (0.06 mol) of concentrated sulphuric acid were added dropwise whilst stirring and cooling. The mixture was stirred for a further 2 hours at room temperature, the ether was decanted, and the oil was washed with ether and stripped *in vacuo*. 115.0 g of a product 89.7% of the theoretical yield) of melting point 44—50°C were obtained.

EXAMPLE 3.

N-(3-Dimethylaminopropyl)-carbamic acid propyl ester benzoate
14.1 g (0.075 mol) of N-(3-dimethylaminopropyl)-carbamic acid propyl ester were dissolved in 200 ml of ether. 9.15 g (0.075 mol) of benzoic acid in 30 ml of tetrahydrofuran were added dropwise whilst stirring. The mixture was stirred for a further 2 hours, the solvent was distilled off and the oil was stripped *in vacuo*. 23.1 g of a product (99.4% of the theoretical yield) having an n_D^{20} value of 1.5070 were obtained.

EXAMPLE 4.

75 N-(3-Dimethylaminopropyl)-carbamic acid ethyl ester chloride
27.2 g (0.1 mol) of N-(3-dimethylaminopropyl)-carbamic acid ethyl ester hydrogen sulphate were dissolved in 50 ml of water and to this solution was slowly added a solution of 24.4 g (0.1 mol) of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 60 ml of water, whilst stirring. The mixture was stirred for 15 minutes, 100 ml of ethanol were added, the precipitated barium sulphate was filtered off with suction and the aqueous solution was treated with active charcoal, filtered, concentrated and stripped *in vacuo*.
14.7 g of oil having an n_D^{20} value of 1.4900 were obtained.

EXAMPLE 5.

N-(3-Dimethylaminopropyl)-carbamic
acid butyl ester chloride

21.0 g (0.1 mol) of N-(3-dimethylamino-
propyl)-carbamic acid ethyl ester chloride were
suspended in 100 ml of *n*-butanol. Dry hydro-
gen chloride gas was passed into the suspension
for a short time and the mixture was heated
for 6 hours at 100–115°C whilst stirring,
whereby the hydrochloride dissolved and a few
ml of liquid distilled off. The material was
then concentrated and the residue was stripped
in *vacuo*.

18.0 g of a product having an $n_{D_{20}}$ value of
1.4750 were obtained.

EXAMPLE 6.

N-(3-Dimethylaminopropyl)-carbamic
acid butyl ester chloride

4.6 g (0.2 g atom) of sodium were dis-
solved in 200 ml of *n*-butanol. 21.0 g (0.1
mol) of N-(3-dimethylaminopropyl)-carbamic
acid ethyl ester chloride were added thereto
and the mixture was boiled for 6 hours under
reflux. It was concentrated; treated with water;
extracted with ether, the ether phase was dried
over magnesium sulphate; dry hydrogen
chloride gas was passed in whilst stirring and
cooling; the ethereal solution was decanted and
the supernatant oil was stripped in *vacuo*.

13.1 g of a product having an $n_{D_{20}}$ value
of 1.4735 were obtained.

EXAMPLE 7.

N-(3-Dimethylaminopropyl)-thiocarbamic
acid S-ethyl ester chloride

12.25 g (0.1 mol) of chlorothioformic acid
S-ethyl ester were dissolved in 50 ml of abso-
lute ether. 110.2 g (0.1 mol) of N,N-dimethyl-
propanediamine-(1,3) in 100 ml of ether were
slowly added dropwise at 30 to 36°C, whilst
stirring. The mixture was stirred for a further
1 hour and filtered with suction.

22.0 g of a product of melting point 90–
94°C were obtained.

EXAMPLE 8.

N-(3-Dimethylaminopropyl)-carbamic
acid ethyl ester chloride

20.4 g (0.2 mol) of N,N-dimethylpropane-
diamine-1,3, were boiled for 3 hours under
reflux with 80 ml of diethyl carbonate. The
mixture was then distilled and 5.2 g of N-(3-
dimethylaminopropyl)-carbamic acid ethyl
ester, having a boiling point of 123°C
and an $n_{D_{20}}$ value of 1.4486, were obtained.
The product was dissolved in 100 ml of abso-
lute ether, dry hydrogen chloride gas was in-
troduced, the ethereal solution was decanted
and the residual oil was stripped in *vacuo*.

5.9 g of a product having an $n_{D_{20}}$ value
of 1.4915 were obtained.

Other compounds of the present invention,
for example those listed in the Table above
but not described in Examples 1 to 8, may
be obtained by a procedure analogous to any
one of the procedures described in Examples
1 to 8 above.

EXAMPLE 9.

Steamed compost soil was inoculated with
mycelium of *Pythium ultimum*. After uni-
formly mixing the active materials indicated
in the Table, in the form of powder prepa-
rations, with the infected soil, 25 marrowfat
peas of the "Wonder of Kelvedon" variety
were sown for each concentration in earthen-
ware dishes holding 1 litre of soil, without a
waiting period. The Table records the number
of germinated healthy peas and the root assess-
ment (1 to 4) after a period of cultivation of
3 weeks at 25–29°C. The hitherto known
CAPTAN (N-trichloromethyl-thio-tetrahydro-
phthalimide) was used as the comparison
material.

Root Assessment:

- 4 = white roots without fungal necroses.
- 3 = white roots, slight fungal necroses.
- 2 = brown roots with more pronounced
fungal necroses.
- 1 = pronounced fungal necroses, roots
rotted.

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Preparation containing as active substance	Active substance/ liter of soil	Number of healthy peas	Root Assessment (1—4)
N-(3-Dimethylaminopropyl)- thiocarbamic acid S-ethyl ester chloride	50 mg	19	4
	100 mg	20	4
	200 mg	24	4
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen oxalate	50 mg	11	3
	100 mg	16	4
	200 mg	22	4
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester formate	50 mg	18	4
	100 mg	19	4
	200 mg	18	4
CAPTAN	50 mg	4	1
	100 mg	6	1
	200 mg	13	1
Steamed soil (3 control experiments)	A	24	4
	B	24	4
	C	25	4
Untreated soil (3 control experiments)	A	5	1
	B	2	1
	C	2	1

EXAMPLE 10.

Steamed compost soil was inoculated with mycelium of *pythium ultimum*. Peas of the "Wonder of Kelvedon" variety, disinfected with 50% strength preparations containing the active materials indicated in the Table, were sown 2—3 cm deep in earthenware dishes holding 0.5 litres of the inoculated soil;

25 peas per concentration were used. After a period of cultivation of 14 days at 25—29°C the number of healthy germinated peas was recorded. A comparison was made with the hitherto known materials MIANEB (manganese ethylene-bis-dithiocarbamate) and CAPTAN (N-trichloromethylthio-tetrahydrophthalimide).

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Preparation containing as active substance	Number of healthy germinated peas		
	0.5 g of active substance/ kg of seed	1.0 g of active substance/ kg of seed	2.0 g of active substance/ kg of seed
N-(3-Dimethylaminopropyl)- thiocarbamic acid S-ethyl ester chloride	21	24	24
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen oxalate	19	18	20
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester formate	16	20	22
N-(3-Dimethylaminopropyl)- carbamic acid ethyl ester benzoate	5	19	18
N-(3-Dimethylaminopropyl)- carbamic acid ethyl ester chloride	15	15	22
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester chloride	3	9	23
N-(3-Dimethylaminopropyl)- carbamic acid butyl ester chloride	4	9	24
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester benzoate	13	21	25
MANEB	1	8	6
CAPTAN	9	6	13
Steamed soil	A	22	
Seed not disinfected	B	24	
(3 control experiments)	C	25	
Untreated soil	A	2	
Seed not disinfected	B	7	
(3 control experiments)	C	2	

EXAMPLE III.

Disinfection experiment in open soil

3 batches each of 100 marrowfat peas of the "Sperling Salout" variety were sown for each preparation and concentration. The active substances of the present invention used for disinfecting the seeds (and indicated in the Table below) were used in the form of 50% strength powder-form preparations and the materials used for comparison had an active substance content of 92%. (MANEB, that is

manganese - ethylene - bis - dithiocarbamate) and 80% (TMTD, that is tetramethyl- thiuram-disulphide). The healthy germinated peas were counted after a period of cultivation of 14 days. The experiment was carried out at high soil temperatures (20—25°C at a depth of 10 cm). Artificial watering by sprinkling was carried out as required. The following Table contains the average value of the batches of 3 experiments each using 100 peas.

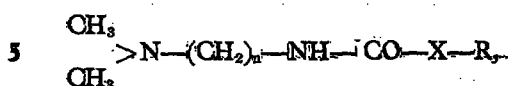
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Preparation containing as active substance	Number of healthy germinated peas as a %	
	1.5 g of preparation per kg of seed	3.0 g of preparation per kg of seed
N-(3-Dimethylaminopropyl)- thiocarbamic acid S-ethyl ester chloride	77	78
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen oxalate	64	74
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester formate	71	76
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester benzoate	64	75
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen sulphate	74	—
TMTD	45	63
MANEB	51	66
Untreated seed	5	5

WHAT WE CLAIM IS:—

1. A salt of a compound of the general formula



in which R represents an aliphatic hydrocarbon group, X represents an oxygen or sulphur atom and n represents 2, 3 or 4, with an inorganic or organic acid.

2. A salt as claimed in claim 1, wherein R represents an aliphatic hydrocarbon group containing 2 to 4 carbon atoms.

3. N - (3 - Dimethylaminopropyl) - carbamic acid ethyl ester chloride.

4. N - (3 - Dimethylaminopropyl) - carbamic acid ethyl ester benzoate.

5. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester chloride.

6. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester formate.

7. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester propionate.

8. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester valerate.

9. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester hydrogen oxalate.

10. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester malonate.

11. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester succinate.

12. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester cyanoacetate.

13. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester chloroacetate.

14. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester dichloroacetate.

15. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester trichloroacetate.

16. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester benzoate.

17. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester furan-2-carboxylate.

18. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester *p*-toluenesulphonate.

19. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester hydrogen sulphate.

20. N - (3 - Dimethylaminopropyl) - carbamic acid butyl ester chloride.

21. N - (3 - Dimethylaminopropyl) - thiocarbamic acid S-ethyl ester chloride.

22. N - (3 - Dimethylaminopropyl) - thiocarbamic acid S-propyl ester chloride.

23. A process for the manufacture of a salt of a compound of the general formula I

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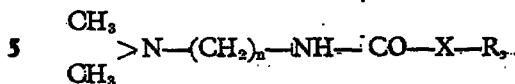
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Preparation containing as active substance	Number of healthy germinated peas as a %	
	1.5 g of preparation per kg of seed	3.0 g of preparation per kg of seed
N-(3-Dimethylaminopropyl)- thiocarbamic acid S-ethyl ester chloride	77	78
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen oxalate	64	74
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester formate	71	76
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester benzoate	64	75
N-(3-Dimethylaminopropyl)- carbamic acid propyl ester hydrogen sulphate	74	—
TMTD	45	63
MANEB	51	66
Untreated seed	5	5

WHAT WE CLAIM IS:—

1. A salt of a compound of the general formula



in which R represents an aliphatic hydrocarbon group, X represents an oxygen or sulphur atom and n represents 2, 3 or 4, with an inorganic or organic acid.

10 2. A salt as claimed in claim 1, wherein R represents an aliphatic hydrocarbon group containing 2 to 4 carbon atoms.

3. N - (3 - Dimethylaminopropyl) - carbamic acid ethyl ester chloride.

15 4. N - (3 - Dimethylaminopropyl) - carbamic acid ethyl ester benzoate.

5. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester chloride.

20 6. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester formate.

7. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester propionate.

8. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester valerate.

25 9. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester hydrogen oxalate.

10. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester malonate.

11. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester succinate.

12. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester cyanoacetate.

13. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester chloroacetate.

14. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester dichloroacetate.

15. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester trifluoroacetate.

16. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester benzoate.

17. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester furan-2-carboxylate.

18. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester *p*-toluenesulphonate.

19. N - (3 - Dimethylaminopropyl) - carbamic acid propyl ester hydrogen sulphate.

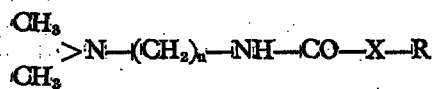
20. N - (3 - Dimethylaminopropyl) - carbamic acid butyl ester chloride.

21. N - (3 - Dimethylaminopropyl) - thiocarbamic acid S-ethyl ester chloride.

22. N - (3 - Dimethylaminopropyl) - thiocarbamic acid S-propyl ester chloride.

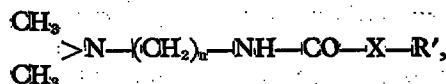
23. A process for the manufacture of a salt of a compound of the general formula I





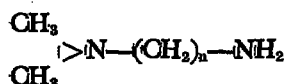
in which R represents an aliphatic hydrocarbon group, X represents an oxygen or sulphur atom and n represents 2, 3 or 4, with an inorganic or organic acid, wherein

- 5 a) a compound of the general formula I is neutralised, in a known manner, with an inorganic or organic acid or
- 10 b) the acid residue of a salt of a compound of the general formula I, in which R, X and n have the meanings given above, is replaced, in a known manner, by another acid residue by double decomposition of two salts, or
- 15 c) the ester group R' of a salt of a compound of the general formula



in which R' represents an aliphatic hydrocarbon group and X and n have the meanings given above, is replaced, in a known manner, by an ester group R, R having the meaning given above, by trans-esterification, or

- 20 d) a compound of the general formula

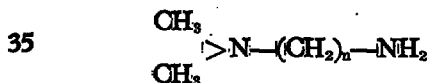


- 25 in which n has the meaning given above, or a salt thereof with a hydrohalic acid, is reacted, in a known manner, with a chloroformic acid ester or thioester of the general formula



- 30 in which R and X have the meanings given above, and, if desired, the acid residue in the resulting chloride is replaced, in a known manner, by another acid residue by double decomposition of two salts, or

e) a compound of the general formula



- 35 in which n has the meaning given above, or a salt thereof with a hydrohalic acid, is reacted, in a known manner, with a carbonic acid ester, thioester or dithioester of the
- 40 general formula



in which R' represents an aliphatic hydrocarbon group, X' represents an oxygen or

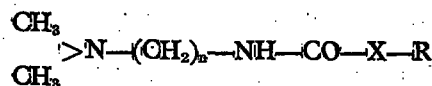
sulphur atom and R and X have the meanings given above, and the resulting compound of the general formula I is neutralised, in a known manner, with an inorganic or organic acid.

24. A process as claimed in claim 23, wherein R represents an aliphatic hydrocarbon group containing 2 to 4 carbon atoms.

25. A process as claimed in claim 23, conducted substantially as described in any one of Examples 11 to 8 herein.

26. A process as claimed in claim 23, conducted substantially as described in any one of Examples 5 to 8 herein.

27. A fungicidal preparation which comprises a salt of a compound of the general formula I



in which R represents an aliphatic hydrocarbon group, X represents an oxygen or sulphur atom and n represents 2, 3 or 4, with an inorganic or organic acid, in admixture or conjunction with a suitable carrier.

28. A fungicidal preparation as claimed in claim 27, wherein the preparation contains 2 or more salts as defined in claim 27.

29. A fungicidal preparation as claimed in claim 27 or 28, wherein R represents an aliphatic hydrocarbon group containing 2 to 4 carbon atoms.

30. A fungicidal preparation as claimed in any one of claims 27 to 29, wherein the salt or at least one of the salts is a salt of a monocarboxylic or polycarboxylic acid or of a sulphonic acid.

31. A fungicidal preparation as claimed in any one of claims 27 to 29, wherein the salt or at least one of the salts is a salt of a mineral acid.

32. A fungicidal preparation as claimed in claim 27, and having a composition substantially as described in any one of Examples 9 to 11 herein.

33. A method of treating a seed, wherein a seed is treated with a salt as claimed in claim 1.

34. A method as claimed in claim 33, wherein the seed is treated with 2 or more salts as claimed in claim 1.

35. A method as claimed in claim 33 or 34, wherein the seed is treated with at least one compound as claimed in claim 2.

36. A method as claimed in claim 33 or 34, wherein the seed is treated with the compound claimed in any one of claims 3 to 22.

37. A method as claimed in claim 33, wherein the seed is treated with a preparation as claimed in any one of claims 27 to 31.

38. A method as claimed in claim 33, conducted substantially as described in Example 10 or 11 herein.



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39. A method of treating a crop area, wherein a crop area is treated with a salt as claimed in claim 1.

5 40. A method as claimed in claim 39, wherein the crop area is treated with 2 or more salts as claimed in claim 1.

41. A method as claimed in claim 39 or 40, wherein the crop area is treated with at least one compound as claimed in claim 2.

10 42. A method as claimed in claim 39 or 40, wherein the crop area is treated with the compound claimed in any one of claims 3 to 22.

15 43. A method as claimed in claim 39, wherein the crop area is treated with a preparation as claimed in any one of claims 27 to 31.

20 44. A method as claimed in claim 39, conducted substantially as described in Example 9 herein.

45. A method of protecting a living plant

against phytopathogenic fungi, wherein a living plant is treated with a salt as claimed in claim 1.

25 46. A method as claimed in claim 45, wherein the living plant is treated with 2 or more salts as claimed in claim 1.

47. A method as claimed in claim 45 or 46, wherein the living plant is treated with at least one compound as claimed in claim 2.

30 48. A method as claimed in claim 45 or 46, wherein the living plant is treated with the compound claimed in any one of claims 3 to 22.

35 49. A method as claimed in claim 45, wherein the living plant is treated with a preparation as claimed in any one of claims 27 to 31.

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