

1049.344



# PATENT SPECIFICATION

NO DRAWINGS

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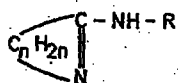
## COMPLETE SPECIFICATION

### New Fungicidal Compositions

We, J. R. GEIGY A.G. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, 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 concerns new heterocyclic compounds having excellent fungicidal properties, their salts with inorganic and organic acids, their quaternary salts, as well as fungicidal active compositions for combating fungi, which compositions contain heterocyclic compounds and/or their salts as active ingredients.

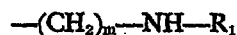
It has been found that heterocyclic compounds with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I



I

wherein

R represents an alkyl radical containing 4 to 20 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, an aralkyl radical, a monoalkylamino radical with 4 to 12 carbon atoms, the benzylamino radical, an alkoxy-polyethyleneoxy-alkyl radical or the group



wherein

R<sub>1</sub> represents an alkyl radical with from 1 to 20 carbon atoms, a o-, m- or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl or azacycloheptene - (7) - yl radicals, and

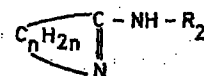
[Price 4s. 6d.]

m is an integer from 2 to 6, and n is an integer from 3 to 13, but only 3, 5 or 7 of the corresponding carbon atoms being ring members, as well as their salts with inorganic and organic acids or their quaternary salts, have excellent fungicidal properties. Heterocyclic compounds of formula I in which R is an alkyl radical with from 16—20 carbon atoms or the group



wherein R<sub>1</sub> is an azacycloheptene - (7) - yl radical and m is the integer 2 or 6 are known substances, but it was not known until now that they exert a fungicidal activity.

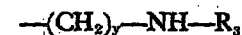
New heterocyclic compounds of this group are compounds of the more restricted general formula II



II

wherein

R<sub>2</sub> represents an alkyl radical with from 4 to 15 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, a monoalkylamino radical with 4 to 12 carbon atoms, the benzylamino radical, an alkoxy-polyethyleneoxy - alkyl radical or the group



wherein R<sub>3</sub> represents an alkyl radical with from 1 to 20 carbon atoms, a o-, m- or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl radical, and y represents an integer from 1 to 6, and

n being defined as in formula I.

These new compounds are obtained by reacting equivalent amounts of a compound of the general formula III



(III)

wherein  $\text{R}_2$  represents an alkyl radical having 1 to 3 carbon atoms,

A represents oxygen or sulphur, and

10 n has the definition given under formula I, possibly in the presence of an organic solvent and of a tertiary amine as catalyst, and of a primary amine of the general formula IV



wherein  $\text{R}_2$  has the meaning given above.

15 As solvents, e.g. aromatic hydrocarbons, alcohols, esters, ketones, ethers are used.

20 Examples of tertiary amines are pyridine, trimethylamine, triethylamine, triethanolamine etc. In the reaction, the radical  $-\text{AR}_2$  is split off and an alcohol or mercaptan is formed.

By the term "salts" are meant salts of the compounds of the general formula I with inorganic and organic acids as well as the quaternary salts of said compounds. The salts with inorganic and organic acids are obtained by reacting, optionally, in the presence of an inert organic solvent or water, compounds of the general formula I with equivalent amounts of an inorganic or organic acid such as hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, acetic acid, propionic acid, sorbic acid, oxalic acid, succinic acid, phthalic acid, p-toluene sulphonic acid.

35 The quaternary salts are obtained by reacting, optionally, in the presence of an inert organic solvent or water, compounds of the general formula I with usual quaternising agents, e.g. reactive esters of the sulphuric acid and toluene sulphonic acid, or methyl iodide, butyl bromide and benzyl chloride.

40 By the grouping  $-\text{C}_n\text{H}_{2n}-$  of the general formulas I and II are meant alkylene radicals with from 3 to 13 carbon atoms, which may be substituted by straight or branched chain alkyl radicals, but 3, 5 or 7 of which are ring members.

45 The alkyl radicals  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  represent straight or branched chain radicals which may be substituted by alkoxy or alkylthio groups with from 1 to 4 carbon atoms as well as by halogen atoms, e.g. chlorine or bromine. Aryl radicals are, e.g. phenylethyl, phenylpropyl and isobutylbenzyl radicals.

55 Examples of compounds of the general formula III are the O-methyl, O-ethyl, O-propyl lactim ether, the methyl ester of the 4-t-butyl, 4-amyl, 4-t-butyl-6-methyl, and 4,6-diisopropyl caprolactam as well as the corres-

60 ponding thioethers of the lactim forms of  $\alpha$ -pyrrolidone,  $\alpha$ -piperidone, caprolactam, enanthlactam and capryl lactam.

The following are examples of amines of formula IV: n-hexylamine, octylamine, decylamine, undecylamine, laurylamine, tridecylamine, myristylamine, polychlorooctylamine, polychlorolaurylamine, benzylamine,  $\beta$ -phenylethylamine,  $\gamma$ -phenylpropylamine,  $\alpha$ -methylbenzylamine,  $\alpha$ -isobutylbenzylamine,  $\gamma$ -methoxypropylamine,  $\gamma$ -ethoxypropylamine,  $\gamma$ -(polyethoxy)-propylamine, N-hexyl-1,2-diaminoethane, N-octyl-1,2-diaminoethane, N-dodecyl-1,2-diaminoethane, N-octyl-1,3-diaminopropane, N-hexyl-1,2-diaminocyclohexane, N-phenyl-1,3-diamino-propane, N-o-, N-m-, N-p-chlorophenyl-1,3-diaminopropane.

The compounds of formula I or their salts are suitable in particular as active substances for fungicidal compositions which can be applied in various ways. Due to their slight toxicity to warm blooded animals and the absence of phytotoxicity in the concentrations applied in practice, which vary between 0.1 to 2% calculated on the active substance, the compounds of formula I are particularly suitable for plant protection. The use of the active substances as fungicides in orchards is of particular importance. In addition the active substances according to the invention can be used as dry seed dressing agents as they have an excellent action, e.g. on *Tilletia tritici*, *Fusarium culmorum* and they do not inhibit germination.

95 The following examples describe the production of the active substances according to the invention. Parts are given therein as parts by weight, if not stated otherwise, and the temperatures are in degrees Centigrade.

#### EXAMPLE 1.

100 12.7 Parts of O-methyl caprolactim, 18.5 parts of n-dodecylamine, 200 parts by volume of ethanol and 1.0 part of triethylamine are refluxed for 20 hours. The main amount of the ethanol is then evaporated off in vacuo and the residue is taken up in ether and washed with water. On evaporating the ether solution, the 7-dodecylamino-3,4,5,6-tetrahydro-2H-azepine obtained is recrystallised from petroleum ether. M.P. 53—54°.

110 On dissolving in the equivalent amount of dilute hydrochloric acid, the hydrochloride is obtained. M.P. 148—149° (recrystallised from water or acetone).

#### EXAMPLE 2.

115 14.3 parts of 2-methylthio-3,4,5,6-tetrahydro-2H-azepine 200 parts by volume of benzene, 18.6 parts of laurylamine and 1 part of triethylamine are refluxed for 20 hours. The solution is concentrated in vacuo and the residue is recrystallised from petroleum ether; the 7-laurylamino-3,4,5,6-

tetrahydro - 2H - azepine melts at 52—54°. The hydrochloride obtained as described in example 1 melts at 149—150°.

- 5 28 Parts of 7 - laurylamino - 3,4,5,6-tetrahydro - 2H - azepine are dissolved in 100 parts by volume of anhydrous benzene. To this solution are added, dropwise at 20°, 13 parts of dimethyl sulfate and the obtained solution is then refluxed for 1 hour. On
- 10 evaporating the benzene solution, the quaternary salt of the 7 - laurylamino - 3,4,5,6-tetrahydro - 2H - azepine is obtained as viscous non-distillable oil.

- 15 In analogous manner, the quaternary salts of the 7 - laurylamino - 3,4,5,6 - tetrahydro-2H - azepine and diethyl sulfate or n-butylbromide are obtained as viscous non-distillable oils.

## EXAMPLE 3.

66.5 Parts of -caprolactim-o-methyl ether, 20  
5.0 parts of triethylamine and 72.0 parts of monooctyl hydrazine are refluxed in 500 parts by volume of benzene for 18 hours. The solvent is evaporated off under water jet vacuum at 50° and the residue is distilled 25  
under high vacuum. 81 Parts of 7 - octylhydrazino - 3,4,5,6 - tetrahydro - 2H - azepine are obtained, B.P. 128—131°/0.03 Torr. The hydrochloride crystallised from benzene melts at 146—150°. 30

In the following Table I compounds of the general formula II are listed which are obtained in the manner described in the above examples from equivalent amounts of compounds of the general formula III and amines 35 of the general formula IV.

TABLE I

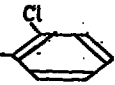
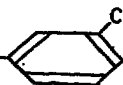
| Nr | n | R <sub>2</sub>                                                                                                                                            | Melting or Boiling Point | Salt                                                  |
|----|---|-----------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|-------------------------------------------------------|
| 1  | 5 | —C <sub>6</sub> H <sub>13</sub> (n)                                                                                                                       | 105—109°/0.002 mm        | hydrochloride<br>M.P. 146—147°<br>(isopropanol-ether) |
| 2  | 5 | —C <sub>8</sub> H <sub>17</sub> (n)                                                                                                                       | 110—117°/0.001 mm        | hydrochloride<br>M.P. 152—154°<br>(isopropanol-ether) |
| 3  | 5 | —CH <sub>2</sub> —CH <sub>2</sub> —NH—C <sub>6</sub> H <sub>13</sub> (n)                                                                                  | 113—115°/0.002 mm        |                                                       |
| 4  | 5 | —CH <sub>2</sub> —CH <sub>2</sub> —NH—C <sub>8</sub> H <sub>17</sub> (n)                                                                                  | 130—131°/0.003 mm        |                                                       |
| 5  | 5 | —(CH <sub>2</sub> ) <sub>3</sub> —O—(CH <sub>2</sub> ) <sub>2</sub> —O—(CH <sub>2</sub> ) <sub>2</sub><br> <br>O<br> <br>CH <sub>3</sub> —CH <sub>2</sub> | 142—147°/0.01 mm         |                                                       |
| 6  | 5 | —(CH <sub>2</sub> ) <sub>3</sub> —NH—                                  | 150°/0.0001 mm *)        |                                                       |
| 7  | 5 | —(CH <sub>2</sub> ) <sub>3</sub> —NH—                                  | 160°/0.0001 mm *)        |                                                       |

TABLE I (Continued)

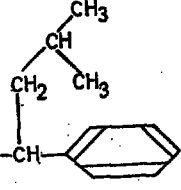
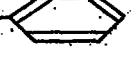
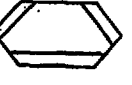
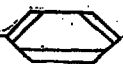
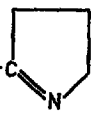
| Nr | n | R <sub>2</sub>                                                                                     | Melting or Boiling Point | Salt                                        |
|----|---|----------------------------------------------------------------------------------------------------|--------------------------|---------------------------------------------|
| 8  | 5 | $-(CH_2)_3-NH-$   | 150°/0.0001 mm *)        | hydrochloride<br>M.P. 218—220°<br>(acetone) |
| 9  | 5 | $-CH_2-CH_2-NH-$  | 120—121° (acetone)       |                                             |
| 10 | 5 |                   | 106—107° (acetone)       |                                             |
| 11 | 5 | $-CH_2-$          | 76 — 77°                 |                                             |
| 12 | 5 | $-CH_2-CH_2-$   | 120—121°/0.01 mm         |                                             |
| 13 | 5 | $-C_8H_2Cl_{17-z}$                                                                                 | oil                      |                                             |
| 14 | 5 | $-(CH_2)_6-OCH_3$                                                                                  |                          |                                             |
| 15 | 5 | $-(CH_2)_6-S-n-C_8H_7$                                                                             |                          |                                             |
| 16 | 5 | $-C_{14}H_{29}$                                                                                    | 56 — 58° (acetone)       |                                             |
| 17 | 5 | $-NH-C_4H_9$                                                                                       | 144—155°/12 mm           | hydrochloride<br>M.P. 153—157°<br>(acetone) |
| 18 | 5 | $-NH-C_6H_{13}$                                                                                    | 105—109°/0.01 mm         | hydrochloride<br>M.P. 155—158°<br>(acetone) |
| 19 | 5 | $-NH-C_8H_{17}$                                                                                    | 128—131°/0.03 mm         | hydrochloride<br>M.P. 146—150°<br>(benzene) |
| 20 | 5 | $-NH-C_{10}H_{21}$                                                                                 | 145—149°/0.01 mm         |                                             |
| 21 | 5 | $-NH-C_{12}H_{25}$                                                                                 | 159—163°/0.01 mm         |                                             |
| 22 | 5 | $-NH-CH_2-$     | 140—145°/0.01 mm         | oxalate<br>M.P. 156—157°<br>(ethanol)       |

TABLE I (Continued)

| Nr. | n | R <sub>2</sub>                                                                                                  | Melting or Boiling Point      | Salt |
|-----|---|-----------------------------------------------------------------------------------------------------------------|-------------------------------|------|
| 23  | 3 | $-\text{C}_8\text{H}_{17}$                                                                                      | 49 — 50°<br>101—103° 0.001 mm |      |
| 24  | 3 | $-\text{C}_{12}\text{H}_{25}$                                                                                   | 64—65°<br>129—132° 0.01 mm    |      |
| 25  | 3 | $-\text{CH}_2-$                | 81—82°<br>125—129° 0.01 mm    |      |
| 26  | 3 | $-\text{C}_8\text{H}_2\text{Cl}_{17-z}$                                                                         | oil                           |      |
| 27  | 3 | $-(\text{CH}_2)_2-\text{NH}-$  | 195—201°                      |      |
| 28  | 3 | $-(\text{CH}_2)_6-\text{NH}-$  | 198—203                       |      |

\*) Molecular distillation.

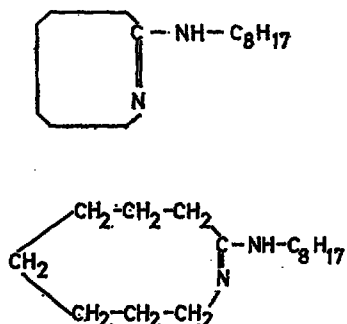
In an analogous manner the compounds of the general formula I listed in Table II are obtained.

TABLE II

| Nr | n  | Ring members | Alkyl branching    | R                             | Melting or Boiling Point | Hydrochloride     |
|----|----|--------------|--------------------|-------------------------------|--------------------------|-------------------|
| 29 | 7  | 7            |                    | $-\text{C}_8\text{H}_{13}$    | 121 — 124°/0.1           |                   |
| 30 | 7  | 7            |                    | $-\text{C}_8\text{H}_{17}$    | 113 — 114°/0.005         |                   |
| 31 | 7  | 7            |                    | $-\text{C}_{10}\text{H}_{21}$ | 146 — 149°/0.1           |                   |
| 32 | 7  | 7            |                    | $-\text{C}_{12}\text{H}_{25}$ | 150°/0.001*              |                   |
| 33 | 7  | 7            |                    | $-\text{C}_{14}\text{H}_{29}$ | M.P. 54—56°<br>(acetone) |                   |
| 34 | 10 | 5            | 4-amyl             | $-\text{C}_8\text{H}_{17}$    | 125°/0.001*              | 171—173° (water)  |
| 35 | 10 | 5            | 4-amyl             | $-\text{C}_{10}\text{H}_{21}$ | 140°/0.001*              | 181—182° (water)  |
| 36 | 10 | 5            | 4-amyl             | $-\text{C}_{12}\text{H}_{25}$ | 160°/0.001*              | 170—171°(acetone) |
| 37 | 10 | 5            | 4-amyl             | $-\text{C}_{14}\text{H}_{29}$ | 170°/0.001*              | 166—167°(acetone) |
| 38 | 9  | 5            | 4-t-butyl          | $-\text{C}_8\text{H}_{17}$    | 120°/0.001*              | 190—191°(acetone) |
| 39 | 9  | 5            | 4-t-butyl          | $-\text{C}_{10}\text{H}_{21}$ | 135°/0.001*              | 184—185°(acetone) |
| 40 | 9  | 5            | 4-t-butyl          | $-\text{C}_{12}\text{H}_{25}$ | 145°/0.001*              | 180—181°(acetone) |
| 41 | 9  | 5            | 4-t-butyl          | $-\text{C}_{14}\text{H}_{29}$ | 160°/0.001*              | 170—172°(acetone) |
| 42 | 10 | 5            | 4-t-butyl-6-methyl | $-\text{C}_{12}\text{H}_{25}$ | 150°/0.001*              | 46—48° (acetone)  |
| 43 | 13 | 5            | 4,6-diiso-butyl    | $-\text{C}_{12}\text{H}_{25}$ | 150°/0.001*              |                   |

\*) Molecular distillation.

The two following compounds are obtained in the same manner as described in examples 1 and 2 from enanth lactam and capryl lactam by reaction with octylamine:



The compounds of structure I are suitable as active substances in fungicidal compositions for the most various forms of application such as inhibition and repression of the growth of

fungi and bacteria on plants and parts thereof as well as the protection of organic materials of all types such as wood, textiles, furs, leather paper, synthetic substances etc. from attack and decomposition by fungi and bacteria. For these purposes the active substances are employed in a finely distributed form as such or combined with suitable carriers and distributing agents. They can also be used in combination with other fungicidally active substances as well as with fungistatica and bacteriostatica. To increase the range of action, also insecticidally or nematocidally active substances etc. can be added to the active substances used according to the invention.

To produce fungicidal compositions according to the invention the active substances can be mixed, for example, with solid, pulverulent carriers such as, e.g. talcum, kaolin, loess, chalk or ground limestone. If desired, the pulverulent agents obtained can be made suspendable in water by the addition of suit-

able wetting and dispersing agents such as sulphite waste liquor. In addition, the active substances as such in solid, finely milled form, can be suspended in water with the aid of capillary active substances, or they can be emulsified in water, after dissolving them in organic solvents, with the aid of suitable emulsifying agents. Also, the active substances can be dissolved in organic solvents, e.g. in chlorinated hydrocarbons such as trichloroethylene, or in medium petroleum fractions, possibly with the addition of auxiliary solvents such as acetone or higher ketones. Finally, the active substances can also be distributed in the air in the form of aerosols, smoke or mist, particularly in storerooms and greenhouses.

The fungicidal active substances are applied to an organic material to be protected generally either by admixture therewith, by spraying or by impregnating with organic-aqueous or aqueous solutions of the active substance which can contain the active substance in dispersion or suspension.

The following examples further illustrate the production of some fungicidal agents:

#### EXAMPLE 4.

20 parts of 4 - tert.butyl - 7 - myristylamino - 3,4,5,6 - tetrahydro - 2H - azepine are finely milled in a ball mill with 4 parts of a polyvinyl pyrrolidone dispersing agent and 76 parts of water. The paste so obtained is suspended in water and is used for the combating of fungi, particularly in orchards.

#### EXAMPLE 5.

50 parts of 7 - octylamino - 3,4,5,6 - tetrahydro - 2H - azepine, 2 parts of an adhesive having a polyvinyl alcohol base, 10 parts of sulphite waste liquor, 16 parts of champagne chalk, 20 parts of kaolin and 2 parts of a wetting agent having an alkyl and aryl sulphonate base are milled together, mixed, and again milled. A 50% wettable powder is obtained which can be suspended in water

and is suitable in particular for use in fruit cultivation.

#### EXAMPLE 6.

10 parts of 7 - octylhydrazino - 3,4,5,6-tetrahydro - 2H - azepine are dissolved in 80 parts of dimethyl formamide and 10 parts of an alkyl-aryl sulphonate are mixed into this solution until homogeneity is attained. In this way an emulsifiable solution is obtained which can be diluted to any concentration desired.

#### EXAMPLE 7.

10 parts of 9 - dodecylamino - 3,4,5,6,7,8-hexahydro - 2H - azonine are dissolved in 15 parts of dimethyl sulphoxide and 65 parts of cyclohexanone. 10 Parts of an alkylaryl polyethylene oxide (ratio 1:10) are mixed into this solution until homogeneity is attained. An emulsifiable solution is obtained which can be diluted to any concentration desired.

#### EXAMPLE 8.

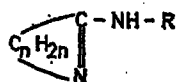
The fungicidal activity of the compounds of general formula I was determined by the germination test with spores of the following types of fungi: *Alternaria tenuis*, *Botrytis cinerea*, *Clasterosporium c.*, *coniothyrium dipl.*, *Fusarium culm*, *Mucor spec.*, *Penicillium spec.*, and *Stemphyllium cons.*

A determined amount of a 1%, 0.1% and 0.01% solution of active substances in acetone was placed, — all under equal conditions — in four Petri dishes of identical size. The solvent was evaporated whereupon a level coating of active substance ready for inoculation was obtained, in each of the four dishes. After inoculation, the dishes were kept for 168 hours at 20°C in an atmosphere of 80% humidity. The germinated spores were then counted. The following table shows the values at which at least a 90% inhibition of germination was attained. The value "1" in the Table represents at least a 90% inhibition of germination attained by the residue of one cc. of the aforesaid 0.1% solution of active substance in acetone (= 13 γ active substance per sq.cm.)

|                                                                             | Alt.<br>ten | Botr.<br>cin | Clast<br>c | Coni<br>dipl. | Fus<br>culm. | Muc.<br>Spec. | * Pen<br>Spec. | Stem<br>cons |
|-----------------------------------------------------------------------------|-------------|--------------|------------|---------------|--------------|---------------|----------------|--------------|
| 7-methylamino- $\Delta^{1,7}$ -azacycloheptene                              | >10         | >10          | >10        | >10           | >10          | >10           | >10            | >10          |
| Cefelin et al<br>Collection Czechoslov.<br>Chem. Commun.<br>25, 2522 (1960) |             |              |            |               |              |               |                |              |
| 7-n-dodecylamino- $\Delta^{1,7}$ -azacycloheptene                           | 10          | 1            | 0.1        | 0.1           | 1            | 0.1           | 1              | 10           |
| 7-[ $\beta$ -(n-octylamino)-ethylamino]- $\Delta^{1,7}$ -azacycloheptene    | 10          | 1            | 1          | 1             | 10           | 1             | 10             | 10           |
| quaternary 7-n-octylamino- $\Delta^{1,7}$ -azacycloheptenedimethylsulfate   | 1           | 1            | 0.1        | 1             | 1            | 0.1           | 1              | 1            |

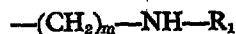
## WHAT WE CLAIM IS:—

1. Fungicidal composition which comprises as the active ingredient at least one heterocyclic compound with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I



I

- wherein
- 10 R represents an alkyl radical containing from 4 to 20 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, an aralkyl radical, a monoalkylamino radical with 4 to 12 carbon atoms,
- 15 the benzylamino radical, an alkoxypolyethyleneoxy-alkyl radical or the group

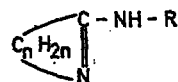


wherein

- 20  $\text{R}_1$  represents an alkyl radical with from 1 to 20 carbon atoms, a o-, m- or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl or azacycloheptene - (7) - yl radicals, and
- 25 m is an integer from 2 to 6, and n is an integer from 3 to 13, but only 3, 5 or 7 of the corresponding carbon atoms being ring members, and/or its salts with inorganic or organic acids and/or its quaternary salts, these active ingredients being combined with suitable solid pulverulent carriers and/or with high boiling hydrocarbons and/or with distributing agents containing capillary active substances.

- 35 2. A method for combatting fungi and preventing or retarding the growth of fungi

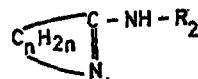
on plants and parts thereof as well as for the protection of organic materials from attack and decomposition by fungi which comprises treating the surfaces of said plants and organic materials with fungicidally active amounts of at least one heterocyclic compound with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I



I

wherein n and R have the meanings given in claim 1, and/or with acid addition salts or quaternary salts of such heterocyclic amines.

3. New heterocyclic compounds with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the more restricted formula II



II

wherein

$\text{R}_2$  represents an alkyl radical with from 4 to 15 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, a monoalkyl-amino radical with 4 to 12 carbon atoms, the benzyl-amino radical, an alkoxypolyethyleneoxy-alkyl radical or the group



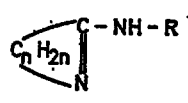
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|                                                                             | Alt.<br>ten | Botr.<br>cin | Clast<br>c | Coni<br>dipl. | Fus<br>culm. | Muc.<br>Spec. | * Pen<br>Spec. | Stem<br>cons |
|-----------------------------------------------------------------------------|-------------|--------------|------------|---------------|--------------|---------------|----------------|--------------|
| 7-methylamino- $\Delta^{1,7}$ -azacycloheptene                              | >10         | >10          | >10        | >10           | >10          | >10           | >10            | >10          |
| Cefelin et al<br>Collection Czechoslov.<br>Chem. Commun.<br>25, 2522 (1960) |             |              |            |               |              |               |                |              |
| 7-n-dodecylamino- $\Delta^{1,7}$ -azacycloheptene                           | 10          | 1            | 0.1        | 0.1           | 1            | 0.1           | 1              | 10           |
| 7-[ $\beta$ -(n-octylamino)-ethylamino]- $\Delta^{1,7}$ -azacycloheptene    | 10          | 1            | 1          | 1             | 10           | 1             | 10             | 10           |
| quaternary 7-n-octylamino- $\Delta^{1,7}$ -azacycloheptenedimethylsulfate   | 1           | 1            | 0.1        | 1             | 1            | 0.1           | 1              | 1            |

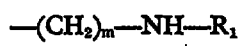
WHAT WE CLAIM IS:—

1. Fungicidal composition which comprises as the active ingredient at least one heterocyclic compound with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I



I

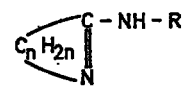
wherein  
10 R represents an alkyl radical containing from 4 to 20 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, an aralkyl radical, a monoalkylamino radical with 4 to 12 carbon atoms,  
15 the benzylamino radical, an alkoxypolyethyleneoxy-alkyl radical or the group



wherein  
20  $\text{R}_1$  represents an alkyl radical with from 1 to 20 carbon atoms, a o-, m- or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl or azacycloheptene - (7) - yl radicals, and  
25 m is an integer from 2 to 6, and n is an integer from 3 to 13, but only 3, 5 or 7 of the corresponding carbon atoms being ring members, and/or its salts with inorganic or organic acids and/or its quaternary salts, these active ingredients being combined with suitable solid pulverulent carriers and/or with high boiling hydrocarbons and/or with distributing agents containing capillary active substances.

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35 2. A method for combatting fungi and preventing or retarding the growth of fungi

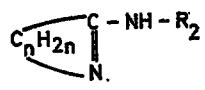
on plants and parts thereof as well as for the protection of organic materials from attack and decomposition by fungi which comprises treating the surfaces of said plants and organic materials with fungicidally active amounts of at least one heterocyclic compound with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I



I

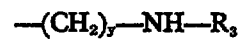
wherein n and R have the meanings given in claim 1, and/or with acid addition salts or quaternary salts of such heterocyclic amines.

3. New heterocyclic compounds with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the more restricted formula II



II

wherein  
R<sub>2</sub> represents an alkyl radical with from 4 to 15 carbon atoms, which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, a monoalkyl-amino radical with 4 to 12 carbon atoms, the benzylamino radical, an alkoxypolyethyleneoxy-alkyl radical or the group



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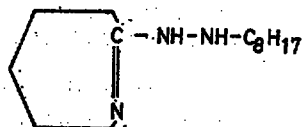
wherein  $R_3$  represents an alkyl radical with from 1 to 20 carbon atoms, a o-, m- or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl radical, and y represents an integer from 1 to 6, and

- 5 n being defined as in claim I, and their salts with organic or inorganic acids and their quaternary salts.

4. The compound of the formula



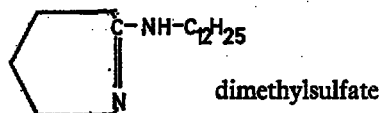
5. The compound of the formula



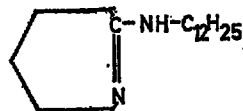
6. The compound of the formula



- 15 7. The quaternary compound of the formula



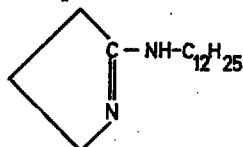
8. The compound of the formula



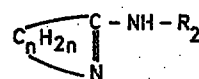
9. The compound of the formula



10. The compound of the formula



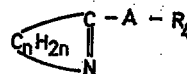
- 25 11. Process for the production of new heterocyclic compounds with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the more restricted general formula II



(II)

wherein  $R_2$  and n have the meanings given in claim 3, which comprises reacting equivalent amounts of a compound of the general formula III

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(III)

wherein  $R_4$  represents an alkyl radical having from 1 to 3 carbon atoms,

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A represents oxygen or sulphur and

n represents a whole number from 3 to 13, but only 3, 5 or 7 of the corresponding carbon atoms being ring members, and of a primary amine of the general formula IV

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wherein  $R_2$  has the meaning given in claim 3, and if desired converting the reacting products so obtained into their salts with organic and inorganic acids or into their quaternary salts.

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12. Fungicidal composition which comprises as the active ingredient at least one heterocyclic compound with one nitrogen atom as ring hetero atom and 4 to 8 carbon atoms as ring members of the general formula I given in claim 1 in which R represents an alkyl radical containing from 6 to 20 carbon atoms which may be substituted by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, an aralkyl radical an alkoxypolyethyleneoxy-alkyl radical or the group:

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wherein  $R_1$  represents hydrogen, an alkyl radical having from 6 to 20 carbon atoms, an o-, m-, or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl or azacycloheptene - (7) - yl radicals and

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m is an integer from 2 to 6 and

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n is an integer from 3 to 5, and/or its salts with inorganic or organic acids, these active ingredients being combined with suitable solid pulverulent carriers and/or with high boiling point hydrocarbons and/or with distributing agents containing capillary active substances.

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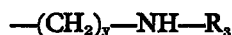
13. A method of combatting fungi or retarding the growth of fungi on plants or parts thereof as well or for the protection of

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organic materials from attack and decomposition by fungi as claimed in claim 2 in which n and R have the meanings given in claim 11.

- 5 14. New heterocyclic compounds of the general formula II given in claim 3 in which  $R_2$  represents an alkyl radical having from 6 to 15 carbon atoms, which may be substituted, by halogen atoms or by an alkoxy or an alkylthio group with from 1 to 4 carbon atoms, an alkoxy-polyethyleneoxy-alkyl radical or the group



- 15 wherein  $R_3$  represents an alkyl radical having from 6 to 20 carbon atoms, an o-, m-, or p-chlorophenyl radical or the alkyl substituted azacyclopentene - (5) - yl radical and y represents a whole number from 1 to 6, and

- 20 n represents a whole number from 3 to 5, and their salts with organic and inorganic acids.

- 25 15. Process for the production of new heterocyclic amines and, if desired, their salts with organic and inorganic acids, as claimed in claim 11 in which  $R_2$  and n have the meanings given in claim 14 and A and  $R_4$  have the meanings given in claim 11.

16. A fungicidal composition substantially as hereinbefore described with reference to

and as illustrated in any of Examples 5 to 9.

17. New heterocyclic amines and salts thereof with organic and inorganic acids as hereinbefore described with reference to and as illustrated in Example 1 or 2.

18. Quaternary salts of the heterocyclic compounds claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in Example 2.

19. Process for the production of new heterocyclic amines and salts thereof with organic and inorganic acids substantially as hereinbefore described with reference to and as illustrated in Example 1 or 2.

20. Process for the production of quaternary salts of the heterocyclic compounds claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in Example 2.

21. A method for combatting fungi and preventing or retarding the growth of fungi on plants and parts thereof as well as for the protection of organic materials from attack and decomposition by fungi according to claim 2 substantially as hereinbefore described with reference to and as illustrated in Example 8.

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Chartered Patent Agents.