

PATENT SPECIFICATION

(11) 1351034

1351034

- (21) Application No. 40992/71 (22) Filed 2 Sept. 1971
 (31) Convention Application No. P 20 44-205.1
 (32) Filed 7 Sept. 1970 in
 (33) Germany (DT)
 (44) Complete Specification published 24 April 1974
 (51) International Classification C07D 49/38; A01N 9/16; A61K 27/00
 (52) Index at acceptance
 C2C 1416 213 220 22Y 247 250 252 25Y 30Y 311 313 314
 31Y 326 338 339 340 34Y 364 366 368 36Y 385
 511 520 522 662 694 695 790 791 79Y SB

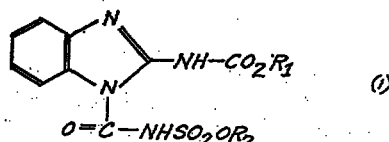


(54) BENZIMIDAZOLES

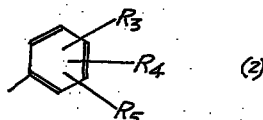
(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Bruning, a body corporate recognised under German law, of 6230 Frankfurt Main 80, Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to benzimidazoles, a process for their manufacture and to pesticidal and pharmaceutical preparations containing them.

The present invention provides benzimidazoles of the general formula (1)



- 10 in which R_1 represents an alkyl group having 1 to 4 carbon atoms and R_2 represents an alkyl group having 1 to 4 carbon atoms which may be substituted by one or more halogen atoms and/or alkoxy groups having 1 to 4 carbon atoms, a cyclohexyl group, or a radical of the formula (2)



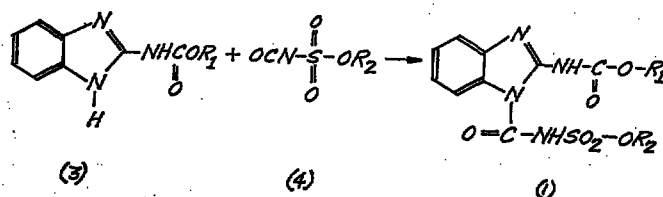
- 15 in which R_3 , R_4 and R_5 , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, a carbalkoxy group having 1 to 4 carbon atoms in the alkoxy group, a halogen atom or a cyano, nitro, trifluoromethyl, phenyl or phenylazo ($\text{C}_6\text{H}_5\text{—N=N—}$) group.

- 20 Among the benzimidazoles of the formula (1) those are preferred in which R_1 represents an alkyl group having 1 to 4 carbon atoms and R_2 represents an alkyl group having 1 to 3 carbon atoms which may be substituted by one or more chlorine and/or fluorine atoms, or a radical of the formula (2) in which R_3 , R_4 and R_5 , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 or 2 carbon atoms, a carbalkoxy group having 1 or 2 carbon atoms in the alkoxy group, a chlorine atom, a bromine atom, a trifluoromethyl group or a cyano group.

- 25 The present invention also provides a process for the manufacture of benzimidazoles of the formula (1) which comprises reacting a carbalkoxy-aminobenzimidazole of the formula (3) with an alkoxy- or aryloxy-sulfonyl isocyanate of the formula (4) as follows:

[Price 25p]

12



R_1 and R_2 having the meanings given above.

To carry out the reaction the benzimidazole derivative (3) is preferably suspended in an inert solvent and while stirring the latter, the liquid or solid isocyanate (4) is added, whereupon the exothermic reaction starts. In general, the reaction product separates in the form of crystals after a short period of time.

To complete the reaction, the reaction mixture is preferably stirred for 10 to 15 hours. After that the reaction product, which is obtained in a good to very good yield, is separated from the reaction mixture by filtration.

Suitable inert solvents to carry out the reaction are preferably those which are slightly or weakly polar and have a low boiling point, for example methylene chloride, carbon tetrachloride, benzene; ethers, for example diethyl ether or tetrahydrofuran; esters, for example methyl acetate, and preferably chloroform.

The carbalkoxy-aminobenzimidazoles used as starting material may be prepared by reacting the sulfate salt of S-alkyl-pseudothiourea (obtained from dialkyl sulfate and thio-urea) with two equivalents of a chloroformic acid ester of the general formula ClCO_2R_1 . The product thus obtained reacts with ortho-phenylene diamine to yield the desired carbalkoxy-aminobenzimidazole (cf. J. Amer. Chem. Soc. volume 56, page 144 (1934)).

The alkoxysulfonyl isocyanates used can be prepared by the process described in German Patent 1,300,556. In this process the sulfochloride prepared from chlorosulfonyl isocyanate and 2, 4, 6-trichlorophenol is reacted with the corresponding alcohols and the reaction product obtained is heated at 120—140° C.

The phenyloxy-sulfonyl isocyanates are prepared by the process disclosed in German Patent 1,230, 017 by heating at 120 to 130°C the corresponding phenols with at least an equimolar amount of chlorosulfonyl isocyanate in chlorobenzene.

Halogen-substituted alkoxy-sulfonyl isocyanates are obtained in the same way by reacting the corresponding α -halogenated alcohols with chlorosulfonyl isocyanate.

The following sulfonyl isocyanates (4) are preferably used as starting material: methoxy, ethoxy, propoxy, butoxy-, or cyclohexyloxy-sulfonyl isocyanate; 2-chloro-ethoxy-, 2,2,2-trichloroethoxy 2,2,2-trifluoroethoxy, 2-methoxyethoxy- or 2-ethoxy-ethoxy-sulfonyl isocyanate; phenoxy-, 3-chlorophenoxy-, 2-chlorophenoxy-, 2,3-dichlorophenoxy-, 2,5-dichlorophenoxy-, 2,4-dichloro-phenoxy-, 2,6-dichlorophenoxy-, 4-chlorophenoxy, 3,4-dichlorophenoxy, 3,5-dichlorophenoxy-, 2,4,5-trichlorophenoxy-, or 2,4,6-trichlorophenoxy-sulfonyl isocyanate; the corresponding bromo- and fluoro-derivatives, as well as mixed halogen-derivatives, for example 2-chloro-4-bromophenoxy-sulfonyl isocyanate; 2-methylphenoxy-, 3-methylphenoxy-, 4-methylphenoxy-, 2,3-, 2,4-, and 2,6-dimethylphenoxy-, or 2,4,6-trimethyl-phenoxy-sulfonyl isocyanate; the corresponding ethyl, propyl, isopropyl, butyl, isobutyl-, or tert. butyl derivatives, as well as mixed derivatives.

It is also possible to use phenoxy-sulfonyl isocyanates containing both halogen atoms and alkyl groups, for example 2-chloro-6-methyl-, 2-chloro-4-methyl-, 4-chloro-2-methyl-, 4-chloro-3-methyl-, 4-chloro-2,6-dimethyl-, 6-chloro-2,4-dimethyl-, 2,6-dichloro-4-methyl-, 4,6-dichloro-2-methyl-, 4,6-dibromo-2-methyl-phenoxy-sulfonyl isocyanate; phenoxy-sulfonyl isocyanates substituted in the 2-, 3-, 4-, and/or 6-position by cyano, nitro and/or trifluoromethyl groups; 2-methoxy-, 3-methoxy-, 4-methoxy-2-ethoxy-, 4-ethoxy-, 2-carbethoxy-phenoxy-sulfonyl isocyanates, 4-phenylphenoxy- or phenylazophenoxy-sulfonyl isocyanate. Especially preferred are alkoxy- and phenoxy-sulfonyl isocyanates carrying one or several chlorine atoms.

The benzimidazoles according to the present invention exhibit a good anthelmintic effect, especially against ascarides and oxyuris. The present invention therefore provides a pharmaceutical composition comprising as active ingredient a benzimidazole of the general formula (1) in admixture or conjunction with a pharmaceutically suitable carrier. In addition, the compounds of the invention have a pesticidal action, for example, an acaricidal, ovicidal and especially a fungicidal action. They are well absorbed by the leaves and roots of plants and thus act as systemic fungicides. They can be used to combat fungus diseases of plants either prophylactically or curatively.

The present invention therefore also provides pesticidal compositions comprising

	as active ingredients benzimidazoles of the general formula (1) together with solid or liquid carrier substances, and, if desired, adhesives, wetting agents, dispersion media and/or grinding auxiliaries. They can be used in the form of wettable powders, emulsions, suspensions, dusts or granules. If desired, they can be mixed with other fungicides with which they form compatible mixtures.	
5	Suitable carrier materials are mineral substances, for example aluminium silicates, argillaceous earths, kaolin, chalk, siliceous chalk, talc, kieselguhr or hydrated silicic acid, or preparations of said mineral substances with special additives, for example chalk with sodium stearate. Carrier materials for liquid preparations are all suitable and common solvents, for example, toluene, xylene, diacetone alcohol, cyclohexanone, isophorone, gasolines, paraffin oils, dioxane, dimethyl formamide, dimethyl sulfoxide, ethyl acetate, tetrahydrofuran and chlorobenzene.	5
10	As adhesives there can be used glutinous cellulose products or polyvinyl alcohols. As wetting agents there can be used all suitable emulsifiers, for example hydroxyethylated alkylphenols, salts of aryl or alkylaryl-sulfonic acids, salts of oleylmethyl-taurine, salts of phenyl alkyl (12—16C)-sulfonic acids or soaps.	10
15	Suitable dispersion media are salts of lignin sulfonic acid, salts of naphthalene-sulfonic acid or salts of oleylmethyl-taurine.	15
20	As grinding auxiliaries suitable inorganic or organic salts can be used, for example sodium sulfate, ammonium sulfate, sodium carbonate, sodium bicarbonate, sodium thiosulfate, sodium stearate or sodium acetate.	20
	The following Examples illustrate the invention.	
	A) Preparation of benzimidazoles according to the invention.	
	EXAMPLE 1.	
25	1-(2'-chloro-4'-bromophenoxy)sulfonylcarbamoyle-2-carbomethoxy-aminobenzimidazole (I)	25
30	12 Parts by weight of 2-carbomethoxy-aminobenzimidazole were suspended in 500 parts by volume of absolute chloroform. 20 Parts by weight of 2-chloro-4-bromophenoxy sulfonyl isocyanate were added while stirring. After 15 to 20 minutes the reaction mixture became distinctly brighter and the reaction product separated in the form of crystals. To complete the reaction, the reaction mixture was stirred for another 20 hours at room temperature. The crystals were then filtered off, washed with chloroform and dried at room temperature in high vacuum. 27 Parts by weight of pure reaction product were obtained, corresponding to a yield of 85% of the theoretical yield. The product melted at 161—162°C with decomposition.	30
35	$C_{18}H_{12}BrClN_4O_6S$ (503.5)	35
	Analysis:	
	Calc: C 38,2; H 2,4; N 11,1; S 6,4; Br 15,9; Cl 7,1	
	found: C 38,3; H 2,4; N 11,1; S 6,5; Br 16,0; Cl 7,0	
40	The compounds listed in the following Table 1 were prepared in an analogous manner.	40

TABLE I

No.	Chemical designation	Melting Point °C (with decomposition)	Molecular formula (mol. weight) Analysis values in %
II	1-phenoxysulfonylcarbonyl-2-carbomethoxyaminobenzimidazole	155	$C_{16}H_{14}N_4O_6S$ (390) calc: C 49,2; H 3,6; N 14,4; S 8,2 found: C 49,2; H 3,9; N 14,8; S 8,0
III	1-(4'-chlorophenoxysulfonylcarbonyl)-2-carbomethoxyaminobenzimidazole	167 — 168	$C_{18}H_{13}ClN_4O_6S$ (424,5) calc: C 45,3; H 3,1; N 13,2; S 7,6 found: C 44,9; H 3,8; N 13,1; S 7,7
IV	1-(4'-methoxyphenoxysulfonylcarbonyl)-2-carbomethoxyaminobenzimidazole	160 — 161	$C_{17}H_{16}N_4O_7S$ (420) calc: C 48,5; H 3,8; N 13,3; S 7,6 found: C 48,4; H 4,4; N 13,6; S 7,6
V	1-(2',4'-dimethylphenoxysulfonylcarbonyl)-2-carbomethoxyaminobenzimidazole	158 — 159	$C_{18}H_{18}N_4O_6S$ (418)
VI	1-(2'-methylphenoxysulfonylcarbonyl)-2-carbomethoxyaminobenzimidazole	160 — 162	$C_{17}H_{16}N_4O_6S$ (404) calc: N 13,9; S 7,9 found: N 13,8; S 7,5
VII	1-(3'-methylphenoxysulfonylcarbonyl)-2-carbomethoxyaminobenzimidazole	161 — 162	$C_{17}H_{16}N_4O_6S$ (404) calc: C 50,5; H 4,0; N 13,9; S 7,9 found: C 50,4; H 4,2; N 13,8; S 8,0

No.	Chemical designation	Melting Point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
VIII	1-(4'-t-butylphenoxysulfonylcarbonyl)- 2-carbomethoxyaminobenzimidazole	174	$C_{26}H_{28}N_4O_6S$ calc: C 53.6; H 5.2; N 12.5; S 7.2 found: C 53.7; H 5.0; N 12.6; S 6.9	(447)
IX	1-(2'-chloro-4'-methylphenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	161 — 162	$C_{17}H_{16}ClN_4O_6S$ calc: N 12.8; S 7.3 found: N 12.5; S 7.0	(438.5)
X	1-(2'-methyl-4',6'-dibromophenoxy- sulfonylcarbonyl)-2-carbomethoxy- aminobenzimidazole	180 — 181	$C_{17}H_{14}Br_2N_4O_6S$ calc: N 10.0; S 5.7 found: N 10.4; S 6.0	(562)
XI	1-(2'-chloro-6'-methylphenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenzimid- azole	159 — 161	$C_{17}H_{15}ClN_4O_6S$ calc: C 46.5; H 3.4; N 12.8; S 7.3 found: C 46.0; H 3.6; N 12.2; S 7.0	(438.5)
XII	1-(2',6'-dichlorophenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	156 — 158	$C_{16}H_{12}Cl_2N_4O_6S$ calc: N 12.2; S 7.0 found: N 12.3; S 6.7	(459)
XIII	1-(2',4'-dichlorophenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	151 — 153	$C_{16}H_{12}Cl_2N_4O_6S$ calc: C 41.8; H 2.6; N 12.2; S 7.0 found: C 41.6; H 2.9; N 12.4; S 7.2	(459)

No.	Chemical designation	Melting Point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
XIV	1-(2',4',6'-trimethylphenoxysulfonyl- carbamoyl)-2-carbomethoxyaminobenz- imidazole	168 — 169	$C_{19}H_{20}N_4O_6S$	(432)
XV	1-(2',6'-diethylphenoxysulfonyl- carbamoyl)-2-carbomethoxyaminobenz- imidazole	162 — 165	$C_{20}H_{22}N_4O_6S$ calc: C 53.8; H 4.9; N 12.5; S 7.2 found: C 54.1; H 5.0; N 12.6; S 7.1	(446)
XVI	1-(4'-bromophenoxysulfonyl(carbamoyl))- 2-carbomethoxyaminobenzimidazole	178	$C_{19}H_{13}BrN_4O_6S$	(469)
XVII	1-(2'-methyl-4',6'-dichlorophenoxy- sulfonyl(carbamoyl))-2-carbomethoxy- aminobenzimidazole	181 — 182	$C_{17}H_{14}Cl_2N_4O_6S$ calc: C 43.1; H 3.0; N 11.8; S 6.8 found: C 43.1; H 3.2; N 12.1; S 7.0	(473)
XVIII	1-(2'-ethoxyphenoxysulfonyl- carbamoyl)-2-carbomethoxyaminobenz- imidazole	170	$C_{18}H_{18}N_4O_7S$ calc: N 12.9; S 7.4 found: N 12.9; S 7.5	(434)
XIX	1-(2'-methyl-4'-chlorophenoxysulfonyl- carbamoyl)-2-carbomethoxyaminobenz- imidazole	165	$C_{17}H_{16}ClN_4O_6S$ calc: C 46.5; H 3.4; N 12.8; S 7.3 found: C 46.6; H 3.7; N 12.8; S 7.4	(438.5)

No.	Chemical designation	Melting point °C (with decomposition)	Molecular formula Analysis values in %	(Mol. weight)
XX	1-(4'-cyanophenoxy)sulfonylcarbonyl)- 2-carbomethoxyaminobenzimidazole	97	$C_{17}H_{18}N_6O_6S$ calc: S 7,7 found: S 7,1	(415)
XXI	1-(2'-methoxyphenoxy)sulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	156	$C_{17}H_{18}N_4O_7S$ calc: C 48,5; H 3,8; N 13,3; S 7,6 found: C 48,5; H 4,1; N 13,1; S 7,4	(420)
XXII	1-(4'-ethoxyphenoxy)sulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	134	$C_{18}H_{18}N_4O_7S$ calc: N 12,9 found: N 12,2	(434)
XXIII	1-(3'-chlorophenoxy)sulfonylcarbonyl)- 2-carbomethoxyaminobenzimidazole	163	$C_{16}H_{13}ClN_4O_6S$ calc: C 45,3; H 3,1; N 13,2; S 7,6 found: C 44,8; H 3,0; N 13,0; S 7,4	(424,5)
XXIV	1-(2',6'-dichloro-4'-methylphenoxy- sulfonylcarbonyl)-2-carbomethoxy- aminobenzimidazole	153 — 155	$C_{17}H_{14}Cl_2N_4O_6S$ calc: C 43,1; H 3,0; N 11,8; S 6,8 found: C 42,7; H 3,0; N 11,80; S 6,8	(473)
XXV	1-(2',4',6'-trichlorophenoxy)sulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	170	$C_{16}H_{11}Cl_3N_4O_6S$ calc: C 38,9; H 2,2; N 11,3; S 6,5 found: C 39,0; H 2,3; N 11,6; S 6,4	(493,5)

No.	Chemical designation	Melting point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
XXVI	1-(4'-methoxyphenoxysulfonylcarbonyl)- 2-carbomethoxyaminobenzimidazole	162 — 164	$C_{17}H_{16}N_4O_6S$ calc: N 13,9; S 7,9 found: N 14,1; S 7,7	(404)
XXVII	1-(3'-carbomethoxyphenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	115 — 120	$C_{18}H_{16}N_4O_6S$ calc: N 13,5; S 7,7 found: N 13,9; S 7,8	(416)
XXVIII	1-(2',5'-dimethylphenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	190 — 194	$C_{18}H_{18}N_4O_6S$ calc: N 13,4; S 7,6 found: N 13,6; S 7,8	(418)
XXIX	1-(2',6'-dimethylphenoxysulfonyl- carbonyl)-2-carbomethoxyaminobenz- imidazole	165	$C_{18}H_{18}N_4O_6S$ calc: N 13,4; S 7,6 found: N 13,8; S 7,6	(418)
XXX	1-methoxysulfonylcarbonyl-2-carbo- methoxyaminobenzimidazole	132 — 135	$C_{11}H_{12}N_4O_6S$ calc: N 17,1; S 9,8 found: N 17,0; S 9,7	(328)
XXXI	1-methoxysulfonylcarbonyl-2-carbo- methoxyaminobenzimidazole	124	$C_{13}H_{14}N_4O_6S$ calc: C 42,1; H 4,1; N 16,4; S 9,4 found: C 42,0; H 4,1; N 16,2; S 9,1	(342)

No.	Chemical designation	Melting point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
XXXII	1-(2',2',2'-trichloroethoxysulfonyl-carbamoyl)-2-carboethoxyaminobenzimidazole	172 — 174	$C_{12}H_{11}Cl_3N_4O_6S$ calc: C 23,8; N 12,6 found: C 23,6; N 12,6	(445,5)
XXXIII	1-propyloxysulfonylcarbamoyl-2-carboethoxyaminobenzimidazole	148	$C_{13}H_{16}N_4O_6S$ calc: C 43,8; H 4,5; S 9,0 found: C 44,0; H 5,3; S 9,4	(356)
XXXIV	1-(2',4',6'-trichlorophenoxysulfonyl-carbamoyl)-2-carboethoxyaminobenzimidazole	171 — 177	$C_{17}H_{13}Cl_3N_4O_6S$ calc: C 40,2; H 2,6; N 11,0; S 6,4 found: C 40,1; H 2,6; N 11,3; S 6,5	(507,5)
XXXV	1-(2',6'-dichloro-4'-methylphenoxy-sulfonylcarbamoyl)-2-carboethoxyaminobenzimidazole	164 — 167	$C_{18}H_{16}Cl_2N_4O_6S$ calc: C 44,3; H 3,3; N 11,5; S 6,6 found: C 44,5; H 3,4; N 11,6; S 6,8	(487)
XXXVI	1-(3'-chlorophenoxysulfonylcarbamoyl)-2-carboethoxyaminobenzimidazole	174	$C_{17}H_{16}ClN_4O_6S$ calc: C 46,5; H 3,4; N 12,8; S 7,3 found: C 46,4; H 3,6; N 12,6; S 7,2	(438,5)
XXXVII	1-(2',4'-dichloro-6'-methylphenoxy-sulfonylcarbamoyl)-2-carboethoxyaminobenzimidazole		$C_{18}H_{16}Cl_2N_4O_6S$ calc: C 44,3; H 3,3; N 11,5; S 6,6 found: C 44,3; H 3,5; N 11,5; S 6,7	(487)

No.	Chemical designation	Melting point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
XXXVIII	1-(2'-chlorophenoxy)sulfonylcarb- amoyl)-2-carbomethoxyamino- benzimidazole	152	$C_{16}H_{13}ClN_4O_6S$ (424.5) calc: C 45.3; H 3.1; N 13.2; S 7.6 found: C 45.1; H 3.4; N 13.3; S 7.9	
XXXIX	1-(2',4',5'-trichlorophenoxy- sulfonylcarbamoyl)-2-carbo- methoxyaminobenzimidazole	159 — 160	$C_{16}H_{11}Cl_3N_4O_6S$ (493.5) calc: C 38.9; H 2.2; N 11.3; S 6.5 found: C 39.0; H 2.2; N 11.6; S 6.7	
XL	1-(3',4'-dichlorophenoxy)sulfonyl- carbamoyl)-2-carbomethoxyamino- benzimidazole	159 — 162	$C_{16}H_{13}Cl_2N_4O_6S$ (459) calc: C 41.8; H 2.6; N 12.2; S 7.0 found: C 41.6; H 2.6; N 12.1; S 6.9	
XLI	1-(2',3'-dichlorophenoxy)sulfonyl- carbamoyl)-2-carbomethoxyamino- benzimidazole	155 — 157	$C_{16}H_{13}Cl_2N_4O_6S$ (459) calc: C 41.8; H 2.6; N 12.2; S 7.0 found: C 41.5; H 2.7; N 12.4; S 6.8	
XLII	1-(3',5'-dichlorophenoxy)sulfonyl- carbamoyl)-2-carbomethoxyamino- benzimidazole	159 — 160	$C_{16}H_{13}Cl_2N_4O_6S$ (459) calc: C 41.8; H 2.6; N 12.2; S 7.0 found: C 41.4; H 2.6; N 12.4; S 6.7	
XLIII	1-(2',5'-dichlorophenoxy)sulfonyl- carbamoyl)-2-carbomethoxyamino- benzimidazole	152	$C_{16}H_{13}Cl_2N_4O_6S$ (459) calc: C 41.8; H 2.6; N 12.2; S 7.0 found: C 41.4; H 2.7; N 12.4; S 7.0	

21

No.	Chemical designation	Melting point °C (with decomposition)	Molecular formula Analysis values in %	(mol. weight)
XLIV	1-(1',3'-dichloropropoxy-(2')-sulfonylcarbamoyl)-2-carbo-methoxyaminobenzimidazole	154	$C_{13}H_{14}Cl_2N_4O_6S$ calc: C 36.7; H 3.3; N 13.2; S 7.5 found: C 38.8; H 3.7; N 13.4; S 7.6	(425)
XLV	1-(2',2',2'-trifluoroethoxy-sulfonylcarbamoyl)-2-carbo-methoxyaminobenzimidazole	171	$C_{13}H_{11}F_3N_4O_6S$	(396)
XLVI	1-(3',trifluoromethylphenoxy-sulfonylcarbamoyl)-2-carbo-methoxyaminobenzimidazole	149 — 150	$C_{17}H_{13}F_3N_4O_6S$	(458)

B) Examples of application

Example 1.

Cucumbers in the three-leave stage were strongly infested with conidia of cucumber mildew (*Erysiphe cichoracearum*) and five days after the infestation the plants were drip-sprayed with liquors containing decreasing amounts of the following compounds:

XXX, XXVII, XXVI, XXXII, XXV, III, II, IV, VI, VII, and V.

As comparative agent a commercial preparation on the basis of dinocap (2,4-dinitro-6-(2-octyl)-phenylcrotonate) was used. The active ingredients were applied in concentrations of 100, 50, 25, 12, 6, 3, 1.5 and 0.75 milligrams per liter of spray liquor. After drying of the liquor the plants were placed in the greenhouse and the degree of infestation was evaluated after two weeks.

The following Table 2 shows that the novel compounds have an excellent efficiency superior to that of the comparative substance.

5

10

15

TABLE 2

Compound	Efficiency in % against (<i>Erysiphechioracearum</i>) mg of active ingredient per liter of spray-liquor							
	100	50	25	12	6	3	1,5	0,75
XXX	100	100	100	100	100	97	95	90
XXVII	100	100	99	97	95	90	85	70
XXVI	100	100	99	97	95	90	85	75
XXXII	100	100	100	98	97	95	85	70
XXV	100	100	100	100	98	95	90	85
III	100	100	100	100	98	95	92	85
II	100	100	100	98	93	87	80	75
IV	100	100	100	95	90	85	82	78
VI	100	100	100	97	93	90	85	80
VII	100	100	100	100	99	97	95	90
V	100	100	100	100	98	97	95	92
comparative agent	100	100	90	80	55	25	0	0
untreated	0	0	0	0	0	0	0	0

Example 2.

Loamy sandy soil was treated with compounds XXX, XXXII, XXVI, XXIX, and XXVIII, respectively, in amounts of 10, 5, 2.5 and 1.25 milligrams of active ingredient per kilogram of soil and thoroughly mixed. As comparative agent a commercial preparation on the basis of dinocap was used in the same amounts. The soil was filled into pots, and wheat of the type Heine VII was sown in the pots which were then placed in a greenhouse. 7 Weeks after sowing when the plants had developed 6 leaves they were strongly infested with conidia of powdery mildew of cereals (*Erysiphe graminis*), 7 days after infestation they were examined and the efficiency of the compounds against mildew was ascertained on a percent basis.

The results summarized in Table 3 show that the compounds of the invention have a very good fungicidal action whereas the comparative agent did not exhibit any action. The mode of treatment clearly shows that the compounds of the invention were taken up by the roots and had a systemic effect.

TABLE 3

23

Compound	Efficiency in % against mildew of wheat after treatment of soil with mg of active ingredient/kg of soil			
	10	5	2,5	1,25
XXX	100	100	98	90
XXXII	100	100	95	90
XXVI	100	98	93	85
XXIX	100	100	98	93
XXVIII	100	90	85	80
comparative agent	0	0	0	0
untreated	0	0	0	0

Example 3.

Plants of wheat in the three-leave stage were infested with conidia of powdery mildew of cereals (*Erysiphe graminis*) and three days after infestation the plants were treated with preparations containing the following compounds:

II, III, XII, XIII, I, IX, X, XXV, XVII, XXVI, IV, VIII, XXIX, XV, V, XXVIII, VI, VII, XXVII,

in concentrations of 500, 250, 125, 60, 30, 15 and 7.5 milligrams of active ingredient per liter of spray liquor. As comparative agent a commercial preparation on the basis of dinocap was used in the same concentrations. The experiment was repeated four times.

14 Days after the treatment the wheat was examined to determine mildew infestation. The results are summarized in Table 4.

Example 4.

Plants of wheat were infested in the three-leave stage with conidia of powdery mildew of cereals (*Erysiphe graminis*) and 6 days after infestation the plants were treated with preparations containing the following compounds:

II, III, XXVI, IV, VIII, XII, XXIX, XV, XIII, V, XXV, X, XVII, I, IX, XXVIII, VI, VII, XXVII

in concentrations of 500, 250, 125, 60, 30 and 15 milligrams of active ingredients per liter of spray liquor. As comparative agent a commercial preparation on the basis of dinocap was used in the same concentrations. The experiment was repeated four times.

14 Days after treatment the plants were examined to determine the degree of infestation. The results are summarized in Table 5.

Example 5.

Plants of wheat in the two-leave stage were treated with the following compounds: II, III, XXVI, IV, VIII, VI, VII, XXVII, XII, XXIX, XV, XIII, V, I, IX, XXVIII, XXV, XVII, X

in concentrations of 4,000, 2,000, 1,000, 500, and 250 milligrams of active ingredient per liter of spray liquor. As comparative agent a commercial preparation on the basis of dinocap was used in the same concentrations. The experiment was repeated three times. After drying of the coating of active ingredient the plants were again placed in the greenhouse and, after they had developed the fifth leave, were strongly infested with conidia of mildew of cereals (*Erysiphe graminis*), and were then kept in a moist atmosphere for 24 hours. Subsequently they were brought again into the greenhouse.

After an incubation time of 14 days the plants were examined to determine the infestation with *Erysiphe graminis*. The result is listed in Table 6. It can be seen that all compounds of the invention had an excellent systemic action against mildew in contrast with the comparative agent.

5

Example 6.

5

Seeds of wheat were thoroughly mixed in a drum with the same compounds as used in Example 5 in amounts of 400, 200, 100, and 50 grams of active ingredient per 100 kilograms of seeds. As comparative agents a commercial treating agent on the basis of mercury and a commercial preparation on the basis of dinocap were used.

10

Subsequently, 10 treated grains were sown together in pots in five repetitions, and after development of the fifth leaf the plants were strongly infested with conidia of mildew of cereals (*Erysiphe graminis*). After a time of incubation of 14 days the plants were examined to determine their infestation with mildew. The result is summarized in Table 7.

10

15

Example 7.

15

Loamy soil was mixed for 10 minutes with the compounds indicated in Example 5 in amounts of 10, 5, 2.5 and 1.25 milligrams per kilogram of soil. As comparative agent a commercial preparation against mildew on the basis of dinocap was used in the same amounts. Pots were filled with the treated soil and 10 wheat grains were sown in each pot in four repetitions. After germination of the wheat when they had developed the fourth or fifth leaf the plants were strongly infested with conidia of mildew of cereals. 10 Days after infestation the plants were examined. The result is listed in Table 8.

20

20

Example 8.

25

Cucumber plants in the two-leave stage were strongly infested with conidia of cucumber mildew (*Erysiphe cichoracearum*) and subsequently placed in a moist atmosphere at 23°C for 24 hours. 5 Days after infestation, the plants were treated 3 times with the compounds indicated in Example 5 in amounts of 100, 50, 25, 12, 6 and 3 milligrams of active ingredient per liter of spray liquor. As comparative agent a commercial preparation on the basis of dinocap was used. After drying of the spray liquor the plants were placed in the greenhouse, and after an incubation time of 14 days, were examined to determine the degree of mildew. The results are listed in Table 9.

25

30

30

TABLE 4

Compound	Efficiency in % against powdery mildew of wheat with mg of active ingredient per liter of spray liquor						
	500	250	120	60	30	15	7,5
II	100	100	97	97	95	85	85
III	100	100	100	97	95	90	85
XII	100	100	100	97	95	90	80
XIII	100	100	100	95	90	85	85
I	100	100	98	95	90	85	80
IX	100	100	95	90	85	85	80
X	100	97	95	90	85	80	75
XXV	100	100	100	97	97	95	75
XVII	100	100	97	95	90	85	70
XXVI	100	97	97	90	85	75	40
IV	100	100	100	97	95	90	85
VIII	100	97	95	90	85	65	55
XXIX	100	100	95	95	85	65	0
XV	100	100	97	95	90	85	75
V	100	100	100	97	95	90	85
XXVIII	100	97	95	90	85	75	65
VI	100	100	97	95	95	85	75
VII	100	100	97	95	90	85	75
XXVII	100	100	97	95	90	90	85
comparative agent	100	85	70	60	35	0	0
untreated	0	0	0	0	0	0	0

25

TABLE 5.

Compound	Efficiency in % against powdery mildew of wheat with mg of active ingredient per liter of spray liquor					
	500	250	120	66	30	15
II	97	95	90	85	65	40
III	100	97	97	95	90	65
XXVI	97	95	90	85	65	40
IV	97	95	90	85	65	40
VIII	97	95	90	85	75	40
XII	100	97	95	85	65	0
XXIX	100	97	97	90	90	75
XV	100	97	95	85	65	0
XVIII	100	100	97	95	90	65
V	100	97	95	90	75	65
XXV	100	100	100	97	95	90
X	100	97	90	75	65	0
XVII	100	97	95	85	75	65
I	100	97	95	90	75	0
IX	97	95	85	75	65	0
XXVIII	97	97	95	90	65	40
VI	97	95	90	85	65	40
VII	97	95	90	90	75	40
XXVII	100	97	95	90	90	85
comparative agent	85	70	55	30	0	0
untreated	0	0	0	0	0	0

TABLE 6

27

Compound	Efficiency in % against powdery mildew of wheat with mg of active ingredient per liter of spray liquor				
	4000	2000	1000	500	250
II	100	97	95	90	65
III	100	97	95	90	75
XXVI	97	95	85	75	65
IV	100	97	95	90	65
VIII	100	97	95	90	65
VI	100	95	90	85	65
VII	100	95	90	75	40
XXVII	100	95	90	85	65
XII	100	100	97	95	90
XXIX	100	97	97	95	85
XV	100	97	90	85	65
XIII	100	100	97	97	90
V	100	97	90	85	65
I	100	97	95	90	85
IX	100	97	95	85	65
XXVIII	100	95	90	85	65
XXV	100	100	97	90	85
XVII	100	100	97	97	90
X	100	100	97	95	90
comparative agent	0	0	0	0	0
untreated	0	0	0	0	0

TABLE 7

Compound	Efficiency in % against mildew in wheat after seed treatment with grams of active ingredient per 100 kg. of seed			
	400	200	100	50
II	100	95	85	40
III	97	90	85	65
XXVI	85	75	65	0
IV	100	95	90	65
VIII	97	95	90	75
VI	100	97	90	40
VII	98	97	90	65
XXVII	95	90	75	0
XII	100	95	90	85
XXIX	100	95	85	75
XV	97	95	85	75
XIII	100	97	95	90
V	97	95	85	0
I	97	95	90	85
IX	95	90	85	75
XXVIII	95	90	75	0
XXV	97	95	90	75
XVII	100	100	97	85
X	97	95	85	75
comparative agent	0	0	0	0
comparative agent	0	0	0	0
untreated	0	0	0	0

TABLE 8

29

Compound	Efficiency in % against mildew in wheat after soil treatment with mg of active ingredient per kg of soil			
	10	5	2,5	1,25
II	100	97	95	85
III	100	97	95	85
XXVI	100	97	95	65
IV	100	97	90	85
VIII	95	90	85	75
VI	100	97	97	90
VII	100	100	95	85
XXVII	100	97	90	65
XII	100	97	95	95
XXIX	100	97	90	65
XV	100	97	90	75
XIII	100	100	97	85
V	100	97	95	85
I	100	97	95	75
IX	100	97	95	75
XXVIII	97	95	85	75
XXV	100	97	97	90
XVII	100	97	97	95
X	100	97	95	85
comparative agent	0	0	0	0
untreated	0	0	0	0

TABLE 9

Compound	Efficiency in % against cucumber mildew with mg of active ingredient per liter of spray liquor					
	100	50	25	12	6	3
II	100	97	97	95	90	85
III	100	100	97	97	90	85
XXVI	100	97	97	90	85	65
IV	100	100	97	90	85	65
VIII	100	100	97	95	85	75
VI	100	97	95	90	85	65
VII	100	100	100	97	95	85
XXVII	100	97	95	90	65	0
XII	100	100	100	97	95	85
XXIX	100	100	97	95	90	85
XV	100	100	97	97	95	85
XIII	100	100	100	100	95	85
V	100	100	97	95	90	65
I	100	100	97	95	90	80
IX	100	100	97	95	90	80
XXVIII	100	97	90	75	40	0
XXV	100	100	100	97	95	90
XVII	100	100	100	97	95	90
X	100	100	97	95	90	80
comparative agent	100	90	75	60	30	0
untreated	0	0	0	0	0	0

Example 9.

Cucumber plants in the two-leave stage were treated with the compounds indicated in Example 5 in amounts of 1000, 500, 250 and 125 milligrams per liter of spray liquor. After drying of the coating, the plants were brought into a greenhouse. After the plants thus treated had developed the fifth or sixth leaf they were strongly infested with conidia of cucumber mildew (*Erysiphe cichoracearum*), kept in a moist atmosphere and, after 24 hours were brought again in to the greenhouse. After an incubation time of 14 days the plants were examined to determine the degree of mildew. The result is listed in Table 10.

Example 10.

Plants of cucumbers having 2 leaves were treated on the lower side of the leaves only with the compounds indicated in Example 5, while care was taken that no active ingredient came into contact with the upper sides. The compounds were used in amounts of 200, 100, 50 and 25 milligrams of active ingredient per liter of spray liquor. As comparative agent a commercial preparation on the basis of dinocap was used in the same concentration.

After drying of the coating the untreated upper sides of the leaves were cautiously infested with conidia of cucumber mildew and the plants were placed in a moist atmosphere. After 24 hours the plants were brought into the greenhouse and 14 days later they were examined to determine the degree of infestation with mildew. The result is listed in Table 11.

TABLE 10

Compound	Efficiency against cucumber mildew in % with mg of active ingredient per liter of spray liquor			
	1000	500	250	125
II	90	85	75	65
III	97	95	85	75
XXVI	75	40	0	0
IV	97	95	85	65
VIII	75	65	0	0
VI	90	85	75	65
VII	97	95	90	85
XXVII	85	75	40	0
XII	97	95	75	60
XXIX	75	65	0	0
XV	100	95	75	60
XIII	100	95	85	70
V	75	65	40	0
I	97	90	75	60
IX	97	95	75	65
XXVIII	90	85	75	40
XXV	97	95	85	65
XVII	100	97	90	75
X	97	85	65	0
comparative agent	0	0	0	0
untreated	0	0	0	0

TABLE 11

Compound	Efficiency in % against cucumber mildew with mg of active ingredient per liter of spray liquor			
	200	100	50	25
II	85	65	0	0
III	95	85	65	0
XXVI	65	40	0	0
IV	95	85	65	0
VIII	95	90	75	65
VI	90	75	65	0
VII	90	85	65	0
XXVII	85	75	65	0
XII	95	90	85	75
XXIX	75	65	0	0
XV	97	90	75	40
XIII	97	95	90	85
V	95	90	65	0
I	97	95	90	75
IX	90	85	75	75
XXVIII	75	65	40	0
XXV	100	97	90	75
XVII	100	97	95	90
X	90	85	75	65
comparative agent	0	0	0	0
untreated	0	0	0	0

Example 11.

Loamy soil was thoroughly mixed for 10 minutes with the compounds indicated in Example 5 in amounts of 10, 5, 2.5 and 1.25 milligrams per kilogram of soil. As comparative agent a commercial preparation on the basis of dinocap was used. Pots were filled with the treated soil, cucumber seeds were sown in the pots in 5 repetitions and the pots were placed in a greenhouse. After the cucumber plants had developed their fifth leaf they were strongly infested with conidia of cucumber mildew, kept for 24 hours in a moist atmosphere and brought again into the greenhouse. After a time of incubation of 14 days, the cucumber plants were examined to determine the degree of infestation with mildew. The result is summarized in Table 12.

Example 12.

Cucumber seeds were thoroughly mixed for 10 minutes in a drum with the compounds indicated in Example 5 in amounts of 400, 200, 100 and 50 grams of active ingredient per 100 kilograms of seeds. As comparative agent two commercial preparations, one on the basis of mercury and the other on the basis of dinocap, were used in the same amounts, but calculated on the preparations. The treated seeds were sown in pots in 5 repetitions. When the plants had developed their fifth leaf they were strongly infested with conidia of cucumber mildew and placed at once in a moist atmosphere of 23°C. After a residence time of 24 hours, the plants were brought into a greenhouse where they were examined after 14 days to determine the degree of infestation with mildew. The result is indicated in Table 13.

TABLE 12

Compound	Efficiency in % against cucumber mildew after soil treatment with mg of active ingredient per kg of soil			
	10	5	2,5	1,25
II	100	100	97	75
III	100	100	97	75
XXVI	100	100	97	85
IV	100	100	97	95
VIII	100	100	97	90
VI	100	97	95	75
VII	100	100	97	85
XXVII	100	100	95	75
XII	100	100	97	95
XXIX	100	100	97	97
XV	100	97	95	85
XIII	100	100	100	95
V	100	100	95	75
I	100	100	97	90
IX	100	100	97	90
XXVIII	100	97	95	85
XXV	100	100	97	97
XVII	100	100	97	95
X	100	100	97	85
comparative agent	0	0	0	0
untreated	0	0	0	0

TABLE 13

Compound	Efficiency against cucumber mildew in % after seed treatment with mg of active ingredient per 100 kg of seeds			
	400	200	100	50
II	100	97	95	85
III	100	97	90	85
XXVI	95	85	75	65
IV	100	97	90	85
VIII	100	97	90	75
VI	97	97	90	85
VII	97	95	90	75
XXVII	97	95	90	40
XII	97	95	90	70
XXIX	97	95	90	85
XV	95	90	85	80
XIII	100	95	90	75
V	97	95	90	75
I	97	95	85	65
IX	97	95	90	75
XXVIII	97	95	75	65
XXV	100	97	90	75
XVII	95	90	80	70
X	97	95	90	75
comparative agent	0	0	0	0
comparative agent	0	0	0	0
untreated	0	0	0	0

Example 13.

Sugar beet plants were treated with the compounds indicated in Example 5 in amounts of 25, 12.5, 6 and 3 milligrams of active ingredient per liter of spray liquor. As comparative agents commercial preparations on the basis of copper oxychloride and on the basis of maneb (manganese (ethylene-bis-dithiocarbamate)) were chloride and on the basis of the coating, the plants were strongly infested with spores of *Cercospora beticola* and then placed in a moist atmosphere of 25°C. After a residence time of 24 hours, the plants were brought into the greenhouse and examined after an incubation time of 21 days to determine the degree of infestation with *Cercospora beticola*. The result is listed in Table 14.

Example 14.

Sugar beet plants were strongly infested with spores of *Cercospora beticola* and placed at once in a moist atmosphere of 25°C. After 24 hours the plants were transferred into the greenhouse. 6 Days after infestation the plants were treated with the compounds indicated in Example 5 in concentrations of 250, 120, 60 and 30 milligrams of active ingredient per liter of spray liquor. As comparative agents preparations on the basis of copper oxychloride and maneb were used. After drying of the coating of active ingredient the plants were placed again in the greenhouse where they were examined after an incubation time of 21 days to determine their degree of infestation with *Cercospora beticola*. The result is indicated in Table 15.

TABLE 14

	Efficiency in % against <i>Cercospora beticola</i> in sugar beet with mg of active ingredient per liter of spray liquor				
	25	12	6	3	1,5
II	100	100	97	90	80
III	100	100	97	95	80
XXVI	100	97	95	90	75
IV	100	97	95	90	70
VIII	100	97	95	90	85
VI	100	97	95	85	75
VII	100	97	95	85	70
XXVII	100	100	97	90	85
XII	100	100	97	97	90
XXIX	100	100	97	97	90
XV	100	97	95	95	90
XIII	100	100	100	97	90
V	100	97	95	90	80
I	100	97	97	95	90
IX	100	97	97	95	90
XXVIII	100	100	97	95	85
XXV	100	100	100	97	90
XVII	100	100	100	97	90
X	100	97	95	95	90
comparative agent copper oxychloride.	75	38	0	0	0
comparative agent maneb	90	65	40	25	0
untreated	0	0	0	0	0

TABLE 15

37

Compound	Efficiency in % against <i>Cercospora beticola</i> in sugar beet with mg of active ingredient per liter for spray liquor			
	250	120	60	30
II	100	97	95	85
III	100	100	97	95
XXVI	100	97	95	90
IV	100	97	95	90
VIII	100	95	85	65
VI	100	97	95	85
VII	100	97	95	75
XXVII	100	97	95	85
XII	100	97	95	85
XXIX	100	97	90	85
XV	100	97	95	85
XIII	100	100	97	95
V	100	97	85	65
I	100	97	95	85
IX	97	95	90	85
XXVIII	100	97	95	85
XXV	100	100	97	95
XVII	100	100	97	95
X	100	97	95	85
comparative agent copper oxychloride.	45	20	0	0
comparative agent maneb	60	30	0	0 <
untreated	0	0	0	0

Example 15.

Apple seedlings in the 4-leave stage were artificially infested in the usual manner with conidia of apple mildew (*Podosphaera leucotricha*) and 5 days after infestation the seedlings were treated with the following compounds:

5 II, III, XXVI, IV, VIII, VI, VII, XXVII, XII, XXIX, XV, XIII, V, I, IX, XXVIII, XXV, XVII, X, XXX, XXXI, XXXII, 5

in concentrations of 50, 25, 12, 6 and 3 milligrams of active ingredient per liter of spray liquor. As comparative agent a commercial preparation on the basis of binapacryl (2-sec-butyl-4,6-dinitrophenyl-3-methyl-butenate) was used with the same concentration of active ingredient. The experiment was repeated 4 times. 10

After an incubation time of 14 days the plants were examined to determine the degree of infestation with apple mildew. The result is indicated in Table 16.

Example 16.

15 Tomato plants of the type "Rheinlands Ruhm" in the three leave stage were treated with the compounds indicated in Example 15 in concentrations of 100, 50, 25, 12 and 6 milligrams of active ingredient per liter of spray liquor. As comparative agent maneb was used in the same concentrations. 15

One day after drying of the coating the plants were strongly infested with spores of leaf mould of tomatoes (*Cladosporium fulvum*), placed in a moist atmosphere and, after 24 hours, brought into a greenhouse. 3 Weeks after infestation the plants were examined. The result is summarized in Table 17. 20

TABLE 16

39

Compound	Efficiency in % against apple mildew with mg of active ingredient per liter of spray liquor				
	50	25	12	6	3
II	100	100	97	97	95
III	100	100	100	97	95
XXVI	97	90	85	40	30
IV	100	100	100	97	95
VIII	95	90	75	60	40
VI	100	100	97	97	95
VII	100	100	100	97	95
XXVII	100	100	97	95	90
XII	100	97	95	90	85
XXIX	100	100	97	90	65
XV	100	100	97	95	90
XIII	100	100	100	97	95
V	100	100	100	97	90
I	100	100	100	95	90
IX	100	97	95	90	85
XXVIII	97	95	90	85	75
XXV	100	100	100	97	97
XVII	100	100	97	97	95
X	97	95	90	85	70
XXX	100	100	100	97	95
XXXI	100	97	95	90	95
XXXII	100	100	100	97	97
Comparative Agent	90	85	60	40	0
untreated	0	0	0	0	0

TABLE 17

Compound	Efficiency in % against <i>Cladosporium fulvum</i> on tomato plants with mg of active ingredient per liter of spray liquor				
	100	50	25	12	6
II	100	100	97	95	90
III	100	100	97	95	90
XXVI	100	97	97	95	85
IV	100	100	97	95	90
VIII	100	100	90	85	80
VI	100	100	97	90	75
VII	100	100	97	90	90
XXVII	100	100	97	95	85
XII	100	95	90	75	70
XXIX	100	100	97	97	90
XV	100	100	95	90	75
XIII	100	97	90	85	75
V	100	100	97	95	85
I	100	100	95	90	85
IX	100	95	95	90	80
XXVIII	100	100	97	90	85
XXV	100	100	100	95	95
XVII	100	100	95	90	75
X	100	90	85	75	70
XXX	100	100	100	95	85
XXXI	100	100	95	90	80
XXXII	100	100	100	97	95
Comparative Agent	95	70	50	25	0
untreated	0	0	0	0	0

Example 17.

41

- 5 Tomato plants of the type "Rheinlands Ruhm" in the three-leave stage were strongly infested with conidia of *Cladosporium fulvum*, kept for 24 hours in a moist atmosphere and then placed in a greenhouse. 5 Days after infestation the plants were treated with the compounds indicated in Example 15 and, after drying of the spray liquor, were again brought into the greenhouse. The active ingredients were used in concentrations of 250, 120, 60, 30, and 15 milligrams per liter of spray liquor. As comparative agent a commercial preparation on the basis of zineb (zinc ethylene bisdithiocarbamate) was used in the same concentration of active ingredient.
- 10 3 Weeks after treatment the plants were examined to determine the degree of infestation with *Cladosporium fulvum*. The result is summarized in Table 18.

Example 18.

- 15 Celery plants of the type "Magdeburger Markt" were treated in the four-leave stage with the compounds indicated in Example 15 in concentrations of 500, 250, 120, and 60 milligrams of active ingredient per liter of spray liquor. As comparative agents commercial preparations on the basis of copper oxichloride and one the basis of maneb were used in the same concentrations.
- 20 One day after drying of the spray liquor the plants were strongly infested in the usual manner with spores of *Septoria apii*, placed for 24 hours in a moist atmosphere of 25°C and then brought into a greenhouse. 3 Weeks after infestation the plants were examined. The result is indicated in Table 19.

TABLE 18

Compound	Efficiency in % against <i>Cladosporium fulvum</i> on tomato plants with mg of active ingredient per liter of spray liquor				
	250	120	60	30	15
II	97	95	85	65	40
III	100	97	90	85	75
XXVI	97	90	85	70	60
IV	100	97	95	90	85
VIII	97	95	90	85	70
VI	100	97	95	85	75
VII	97	95	90	85	75
XXVII	100	97	95	90	85
XII	100	97	95	75	70
XXIX	95	90	85	70	65
XV	100	95	90	85	80
XIII	100	100	97	95	90
V	100	97	97	95	90
I	100	97	90	85	75
IX	97	95	90	85	60
XXVIII	100	97	95	90	85
XXV	100	100	97	95	95
XVII	100	100	97	95	90
X	100	97	95	85	75
XXX	100	100	97	90	85
XXXI	97	90	85	75	65
XXXII	100	100	97	90	85
Comparative Agent	70	30	0	0	0
untreated	0	0	0	0	0

TABLE 19

43

Compound	Efficiency in % against <i>Septoria apii</i> on celery with mg of active ingredient per liter of spray liquor			
	500	250	120	60
II	100	97	90	85
III	100	97	90	85
XXVI	97	90	85	65
IV	100	97	95	90
VIII	100	95	90	80
VI	97	95	90	85
VII	100	97	90	85
XXVII	97	95	90	75
XII	100	97	95	90
XXIX	100	97	95	85
XV	100	97	95	90
XIII	100	97	95	90
V	100	97	90	80
I	100	97	95	90
IX	100	97	95	90
XXVIII	97	95	85	75
XXV	100	97	95	90
XVII	100	100	97	95
X	100	97	95	90
XXX	100	97	95	85
XXXI	100	97	95	90
XXXII	100	97	95	95
Comparative agent maneb	70	45	20	0
comparative agent copper oxychloride	85	60	30	0
untreated	0	0	0	0

Example 19.

5 Rice plants in the three-leave stage were treated with the compounds of the invention indicated in Example 15 in concentrations of 500, 250, 120, 60, and 30 milligrams per liter of spray liquor. As comparative agent a commercial preparation on the basis of maneb was used in the same concentrations. After drying of the spray liquor, the plants were strongly infested with spores of *Piricularia oryzae*, placed in a moist atmosphere of 25°C and then brought into a greenhouse. Two weeks after infestation, the plants were examined to determine the degree of disease. The result is summarized in Table 20.

Example 20.

10 Kidney beans were thoroughly mixed for 10 minutes in a drum with the following compounds of the invention in concentrations of 200, 100, 50, 25, and 12.5 grams of active ingredient per 100 kilograms of beans:

15 II, III, XXVI, IV, VIII, VI, VII, XXVII, XII, XXIX, XV, XIII, V, I, IX, XXVIII, XXV, XVII, X, XXX, XXXI, XXXII, XIX, XVI, XIV.

As comparative agent a preparation on the basis of pentachloronitrobenzene was used in the same concentrations. The experiment was repeated 4 times. One day after the treatment equal numbers of beans were sown in pots in a soil strongly infested with *Rhizoctonia solani* and the pots were placed in the greenhouse.

20 3 Weeks after germination the healthy plants were counted. The result is indicated in Table 21.

TABLE 20

Compound	Efficiency in % against <i>Piricularia oryzae</i> on rice with mg of active ingredient per liter of spray liquor				
	500	250	120	60	30
II	100	95	90	65	50
III	100	95	90	65	50
XXVI	100	95	90	85	75
IV	100	100	97	95	85
VIII	95	90	85	70	65
VI	100	97	95	90	85
VII	100	97	95	90	85
XXVII	95	90	75	65	50
XII	95	90	70	65	55
XXIX	95	90	80	70	65
XV	100	97	90	85	75
XIII	100	97	95	90	80
V	100	100	97	95	90
I	97	90	85	70	65
IX	95	85	75	65	50
XXVIII	95	85	80	70	60
XXV	100	100	97	95	90
XVII	100	97	90	85	65
X	95	90	85	65	50
XXX	100	100	97	90	85
XXXI	97	90	85	70	65
XXXII	100	97	95	90	85
Comparative Agent	70	45	0	0	0
untreated	0	0	0	0	0

TABLE 21

Compound	Efficiency in % against <i>Rhizoctonia solani</i> in dwarf beans after seed treatment with g of active ingredient per 100 kg of seed				
	200	100	50	25	12.5
II	100	90	90	80	70
III	100	100	95	90	80
XXVI	100	100	100	90	80
IV	100	100	90	80	70
VIII	100	90	80	70	65
VI	100	100	95	90	80
VII	100	95	90	80	75
XXVII	100	100	100	90	85
XII	100	95	90	85	70
XXIX	100	100	95	90	85
XV	100	90	85	75	70
XIII	100	100	90	80	70
V	100	90	85	80	70
I	100	95	90	80	75
IX	100	95	80	75	60
XXVIII	100	90	85	70	65
XXV	100	100	100	95	90
XVII	100	90	85	70	65
X	100	90	85	70	65
XXX	100	100	90	85	75
XXXI	100	90	85	70	65
XXXII	100	100	100	95	80
XIX	100	95	90	85	75
XVI	100	95	85	70	65
XIV	100	90	80	65	60
Comparative Agent	90	60	45	30	0
untreated	0	0	0	0	0

Example 21.

A wettable powder containing 1-(2'-chloro-4'-bromophenoxy-sulfonylcarbonyl)-2-carbomethoxy-aminobenzimidazole (I) as active ingredient was prepared by mixing

- 5 20 % by weight of active ingredient
 13 % by weight of highly dispersed silicic acid (Silcasil Z)
 49 % by weight of magnesium-aluminum silicate (Sillitin Z)
 10 % by weight of sulfite waste liquor
 1 % by weight of oleyl methyl tauride (Hostapon (registered Trade Mark) T)
 7 % by weight of wetting agent

- 10 Preparations of the other compounds II to XLVI were made in an analogous manner. 10

Example 22.

- 15 Albino rats were orally infested each with 1,000 eggs of *Heterakis spumosa*. After termination of the prepotent period (about 7 weeks), the compounds listed in following Table 22 were administered once p.o. or s.c. The results were evaluated one week after administration. For this purpose the animals were killed, dissected and the living and dead parasites were counted. 15

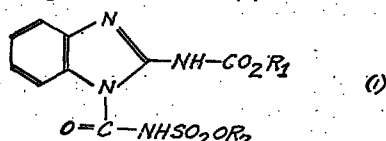
The results are summarized in the following Table 22.

TABLE 22

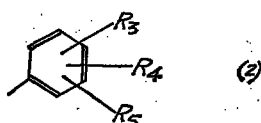
Compound	administration against <i>Heterakis spumosa</i> with mg of active ingredient per kg of body weight s.c. and p.o.	efficiency % of dead parasites	tolerated maximum dose in mg/kg of rat (s.c. and p.o.)
XXV	1 × 200 s.c.	100	800 s.c.
	1 × 200 p.o.	100	800 p.o.
XLIII	1 × <1000 s.c.	100	800 s.c.
	1 × 1000 p.o.	100	1600 p.o.
XXX	1 × 100 s.c.	100	200 s.c.
	1 × 150 p.o.	100	200 p.o.
XLI	1 × 300 s.c.	100	400 s.c.
	1 × 600 p.o.	100	1600 p.o.
XLII	1 × 300 s.c.	100	400 s.c.
	1 × 200 p.o.	100	800 p.o.
XLIV	1 × 150 s.c.	100	200 s.c.
	1 × 400 p.o.	100	800 p.o.
XXXIV	1 × 300 s.c.	100	400 s.c.
	1 × 600 p.o.	100	800 p.o.

WHAT WE CLAIM IS:—

1. Benzimidazoles of the general formula (1)



in which R_1 represents an alkyl group having 1 to 4 carbon atoms and R_2 represents an alkyl group having 1 to 4 carbon atoms which may be substituted by one or more halogen atoms and/or alkoxy groups having 1 to 4 carbon atoms, a cyclohexyl group, or a radical of the formula (2)



in which R_3 , R_4 and R_5 , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, a carbalkoxy group having 1 to 4 carbon atoms in the alkoxy group, a halogen atom or a cyano, nitro, trifluoromethyl, phenyl or phenylazo ($C_6H_5-N=N-$) group.

2. A benzimidazole as claimed in claim 1, in which R_1 represents an alkyl group having 1 to 4 carbon atoms, and R_2 represents an alkyl group having 1 to 3 carbon atoms which may be substituted by one or more chlorine and/or fluorine atoms, or a radical of the formula (2) in which R_3 , R_4 and R_5 , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, an alkoxy group having 1 or 2 carbon atoms, a carbalkoxy group having 1 or 2 carbon atoms in the alkoxy group, a chlorine atom, a bromine atom, a trifluoromethyl group or a cyano group.

3. 1-(2',4'-dichlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

4. 1-(3'-chlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxyaminobenzimidazole.

5. 1-(2',4',6'-trichlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

6. 1-(2',2',2'-trichloroethoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

7. 1-(2'-chlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

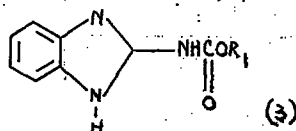
8. 1-(2',4',5'-trichlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

9. 1-(3',4'-dichlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

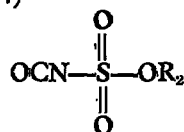
10. 1-(2',5'-dichlorophenoxy-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

11. 1-(1',3'-dichloropropoxy-(2')-sulfonyl-carbamoyl)-2-carbomethoxy-aminobenzimidazole.

12. A process for the manufacture of a benzimidazole as claimed in claim 1, which comprises reacting a carbalkoxy-aminobenzimidazole of the general formula (3)



in which R_1 has the meaning specified in claim 1, with an alkoxy- or aryloxy-sulfonyl isocyanate of the general formula (4)



(4)

in which R_2 has the meaning specified in claim 1.

5 13. A process as claimed in claim 12, substantially as described in Example A1 herein.

14. A benzimidazole as claimed in claim 1 manufactured by the process claimed in claim 12 or claim 13.

10 15. A pesticidal composition comprising as active ingredient a benzimidazole as claimed in claim 1 together with a solid or liquid carrier.

16. A pharmaceutical preparation comprising as active ingredient a benzimidazole as claimed in claim 1 in admixture or conjunction with a pharmaceutically suitable carrier.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

