

1.182.584



PATENT SPECIFICATION

NO DRAWINGS

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Date of filing Complete Specification: 24 Feb., 1967.

Date of Application (No. 14271/66): 31 March, 1966.

Complete Specification Published: 25 Feb., 1970.

1.182.584

Index at acceptance:—C2 C(1E7D1, 1E7D2, 1E7F1, 1E7J, 1E7L, 1E7N5, 1J3C3, 1Q2, 1Q6C, 1Q7B, 1Q8A, 1Q9A, 1Q9B, 1Q9F2, 1Q11G, 2C4, 2C6D, 2C7A1, 2C7A2, 2C7A5, 2D6, 2D19, 2D43C, 2D43F, 2D43H, 2D43S4, 3A13B3, 3A14A3A, 3A14A8D, 200, 213, 214, 215, 22Y, 220, 221, 225, 226, 246, 247, 25Y, 250, 251, 252, 255, 28X, 30Y, 305, 31Y, 313, 314, 32Y, 320, 321, 322, 323, 325, 326, 327, 332, 337, 338, 339, 34Y, 341, 342, 351, 352, 36Y, 360, 361, 362, 364, 366, 368, 50Y, 500, 601, 610, 62X, 626, 630, 650, 652, 656, 660, 662, 667, 670, 671, 672, 677, 713, 72X, 723, 743, 744, 747, 761, 762, 79Y, 791, 17X—186—272, 171—27X—289, 172—195—285, 173—197—288, 176—270—277, 178—188—283, 182—193—276, KD, KR, KS, LA, LH, LK, LW, LY, LZ, MD, MF); A2 Q(6, 16B2, 16C); A5 E(1C4B2, 1C4B3, 1C4B4, 1C17)

International Classification:—C 07 d 51/42

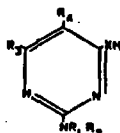
COMPLETE SPECIFICATION

Pyrimidine Derivatives and the use thereof as Fungicides

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company 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 fungicidal compositions containing as an active ingredient a pyrimidine derivative, to new pyrimidine derivatives, to processes for making new pyrimidine derivatives and to methods for combating plant fungal diseases.

According to the invention we provide a fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:—



or ether thereof

wherein R_1 and R_2 are:

- hydrogen,
- a substituted or unsubstituted hydrocarbon,
- a heterocyclic ring,
- a benzylidene-imino group,

an amino or sulphur-free substituted amino group,

a cyano group,

a substituted or unsubstituted carbamoyl group,

an $R.CO-$ or $R.SO_2$ group where R is a substituted or unsubstituted hydrocarbon group,

or R_1 and R_2 , together with the adjacent N-atom, form a substituted or unsubstituted heterocyclic ring which may contain one or more additional heterocyclic atoms; and wherein R_3 and R_4 , are:

hydrogen,

halogen,

a substituted or unsubstituted hydrocarbon group bonded directly to a carbon atom of the pyrimidine ring or through an O— or S— atom thereto,

a heterocyclic-substituted alkyl radical,

a nitro group,

an azophenyl group,

an alkylsulphonyl group,

or R_3 and R_4 together form a substituted or unsubstituted alkylene or alkenylene bridging group;

and wherein X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.

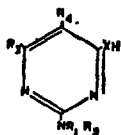
Preferred fungicidal compositions according to the invention comprising as an active

[Price 5s. 0d.]

Price 25p

SEE BRANCH SHEET ATTACHED

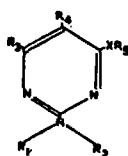
ingredient a pyrimidine derivative of the formula:—



or ether thereof

- 5 wherein R_1 is hydrogen, alkyl, or substituted or unsubstituted aralkyl; R_2 is hydrogen, alkyl, alkenyl, unsubstituted aryl or halo-, alkyl-, or alkoxy-carbonyl-substituted aryl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, halo-alkylcarbonyl, heterocyclic, heterocyclic-substituted alkyl, carbamoyl, or R_1 and R_2 together with the adjacent N-atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms; R_3 and R_4 are hydrogen, halogen, alkyl, aralkyl, alkenyl, alkylthioalkyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, arylazo, or heterocyclic alkyl which may contain an N-atom, unsubstituted or substituted aryl or aryloxy or arylthio, azophenyl, alkylamino or alkylsulphonyl; and X is an atom or oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.

More particularly the invention provides a fungicidal composition comprising as an active ingredient a pyrimidine derivative of the general formula:



wherein:

R_1 stands for hydrogen, alkyl or phenyl-alkyl

- 35 R_2 is hydrogen, alkyl, alkenyl, halo-, alkyl-, or alkoxy-carbonyl-substituted phenyl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, haloalkylcarbonyl, a nitrogen-containing monocyclic heterocyclic radical, phenylalkyl, an alkyl group substituted by a 6-membered heterocyclic nitrogen-containing radical, cycloalkyl, carbamoyl, or a nitro substituted phenylsulphonyl group; or

- 45 R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms, or form a guanidino, N-halophenyl-guanidino or benzyldine-hydrazino group.

- 50 R_3 is hydrogen, halogen, alkyl, alkylthio-alkyl, or unsubstituted or halo- or alkoxy-substituted phenyl;

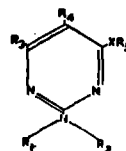
R_4 is hydrogen, halogen, alkyl, phenylalkyl, alkenyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, phenylazo, monocyclic heterocyclic substituted alkyl, phenyl, phenyloxy or halo-, or alkyl-substituted phenylthio, alkylsulphonyl, phenylalkylthio-, alkyl-, or halo-substituted phenylalkyl, or a —CHO group, or

R_3 and R_4 together form an alkylene or alkenylene bridging group;

X is an atom of oxygen or sulphur

R_5 is hydrogen, hydroxyalkyl, phenylalkyl, alkenyl, alkoxy-carbonyl-alkyl, alkylcarbonyl-alkyl, dialkylaminoalkyl, alkylthioalkyl or alkoxyalkyl; and a carrier for the active ingredient comprising a solid diluent or a liquid diluent containing a surface active agent.

The invention also provides a fungicidal composition comprising as an active ingredient a pyrimidine derivative of the general formula:



wherein

R_1 is hydrogen, alkyl or phenylalkyl;

R_2 is hydrogen, alkyl, unsubstituted or halo-, alkyl- or alkoxy-carbonyl-substituted phenyl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, phenyl-alkyl, heterocyclic-substituted alkyl or carbamoyl; or

R_1 and R_2 together with the adjacent nitrogen form a heterocyclic ring which may contain one or more additional heterocyclic atoms;

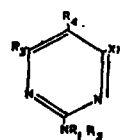
R_3 is hydrogen, alkyl, phenyl or alkylthio-alkyl

R_4 is hydrogen, halogen, alkyl, phenyl-alkyl, alkenyl, alkoxyalkyl, hydroxyhaloalkyl, an alkyl group substituted by a nitrogen-containing monocyclic heterocyclic radical, or alkylsulphonyl;

X is oxygen or sulphur;

R_5 is hydrogen, hydroxyalkyl, alkyl-carbonylalkyl, dialkylamino-alkyl, or alkylthioalkyl; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.

Particularly preferred compositions according to the invention comprise as an active ingredient a pyrimidine derivative of the formula:

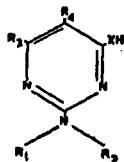


or an ether thereof, wherein R_1 and R_2 are hydrogen or lower alkyl groups, or R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring; R_3 is a lower alkyl group; R_4 is a lower alkyl or alkenyl group; and X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a wetting agent. by the terms "lower alkyl" and "lower alkenyl" in this specification are intended groups containing from 1 to 8 carbon atoms.

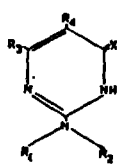
Especially preferred compositions are those comprising compounds wherein in the structural formula in the preceding paragraph, R_1 , R_2 and R_3 are methyl or ethyl groups; R_4 is an alkyl or alkenyl group containing from 1 to 5 carbon atoms; and X is an atom of oxygen or sulphur.

The invention also includes compositions wherein the active ingredient is a pyrimidine derivative as defined in any of the preceding paragraphs and in which the group XH is etherified having an ether group comprising an alkyl, hydroxyalkyl, aralkyl, alkenyl, alkoxyalkyl, alkylcarbonylalkyl, alkylthioalkyl residue.

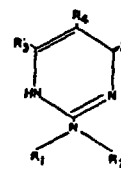
The pyrimidine derivatives are, for convenience, referred to throughout the present specification and claims as having the formula:—



where X is sulphur or oxygen. The compounds, however, also exist with tautomeric structures of the following form:—

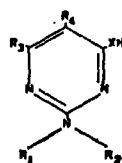


or

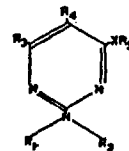


and the present invention is to be understood as including the tautomeric forms of such compounds.

Specific pyrimidine derivatives of the invention which have been found to be particularly useful are listed in Tables I to III below. In Table I are listed hydroxypyrimidines and in Tables II and III there are set out various O— and S— etherified pyrimidine derivatives. The groups NR_1R_2 , R_3 and R_4 in Table I, and additionally the group XR_5 in Tables II and III correspond to Formula I and II below. In all three of these Tables melting points (m.p.) and boiling points (b.p.) are expressed in degrees Centigrade.



FORMULA I
(Table I)



FORMULA II
(Table II)

In this specification the numbering of pyrimidine ring is as follows:—

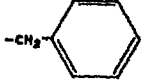
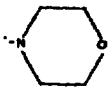
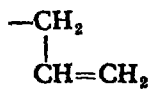
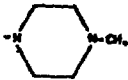


It may be noted that the 4- and 6- positions are equivalent.

TABLE I

HYDROXYPYRIMIDINES (wherein X of Formula I is O)

The compounds marked * are new compounds

Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics
*1	—NH.CN	CH ₃	nC ₄ H ₉	m.p. 295—298°
*2	—N(CH ₃) ₂	CH ₃	nC ₅ H ₁₁	m.p. 84°
*3	—N(CH ₃) ₂	CH ₃	nC ₃ H ₇	m.p. 120°
4	—N(CH ₃) ₂	CH ₃	nC ₄ H ₉	m.p. 102°
*5	—N(CH ₃) ₂	CH ₃	nC ₆ H ₁₃	m.p. 80°
6	—NH ₂	CH ₃	nC ₄ H ₉	m.p. 257°
7	—N(CH ₃) ₂	CH ₃	Br	m.p. 232—233°
8	—NH ₂	CH ₃		m.p. 277.5—278.5°
*9		CH ₃	nC ₄ H ₉	m.p. 149°
*10		CH ₂	nC ₄ H ₉	m.p. 192—195°
*11	—N(CH ₃) ₂	C ₂ H ₅	H	m.p. 140°
12	—N(CH ₃) ₂	CH ₃		m.p. 174°
*13	—NH—C ₆ H ₄ .Br(p)	CH ₃	nC ₄ H ₉	m.p. 176°
*14	—NH—C ₆ H ₄ —CO.OC ₂ H ₅ (p)	CH ₃	nC ₄ H ₉	m.p. 147—150°
*15	—NH—C ₆ H ₄ —CH ₃ (p)	CH ₃	nC ₄ H ₉	m.p. 185—187°
*16		CH ₃	nC ₄ H ₉	m.p. 162—164°

C
p

*

*

*1

*2

*2

*2

*23

*25

26

*27

*28

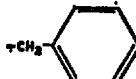
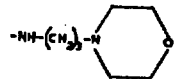
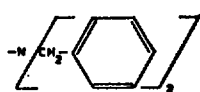
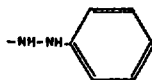
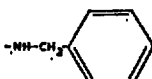
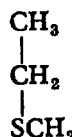
*29

*30

*31

*32

TABLE I (Continued)

Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics
*17	—N(CH ₃) ₂	CH ₃		m.p. 188—190°
*18	—N(CH ₃) ₂		nC ₄ H ₉	m.p. 182°
*19	—N(CH ₃) ₂	CH ₃	—CH(CH ₃) ₂	m.p. 181—183°
*20		CH ₃	nC ₄ H ₉	m.p. 139—141°
*21		CH ₃	nC ₄ H ₉	m.p. 151°
*22	—NH—CO—NH ₂	CH ₃	nC ₄ H ₉	m.p. 207°
*23		CH ₃	nC ₄ H ₉	m.p. 185°
*25	—N(nC ₄ H ₉) ₂	CH ₃	nC ₄ H ₉	m.p. 145—148°
26	—NH—NH ₂	CH ₃	nC ₄ H ₉	m.p. 201—212°
*27	—NH—CO—CH ₃	CH ₃	nC ₄ H ₉	m.p. 153°
*28	—NH—CH(CH ₃) ₂	CH ₃	nC ₄ H ₉	m.p. 135—137°
*29		CH ₃	nC ₄ H ₉	m.p. 76°
*30	NHC ₂ H ₅	CH ₃	nC ₄ H ₉	m.p. 159°
*31	—N(CH ₃) ₂		H	m.p. 118°
*32	—N(CH ₃) ₂	CH ₃	CH ₃ .CH ₂ .OCH ₂ .CH ₂ —	m.p. 104—105°

ical
acteristics

295—298°

84°

120°

102°

80°

257°

232—233°

—278.5°

49°

92—195°

40°

74°

76°

17—150°

35—187°

52—164°

TABLE I (Continued)

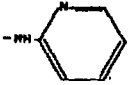
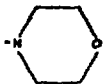
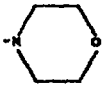
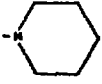
Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics	Compound No.
*33	—N(CH ₃) ₂	H	<i>n</i> C ₄ H ₉	m.p. 84°	*53
*34	—NH <i>n</i> C ₄ H ₉	CH ₃	<i>n</i> C ₄ H ₉	m.p. 143°	
*35	—N(CH ₃) ₂	CH ₃	CH ₃ —SO ₂ —	m.p. 235°	
37	—NH ₂	CH ₃	CH ₂ CH=CH ₂	m.p. 266–267°	*54
38	—N(CH ₃) ₂	CH ₃	CH(OH)CCl ₃	m.p. 221–222° (with decomposition)	
39	—N(CH ₃) ₂	H	CH(OH)CCl ₃	m.p. 228–229° (with decomposition)	
*40	—NH—CH ₃	CH ₃	CH(OH)CCl ₃	m.p. 196°	*55
41		CH ₃	H	m.p. 205–207°	*56
*42	—NH.OH ₂ .CH=CH ₂	CH ₃	<i>n</i> C ₄ H ₉	m.p. 165–167°	57
43	N(CH ₃) ₂	H	NO ₂	m.p. 301°	
*44		CH ₃	CH ₃	m.p. 201°	
*45		<i>n</i> C ₃ H ₇	H	m.p. 174–175°	*58
					*60
					61
*46		CH ₃	CH ₃	m.p. 157°	*62
					*63
					*64
*47	—N(CH ₃) ₂	CH ₃	C ₂ H ₅	m.p. 141°	*65
48	—N(CH ₃) ₂	H	H	m.p. 175–176°	*66
49	—NH ₂	CH ₃	<i>n</i> C ₅ H ₁₁	m.p. 234°	*67
50	—NH ₂	CH ₃	<i>n</i> C ₆ H ₁₃	m.p. 236°	*68
51	—NH ₂	CH ₃	CH ₃	m.p. 304–306°	
*52	N(CH ₃) ₂	<i>n</i> C ₃ H ₇	H	m.p. 127°	

TABLE I (Continued)

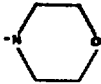
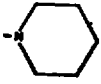
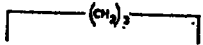
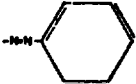
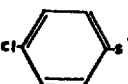
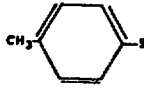
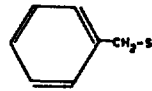
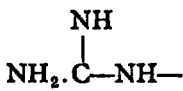
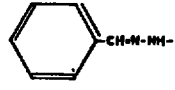
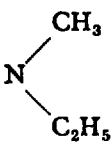
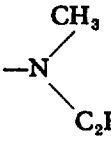
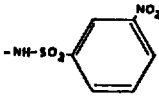
Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics
*53		CH ₃	<i>n</i> C ₃ H ₇	m.p. 238°
*54		CH ₃	<i>n</i> C ₄ H ₉	m.p. 126°
*55	N(CH ₃) ₂		H	m.p. 243°
*56	N(CH ₃) ₂			m.p. 224—225°
57	N(CH ₃) ₂	CH ₃		m.p. 147—150°
*58	N(CH ₃) ₂	CH ₃	<i>n</i> C ₈ H ₁₇	m.p. 57°
*60	N(CH ₃) ₂	<i>n</i> C ₆ H ₁₃	H	m.p. 80—81°
61	NH.NH ₂	CH ₃	<i>n</i> C ₃ H ₇	m.p. 216—218°
*62	NH.C ₃ H ₇ <i>n</i>	CH ₃	<i>n</i> C ₄ H ₉	m.p. 154°
*63	N(CH ₃) ₂	CH ₃	<i>iso</i> C ₄ H ₉	m.p. 150°
*64	N(CH ₃) ₂	H	CH ₂ =CH—CH ₂	m.p. 94°
*65	N(CH ₃) ₂	CH ₃	(CH ₃) ₂ .CH.CH ₂ .CH ₂	m.p. 151°
*66	NH.CO.CF ₃	CH ₃	<i>n</i> C ₄ H ₉	m.p. 128—129°
*67	N(CH ₃) ₂	<i>n</i> C ₃ H ₇	C ₂ H ₅	m.p. 103—104°
*68	N(CH ₃) ₂	CH ₃		m.p. 210°

TABLE I (Continued)

Compound No.	NR ₁ R ₂	R ₃	R ₄	Physcial Characteristics
*69	NH COCH ₂ Cl	CH ₃	<i>n</i> C ₄ H ₉	m.p. 156°
*70	N(CH ₃) ₂	C ₂ H ₅	<i>n</i> C ₄ H ₉	m.p. 100°
*71	N(CH ₃) ₂	CH ₃		m.p. 220°
*72	N(CH ₃) ₂	CH ₃		m.p. 175—176°
*73		CH ₃	<i>n</i> C ₃ H ₇	m.p. 291—293°
74		CH ₃	<i>n</i> C ₃ H ₇	m.p. 199°
*75		CH ₃	<i>n</i> C ₄ H ₉	m.p. 101°
*76		CH ₃	<i>n</i> C ₃ H ₇	m.p. 116—117°
*77	—N(C ₂ H ₅) ₂	CH ₃	<i>n</i> C ₃ H ₇	m.p. 114—115°
*78		CH ₃	CH ₂ =CH—CH ₂ —	m.p. 233—234°

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TABLE I (Continued)

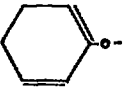
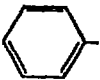
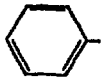
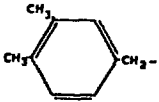
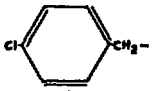
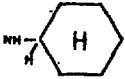
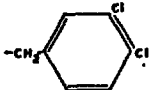
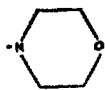
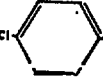
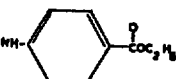
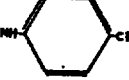
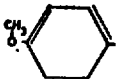
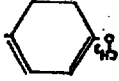
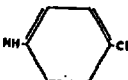
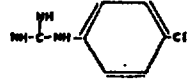
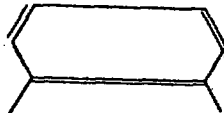
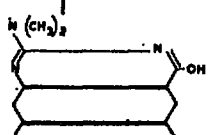
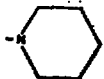
Physical Characteristics	Compound No.	NR_1R_2	R_3	R_4	Physical Characteristics
156°	*79	$\text{NH} \cdot \text{CO} \cdot \text{CH}_3$	H		m.p. 230—231°
100°	80	NH_2	H		m.p. 268—270°
220°	*81	$\text{NH} \cdot \text{CO} \cdot \text{CH}_3$	H		m.p. 307°
175—176°	*82	$\text{N}(\text{CH}_3)_2$	CH_3		m.p. 182°
291—293°	*83	$\text{N}(\text{CH}_3)_2$	CH_3		m.p. 220°
199°	*84		CH_3	$n \text{ C}_3\text{H}_7$	m.p. 220°
101°	85	$\text{N}(\text{CH}_3)_2$	CH_3		m.p. 140°
116—117°	*86		H	$\text{CH}(\text{OH})\text{CCl}_3$	m.p. 202—203°
114—115°					
233—234°					

TABLE I (Continued)

Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics	Compound No.
*87		H	CH(OH)CCl ₃	m.p. 205°	101
*88		CH ₃	CH(OH)CCl ₃	m.p. 213°	102
*89	—NHC ₂ H ₅	H	CH(OH)CCl ₃	m.p. 188—190°	
*90	N(C ₂ H ₅) ₂	CH ₃	C ₂ H ₅	m.p. 121—122°	
*91	N(C ₂ H ₅) ₂	CH ₃	—CH ₂ —CH=CH ₂	m.p. 110—111°	
*92	N(CH ₃) ₂	H	C ₂ H ₅	m.p. 124—125°	*103
*93	N(CH ₃) ₂		CH ₂ =CH·CH ₂ —	m.p. 196°	104
*94	N(CH ₃) ₂		H	m.p. 260—261°	
*95	N(CH ₃) ₂		C ₂ H ₅	m.p. 175°	105
*96		CH ₃	n C ₈ H ₇	—219° m.p. 217	*106
*97		CH ₃	n C ₈ H ₇	m.p. 216—218°	107
*98	N(CH ₃) ₂		H	m.p. 280°—281	*108
*99	NHC ₂ H ₅		H	m.p. 199°	
100	NH ₂	CH ₃	C ₂ H ₅	m.p. 288—289°	

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TABLE I (Continued)

Compound No.	NR ₁ R ₂	R ₃	R ₄	Physical Characteristics
101	NH ₂	Cl	H	m.p. 261°
102		CH ₃	Br	m.p. 267—269°
*103		CH ₃	CH ₃	m.p. 268—270°
104	NH CH (CH ₃) ₂			m.p. 212—213°
105	N(CH ₃) ₂	CH ₃	H	m.p. 175—176°
*106	N(CH ₃) ₂			m.p. above 340°
107		CH ₃	CHO	m.p. 235°
*108		CH ₃	H	m.p. 220—222°

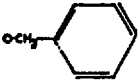
In the above table the compounds numbered 42, 91, 92, 93, 103 and 106 were prepared by the procedure set out in Example 1 below, using the appropriate reactants. The compounds numbered 40, 86, 87, 88 and 89 were prepared by a method analogous to that described in the literature by Hull, J.C.S. 1957, 484.

TABLE II

ETHERIFIED HYDROXYPYRIMIDINES of general Formu II

(wherein X = O)

All these compounds are new compounds

Compound No.	NR ₁ R ₂	R ₃	R ₄	XR ₅	Physical Characteristics
*109	-N(CH ₃) ₂	CH ₃	nC ₄ H ₉	O-CH ₂ -CH ₂ -OH	b.p. 126—128°/ 0.4 mm
*110	-N(CH ₃) ₂	CH ₃	nC ₄ H ₉	O-CH ₂ -CH ₂ -N(C ₂ H ₅) ₂	b.p. 126—128°/ 0.23 mm
*111	N(CH ₃) ₂	H	H		b.p. 118—120°/ 0.1 mm
*112	N(CH ₃) ₂	H	H	O-CH ₂ -CH=CH ₂	b.p. 60—65°/ 0.1 mm
*113	N(CH ₃) ₂	CH ₃	CH ₃	O-CH ₂ -CH ₂ OH	m.p. 79—80°

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*12

*12

*12

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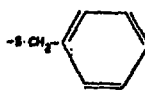
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TABLE III

SULPHUR-CONTAINING PYRIMIDINES of General Formula II

(wherein X = S)

Compound No.	NR ₁ R ₂	R ₃	R ₄	XR ₅	Physical Characteristics
*114	—N(CH ₃) ₂	CH ₃	nC ₄ H ₉	—SH	m.p. 105—106°
*115	—N(CH ₃) ₂	CH ₃	nC ₄ H ₉	—S—CH ₂ —C(=O)—CH ₃	m.p. 48°
*116	—N(CH ₃) ₂	CH ₃	C ₂ H ₅	SH	m.p. 140—141°
*117	—N(CH ₃) ₂	CH ₃	nC ₄ H ₉	—S—CH ₂ —CH ₂ —N(CH ₃) ₂	b.p. 153°/0.23 mm η _D ²⁵ 1.5452
*118	—N(CH ₃) ₂	CH ₃	nC ₄ H ₉	—S—CH ₂ —CH ₂ S—C ₂ H ₅	b.p. 160°/0.33 mm η _D ²⁵ 1.5670
*119	N(CH ₃) ₂	CH ₃	nC ₄ H ₉	—S—CH ₂ — 	m.p. 52—53°
*121	N(CH ₃) ₂	CH ₃	CH ₃	SH	m.p. 162—163°
*122	N(CH ₃) ₂	CH ₃	nC ₄ H ₉	S·CH ₂ ·CH ₂ OC ₂ H ₅	b.p. 146°/0.5 mm
*123	N(CH ₃) ₂	CH ₃	H	SH	m.p. 154—155°
124	N(CH ₃) ₂	H	H	SH	m.p. 149°
*125	N(CH ₃) ₂	CH ₃	nC ₄ H ₉	S·CH ₂ ·C(=O)·C ₂ H ₅	m.p. 64°
*126	N(CH ₃) ₂	CH ₃	nC ₄ H ₉	S·CH ₂ ·CH ₂ ·N(C ₂ H ₅) ₂	b.p. 150°/0.22 mm η _D ²⁵ 1.5411

We have found that the fungicidal properties of the pyrimidine derivatives of the invention are decreased if both R₃ and R₄ are hydrogen, or if R₄ is an alkyl radical containing more than 7 carbon atoms.

A particularly useful pyrimidine derivative is that in which R₁ and R₂ are both methyl, R₃ is methyl, R₄ is nC₄H₉, and XR₅ is OH, that is compound No. 4 in the foregoing Table I, (page 6). Other particularly useful pyrimidine derivatives are those having the following compound numbers in the foregoing Tables:— 2, 3, 9, 12, 28, 30, 37, 62, 70, 75, 91, 116, 117, and 126. According to a pre-

ferred embodiment of the invention, we provide fungicidal compositions comprising as active ingredient, 2 - dimethylamino - 4 - methyl - 5 - n - butyl - 6 - hydroxypyrimidine or 2 - ethylamino - 4 - methyl - 5 - n - butyl - 6 - hydroxypyrimidine. The latter two compounds have been accorded the British Standard Names dimethirimol and ethirimol, respectively, and are numbered 4, and 30, in Table I above.

The fungicidal compositions of the invention possess activity against a wide variety of fungal diseases including the following specific diseases:—

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	<i>Puccinia recondita</i> (rust1-brown) on wheat	grains may include fillers, and suspending agents.	
	<i>Phytophthora infestans</i> (late blight) on tomatoes	The compositions may also be in the form of liquid preparations to be used as dips or sprays which are generally aqueous disper-	70
5	<i>Sphaerotheca fuliginea</i> (powdery mildew) on cucumber	sions or emulsions containing the active ingredient in the presence of one or more surface active agents such as, for example, wetting agents, dispersing agents, emulsifying agents or suspending agents.	75
	<i>Erysiphe graminis</i> (powdery mildew) on wheat and barley	Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include, for example, quaternary ammonium compounds for example cetyltrimethyl-ammonium bromide. Suitable agents of the anionic type include, for example, soaps, salts of aliphatic monoesters of sulphuric acid, for example sodium lauryl sulphate, salts of sulphonated aromatic compounds, for example sodium dodecyl-benzenesulphonate, sodium, calcium or ammonium lignosulphonate, butyl-naphthalene sulphonate, and a mixture of the sodium salts of diisopropyl- and triisopropyl-naphthalene sulphonic acids. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol or cetyl alcohol, or with alkyl phenols such as octylphenol, nonylphenol and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins. Suitable suspending agents are, for example, hydrophilic colloids, for example polyvinylpyrrolidone and sodium carboxymethylcellulose, and the vegetable gums, for example gum acacia and gum tragacanth.	80
10	<i>Podosphaera leucotricha</i> (powdery mildew) on apple		85
	<i>Uncinula necator</i> (powdery mildew) on vine		90
	<i>Plasmopara viticola</i> (downy mildew) on vine		95
	<i>Piricularia oryzae</i> (blast) on rice		100
15	<i>Venturia inaequalis</i> (scab) on apple		105
	<i>Pythium ultimum</i> (seedling rot)		110
	<i>Fusarium culmorum</i> (stem rot)		115
20	A particularly useful feature of the activity of the pyrimidine derivatives listed above is their systemic effect, that is to say, their ability to move throughout the plant to reach any part thereof bearing a fungal infection and to combat the infection.		120
25	The fungicidal compositions of the invention can be used to combat plant pathogens in a number of ways. Thus they can be applied to the foliage of an infected plant, to seed or to the soil in which plants are growing or to be planted.		125
30	In a further aspect the invention includes a method for the combating of undesired fungal infections in growing plants which comprises applying to the locus of the plant a pyrimidine derivative as hereinbefore defined.		130
35	In yet a further aspect the invention includes a method for treating agricultural soil to combat pathogens on plants comprising applying to the soil a pyrimidine derivative as hereinbefore defined.		
40	The invention includes therefore a method of combating plant pathogens in which a plant susceptible to such pathogens, or seed thereof, is treated with pyrimidine derivative as hereinbefore defined.		
45	The compositions may be used for agricultural and horticultural purposes and the type of composition used in any instance will depend upon the particular purpose for which it is to be used.		
50	The compositions may be in the form of dusting powders or granules wherein the active ingredient is mixed with a solid diluent or carrier. Suitable solid diluents or carriers may be, for example, kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, Fuller's earth, gypsum, Hewitt's earth, diatomaceous earth and China clay. Compositions for dressing seed, for example, may comprise an agent assisting the adhesion of the composition to the seed, for example a mineral oil.		
55	The compositions may also be in the form of dispersible powders or grains comprising, in addition to the active ingredient, a surface active agent to facilitate the dispersion of the powder or grains in liquids. Such powders or		
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The pyrimidine derivatives may also be conveniently formulated by admixing them with fertilizers. A preferred composition of this type comprises granules of fertiliser material, incorporating, for example coated with, a pyrimidine derivative. The fertiliser material may, for example, comprise nitrogen or phosphate-containing substances.

- The compositions which are to be used in the form of aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient or ingredients, the said concentrate to be diluted with water before use.
- These concentrates are often required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water in order to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may conveniently contain from 10—85% by weight of the active ingredient or ingredients and generally from 25—60%, by weight of the active ingredient or ingredients. When diluted to form aqueous preparations, such preparations may contain varying amounts of the active ingredient or ingredients depending upon the purpose for which they are to be used, but an aqueous preparation containing between 0.001% and 1.0%, by weight of

active ingredient or ingredients may be used.

It is to be understood that the fungicidal compositions of this invention may comprise, in addition to a pyrimidine derivative, one or more other compounds having biological activity.

Compositions according to the invention were made up in the following manner and tested against various fungal diseases, and the results of these tests are shown in Tables IV to VI hereinafter. In the tests, both a protectant and an eradicant test were carried out, and in the protectant test the plants were sprayed so that the leaves were wetted with a solution or suspension containing 500 parts per million of the active compound and 0.1% of a wetting agent, and after 24 hours were inoculated with the disease, the extent of which was assessed visually at the end of the test. In the eradicant test, the plants were inoculated with the disease and then sprayed (so that the leaves were wetted) after a number of days depending on the disease with a solution or suspension containing 500 parts per million of the active compound and 0.1% of a wetting agent. The results are shown in Tables IV to VI as a grading giving the percentage amount of disease as follows. The time in days stated in the headings to the tables is the period between spraying and assessment of the disease.

Grading	Percentage Amount of Disease
0	61 to 100
1	26 to 60
2	6 to 25
3	0 to 5

TABLE IV

Compound No.	Puccinia recondita (Rust)		Phyto-phthora infestans (Late Blight)		Sphaero-theca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podo-sphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmo-para viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7 — 14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
1	—	—	—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—
2	0	0	1	—	3	3	3	—	3	—	3	—	1	—	1	—	0	—	0	—
3	3	0	—	—	3	3	3	0	3	—	3	1	0	—	3	—	—	—	—	—
4	3	0	—	—	3	3	3	3	3	—	3	3	1	—	0	—	—	—	—	—
5	2	0	1	—	3	1	3	2	—	—	—	—	0	—	3	—	—	—	—	—
6	0	0	1	—	3	3	3	1	—	—	1	—	0	—	2	—	0	—	1	—
7	0	0	0	—	2	1	3	1	—	—	0	—	1	—	3	—	3	—	1	—
8	0	0	1	—	0	0	0	1	—	—	0	—	0	—	3	—	0	—	0	—
9	0	0	2	—	3	3	3	2	—	—	1	—	0	—	2	—	2	—	1	—
10	0	1	2	—	0	0	0	0	—	—	1	—	0	—	3	—	—	—	—	—
11	0	1	3	—	0	0	0	0	—	—	0	—	0	—	3	—	0	—	1	—
12	0	0	0	—	3	3	3	2	—	—	3	3	0	—	3	—	1	—	0	—
13	0	0	1	—	0	3	3	—	—	—	—	—	—	—	0	—	—	—	—	—

TABLE IV (Continued)

Compound

Compound No.	Puccinia recondita (Rust)		Phyto-phthora infestans (Late Blight)		Sphaero-theca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podo-sphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmo-para viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7 — 14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
14	0	0	1	—	3	3	1	—	—	—	2	—	0	—	3	—	—	—	—	—
15	0	0	2	—	0	2	0	—	0	—	2	—	0	—	3	—	0	—	0	—
16	0	0	0	—	0	3	0	—	0	—	2	—	0	—	3	—	2	—	2	—
17	0	0	1	—	3	1	2	—	0	—	0	—	0	—	3	—	2	—	—	—
18	0	0	0	—	0	0	0	—	0	—	1	—	0	—	3	—	1	—	1	—
19	—	—	—	—	2	0	—	—	0	—	0	—	0	—	1	—	0	—	1	—
20	0	0	1	—	2	3	1	—	—	—	—	—	2	—	2	—	—	—	—	—
21	0	0	2	—	3	3	0	—	1	—	1	—	0	—	0	—	1	—	0	—
22	0	0	3	—	0	0	1	—	—	—	—	—	—	—	2	—	—	—	—	—
23	0	0	0	—	3	3	1	—	3	—	2	—	0	—	1	—	1	—	0	—
25	0	0	0	—	3	3	0	—	2	—	0	—	0	—	2	—	2	—	1	—
26	0	0	1	—	0	0	0	—	3	—	0	—	0	—	3	—	0	—	0	—
27	0	0	0	—	3	3	3	—	0	—	3	3	0	—	2	—	1	—	2	—
28	0	0	2	—	3	3	3	1	3	—	0	—	1	—	0	—	3	—	0	—

TABLE IV (Continued)

Compound No.	Puccinia recondita (Rust)		Phyto-phthora infestans (Late Blight)		Sphacro-theca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podo-sphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmo-para viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7-14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
29	1	0	2	—	2	3	2	—	3	—	0	—	0	—	1	—	0	—	0	—
30	0	0	2	—	3	3	3	1	3	—	3	3	0	—	1	—	0	—	1	—
32	0	0	0	—	1	0	0	—	0	—	0	—	1	—	2	—	0	—	0	—
33	3	0	—	—	2	2	3	—	3	—	2	—	—	—	—	—	—	—	—	—
34	0	0	1	—	3	3	2	1	3	—	2	—	—	—	0	—	1	—	0	—
35	0	0	—	—	3	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
37	0	0	3	—	3	3	2	—	3	—	3	—	0	—	1	—	0	—	1	—
38	0	0	3	—	3	1	1	—	1	—	1	—	0	—	0	—	0	—	2	—
39	3	0	—	—	1	0	0	—	0	—	0	—	0	—	0	—	1	—	0	—
40	1	0	0	—	3	3	2	—	—	—	—	—	—	—	—	—	—	—	—	—
41	0	0	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
43	2	0	0	—	0	—	0	—	1	—	—	—	0	1	1	—	2	—	1	—
44	0	0	0	—	0	0	0	—	0	—	1	—	1	—	0	—	1	—	0	—
45	0	0	0	0	0	0	0	0	2	—	0	—	0	—	3	0	0	—	0	—
46	0	0	0	—	0	0	0	—	0	—	0	—	0	—	0	—	0	—	1	—
47	2	0	1	0	3	3	0	—	0	—	0	—	1	—	—	0	—	0	—	—

TABLE IV (Continued)

TABLE IV (Continued)

Compound No.	Puccinia recondita (Rust)		Phytophthora infestans (Late Blight)		Sphaerotheca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podosphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmopara viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7—14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
63	—	—	—	—	3	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
64	3	3	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
65	0	0	0	0	3	3	0	—	2	—	—	—	1	—	0	—	0	—	0	—
66	0	0	0	0	3	3	1	—	3	—	—	—	0	—	1	—	0	—	0	—
67	0	0	0	0	3	3	0	—	0	—	—	—	0	—	0	—	3	—	3	—
68	1	0	0	—	0	0	0	—	0	—	—	—	0	—	0	—	0	—	0	—
69	1	0	0	0	3	2	0	—	1	—	—	—	0	—	3	—	1	—	3	—
70	0	0	0	0	3	3	3	—	3	—	3	—	—	—	1	—	3	—	0	—
71	0	0	0	—	0	0	0	—	2	—	—	—	0	—	0	—	0	—	1	—
72	0	0	0	—	0	0	0	—	0	—	—	—	0	—	0	—	0	—	0	—
73	0	0	2	—	0	0	1	—	3	—	—	—	—	—	2	—	—	—	1	—
74	1	0	0	—	0	0	1	—	0	—	—	—	—	—	2	—	1	—	0	—
75	0	0	—	—	3	3	3	—	3	—	—	—	3	—	1	—	1	—	0	—
76	0	0	—	—	3	3	3	—	3	—	—	—	—	—	—	—	0	—	—	—
77	3	0	—	—	2	3	—	—	—	—	—	—	3	—	2	—	3	—	—	—

TABLE IV (Continued)

Compound No.	Puccinia recondita (Rust)		Phyto-phthora infestans (Late Blight)		Sphaero-theca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podosphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmopara viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7-14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
90	0	0	—	—	3	3	2	—	3	—	1	—	0	—	0	—	0	0	—	—
91	1	1	—	—	3	3	3	—	3	—	—	—	2	—	2	—	—	0	—	—
100	0	0	0	—	2	0	3	—	0	—	1	—	0	—	3	—	0	1	—	—
101	2	0	1	—	3	0	0	—	0	—	0	—	2	—	0	—	0	0	—	—
102	0	0	0	—	0	0	1	—	1	—	2	—	3	—	3	—	2	0	—	—
103	0	0	0	—	0	0	0	—	0	—	0	—	3	—	3	—	1	0	—	—
104	2	0	2	—	0	1	0	—	3	—	0	—	1	—	3	—	1	2	—	—
105	0	0	—	0	3	3	0	—	0	—	1	—	1	—	0	—	0	0	—	—
106	1	0	0	—	0	0	0	—	1	—	0	—	2	—	2	—	3	2	—	—
107	0	0	3	—	0	0	0	—	0	—	0	—	1	—	3	—	1	2	—	—
108	0	0	—	—	2	0	0	—	0	—	2	—	1	—	1	—	1	0	—	—

TABLE V

Compound No.	Puccinia recondita (Rust)		Phytophthora infestans (Late Blight)		Sphaerotheca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podosphaera leucotricha (Powdery mildew)		Uncinula necator (Powdery mildew)		Plasmopara viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
109	1	0	0	—	3	3	—	—	0	—	0	—	0	—	1	—	0	—	2	—
110	0	0	2	—	3	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
111	0	0	0	—	0	0	3	—	0	—	1	—	3	—	1	—	3	—	1	—
112	0	0	0	—	0	0	1	—	1	—	0	—	0	—	0	—	0	—	1	—
113	2	0	0	—	0	0	0	—	0	—	0	—	0	—	1	—	0	—	2	—

TABLE VI

Compound No.	Puccinia recondita (Rust)		Phyto-phthora infestans (Late Blight)		Sphaero-theca fuliginea (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Erysiphe graminis (Powdery mildew)		Podosphaera leucotricha (Powdery mildew)		Ucinula necator (Powdery mildew)		Plasmo-para viticola (Downy mildew)		Piricularia oryzae (Blast)		Venturia Inaequalis (Scab)	
	Wheat 10 days		Tomato 4 days		Cucumber 10 days		Wheat 10 days		Barley 10 days		Apple 7-14 days		Vine 14 days		Vine 7 days		Rice 7 days		Apple 14 days	
	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad	Prot	Erad
114	0	0	0	—	3	3	0	—	1	—	1	—	0	—	0	—	0	—	0	—
115	1	0	0	—	3	3	0	—	0	—	1	—	0	—	0	—	0	—	0	—
116	1	0	0	—	3	3	2	—	0	—	3	—	1	—	2	—	2	—	2	—
117	2	0	0	—	3	0	3	—	3	—	3	—	0	—	0	—	3	—	2	—
118	1	1	0	—	0	1	3	—	3	—	3	—	0	—	0	—	3	—	1	—
119	1	0	0	—	3	2	3	—	3	—	3	—	0	—	1	—	1	—	1	—
121	0	0	0	—	0	0	0	—	3	—	2	—	0	—	2	—	1	—	1	—
122	0	0	0	—	1	1	0	—	3	—	2	0	0	—	0	—	0	—	1	—
123	0	0	0	—	0	1	0	—	0	—	3	—	2	—	2	—	3	—	3	—
124	0	0	0	—	0	0	1	—	0	—	3	—	0	—	2	—	1	—	2	—
125	0	0	1	—	1	0	0	—	1	—	0	—	0	—	1	—	0	—	0	—
126	1	0	—	—	2	2	3	—	3	—	3	—	0	—	0	—	0	—	3	—

25

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45

5 In a further test, pots of natural soil were treated with granules comprising, on a weight basis, 5% of active ingredient in the form of the compound numbered 4 in Table I above and 95% of Fuller's Earth granules. The preparation of these granules is described in Example 19 below. The amount of granules added to each pot was 0.16 grams.

10 Five wheat seeds were sown in each pot. A similar series was set up without granules. After 10 days all the pots were inoculated with

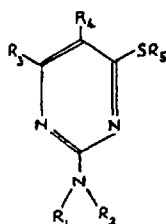
mildew (*Erysiphe graminis*) by dusting with spores from infected plants. After a further 3 weeks the plants were assessed for mildew attack. By using a standard chart, the percentage leaf area infected was estimated as one of the following categories: 0, 1%, 5%, 25%, 50% and 100%. In the Table VII below, setting out the results of the tests, each figure represents the mean leaf area infected for the five plants in a pot.

TABLE VII

	Replicates				Mean
	% leaf area infected				
Pots and granules	0	0	0	0	0
Untreated pots	50	50	50	35	46

25 According to a further feature of the invention, we provide novel hydroxypyrimidines as listed, and indicated as novel by an asterisk, in Table I hereinabove.

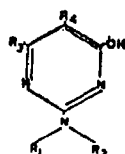
30 According to a further feature of the invention, we provide novel etherified hydroxypyrimidines as listed in Table II above. With the invention also we provide novel sulphur-containing pyrimidines of the general formula:



35 where R1, R2, R3, and R4 have the meanings assigned to them in Claim 1 and R5 is hydrogen or an alkyl, hydroxyalkyl, arylalkyl, alkenyl, alkoxyalkyl, alkylcarbonyl-alkyl or alkylthioalkyl radical provided that it is not a methyl or benzyl radical.

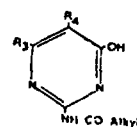
40 In particular, we provide the novel compounds listed in Table III above.

The invention also provides a method of preparing hydroxypyrimidines having the general formula:



wherein R1 stands for hydrogen, alkyl, or phenylalkyl; R2 is hydrogen, alkyl, alkenyl, halo-, alkyl-, or alkoxyalkyl-substituted phenyl, cyano, a nitrogen-containing monocyclic heterocyclic radical, phenylalkyl, an alkyl group substituted by a 6-membered heterocyclic nitrogen-containing radical, cycloalkyl or a nitro-substituted phenylsulphonyl group; or R1 and R2 together with the adjacent nitrogen atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms, or form a guanidino or N-halophenyl-guanidino group; R3 is hydrogen, halogen, alkyl, alkylthioalkyl or unsubstituted or halo- or alkoxy-substituted phenyl; R4 is hydrogen, halogen, alkyl, phenylalkyl, alkenyl, alkoxyalkyl, phenylazo, phenyl, or alkyl- or halo-substituted phenylalkyl, or R3 and R4 together form an alkylene or alkenylene bridging-group; which comprises condensing the appropriate guanidine with a suitably substituted beta-keto ester, if necessary in the presence of a base.

The invention also provides a process for preparing acyl pyrimidine derivative which comprises acylating the appropriate 2-amino pyrimidine. Thus hydroxy pyrimidines of the formula:—



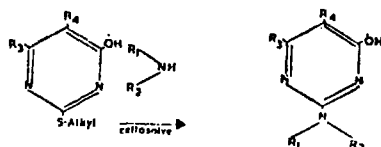
75 where R1 and R2 have any of the meanings defined above may be prepared by acylating the corresponding 2-aminopyrimidine.

The invention also provides a method of preparing the pyrimidine derivatives of the

invention which comprises carrying out the process set out in the penultimate paragraph above and then subsequently effecting the further step of

- 5 (a) hydrolysing the appropriate pyrimidine derivative containing a cyanamino group in position 2 thus preparing the corresponding 2-ureido-derivative; or
- (b) reacting the appropriate 6-hydroxy-
10 pyrimidine with phosphorous pentasulphide to produce the corresponding 6-mercapto derivative; or
- (c) react the appropriate 6-mercapto pyrimidine with the appropriate organic
15 halide to obtain the corresponding thioether. The pyrimidine derivatives of the invention may also be prepared by

- (a) reacting the corresponding 2-alkylthio-
20 pyrimidine with the appropriate amine, for example as represented by the equation:—



the 2-alkylthiopyrimidine being preferably a 2-methylthiopyrimidine; or

- (b) reacting the appropriate 6-halo-
25 pyrimidine with a hydroxy compound to produce the corresponding 6-etherified pyrimidine derivative; or
- (c) reacting the appropriate 5-halo-
30 pyrimidine derivative with a mercapto to form the corresponding 5-mercapto ether.

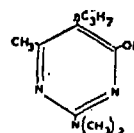
- Various other methods well-known to those skilled in the art may be used to prepare the fungicidally-active pyrimidine derivatives and in so far as these methods are pertinent
35 to the preparation of new compounds they form part of the present invention. Tech-

niques used to produce the pyrimidine derivatives include photochemical Claisen rearrangements and Schotten-Baumann reactions.

The invention is illustrated by the following
40 Examples, those numbered 1—14 exemplifying methods of preparing the pyrimidine compounds listed in Tables I, II and III above, while those numbered 15—22 are illustrative of fungicidal compositions containing
45 various of the pyrimidines derivatives as active ingredient. In the latter group all references to percentage amounts of constituents are by weight and are based on the weight of the composition as a whole.

EXAMPLE 1

The hydroxypyrimidine having the
50 formula:—



was prepared as follows:

To a solution of sodium (0.2 mole 4.6 g.)
55 in dry methanol (120 ml.) was added asymdimethylguanidine sulphate (0.1 mole, 27.2 g.) and the mixture was refluxed for 30 minutes. Ethyl n-propyl acetoacetate (0.2
60 mole, 34.4 g.) was added, and the reaction mixture refluxed with stirring for 20 hours. Water (100 ml.) was added to the cooled mixture, which was then neutralised with
65 acetic acid and extracted exhaustively with methylene chloride. The methylene chloride solution was dried (Na₂SO₄), the solvent removed, and the crystalline residue recrystallised from ethanol (charcoal) to give
70 needles, m.p. 120° (21 g., 54%).

The following compounds of Table I above were prepared by the above method:—

line deriva-
rearrange-
tions.
the follow- 40
-14 exem-
pyrimidine
I and III
2 are illus-
containing 45
es as active
references
nts are by
ght of the
50
ving the

ole 4.6 g.)
as added
(0.1 mole,
xed for 30
etate (0.2 60
e reaction
20 hours.
the cooled
lised with
ively with 65
e chloride
e solvent
esidue re-
l) to give
70
ole I above
d:—

Compound Numbers

Compound Numbers			
		42	
2	18	47	63
	19	52	65
4	28	55	67
5	30	56	70
6	31	57	75
11	32	58	76
12	33	60	77
17	34	62	82

83

85

90

91, 92, 93

94

95

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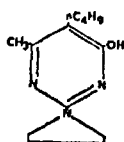
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103

105

EXAMPLE 2

The compound 5 - *n* - Butyl - 4 - hydroxy -
6 - methyl - 2 - pyrrolidinopyrimidine, having
5 the formula:—



was prepared by the following method:

A mixture of 5 - *n* - Butyl - 4 - hydroxy -
6 - methyl - 2 - methyl - thiopyrimidine (10.6
10 g., 0.05 mole), and pyrrolidine (17.75 g.,
0.025 mole) in cellosolve (30 ml.) was re-
fluxed for 16 hours. On cooling the product
separated and was recrystallised from cello-
solve to give colorless needles, m.p. 149°C.,
15 9.8 g. (83%).

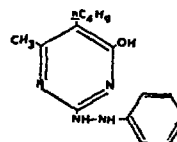
The compounds numbered 16, 20, 21, 25,
29, 44, 45, 46, 53, 54, 84, 96, 97 and 108

in Table I above were also prepared by the
foregoing method using the appropriate re-
actants.

The compounds numbered 13, 14 and 15
were prepared in a similar manner, save
that 48 hours were needed in order to com-
plete the reaction.

EXAMPLE 3

The compound having the formula:



was prepared as follows:

A mixture of 5 - *n* - Butyl - 4 - hydroxy -
6 - methyl - 2 - methyl - thiopyrimidine (5.3
g., 0.025 mole) and phenylhydrazine (20 ml.,
freshly distilled) was heated at 160° for 2
hours. On cooling the product separated, was

20

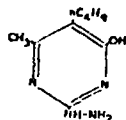
25

30

filtered off, and recrystallised from ethanol to give colourless plates 1.5 g., m.p. 185° dec.

EXAMPLE 4

The compound having the formula:—



was prepared as follows:

A mixture of 5 - *n* - butyl - 4 - hydroxy -

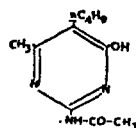
6 - methyl - 2 - methyl - thiopyrimidine (5.3 g., 0.025 mole) hydrazine hydrate (100%, 5 ml.) in absolute ethanol (20 ml) was heated at 100° for 6 hours with exclusion of moisture. On cooling a solid separated which was filtered off, and washed with water. The crude product was purified by dissolving it in dilute hydrochloric acid, filtering, and neutralising the filtrate with sodium hydroxide solution to yield a white crystalline solid, (3 g.), m.p. 201°.

The following compound was also prepared by the method of Example 4.

Compound No.	m.p.	Solvent of Crystallization
10	192—195°	cellosolve

EXAMPLE 5

2 - Acetyl-amino - 5 - *n* - butyl - 4 - hydroxy - 6 - methylpyrimidine having the formula:—

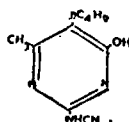


was prepared as follows:

2 - Amino - 5 - *n* - butyl - 4 - hydroxy - 6 - methylpyrimidine (10 g.) in acetic anhydride (40 cc.) was refluxed for 2 hours, concentrated to dryness in vacuo, and the crude product taken up in 5% aqueous sodium hydroxide solution and re-precipitated with acetic acid. The material which separated was filtered off, washed with water, and recrystallised from aqueous ethanol, m.p. 153° (8.6 g., 70%). The following compounds were also prepared by the method of Example 5:—
Compound numbers 66, 69 and 79 and 81.

EXAMPLE 6

5 - *n* - Butyl - 2 - cyanamino - 4 - hydroxy - 6 - methylpyrimidine having the formula:—

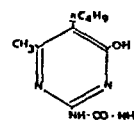


was prepared as follows:

Ethyl-*n*-butyl acetoacetate was condensed with dicyandiamide. The product was recrystallised from ethanol, m.p. 295—298° dec.

EXAMPLE 7

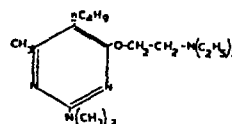
5 - *n* - Butyl - 4 - hydroxy - 6 - methyl - 2 - urcidopyrimidine having the formula:—



was prepared by the hydrolysis of 5 - *n* - Butyl - 2 - cyanamino - 4 - hydroxy - 6 - methylpyrimidine with 10% aqueous hydrochloric acid under reflux for 1 hour, to give the above product, m.p. 207° after recrystallisation from water.

EXAMPLE 8

5 - *n* - Butyl - 4 - (2' - diethylaminoethoxy) - 2 - dimethylamino - 6 - methylpyrimidine having the formula:—



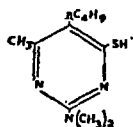
was prepared as follows:

Sodium (0.46 g., 0.02 mole) was dissolved in 2-diethyl-aminoethanol (30 g.). To the solution was added 5 - *n* - butyl - 4 - chloro - 2 - dimethylamino - 6 - methylpyrimidine (0.02 mole), and the reaction mixture stirred at 130—140° for 3 hours. Excess of 2-diethyl-aminoethanol was removed in vacuo, and the residue dissolved in a mixture of methylene chloride and water. The methylene chloride layer was dried (Na₂SO₄), and the solvent removed. Distillation gave the product, b.p. 126°/0.23 mm. $n_D^{25} = 1.5046$.

By a similar method there was also prepared compound numbered 109 having b.p. 126°/0.4 mm. $n_D^{25} = 1.5250$; also compounds Nos. 111, 112 and 113.

EXAMPLE 9

5 - *n* - Butyl - 2 - dimethylamino - 4 - mercapto - 6 - methylpyrimidine having the formula:—



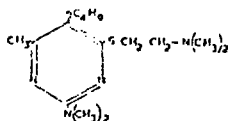
was prepared as follows:

A mixture of 5 - *n* - butyl - 2 - dimethylamino - 4 - hydroxy - 6 - methylpyrimidine (58 g.) and phosphorus pentasulphide (110 g.) in xylene (550 ml.) was refluxed for 6 hours. The mixture was cooled, the xylene decanted and the residue extracted with 5% aqueous sodium hydroxide solution. The alkaline extract was filtered, and the filtrate cooled and acidified to pH 6.0 with glacial acetic acid. The solid obtained was filtered off, and recrystallised from ethanol—water (charcoal) to give the product, 50 g., m.p. 104—105°C.

In a similar manner compound numbered 116 having a m.p. of 140—141° was obtained; also compounds nos. 121, 123 and 124.

EXAMPLE 10

5 - *n* - Butyl - 2 - dimethylamino - 4 - (2 - dimethylaminoethyl)thio - 6 - methylpyrimidine having the formula:—



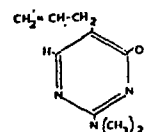
was prepared as follows:

To a mixture of 2 - dimethylaminoethyl chloride hydrochloride (5.76 g., 0.04 mole) and 5 - *n* - butyl - 2 - dimethylamino - 4 - mercapto - 6 - methylpyrimidine (4.5 g., 0.02 mole) in water (50 ml.) was added slowly at room temperature 10N aqueous sodium hydroxide solution (8 ml.). The reaction mixture was stirred overnight and the solution extracted with chloroform. The chloroform extract was washed with water, dried (Mg SO₄), and the solvent removed. Distillation gave the product b.p. 152—153°/0.23 mm., $n_D^{25} = 1.5452$.

In a similar manner were prepared the compounds numbered 115, 118, 119, 122, 125 and 126; Compound No. 118 having b.p. 160°/0.33 mm., $n_D^{25} = 1.5670$.

EXAMPLE 11

The compound 5 - Allyl - 2 - dimethylamino - 4 - hydroxypyrimidine having the formula:—

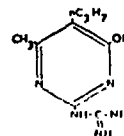


was prepared as follows:—

A solution of 4 - allyloxy - 2 - dimethylaminopyrimidine (1 g.) in dry ethanol (75 ml.) was placed in a quartz flask and irradiated with an Ultraviolet lamp for 16 hrs. The solvent was then removed in vacuo and the residue taken up in petroleum ether and chromatographed using a column (1 cm. x 20 cm.) of silica gel. The product (200 mg) was eluted from the column by means of chloroform. Recrystallisation from a small quantity of ethanol gave needles, m.p. 94°C. Compound No. 37 was prepared by an analogous method.

EXAMPLE 12

The compound 2 - guadino - 4 - hydroxy - 6 - methyl - 5 - *n* - propyl pyrimidine, having the formula:—

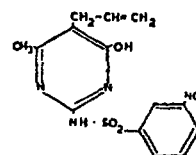


was prepared as follows:—

Sodium hydroxide solution (11N, 40ml., 0.44 mole) was added in portions to a stirred and cooled suspension of biguanide sulphate (43.4 g.) in ethanol (50 ml.), keeping the temperature below 10°C. The mixture was stirred for 5 minutes, ethyl *n*-propylacetoacetate (37.8 g., 0.22 mole) was added in portions below 10°C. and the mixture was stirred at room temperature for 18 hours. The resulting suspension was filtered and the residue washed with ethanol. The residue was shaken with 200 ml. water, filtered, washed with cold water (4 ml. x 50 ml.) and dried at 100°C. Yield, 45 g., m.p. 291—293°C.

EXAMPLE 13

The compound 5 - allyl - 2 - amino - 4 - hydroxy - 6 - methyl - 2 - (m - nitrobenzenesulphonamido)pyrimidine, having the formula:—



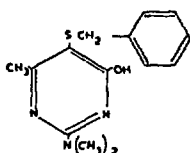
was prepared as follows:—

5 - Allyl - 2 - amino - 4 - hydroxy - 6 - methyl - pyrimidine (4.96 g., 0.03 mole) was suspended in dry dimethylformamide (40 ml.). To the suspension was added m-nitrobenzene

sulphonylchloride (6.66 g., 0.03 mole) and the mixture was stirred at room temperature. A solution of triethylamine (3.09 g., 0.03 mole) in dimethylformamide (5 ml.) was added dropwise; the reaction mixture was stirred for 2 hours and poured onto water (250 ml.). The mixture was allowed to stand at 0°C overnight, and the product filtered off, dried, and recrystallised from methanol. Yield, 4.2 g., m.p. 233—234°C.

EXAMPLE 14

The hydroxypyrimidine having the formula:—



was prepared as follows:—

To a solution of sodium (0.4 mole, 0.92 g.) in ethanol (15 ml.) in an atmosphere of nitrogen was added benzyl mercaptan (0.04 mole, 5 g.) and the whole mixture was stirred for 5 minutes at room temperature. Then ethane-1,2 diol (90 ml.) and 5-bromo-2-dimethylamino - 4 - hydroxy - 6 - methylpyrimidine (0.044 mole, 10.1 g.) were added and the whole stirred for 5 hours at 140°C. Thereafter the reaction mixture was cooled and poured into water (500 ml.), brought to pH 6.0—7.0 with acetic acid to give the product, m.p. 175—176°, after recrystallisation from ethanol.

Compounds numbered 68 and 71 were similarly prepared using the appropriate reactants.

In the following EXAMPLES the words: "LUBROL", "AROMASOL", "DISPERSOL", LISSAPOL, CELLOFAS" are Trade Marks.

EXAMPLE 15

An emulsion concentrate was made up by mixing together the ingredients set out below in the proportions stated and stirring the mixture until all the constituents were dissolved.

Compound No. 4	10%
Ethylene Dichloride	40%
Calciumdodecylbenzenesulphonate	5%
"Lubrol" L	10%
"Aromasol" H	35%

EXAMPLE 16

A composition in the form of grains readily dispersible in a liquid, e.g. water, was prepared by grinding together the first three of the ingredients listed below in the presence of added water and then mixing in the sodium acetate. The resultant mixture was dried and passed through a British Standard mesh sieve,

size 44—100, to obtain the desired size of grains.

Compound No. 4	50%	
"Dispersol" T	25%	60
"Lubrol" APN5	1.5%	
Sodium acetate	23.5%	

EXAMPLE 17

The ingredients listed below were all ground together in the proportions stated to produce a powder formulation readily dispersible in liquids.

Compound No. 4	45%	
"Dispersol" T	5%	70
"Lissapool" NX	0.5%	
"Cellofas" B600	2%	
Sodium acetate	47.5%	

EXAMPLE 18

The active ingredient (Compound No. 4 of Table I) was dissolved in a solvent and the resultant liquid was sprayed onto the granules of Fuller's earth. The solvent was then allowed to evaporate to produce a granular composition.

Compound No. 4	5%	80
Fuller's earth of China clay granules	95%	

EXAMPLE 19

A composition suitable for use as a seed dressing was prepared by mixing all three of the substituents set out below in the proportions stated.

Compound No. 4	50%	
Mineral oil	2%	90
China clay	48%	

EXAMPLE 20

A dusting powder was prepared by mixing, in the proportions stated, the active ingredient with talc.

Compound No. 4	5%	95
Talc	95%	

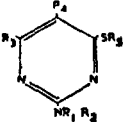
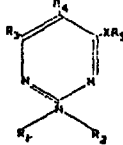
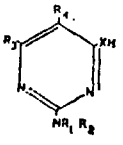
EXAMPLE 21

A Col formulation was prepared by ball-milling the constituents set out below and then forming an aqueous suspension of the ground mixture with water.

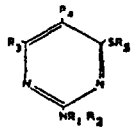
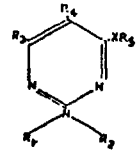
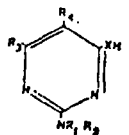
Compound No. 4	40%	
"Dispersol"	10%	105
"Lubrol"	1%	
Water	49%	

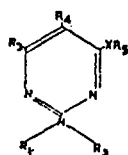
EXAMPLE 22

Formulations similar to those set out in Examples 16—22 above but containing as active ingredient a compound numbered 2, 3, 110

30	31	1,182,584	31
size of -	9, 12, 28, 30, 37, 62, 70, 75, 91, 116, 117 or 126, respectively, from Tables I, II and III above, were prepared by methods similar to those described in each particular Example.		stituted alkyl, carbamoyl, or R ₁ and R ₂ together with the adjacent N-atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms; R ₃ and R ₄ are hydrogen, halogen, alkyl, alkaryl, alkenyl, alkylthioalkyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, arylazo, or heterocyclic alkyl which may contain an N-atom, unsubstituted or substituted aryl or aryloxy, or arylthio, azophenyl alkylamino, or alkylsulphonyl; and X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid containing a surface active agent.
50% 25% 1.5% 23.5%	60	5 WHAT WE CLAIM IS:— (1) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:—	55 60 65
were all stated to dily dis-	65		
45% 5% 0.5% 2% 17.5%	70	10 or other thereof, wherein R ₁ and R ₂ are: hydrogen, a substituted or unsubstituted hydrocarbon, a heterocyclic ring, a benzylidene-imino group, 15 an amino or sulphur-free substituted amino group, a cyano group, a substituted or unsubstituted carbamoyl group, 20 an R.CO— or R.SO ₂ — group where R is a substituted or unsubstituted hydrocarbon group, or R ₁ and R ₂ , together with the adjacent N-atom, form a substituted or unsubstituted heterocyclic ring which may contain one or more additional heterocyclic atoms; 25 and wherein R ₃ and R ₄ are: hydrogen, halogen, 30 a substituted or unsubstituted hydrocarbon group bonded directly to a carbon atom of the pyrimidine ring or through an O— or S— atom thereto, a heterocyclic-substituted alkyl radical, 35 a nitro group, an azophenyl group, an alkylsulphonyl group, or R ₃ and R ₄ together form a substituted or unsubstituted alkylene or alkenylene bridging group; and wherein X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.	
No. 4 ent and into the ent was a granu-	75		
5% 95%	80	wherein: R ₁ stands for hydrogen, alkyl or phenyl-alkyl R ₂ is hydrogen, alkyl, alkenyl, halo-, alkyl-, or alkoxy-carbonyl-substituted phenyl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, haloalkylcarbonyl, a nitrogen-containing monocyclic heterocyclic radical, phenylalkyl, an alkyl group substituted by a 6-membered heterocyclic nitrogen-containing radical, cycloalkyl, carbamoyl, or a nitro-substituted phenylsulphonyl group; or R ₁ and R ₂ together with the adjacent nitrogen atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms, or form a guanidino, N-halophenyl-guanidino or benzylidene-hydrazino group. R ₃ is hydrogen, halogen, alkyl, alkylthio-alkyl, or unsubstituted or halo- or alkoxy-substituted phenyl; R ₄ is hydrogen, halogen, alkyl, phenylalkyl, alkenyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, phenylazo, monocyclic heterocyclic substituted alkyl, phenyl, phenyloxy or halo- or alkyl-substituted phenylthio, alkylsulphonyl, phenylalkylthio-, alkyl-, or halo-substituted phenylalkyl, or a —CHO group; or R ₃ and R ₄ together form an alkylene or alkenylene bridging group; X is an atom of oxygen or sulphur R ₅ is hydrogen, hydroxyalkyl, phenylalkyl, alkenyl, alkoxy-carbonylalkyl, alkylcarbonyl-alkyl, dialkylaminoalkyl, alkylthioalkyl or alkoxyalkyl and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.	75 80 85 90 95 100 105
a seed three of propor-	85	(2) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:—	
50% 2% 48%	90		
mixing, ingredient	95	or other thereof, wherein R ₁ is hydrogen, alkyl, or substituted or unsubstituted aralkyl; R ₂ is hydrogen, alkyl, alkenyl, unsubstituted aryl or halo-, alkyl-, or alkoxy-carbonyl-substituted aryl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, halo-alkylcarbonyl, heterocyclic, heterocyclic-sub-	105 110
by ball- ow and of the	100		
40% 10% 1% 49%	105		
out in ing as d 2, 3,	110		



size of	30	31	1,182,584	31
50%		9, 12, 28, 30, 37, 62, 70, 75, 91, 116, 117 or 126, respectively, from Tables I, II and III above, were prepared by methods similar to those described in each particular Example.	stituted alkyl, carbamoyl, or R ₁ and R ₂ together with the adjacent N-atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms; R ₃ and R ₄ are hydrogen, halogen, alkyl, alkaryl, alkenyl, alkylthioalkyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, arylazo, or heterocyclic alkyl which may contain an N-atom, unsubstituted or substituted aryl or aryloxy, or arylthio, azo-phenyl alkylamino, or alkylsulphonyl; and X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid containing a surface active agent.	55
25%	60	5 WHAT WE CLAIM IS:— (1) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:— 	(3) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the general formula:— 	60
5%		10 or ether thereof, wherein R ₁ and R ₂ are: hydrogen, a substituted or unsubstituted hydrocarbon. a heterocyclic ring, a benzylidene-imino group,	wherein: R ₁ stands for hydrogen, alkyl or phenyl-alkyl R ₂ is hydrogen, alkyl, alkenyl, halo-, alkyl-, or alkoxy-carbonyl-substituted phenyl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, haloalkylcarbonyl, a nitrogen-containing monocyclic heterocyclic radical, phenylalkyl, an alkyl group substituted by a 6-membered heterocyclic nitrogen-containing radical, cycloalkyl, carbamoyl, or a nitro-substituted phenylsulphonyl group; or R ₁ and R ₂ together with the adjacent nitrogen atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms, or form a guanidino, N-halophenyl-guanidino or benzylidene-hydrazino group. R ₃ is hydrogen, halogen, alkyl, alkylthio-alkyl, or unsubstituted or halo- or alkoxy-substituted phenyl; R ₄ is hydrogen, halogen, alkyl, phenylalkyl, alkenyl, alkoxyalkyl, hydroxyhaloalkyl, nitro, phenylazo, monocyclic heterocyclic substituted alkyl, phenyl, phenyloxy or halo- or alkyl-substituted phenylthio, alkylsulphonyl, phenylalkylthio-, alkyl-, or halo-substituted phenylalkyl, or a —CHO group; or R ₃ and R ₄ together form an alkylene or alkenylene bridging group; X is an atom of oxygen or sulphur R ₅ is hydrogen, hydroxyalkyl, phenylalkyl, alkenyl, alkoxy-carbonylalkyl, alkylcarbonyl-alkyl, dialkylaminoalkyl, alkylthioalkyl or alkoxyalkyl and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.	65
re all uted to y dis-	65	15 an amino or sulphur-free substituted amino group, a cyano group, a substituted or unsubstituted carbamoyl group,		
5%		20 an R.CO— or R.SO ₂ — group where R is a substituted or unsubstituted hydrocarbon group,		
5%		or R ₁ and R ₂ , together with the adjacent N-atom, form a substituted or unsubstituted heterocyclic ring which may contain one or more additional heterocyclic atoms; and wherein R ₃ and R ₄ are: hydrogen, halogen,		
5%	70	30 a substituted or unsubstituted hydrocarbon group bonded directly to a carbon atom of the pyrimidine ring or through an O— or S— atom thereto, a heterocyclic-substituted alkyl radical, a nitro group,		
2%		35 an azophenyl group, an alkylsulphonyl group,		
5%		or R ₃ and R ₄ together form a substituted or unsubstituted alkylene or alkenylene bridging group; and wherein X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.		
No. 4 it and o the it was granu-	75	40 (2) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:— 		
5%	80	or ether thereof, wherein R ₁ is hydrogen, alkyl, or substituted or unsubstituted aralkyl; R ₂ is hydrogen, alkyl, alkenyl, unsubstituted aryl or halo-, alkyl-, or alkoxy-carbonyl-substituted aryl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, halo-alkylcarbonyl, heterocyclic, heterocyclic-sub-		
5%		50		
seed ree of popor-	85			
0%				
2%				
8%	90			
ixing, edient				
5%	95			
5%				
ball- and f the	100			
0%				
0%				
1%	105			
0%				
ut in ig as 2, 3,	110			



wherein

R_1 is hydrogen, alkyl or phenylalkyl;

R_2 is hydrogen, alkyl, unsubstituted or halo-, alkyl-, or alkoxy-carbonyl-substituted phenyl, unsubstituted or sulphur-free substituted amino, cyano, alkylcarbonyl, phenylalkyl, heterocyclic-substituted alkyl or carbamoyl; or

R_1 and R_2 together with the adjacent nitrogen form a heterocyclic ring which may contain one or more additional heterocyclic atoms;

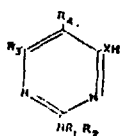
R_3 is hydrogen, alkyl, phenyl or alkylthioalkyl

R_4 is hydrogen, halogen, alkyl, phenylalkyl, alkenyl, alkoxyalkyl, hydroxyhaloalkyl, an alkyl group substituted by a nitrogen-containing monocyclic heterocyclic radical, alkylsulphonyl;

X is oxygen or sulphur;

R_5 is hydrogen, hydroxyalkyl, dialkylaminoalkyl, alkylcarbonylalkyl, or alkylthioalkyl; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.

(5) A fungicidal composition comprising as an active ingredient a pyrimidine derivative of the formula:—



30

or an ether thereof, wherein R_1 and R_2 are hydrogen or lower alkyl groups, or R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring; R_3 is a lower alkyl group; R_4 is a lower alkyl or alkenyl group; and X is an atom of oxygen or sulphur; and a carrier for the active ingredient comprising a solid diluent, or a liquid diluent containing a surface active agent.

(6) A fungicidal composition according to Claim 3 wherein the active ingredient is a compound in which R_1 , R_2 and R_3 are methyl or ethyl groups; R_4 is an alkyl or alkenyl group containing from two to five carbon atoms; and X is an atom of oxygen or sulphur.

(7) A fungicidal composition wherein the active ingredient is a pyrimidine derivative as defined to any of Claims 1 to 4 and in which the group —XII is etherified having an ether group comprising an alkyl, hydroxyalkyl, aralkyl, alkenyl, alkoxy-carbonylalkyl,

alkylcarbonylalkyl, alkylaminoalkyl, or alkylthioalkyl residue.

(8) A fungicidal composition containing as an active ingredient 2 - dimethylamino - 4 - methyl - 5 - n - butyl - 6 - hydroxypyrimidine.

(9) A fungicidal composition containing an active ingredient 2 - ethylamino - 4 - methyl - 5 - n - butyl - 6 - hydroxypyrimidine.

(10) A fungicidal composition containing as an active ingredient at least one of the compounds numbered 2, 3, 9, 12, 28, 30, 37, 62, 70, 75, 91, 116, 117 and 126, in Tables I to III as hereinbefore set forth.

(11) A fungicidal composition according to any of Claims 1—9 in which the solid diluent is an inert substance in powder or granular form.

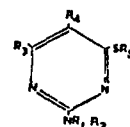
(12) A fungicidal composition according to any of the preceding Claims containing from 0.001% to 85% by weight of the active ingredient.

(13) A fungicidal composition according to any of Claims 1—11 containing from 10 to 85% by weight of the active ingredient.

(14) A fungicidal composition according to any of Claims 1—11 containing from 0.001 to 1.0% by weight of the active ingredient.

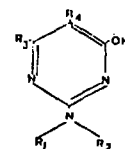
(15) Compounds marked in Tables I and II with an asterisk.

(16) A pyrimidine derivative of the general formula:—



where R_1 , R_2 , R_3 and R_4 have the meanings assigned to them in Claim 1 and R_5 is hydrogen or an alkyl, hydroxyalkyl, arylalkyl, alkenyl, alkoxy-carbonylalkyl, alkylcarbonylalkyl or alkylthioalkyl radical provided that it is not a methyl or benzyl radical.

(17) A process for the preparation of a compound claimed in Claim 15 and corresponding to the general formula:



wherein R_1 stands for hydrogen, alkyl or phenylalkyl; R_2 is hydrogen, alkyl, alkenyl, halo, alkyl- or alkoxy-carbonyl-substituted phenyl, cyano, a nitrogen-containing monocyclic heterocyclic radical, phenylalkyl, an alkyl group substituted by a 6-membered heterocyclic nitrogen-containing radical, cycloalkyl or a nitro-substituted phenylsulphonyl group; or R_1 and R_2 together with the adjacent nitrogen atom form a heterocyclic ring which may contain one or more additional heterocyclic atoms, or form a guanidino or N -halophenyl-guanidino group; R_3 is hydrogen,

- l, or alkyl-
 containing-as 55
 amino - 4 -
 pyrimidine.
 containing an
 4 - methyl -
 dine. 60
 containing as
 of the com-
 30, 37, 62,
 Tables I to 65
 according to
 solid diluent
 or granular
 according to 70
 aining from
 active in-
 according to
 from 10 to 75
 dent.
 according to
 from 0.001
 gredient. 80
 ibles I and
 the general
- halogen, alkyl, alkylthioalkyl or unsubstituted
 or halo- or alkoxy-substituted phenyl; R₄ is
 hydrogen, halogen, alkyl, phenylalkyl, alkenyl,
 alkoxyalkyl, phenylazo, phenyl, or alkyl- or
 5 halo-substituted phenylalkyl, or R₃ and R₄ to-
 gether form an alkylene or alkenylene bridg-
 ing-group; which comprises condensing the
 appropriate guanidine with a suitably sub-
 10 stituted beta-keto ester, if necessary in the
 presence of a base.
 (18) A process for preparing compounds
 claimed in Claim 15 which are acyl deriva-
 tives comprising acylating the appropriate 2-
 amino pyrimidine.
 15 (19) A process according to Claim 17 and
 comprising the further step of:—
 (a) hydrolysing the appropriate
 pyrimidine derivative containing a cyan-
 amino group in position 2 thus preparing
 the corresponding 2-urcideo- derivative; or
 20 (b) reacting the appropriate 6-hydroxy-
 pyrimidine with phosphorous pentasulphide
 to produce the corresponding 6-mercapto
 derivative; or
 25 (c) reacting the appropriate 6-mercapto
 pyrimidine with the appropriate organic
 halide to obtain the corresponding thio-
 ether.
 (20) A process for the preparation of
 30 pyrimidine derivatives as defined in claims 15
 and 16 which comprises:—
 (a) reacting the corresponding 2-alkyl-
 thiopyrimidine with the appropriate amine;
 or
 35 (b) reacting the appropriate 6-halo-
 pyrimidine with a hydroxy compound to
 produce the corresponding 6-etherified
 pyrimidine derivative; or
 (c) reacting the appropriate 5-halo-
 pyrimidine derivative with a mercaptan to
 40 form the corresponding 5-mercapto ether.
 (21) A process for the preparation of
 pyrimidine derivatives bearing an asterisk in
 Tables I to III substantially as described in
 any of Examples 1 to 14. 45
 (22) A pyrimidine derivative which has
 been obtained by the process of any of Claims
 17 to 20.
 (23) A fungicidal composition containing as
 active ingredient the product of any of 50
 Examples 1 to 14.
 (24) A fungicidal composition substantially
 as described, particularly with reference to
 Examples 15 to 23.
 (25) A method for the combating of un- 55
 desired fungal infestations in growing plants
 which comprises applying to the locus of the
 plant a fungicidal composition as claimed in
 any of Claims 1 to 14, 23 and 24.
 (26) A method of combating plant 60
 pathogens, in which a plant susceptible to such
 pathogens, or seed thereof, is treated with a
 pyrimidine derivative as defined in any of
 Claims 1 to 7.
 (27) A method of treating agricultural soil 65
 to combat pathogens on plants comprising
 applying to the soil a pyrimidine derivative
 as defined in any of Claims 1 to 7.
 (28) A fertiliser comprising a pyrimidine
 derivative as defined in any of Claims 1 to 7. 70
 W. SCOTT,
 Agent for the Applicants.

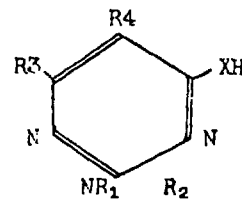
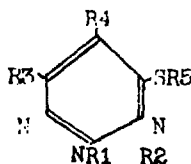
Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
 Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which
 copies may be obtained.

ERRATUM

SPECIFICATION NO. 1,182,584

Page 31, line 9 for

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THE PATENT OFFICE
 26 March 1970

R 122944/28

