

1129,575



PATENT SPECIFICATION

NO DRAWINGS

1,129,575

Date of Application and filing Complete Specification: 16 May, 1967.

No. 22769/67.

Application made in United States of America (No. 552,693) on 25 May, 1966.

Complete Specification Published: 9 Oct., 1968.

© Crown Copyright 1968.

Index at acceptance:—C2 C(1M1A, 1M1C3, 2C4, 2C7A2, 2C7C, 2D44, 5A4, 5B, 5E1); A5 E(1C4B2, 1C4B3, 1C4B4)

Int. Cl.:—C 07 d 85/44, C 07 d 91/44

COMPLETE SPECIFICATION

Heterocyclic Thiocyanates

We, BUCKMAN LABORATORIES, INC., a corporation organised and existing under the laws of the State of Tennessee, United States of America, having its principal place of business at 1256 North McLean Boulevard, Memphis, Tennessee 38108, United States of America, 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 novel organic thiocyanates, their preparation, and their use in controlling fungal growth. More particularly, the products of this invention are useful in combating fungi in industrial and agricultural processes and products.

Many industrial products, both during the process of manufacture and as the finished product, are normally susceptible to fungal degradation if means are not taken to inhibit such degradation. Wood pulp, starch and proteinaceous substances, animal hides, vegetable tanning liquors, and leather are all damaged or degraded by the growth of fungi and other microorganisms or by enzymes produced by such growth. Wet pulp containing more than about 30 percent moisture content is subjected to attack by stain, mould and decay fungi. If not controlled, the result is a loss of useful fiber in badly decayed pulp, difficulty in dispersing partially decayed pulp, a darkening in color, and the development of undesirable odors caused by the growth of the microorganisms. Different species of moulds are encountered at various stages in the manufacture of leather. As an example, soaking provides an environment highly conducive to the growth of microorganisms, and even strong pickle solutions are subject to attack by some microorganisms. Moulds in particular may be troublesome and cause discoloration of the pickled stock, especially if it is held for a period of time. During the chrome tanning process, the chrome tanned

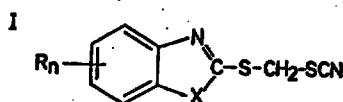
[Price 4s. 6d.]

stock held "in the blue" readily moulds and is discolored. Mould growth may develop on heavy vegetable tan leather during the drying period and produce spots and stains on either the flesh or grain sides.

Certain organic thiocyanates have been used rather extensively as insecticides (Donald E. H. Frear, Chemistry of the Pesticides, 3rd ed., D. Van Nostrand Company, Inc., New York, 1955), but many of these compounds which have proven to be very useful as insecticides do not possess appreciable fungicidal properties.

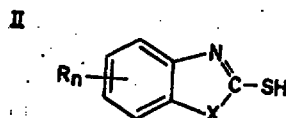
It is an object of the present invention to provide novel organic thiocyanates which have valuable fungicidal properties.

According to one feature of the present invention, there are provided compounds of the general formula



wherein X represents —O—, —NH—, or —S—; R represents a hydrogen or halogen atom, or an alkyl, nitro, amino- or hydroxyl group; and n is 1 or 2.

According to a further feature of the present invention, there is provided a process for the preparation of compounds according to the invention as hereinbefore defined, which comprises reacting a metal salt of a compound of formula:



(wherein X, R and n are as defined above) with chloromethylthiocyanate in an alcoholic solution.

SEE ERRATA SLIP ATTACHED

According to a still further feature of the present invention, there is provided a method of inhibiting the growth and proliferation of fungi in aqueous medium which comprises adding to the said medium a compound according to the invention as hereinbefore defined in an amount sufficient to inhibit the growth and proliferation of the said fungi.

According to a yet further feature of the present invention there is provided a fungicidal composition which comprises at least one compound according to the invention as hereinbefore defined as active ingredient together with a liquid or solid carrier.

The organic thiocyanates of the present invention are prepared by reacting a metal salt, preferably an alkali-metal salt, and more preferably the sodium salt of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, or substituted compounds thereof wherein one or two of the hydrogens attached to the aromatic ring are replaced by halogen, nitro, alkyl, amino, or hydroxyl radicals with chloromethylthiocyanate in an alcoholic solution. Since the reaction between the 2-mercapto compound and the chloromethylthiocyanate is equimolecular, we generally prefer to employ these two reactants in approximately equal molecular proportions. The reaction may be effected at relatively low temperatures.

The compounds of our invention are liquids or solids which are soluble in common organic solvents such as alkyl and aromatic hydrocarbons, alcohols, ketones, esters, ether alcohols, dimethylformamide, dimethylsulphoxide, and other solvents. The addition of a surfactant to the liquid or to the solution renders the compounds of our invention readily dispersible in water. In general, nonionic dispersants are preferred. Examples of such preferred nonionic dispersants include alkylphenoxypolyoxyethylene ethanol or alkylpolyoxyethylene ethanol.

In order to disclose the nature of the invention still more clearly, the following illustrative examples will be given. It is understood, however, that the invention is not to be limited to the specific conditions or details set forth in these examples, except insofar as such limitations are specified in the appended claims.

EXAMPLE 1

Preparation of 2-Thiocyanomethylthiobenzothiazole

The sodium 2-mercaptobenzothiazole used in this example was prepared by reacting 258.5 grams (1.54 moles) of a commercial grade 2-mercaptobenzothiazole with 102.8 grams (1.51 moles) of sodium ethoxide in about 400 milliliters of absolute denatured alcohol (ethanol denatured with isopropanol and methanol). This solution was cooled by means of an ice bath so as to maintain the temperature below 40°C. and treated with

162.4 grams (1.51 moles) of chloromethylthiocyanate. The reaction mixture was maintained at a temperature of 35 to 40°C. overnight and then allowed to stand for a period of 15 days at room temperature. At the end of this period, the reaction mixture was filtered to remove the precipitated sodium chloride. The filter cake was washed first with denatured alcohol and then with methylene chloride. After combining the filtrate and the denatured alcohol wash liquor, an oil layer separated from the mixture. The oil layer so obtained was dissolved in methylene chloride and then the resulting solution was combined with the methylene chloride wash liquor, washed with water, and dried with anhydrous magnesium sulfate. The methylene chloride was removed by evaporation to yield 118.0 grams of 2-thiocyanomethylthiobenzothiazole as an oily liquid. An additional 242.1 grams of 2-thiocyanomethylthiobenzothiazole was recovered from the alcohol phase by extraction with methylene chloride. Experimentally the alcohol phase was diluted with water and extracted three times with methylene chloride; the methylene chloride extracts were combined and dried over anhydrous magnesium sulfate. After evaporating the methylene chloride, the 2-thiocyanomethylthiobenzothiazole remained as a residue, a product which could not be distilled without decomposition even at reduced pressure or recrystallized. The infrared spectrum contained a strong band at 4.62 microns, which is indicative of an organic thiocyanate. Anal. Calcd. for $C_7H_4N_2S_3$: N, 11.8; S, 40.3. Found: N, 11.0; S, 39.5.

EXAMPLE 2

Preparation of 2-Thiocyanomethylthiobenzoxazole

A 250-ml. three-neck, round-bottom flask equipped with stirrer, additional funnel, and thermometer was charged with 150 milliliters of absolute ethanol and 2.3 grams (0.1 mole) of sodium. After the sodium had dissolved, 15.1 grams (0.1 mole) of 2-mercaptobenzoxazole was added and the mixture stirred until a complete solution was obtained. The stirred reaction mixture was cooled and 10.75 grams (0.1 mole) of chloromethylthiocyanate was added dropwise. After the addition was complete, the reaction mixture was stirred at room temperature overnight, then poured into 1.5 liters of water and extracted with four 150-ml. portions of ethyl acetate. The ethyl acetate extracts were combined and washed successively with one 500-ml. portion of water, one 500-ml. portion of two percent sodium hydroxide and one 500-ml. portion of water. The ethyl acetate extract was dried over magnesium sulfate and the ethyl acetate removed under reduced pressure. The residue, a dark oil (14.1 grams), n_D^{25} 1.6372 represented a 63.5 percent yield of a crude product. A por-

tion of t. reduced pr benzoxazo 0.2 mm., contained is indicati Calcd. fo S, 29.30.

Preparat:

A 500-equipped denser, ar 300 millil grams (0. the sodium mole) of 2 and allowe (0.2 mole added drop as the stirr pitate form action mix ture overni water and The dried imidazole, was recryst sample of azole, m.p $C_7H_4N_2S_2$:

Preparation

The 5 - benzothiazol ner as exam mercaptober imidazole. thiocyanome of 91—2.5° Cl, 13.00; 35.40.

Preparation

The 5,6 - thiobenzothi manner as e

tion of this material was distilled under reduced pressure to give 2-thiocyanomethylthiobenzoxazole as a clear liquid, b.p. 154—6° C./0.2 mm., n_D^{25} 1.6427. The infrared spectrum contained a strong band at 4.62 microns, which is indicative of an organic thiocyanate. Anal. Calcd. for $C_7H_4N_2OS_2$: S, 28.82. Found: S, 29.30.

EXAMPLE 3

10 Preparation of 2-Thiocyanomethylthiobenzimidazole

A 500-ml. four-neck, round-bottom flask equipped with stirrer, addition funnel, condenser, and thermometer was charged with 15 300 milliliters of absolute ethanol and 4.6 grams (0.2 mole) of metallic sodium. After the sodium had dissolved, 30.0 grams (0.2 mole) of 2-mercaptobenzimidazole was added and allowed to dissolve and then 21.5 grams (0.2 mole) of chloromethylthiocyanate was added dropwise over a period of five minutes as the stirred solution was cooled. A tan precipitate formed almost immediately and the reaction mixture was stirred at room temperature overnight, then poured into two liters of water and the solid removed by filtration. The dried crude 2-thiocyanomethylthiobenzimidazole, 35.1 grams (79.4 percent yield) was recrystallized from toluene to give a pure sample of 2-thiocyanomethylthiobenzimidazole, m.p. 144—5.5° C. Anal. Calcd. for $C_7H_4N_2S_2$: S, 28.97. Found: S, 28.94.

EXAMPLE 4

35 Preparation of 5 - Chloro - 2 - thiocyanomethylthiobenzothiazole

The 5 - chloro - 2 - thiocyanomethylthiobenzothiazole was prepared in the same manner as example 3, by substituting 5-chloro-2-mercaptobenzothiazole for 2-mercaptobenzimidazole. The recrystallized 5 - chloro - 2 - thiocyanomethylthiobenzothiazole had a m.p. of 91—2.5° C. Anal. Calcd. for $C_7H_3ClN_2S_2$: Cl, 13.00; S, 35.26. Found: Cl, 13.21; S, 35.40.

EXAMPLE 5

45 Preparation of 5,6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole

The 5,6 - dichloro - 2 - thiocyanomethylthiobenzothiazole was prepared in the same manner as example 3, substituting 5,6 - di-

chloro - 2 - mercaptobenzothiazole for 2-mercaptobenzimidazole. The recrystallized 5,6 - dichloro - 2 - thiocyanomethylthiobenzothiazole had a m.p. of 108—10° C. Anal. Calcd. for $C_6H_2Cl_2N_2S_2$: S, 31.31. Found: S, 31.19.

EXAMPLE 6

Preparation of 4,6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole

The 4,6 - dichloro - 2 - thiocyanomethylthiobenzothiazole was prepared in the same manner as example 3, substituting 4,6 - dichloro - 2 - mercaptobenzothiazole for 2-mercaptobenzimidazole. The recrystallized 4,6 - dichloro - 2 - thiocyanomethylthiobenzothiazole had a m.p. of 113—4° C. Anal. Calcd. for $C_6H_2Cl_2N_2S_2$: S, 31.31. Found: 31.30.

Other S-thiocyanomethyl compounds of 2-mercaptobenzothiazoles, 2 - mercaptobenzoxazoles, and 2-mercaptobenzimidazoles may be prepared similarly as will be apparent to those skilled in the art. For example, alkyl, nitro, amino, or hydroxy substituted S-thiocyanomethyl compounds may be prepared by the procedure of example 1 by merely substituting the appropriate substituted 2-mercaptobenzothiazole, substituted 2-mercaptobenzoxazole, or substituted 2-mercaptobenzimidazole for the 2-mercaptobenzothiazole of example 1.

EXAMPLE 7

The effect of several organic thiocyanates on three fungi, *Aspergillus niger*, *Penicillium roqueforti*, and *Chaetomium globosum*, was determined in this example. The pulp-substrate method described in U.S. Patent 3,193,448, was utilized for these tests.

The customary periods of observation were after 7 and 14 days. Growth was recorded after each period on the basis of the following key:

4=excellent

3=good

2=poor

1=very poor, scant, questionable

0=no growth.

The results are summarized in table 1.

TABLE 1

Inhibition of *Aspergillus niger*, *Penicillium roqueforti*, and *Chaetomium globosum* by the compounds listed below in a pulp substrate method after 14 days incubation.

Test organism	Concentration	Compounds tested				
	Parts per million	5-Chloro-2-thiocyanomethylthio- benzothiazole	6-Nitro-2-thiocyanomethylthio- benzothiazole	2-Thiocyanomethylthio- benzimidazole	2-Thiocyanomethylthio- benzoxazole	2-Thiocyanomethylthio- benzothiazole
<i>Aspergillus niger</i>	0.5	—	—	—	—	4
	1	4	4	4	1	1
	3	4	3	4	0	0
	5	0	0	4	0	0
	7	0	0	4	0	0
	10	0	0	4	0	0
	15	0	0	4	0	0
	20	0	0	4	0	0
	25	0	0	4	0	0
	50	0	0	0	0	—
<i>Penicillium roqueforti</i>	0.5	—	—	—	—	3
	1	0*	2*	4	0	0
	3	0*	0*	4	0	0
	5	0*	0*	4	0	0
	7	0*	0*	4	0	0
	10	0*	0*	4	0	0
	15	0*	0*	4	0	0
	20	0*	0*	0	0	0
	25	0*	0*	0	0	0
	50	0*	0*	0	0	—
<i>Chaetomium globosum</i>	0.5	—	—	—	—	4
	1	4	4	4	0	0
	3	4	4	4	0	0
	5	2	3	0	0	0
	7	0	0	0	0	0
	10	0	0	0	0	0
	15	0	0	0	0	0
	20	0	0	0	0	0
	25	0	0	0	0	0
	50	0	0	0	0	—

*7 days incubation.

This es
preservati
tions prev
groundwo
mills.

The lay
ducted up
specimens
2.5±0.1
and meas
Each test
ized glas
sequence
for variou
cyanates c

1. A s
intr
over
buti
tion

Amu
Dip
Pot
Mag
Poly
of
Der

After
wet
was
hour
parti

2-Thiocyanomethylthio-
benzothiazole

4
1
0
0
0
0
0
0
0

3
0
0
0
0
0
0
0
0

- 4
0
0
0
0
0
0
0
0

•

The results are summarized in table 2 wherein the numerical values 0 to 4 have the same meaning as in example 7.

TABLE 2

Inhibition of *Aspergillus niger*, *Pullularia pullulans*, and *Chaetomium globosum* by the compounds listed below in a lap pulp method after 28 days incubation

Test Organism	Concentration Parts per million	Compounds tested	
		2-Thiocyanomethylthiobenzothiazole	2-Thiocyanomethylthiobenzoxazole
<i>Aspergillus niger</i>	10	4	4
	25	4	4
	50	3	0
	75	0	0
	100	0	0
	200	0	0
	400	0	0
<i>Pullularia pullulans</i>	10	4	4
	25	3	0
	50	0	0
	75	0	0
	100	0	0
	200	0	0
	400	0	0
<i>Chaetomium globosum</i>	10	4	4
	25	4	1
	50	0	0
	75	0	0
	100	0	0
	200	0	0
	400	0	0

The com
used dilute
liquid or so
a finely div
phyllite, di
calcium sili
desired, wet
be used. W
increased, t
which may
from a spr

Dusts ma
of one or n
while wetta
50 percent
compounds.

A typical
der compris
organic thio
75 percent
solids, 1 pe
agent, and
persing ager
sodium dode
sulfonate, so
phenoxypoly
agents, such
oxide conde
mercaptans,
Typical disp
sulfonate of
hyde and lig

Liquid cor
are prepared
cyanate com
gether with
For example
of one of the
5 parts of
alkylphenoxy
of one or
sulfoxide or
of these wit
vents.

The comp
used in cor
agents and a
or insecticide

When add
ing organic r
proliferation
compounds
for example
million parts
erial. It will
larger quant
may be used
such larger
operation wit

When used
cyanates of
plant, and so
seedlings em
against attack

The compounds of this invention may be used diluted with a carrier which may be liquid or solid. Dusts may be prepared with a finely divided solid such as talc, clay, pyrophyllite, diatomaceous earth, hydrated silica, calcium silicate, or magnesium carbonate. If desired, wetting and/or dispersing agents may be used. When the proportions of these are increased, there results a wettable powder, which may be taken up in water and applied from a spray.

Dusts may contain 1 percent to 15 percent of one or more compounds of this invention, while wettable powders may contain up to 50 percent or more of one or more of these compounds.

A typical formulation of a wettable powder comprises 20 percent to 50 percent of the organic thiocyanate compound, 45 percent to 75 percent of one or more finely divided solids, 1 percent to 5 percent of a wetting agent, and 1 percent to 5 percent of a dispersing agent. Typical wetting agents include sodium dodecyl sulfate, sodium nonylbenzene sulfonate, sodium dioctyl sulfosuccinate, octylphenoxypolyethoxyethanol, or other nonionic agents, such as the ethylene and/or propylene oxide condensates with long-chained alcohols, mercaptans, amines or carboxylic acids. Typical dispersing agents include the sodium sulfonate of condensed naphthalene-formaldehyde and lignin sulfonates.

Liquid concentrates may also be used. These are prepared by taking up the organic thiocyanate compound in an organic solvent together with one or more surface active agents. For example, there may be mixed 25 parts of one of the organic thiocyanate compounds, 5 parts of a surface-active solvent-soluble alkylphenoxyethoxyethanol and 70 parts of one or more solvents, such as dimethyl sulfoxide or dimethylformamide, or mixtures of these with xylene or other aromatic solvents.

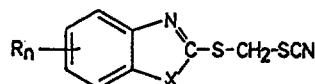
The compounds of this invention may be used in conjunction with other fungicidal agents and also in conjunction with miticides or insecticides or other pesticides.

When added to aqueous systems containing organic material to inhibit the growth and proliferation of fungi, a suitable quantity of compounds according to the invention varies for example from 0.5 to 1,000 parts per million parts of moisture-free organic material. It will be understood, of course, that larger quantities of the organic thiocyanate may be used with no detrimental effect, but such larger quantities increase the costs of operation with limited material benefit.

When used in agriculture, the organic thiocyanates of our invention are used as seed, plant, and soil fungicides for protecting seeds, seedlings emerging from seeds, and plants against attack by fungi.

WHAT WE CLAIM IS:—

1. Compounds of the general formula



(I)

wherein X represents —O—, —NH—, or —S—; R represents a hydrogen or halogen atom, or an alkyl, nitro, amino or hydroxyl group; and n is 1 or 2.

2. 2 - Thiocyanomethylthiobenzothiazole.

3. 2 - Thiocyanomethylthiobenzoxazole.

4. 2 - Thiocyanomethylthiobenzimidazole.

5. 6 - Nitro - 2 - thiocyanomethylthiobenzothiazole.

6. Compounds as claimed in claim 1 wherein R represents a chlorine atom, X represents —S— and n is 1.

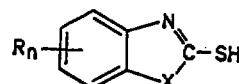
7. 5 - Chloro - 2 - thiocyanomethylthiobenzothiazole.

8. Compounds as claimed in claim 1 wherein R represents a chlorine atom, X represents —S— and n is 2.

9. 5, 6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole.

10. 4, 6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole.

11. A process for the preparation of compounds as claimed in claim 1 which comprises reacting a metal salt of a compound of formula:



(II)

(wherein X, R and n are as defined in claim 1) with chloromethylthiocyanate in an alcoholic solution.

12. A process as claimed in claim 11 wherein the compound of formula II and the chloromethylthiocyanate are reacted in substantially equimolar proportions.

13. A process as claimed in either of claims 11 and 12 wherein the compounds of formula II is used in the form of an alkali metal salt.

14. A process as claimed in claim 13 in which the said alkali metal salt is the sodium salt.

15. A process as claimed in claim 11 substantially as herein described.

16. A process as claimed in claim 11 substantially as herein described in any of Examples 1 to 6.

17. Compounds as claimed in claim 1, when prepared by a process as claimed in any of claims 11 to 16.

18. A method of inhibiting the growth and proliferation of fungi in aqueous medium



The compounds of this invention may be used diluted with a carrier which may be liquid or solid. Dusts may be prepared with a finely divided solid such as talc, clay, pyrophyllite, diatomaceous earth, hydrated silica, calcium silicate, or magnesium carbonate. If desired, wetting and/or dispersing agents may be used. When the proportions of these are increased, there results a wettable powder, which may be taken up in water and applied from a spray.

Dusts may contain 1 percent to 15 percent of one or more compounds of this invention, while wettable powders may contain up to 50 percent or more of one or more of these compounds.

A typical formulation of a wettable powder comprises 20 percent to 50 percent of the organic thiocyanate compound, 45 percent to 75 percent of one or more finely divided solids, 1 percent to 5 percent of a wetting agent, and 1 percent to 5 percent of a dispersing agent. Typical wetting agents include sodium dodecyl sulfate, sodium nonylbenzene sulfonate, sodium dioctyl sulfosuccinate, octylphenoxypolyethoxyethanol, or other nonionic agents, such as the ethylene and/or propylene oxide condensates with long-chained alcohols, mercaptans, amines or carboxylic acids. Typical dispersing agents include the sodium sulfonate of condensed naphthalene-formaldehyde and lignin sulfonates.

Liquid concentrates may also be used. These are prepared by taking up the organic thiocyanate compound in an organic solvent together with one or more surface active agents. For example, there may be mixed 25 parts of one of the organic thiocyanate compounds, 5 parts of a surface-active solvent-soluble alkylphenoxyethoxyethanol and 70 parts of one or more solvents, such as dimethyl sulfoxide or dimethylformamide, or mixtures of these with xylene or other aromatic solvents.

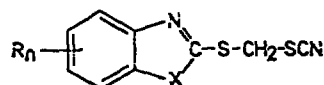
The compounds of this invention may be used in conjunction with other fungicidal agents and also in conjunction with miticides or insecticides or other pesticides.

When added to aqueous systems containing organic material to inhibit the growth and proliferation of fungi, a suitable quantity of compounds according to the invention varies for example from 0.5 to 1,000 parts per million parts of moisture-free organic material. It will be understood, of course, that larger quantities of the organic thiocyanate may be used with no detrimental effect, but such larger quantities increase the costs of operation with limited material benefit.

When used in agriculture, the organic thiocyanates of our invention are used as seed, plant, and soil fungicides for protecting seeds, seedlings emerging from seeds, and plants against attack by fungi.

WHAT WE CLAIM IS:—

1. Compounds of the general formula



(I)

wherein X represents —O—, —NH—, or —S—; R represents a hydrogen or halogen atom, or an alkyl, nitro, amino or hydroxyl group; and n is 1 or 2.

2. 2 - Thiocyanomethylthiobenzothiazole.

3. 2 - Thiocyanomethylthiobenzoxazole.

4. 2 - Thiocyanomethylthiobenzimidazole.

5. 6 - Nitro - 2 - thiocyanomethylthiobenzothiazole.

6. Compounds as claimed in claim 1 wherein R represents a chlorine atom, X represents —S— and n is 1.

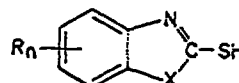
7. 5 - Chloro - 2 - thiocyanomethylthiobenzothiazole.

8. Compounds as claimed in claim 1 wherein R represents a chlorine atom, X represents —S— and n is 2.

9. 5, 6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole.

10. 4, 6 - Dichloro - 2 - thiocyanomethylthiobenzothiazole.

11. A process for the preparation of compounds as claimed in claim 1 which comprises reacting a metal salt of a compound of formula:



(II)

(wherein X, R and n are as defined in claim 1) with chloromethylthiocyanate in an alcoholic solution.

12. A process as claimed in claim 11 wherein the compound of formula II and the chloromethylthiocyanate are reacted in substantially equimolar proportions.

13. A process as claimed in either of claims 11 and 12 wherein the compounds of formula II is used in the form of an alkali metal salt.

14. A process as claimed in claim 13 in which the said alkali metal salt is the sodium salt.

15. A process as claimed in claim 11 substantially as herein described.

16. A process as claimed in claim 11 substantially as herein described in any of Examples 1 to 6.

17. Compounds as claimed in claim 1, when prepared by a process as claimed in any of claims 11 to 16.

18. A method of inhibiting the growth and proliferation of fungi in aqueous medium

which comprises adding to the said medium a compound as claimed in any of claims 1 to 10 and 17 in an amount sufficient to inhibit the growth and proliferation of the said fungi.

19. A method as claimed in claim 18 in which the aqueous medium is wood pulp.

20. A method as claimed in claim 18 substantially as herein described.

10 21. A fungicidal composition which comprises at least one compound as claimed in claim 1 as active ingredient together with a liquid or solid carrier.

15 22. A composition as claimed in claim 21 in which the carrier comprises a finely divided solid.

23. A composition as claimed in claim 22 in which the carrier comprises a wettable powder.

24. A composition as claimed in claim 23 which contains from 20 to 50% by weight of the active ingredient.

25. A composition as claimed in claim 21 in which the carrier comprises an organic liquid.

26. A composition as claimed in claim 25 which also contain one or more surface active agents.

27. A composition as claimed in claim 21 substantially as herein described.

For the Applicants,
FRANK B. DEHN & CO.,
Chartered Patent Agents,

Imperial House,
15—19, Kingsway, London, W.C.2.

x at accept

7.:-C 07 d

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

ERRATA

SPECIFICATION No. 1,129,575

Page 1, line 39, for "microorganisms" read "microorganisms"

Page 7, line 40, for "alkylphenoxyethoxy-ethanol" read "alkylphenoxyethoxy-ethanol"

THE PATENT OFFICE
11th November 1968



* C L M S *

We, BUC
poration or
laws of the
of America,
ness at 11
Memphis, T
America, de
which we pr
to us, and i
performed, t
by the follo
This inver
cyanates, the
controlling f
the products
combating fu
processes and
Many indu
process of n
product, are
degradation i
hibit such d
and proteinac
vegetable tan
damaged or c
and other mic
duced by suc
more than at
tent is subjec
and decay fun
is a loss of
pulp, difficulty
pulp, a darken
ment of undesir
of the microo
moulds are en
the manufactur
soaking provide
ductive to the g
even strong pi
attack by some
particular may
coloration of th
is held for a
chrome tanning
[Price 4s. 6d.]