

PATENT SPECIFICATION

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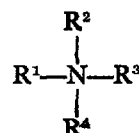
(54) ONIUM METAL BIS-DITHIOCARBAMATE CHELATES

- (71) We, ROHM AND HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, 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:—

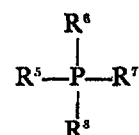
- This invention is concerned with new bis-dithio-carbamate derivatives otherwise referred to herein as onium metal bis-dithiocarbamate chelates and pesticidal compositions containing them.

- In accordance with the present invention there is provided a process for the preparation of onium metal bis-dithiocarbamate chelates which comprises reacting in solution:

- (1) a bisdithiocarbamate of the formula

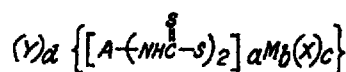
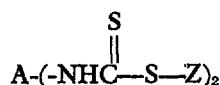


wherein R^1 , R^2 , R^3 and R^4 represent individually alkyl of 1 to 24 carbon atoms, cycloalkyl particularly cyclohexyl, aryl particularly phenyl, benzyl, alkyl-substituted benzyl containing up to 12 alkyl carbon atoms, hydroxy-alkyl of 1 to 4 carbon atoms, or hydrogen except that, when R^1 , R^2 and R^3 each represent hydrogen, R^4 must be a group other than hydrogen or methyl; the group



wherein R^5 , R^6 , R^7 and R^8 represent, individually, alkyl of 1 to 24 carbon atoms, monoalkyl-amino and dialkylamino groups wherein the alkyl radicals contain from 1 to 24 carbon atoms, or aryl particularly phenyl, benzyl and alkyl-substituted benzyl containing up to 12 alkyl carbon atoms.

The novel compounds provided by the invention, which may be more shortly termed "onium metal chelates," are thought to be of the formula:



where A is a phenylene or C_2-C_6 alkylene group and Z is a cation.

- (2) a source of one or more of the following metal ions, namely cadmium, cobalt, copper, iron, manganese, nickel and zinc ions, and

- (3) an onium salt where the onium group is a morpholinium, imidazolium, (C_1-C_6) -alkyl imidazolium, 1 - (2 - hydroxyethyl) - 2 - N-alkylcarbamoylimidazolium wherein the alkyl is 1 to 24 carbon atoms, N- (C_1-C_6) alkyl pyridium, alkylene-diammonium wherein the alkylene is 2 to 6 carbon atoms, the group

wherein A is a straight or branched chain (C₂—C₆)-alkylene group or phenylene;

a is the integer 2 or 4

5 M is at least one of Cd, Co, Cu, Fe, Mn, Ni or Zn particularly one or more of Cu (cupric), Fe (ferric), Mn(manganous) and Zn;

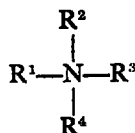
b is the integer 1, 3 or 4;

X is an anion which complexes with the metal M;

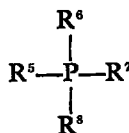
10 C is 0 or an integer from 1 to 4;

d is an integer from 1 to 4; and

Y is morpholinium, imidazolium, (C₁—C₆)-alkyl imidazolium, 1 - (2 - hydroxyethyl) - 2-N - alkylcarbamoylimidazolium wherein the alkyl is 1 to 24 carbon atoms, N-(C₁—C₆)-alkyl pyridinium, alkylenediammonium wherein the alkylene is 2 to 6 carbon atoms, the group



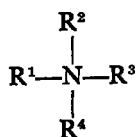
20 wherein R¹, R², R³ and R⁴ represent individually alkyl of 1 to 24 carbon atoms, cycloalkyl particularly cyclohexyl, aryl particularly phenyl, benzyl, alkyl-substituted benzyl containing up to 12 alkyl carbon atoms, hydroxy-alkyl of 1 to 4 carbon atoms, or hydrogen
25 except that, when R¹, R² and R³ each represent hydrogen, R⁴ must be a group other than hydrogen or methyl; the group



30 wherein R⁵, R⁶, R⁷ and R⁸ represent, individually, alkyl of 1 to 24 carbon atoms, monoalkyl-amino and dialkylamino groups wherein the alkyl radicals contain from 1 to 24 carbon atoms, or aryl particularly phenyl, benzyl and alkyl-substituted benzyl containing up to 12
35 alkyl carbon atoms.

Typical (C₁—C₆)-alkyl substituents as referred to above are methyl, ethyl, propyl, isopropyl, butyl, *tert*-butyl, 2-methylbutyl, *sec*-pentyl, 1,1-dimethylbutyl or hexyl. Most of the common anions (X) will complex with the metals (M). Typical X groups are the halides, cyano, thiocyno, nitrate, sulfate, phosphate, acetate and oxalate. X is preferably a halide or mixture of halides.

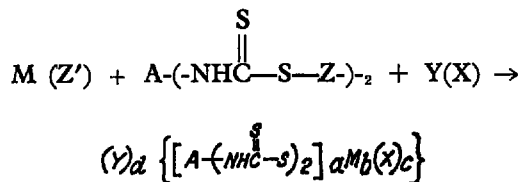
45 Typically Y is the group



where R¹, R², R³ and R⁴ represent (C₁—C₂₄)-allyl (C₁—C₄)-hydroxyalkyl, benzyl or hydrogen with the proviso stated above.

Preparation of the novel onium metal chelates (I) usually involves reacting, in solution, an appropriate transition metal salt, an alkylene bis-dithiocarbamate and an appropriate onium salt Y(X) preferably used in an amount of at least 0.5 equivalent. Typical onium salts would include fluoborate, phosphates, sulfates and nitrates. The onium halides are preferred. Typical metal salts are the halides, acetate, nitrate, phosphate and sulfate. It is preferred that the metal ions be divalent, except for iron, in which case the ferric form is preferred.

The above reaction can be illustrated by the following schematic equation:



wherein the symbols A, M, X, Y, Z, a, b, c and d are as previously defined and Z' is a cation. The bisdithiocarbamate salt must be one which has enough solubility in the reaction mixture for the reaction to occur. The preferred soluble salts are those of the alkali metals.

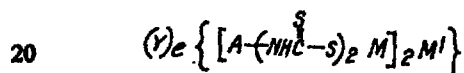
Usually, and preferably, this reaction is carried out in water solution; however, solvents such as methanol, ethanol and isopropanol can also be utilized. There are instances where the onium salt has limited solubility in water and for these it is preferable to dissolve the onium salt in an appropriate solvent, such as alcoholic solvents, for addition to the bis-dithiocarbamate. It is preferred to have the bis-dithiocarbamate/onium salt mixture in solution before addition of the transition metal salt. In certain situations, it may be desirable to effect the reaction in a solvent such as dimethylsulfoxide and then add sufficient water so as to precipitate the onium metal chelates therefrom. Numerous modifications and variations evident to one skilled in the art may be employed within the general concept of the subject process. For example, certain amine hydrochlorides are liquid at room temperature. Where such an amine hydrochloride is used for the Y salt, an excess of this material may be used as the reaction medium either by itself or in conjunction with a small amount of an additional solvent to promote the requisite solubility of the other reactants.

The formation of the onium metal chelates proceeds satisfactorily at temperatures in the

range of 0–50° C. A reactant solution temperature maintained in the range of 20° to 30° C is preferred. Higher temperatures may be used but at these higher temperatures the bis-dithiocarbamate solutions are subject to decomposition, which lowers the yield of the desired product.

The amount of onium salt reactant used, based on the bis-dithiocarbamate reactant, varies with the type of product desired. In the instances where there is no (X) in the structure, i.e., where c equals 0, the theoretical amount of onium salt based on the bis-dithiocarbamate is one-half mole equivalent. In those cases where a halogen (X)₂ is present in the product, a molar equivalent is the theoretical quantity. Excess reagents may be used.

The most usual product formed corresponds to the structure



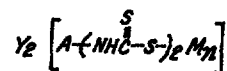
wherein c is 1 or 2 and the symbols A, M and Y have the previously defined meanings and M' may be the same as M or may be a different metal ion selected from the same group of metals specified above for M.

In order to obtain these products, the theoretical amount of metal salts used based on the bis-dithiocarbamate is three-fourths molar equivalent. Mixtures of metal salts may be used and the same theoretical quantity of the metal salt combination applies. Excesses of the metal salt reactant based on the bis-dithiocarbamate may be used and the excess amount is governed by economic and other considerations. For example, excesses of metal salt such as copper sulfate or nickel sulfate can be used. The use of such excess metal salts will result in a mixture of a product of the invention with unused metal salt. An excess of copper sulfate is useful for application to grapes and similar crops while the mixture with excess nickel sulfate may be applied to cereal grains.

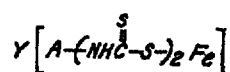
The formulae given herein for the onium metal chelate do not indicate an exact chemical structure by any means; however, it is believed that the metal is present in two main types of bondings. Primarily, the metal forms an ionic bond with the bis-dithiocarbamate radical and, secondarily the metal forms a complex, chelate or coordinate bond with the onium group(s). These two types of bondings have different energy levels and the different metals have different salt-forming and complexing abilities. It is possible to form onium metal complexes according to the invention wherein the same metal is present in both bonding forms or to form compounds wherein different metals are used for each of the two

types of bonding in the same compound.

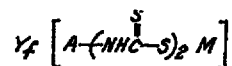
In the case of manganese salts, products are isolated which are thought to correspond to the structure



In the case of ferric salts, products are formed which are thought to correspond to the structure



Accordingly, for this type of onium metal chelate, the theoretical amount of ferric and manganese salt is one-half molar equivalent based on the bis-dithiocarbamate. Products of these types may be represented by the formula



wherein Y, A and M are as previously defined and f is 1 when M is trivalent and 2 when M is divalent.

It was found that when ammonium salts, i.e., NH₄-salts, were used, an onium metal chelate did not form, but only the metal bis-dithiocarbamate was obtained. When monomethylammonium salts, i.e., CH₃NH₃⁺ salts, were tried in the reaction a mixture of metal bis-dithiocarbamate and onium metal chelate was obtained.

The concentration of the solution of the combined bis-dithiocarbamate and onium salt is limited only by the solubility of these reactants in the reaction solvent. Satisfactory results have been obtained wherein the concentration of solids has been varied from 2% to 35%.

Completion of the reaction is usually indicated by formation of a precipitate which constitutes the product being prepared. This precipitate may be recovered from the reaction solution by means well known to one skilled in the art. Typically, this will involve filtration and then drying at elevated temperatures in vacuum. Yields of 90 to 100% of theoretical are normally so obtained. In addition to filtration, means such as centrifugation, settling with subsequent pouring-off of the supernat-

ant liquid and the like are also easily utilized.

By way of illustration and not by way of limitation, several embodiments of this invention have been prepared in accordance with the above-disclosed process. Specific preparations hereinafter following are presented for Examples 1 to 5, 36, 44, 48 and 52 so as to demonstrate more fully the process for the preparation of the onium metal chelates along with the compounds themselves.

EXAMPLE 1

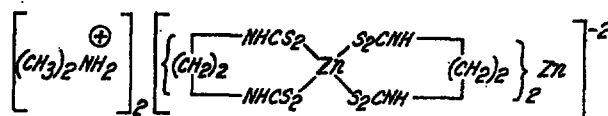
Preparation of

Dimethylammonium Zinc Ethylene-bis-dithiocarbamate Chelate

A 40% dimethylamine solution (20.2 g., 0.1 mole) was diluted with 100 ml. of water

and neutralized to pH 7 by the addition of approximately 10 g. of concentrated hydrochloric acid. To this solution was then added 56.8 g. (0.05 mole) of 32% aqueous disodium ethylene - bis - dithiocarbamate hexahydrate. The resulting orange solution was treated dropwise at 25° C. over 20 minutes with a solution of 5.1 g. (0.0375 mole) of zinc chloride in 20 ml. of water. A white solid precipitated, which was filtered and dried at 40° C. under 10—20 mm vacuum. In this manner, 13.1 g. of dimethylammonium zinc ethylene - bis-dithiocarbamate chelate was obtained which constituted a 92% yield.

The product may be depicted by the following structure:



EXAMPLE 2

Preparation of

Tetramethylammonium Zinc Ethylene-bis-dithiocarbamate Chelate

To a solution of 123 g. (0.8 mole) of tetramethylammonium bromide in 1500 ml. of water was added 454 g. (0.4 mole) of 32% aqueous disodium ethylene-bis-dithiocarbamate hexahydrate. the resulting orange solution was treated dropwise at 25° C. over 30 minutes with 66 g. (0.3 mole) of zinc acetate dihydrate in 250 ml. of water. A white precipitate was filtered off and dried at 50° C. under 10—20 mm. vacuum. In this manner, 123 g. of tetramethylammonium zinc ethylene-bis-dithiocarbamate chelate was obtained.

EXAMPLE 3

Preparation of

Choline Zinc Ethylene-bis-dithiocarbamate Chelate

Anhydrous disodium ethylene - bis - dithiocarbamate, 51 g. (0.2 mole), and choline chloride, 13.9 g. (0.1 mole), were dissolved in 78 ml. of water. This solution was then treated at 25° C. over 5 minutes with 20.4 g (0.15 mole) of zinc chloride in 20 ml. of water. The reaction mixture was stirred over 20 minutes, during which time the temperature rose to 40° C. and the mixture appearance changed from a slightly greenish slime to a white, creamy slurry. The slurry was stirred for 12 hours, then filtered, and the white solid precipitate was washed with 100 ml. of water. The solid was dried under 10—20 mm.

vacuum at 40—50° C. to yield 56.8 g. (92%) of choline zinc ethylene-bisdithiocarbamate chelate.

EXAMPLE 4

Preparation of

Choline Copper Ethylene-bis-dithiocarbamate Chelate

Choline chloride, 55.6 g. (0.4 mole), was dissolved in 750 ml. of water and 51.2 g. (0.2 mole) of anhydrous disodium ethylene-bis-dithiocarbamate was added. The resulting orange solution was treated dropwise at 25° C. over 30 minutes with 37.4 g. (0.150 mole) of copper sulfate pentahydrate in 100 ml. of water. The brown precipitate which formed was filtered off and dried at 40—50° C. under 10—20 mm. vacuum to yield 54 g. (87%) of solid choline copper ethylene-bis-dithiocarbamate chelate.

EXAMPLE 5

Preparation of

Tetrabutylammonium Nickel Ethylene-bis-Dithiocarbamate Chelate

Sodium hydride (67% in mineral oil), 3.9 g. (0.11 mole), was placed in a flame-dried flask and washed with 3 × 50 ml. of xylene. The washed hydride was then covered with 100 ml. of distilled dimethyl sulfoxide. Ethylene diamine (3.0 g., 0.05 mole) was added, and the solution was then treated drop-wise with cooling to 20—25° C. over 30 minutes with 7.6 g. (0.1 mole) of carbon disulfide. A total of 2.17 liters of hydrogen was evolved. The resulting solution of disodium ethylene - bis-

5 dithiocarbamate was treated with 9.3 g. (0.0375 mole) of nickel acetate tetrahydrate to yield a very dark solution. To this solution was added 8.0 g. (0.025 mole) of tetrabutylammonium bromide, and the reaction was stirred for 4 hours. The dimethylsulfoxide solution was then poured into 1500 ml. of water to give a brown solid precipitate. The product was collected by filtration and dried at 25° C. under 10—20 mm. to yield 17 g. (91%) of solid tetrabutylammonium nickel ethylene - bis - dithiocarbamate chelate.

10 The above examples are typical of those in which four units of bis-dithiocarbamate, two ammonium units and three metal units are combined into the onium metal chelate structures. In Table I, appearing later, Examples 1—35 are of this type.

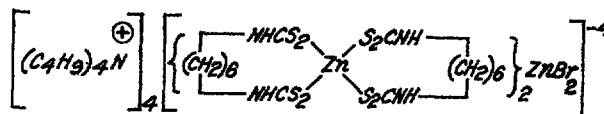
EXAMPLE 36

20 Preparation of Tetrabutylammonium Zinc Hexamethylene-bis-dithiocarbamate Chelate

A solution of disodium hexamethylene - bis - dithiocarbamate was prepared in the following

25 manner. Sodium hydroxide, 8 g. (0.2 mole), was dissolved in 100 ml. of water, and then under nitrogen at 20° C. was added 11.6 g. (0.1 mole) of 1,6 - diamino - hexane. This solution was then treated at 20° C. dropwise with 15.2 g. (0.2 mole) of carbon disulfide, and an orange coloration developed. Twenty-five milliliters of ethanol was added to give a homogeneous system and stirring was continued for 2.5 hours to complete the reaction.

30 The disodium hexamethylene - bis - dithiocarbamate prepared above was treated with 64.4 g. (0.2 mole) of tetrabutylammonium bromide in 100 ml. of water. To the resulting solution was added at 25° C. over 30 minutes 16.4 g. (0.075 mole) of zinc acetate dihydrate dissolved in 100 ml. of water. The white precipitate which formed was then filtered off, washed with water, and dried at 10—20 mm. and 40—50° C. to give 53.5 g. (90% yield) of solid tetrabutylammonium zinc hexamethylene - bis - dithiocarbamate chelate. This product may be depicted by the following structure:



50 This preparation is typical of ones in which the anion (X) is incorporated into the structures. In Table I, Examples 36—43 are of this type.

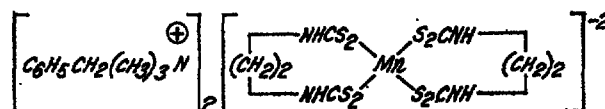
EXAMPLE 44

55 Preparation of Benzyltrimethylammonium Manganese Ethylene-bis-dithiocarbamate Chelate

60 A 35% methanolic solution of benzyltrimethylammonium hydroxide (23.8 g., 0.05 mole) was diluted with 100 ml. of water and neutralized to pH 7 with a 42% aqueous solution of fluoboric acid. To this solution was

then added 28.2 g. (0.025 mole) of 32% aqueous disodium ethylene - bis - dithiocarbamate. To the resulting solution was then added dropwise at 25° C. over a period of 30 minutes 3.0 g. (0.0125 mole) of manganese acetate tetrahydrate dissolved in 50 ml. of water. A tan solid precipitated and was filtered off and dried at 25° C. and 1 mm. (Hg) pressure. In this manner, 8.2 g. (85% yield) of benzyltrimethylammonium manganese ethylene - bis - dithiocarbamate chelate was obtained.

This product may be depicted by the following structure:



80 This exemplifies the type of quaternary ammonium metal chelate wherein two bis-dithiocarbamate units, two quaternary units

and one metal ion are combined. In Table I, Examples 44—47 are of this type.

EXAMPLE 48

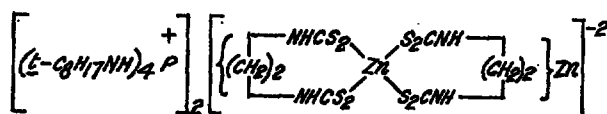
Preparation of

N,N',N'',N''' -Tetrakis-(1,1,3,3-tetramethyl-butylamino)phosphonium Zinc Ethylene-bis-dithiocarbamate (A 1,1,3,3-tetramethyl-butyl Group is often referred to as *t*-octyl)

- 5 To a solution of 29 g. (0.05 mole) of N,N',N'',N''' -tetrakis - (1,1,3,3 - tetramethylbutylamino)phosphonium chloride in
10 500 ml. of methanol was added 28.3 g. (0.025 mole) of 32% aqueous disodium ethylenebis-dithiocarbamate hexahydrate. To the stirred

solution was added 3.45 g. (0.0187 mole) of anhydrous zinc acetate in 75 ml. of methanol plus 5 ml. of water. A slightly yellow gum precipitated and was removed and dried under vacuum to give an orange foam-like solid. The solid was allowed to soak under water for one week and was then filtered off and dried to give 12.8 g. (97% yield) of a slightly tan solid.

The product may be depicted by the following structure:



- 25 Examples 49 and 51 are further examples of the compounds of this invention made from typical quaternary phosphonium compounds.

EXAMPLE 52

Preparation of

- 30 Tetramethylammonium Manganese-zinc Ethylene-bis-dithiocarbamate Chelate
Tetramethylammonium hydroxide (146 g., 0.4 mole) was neutralized to pH 7 with 0.4 mole of concentrated hydrochloric acid and then diluted with 700 ml. of water. To this
35 solution was added 227 g. (0.2 mole) of 32% aqueous disodium ethylene - bis - dithiocarbamate hexahydrate. The resulting aqueous solution was blanketed with nitrogen and there
40 was then added dropwise over a period of 30 minutes a solution of manganous sulfate monohydrate (25.4 g., 0.15 mole) in 200 ml. of water. A precipitate formed. The mixture was stirred for 15 minutes. A sample of the
45 product at this point was somewhat unstable and decomposed upon drying. To the main

reaction mixture was then added 27.2 g. (0.2 mole) of zinc chloride in 100 ml. of water, over a period of 30 minutes. The resulting solid was filtered off, washed with water and dried to give 53.8 g. of light brown solid.

This is typical of a method of preparation in which two or more metals may be incorporated into the onium metal chelate structures. Examples 52—54 are of this type.

In this example the mixed metal onium compound was prepared by carrying out the reaction in successive stages. If desired, mixed metal onium compounds may also be prepared by adding the two metal salts at the same time.

Table I catalogues the substituents of all the examples namely, 1 to 54, along with the decomposition point of the preparations. Following Table I, there is presented in Table II the empirical formula of each example and its corresponding analytical data, both calculated and determined.

TABLE I
Example Substituents



Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range (°C.)
1	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NH}_2$	2			Zn	3	140—145
2	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_4\text{N}$	2			Zn	3	149—150
3	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}$	2			Zn	3	132—133
4	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}$	2			Cu	3	122—125
5	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Ni	3	119
6	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NH}$	2			Zn	3	118—125
7	$(-\text{CH}_2-)_2$	4	$t\text{-C}_4\text{H}_9\text{NH}_2$	2			Zn	3	220—240
8	$(-\text{CH}_2-)_2$	4	$t\text{-C}_8\text{H}_{17}\text{NH}_2$	2			Zn	3	125
9	$(-\text{CH}_2-)_2$	4	$t\text{-C}_{18}\text{H}_{37}\text{NH}_2$	2			Zn	3	120—127
10	$(-\text{CH}_2-)_2$	4	$(\text{HOCH}_2\text{CH}_2)_2\text{NH}_2$	2			Zn	3	130—160
11	$(-\text{CH}_2-)_2$	4	$(\text{HOCH}_2\text{CH}_2)_3\text{NH}$	2			Zn	3	115
				2			Zn	3	96—103

TABLE I Continued

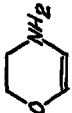
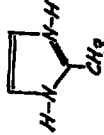
Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range (°C.)
13	$(-\text{CH}_2-)_3$	4	$\text{C}_6\text{H}_5\text{NH}_2$	2			Zn	3	135—150
14	$(-\text{CH}_2-)_3$	4	$\text{C}_6\text{H}_5\text{NH}_2\text{C}_2\text{H}_5$	2			Zn	3	132
15	$(-\text{CH}_2-)_2$	4	$(-\text{CH}_2\text{NH}_2)_3$	1			Zn	3	200—220
16	$(-\text{CH}_2-)_3$	4		2			Zn	3	158—160
17	$(-\text{CH}_2-)_3$	4		2			Zn	3	148

TABLE I (Continued)

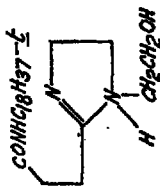
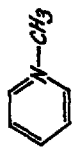
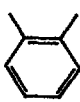
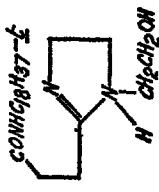
Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range (°C.)
18	$(-\text{CH}_2-)_2$	4		2			Zn	3	127—130
19	$(-\text{CH}_2-)_2$	4		2			Zn	3	123—125
20	$(-\text{CH}_2-)_2$	4	$\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_5$	2			Zn	3	109—111
21	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Zn	3	123—129
22		4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Zn	3	220
23	$(-\text{CH}_2-)_2$	4		2			Cu	3	105—110
24	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	2			Cu	3	115—118

TABLE I (continued)

Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range (°C.)
25	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	2			Ni	3	143
26	$(-\text{CH}_2-)_2$	4	$(\text{C}_3\text{H}_7)_4\text{N}$	2			Zn	3	113
27	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	2			Zn	3	125—130
28	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Zn	3	120
29	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Ni	3	155
30	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	2			Cu	3	107
31	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}$	2			Mn	3	158—162
32	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_4\text{N}$	2			Mn	3	162—165
33	$(-\text{CH}_2-)_3$	4	$(\text{CH}_3)_4\text{N}$	2			Zn	3	171—175
34	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_4\text{N}$	2			Cd	3	159
35	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_4\text{N}$	2			Co	3	250
36	$(\text{CH}_2-)_6$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	4	Br	2	Zn	3	100—110
37	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	4	Br	2	Zn	3	115
38	$(-\text{CH}_2-)_2$	4	$(\text{C}_8\text{H}_7)_4\text{N}$	4	I	2	Zn	3	124

TABLE I (continued)

Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range °C.
39	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	4	Cl	2	Zn	3	103 (1)
40	$(-\text{CH}_2-)_2$	4	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	4	Cl	4	Zn	4	125—129
41	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}- \end{array}$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	4	Br	2	Zn	3	110
42	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	4	Br	2	Cu	3	150
43	$(-\text{CH}_2-)_2$	4	$(\text{C}_4\text{H}_9)_4\text{N}$	4	Br	2	Ni	3	150
44	$(-\text{CH}_2-)_2$	2	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	2			Mn	1	143 (1)
45	$(-\text{CH}_2-)_2$	2	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	2			Mn	1	95 (2)
46	$(-\text{CH}_2-)_2$	2	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	1			Fe+++	1	146 (1)
47	$(-\text{CH}_2-)_2$	2	$(\text{CH}_3)_3\text{NCH}_2\text{C}_6\text{H}_5$	1			Fe+++	1	177 (2)
48	$(-\text{CH}_2-)_2$	4	$(t-\text{C}_8\text{H}_{17}\text{NH})_4\text{P}$	2			Zn	3	110
49	$(-\text{CH}_2-)_2$	4	$\text{C}_6\text{H}_5(\text{C}_{18}\text{H}_{37})\text{P}[\text{N}(\text{CH}_3)_2]_2$	2			Zn	3	115—120
50	$(-\text{CH}_2-)_2$	4	$\text{C}_6\text{H}_5(\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{CH}_2\text{P}(\text{NHC}_4\text{H}_9)_2)$	2			Zn	3	115—130

TABLE I (Continued)

Ex. No.	A	a	Y	d	X	c	M	b	Decomposition Range (°C.)
51	(-CH ₂ -) ₂	4	(C ₆ H ₅) ₃ CH ₂ P	4	Cl	2	Zn	3	124—127
52	(-CH ₂ -) ₂	4	(CH ₃) ₄ N	2			Mn—Zn	3	165—168
53	(-CH ₂ -) ₂	4	HOCH ₂ CH ₂ N(CH ₃) ₃	2			Mn—Zn	3	162—165
54	(-CH ₂ -) ₂	4	HOCH ₂ CH ₂ N(CH ₃) ₃	2			Ni—Zn	3	165—180

(¹) Made from the quaternary ammonium chloride.

(²) Made from the quaternary ammonium fluoborate.

TABLE II

Analysis*

Ex. No.	Empirical Formula	Analysis*				Halogen or Phosphorus	Metal
		C	H	N	S		
1	$C_{20}H_{40}N_{10}S_{16}Zn_3$	20.30 (21.3)	3.54 (3.5)	11.75 (12.4)	43.49 (45.4)	Zn,	18.00 (17.3)
2	$C_{24}H_{48}N_{10}S_{16}Zn_3$	23.80 (24.4)	3.54 (4.1)	11.06 (11.85)	40.94 (43.2)	Zn,	16.80 (16.5)
3	$C_{28}H_{52}N_{10}O_2S_{16}Zn_3$	25.17 (25.1)	4.40 (4.2)	11.05 (11.25)	38.25 (41.15)	Zn,	16.08 (15.75)
4	$C_{28}H_{52}N_{10}O_2S_{16}Cu_3$	23.65 (25.2)	4.40 (4.2)	10.22 (11.3)	35.71 (41.4)	Cu,	16.60 (15.3)
5	$C_{48}H_{96}N_{10}S_{16}Ni_3$	41.57 (38.4)	6.40 (6.4)	6.38 (9.30)	29.98 (34.2)	Ni,	11.24 (11.7)
6	$C_{22}H_{44}N_{10}S_{16}Zn_3$	21.97 (22.8)	4.39 (3.8)	11.37 (12.1)	42.77 (44.3)	Zn,	17.69 (16.9)
7	$C_{24}H_{48}N_{10}S_{16}Zn_3$	21.01 (24.3)	3.17 (4.1)	10.54 (11.85)	43.33 (43.2)	Zn,	21.16 (16.5)
8	$C_{32}H_{64}N_{10}S_{16}Zn_3$	31.81 (29.6)	5.73 (4.9)	10.68 (10.7)	37.45 (39.6)	Zn,	13.83 (15.0)
9	$C_{52}H_{104}N_{10}S_{16}Zn_3$	40.00 (39.6)	7.20 (6.6)	8.74 (8.9)	30.88 (32.5)	Zn,	12.79 (12.4)
10	$C_{24}H_{48}N_{12}O_4S_{16}Zn_3$	22.14 (22.6)	3.60 (3.8)	11.72 (13.2)	41.00 (40.1)	Zn,	18.90 (15.3)
11	$C_{28}H_{56}N_{10}O_6S_{16}Zn_3$	25.37 (25.1)	4.15 (4.2)	10.64 (10.5)	38.24 (38.4)	Zn,	15.40 (14.6)
12	$C_{32}H_{64}N_{10}O_8S_{16}Zn_3$	26.90 (27.0)	4.51 (4.5)	9.77 (9.9)	35.00 (36.1)	Zn,	13.59 (13.7)
13	$C_{28}H_{40}N_{10}S_{16}Zn_3$	25.01 (27.5)	4.05 (3.3)	12.69 (11.4)	41.60 (41.8)	Zn,	16.50 (15.9)

TABLE II (Continued)

Ex. No.	Empirical Formula	Analysis*				Halogen or Phosphorus	Metal
		C	H	N	S		
14	$C_{82}H_{48}N_{10}S_{16}Zn_3$	30.28 (30.0)	4.20 (3.8)	11.60 (11.0)	37.23 (40.0)		Zn, 13.70 (15.2)
15	$C_{13}H_{32}N_{10}S_{16}Zn_3$	19.62 (19.7)	3.46 (2.9)	12.86 (12.8)	43.31 (46.8)		Zn, 18.50 (17.8)
16	$C_{24}H_{44}N_{10}O_2S_{16}Zn_3$	26.70 (23.8)	4.15 (3.6)	11.55 (11.5)	40.94 (42.3)		Zn, 15.50 (16.1)
17	$C_{24}H_{38}N_{12}S_{16}Zn_3$	24.64 (24.0)	3.69 (3.1)	14.09 (14.0)	33.40 (42.6)		Zn, 17.8 (16.2)
18	$C_{68}H_{136}N_{14}O_4S_{16}Zn_3$	41.41 (43.0)	6.73 (6.7)	10.44 (10.3)	25.38 (27.0)		Zn, 10.01 (10.3)
19	$C_{28}H_{40}N_{10}S_{16}Zn_3$	27.20 (27.4)	3.33 (3.3)	10.69 (11.4)	38.07 (41.85)		Zn, 14.72 (16.0)
20	$C_{70}H_{124}N_{10}S_{16}Zn_3$	57.65 (46.3)	8.78 (6.9)	7.83 (7.7)	20.54 (28.3)		Zn, 7.60 (10.8)
21	$C_{48}H_{96}N_{10}S_{16}Zn_3$	36.93 (37.8)	6.58 (6.36)	7.53 (9.21)	32.24 (33.7)		Zn, 13.39 (12.9)
22	$C_{64}H_{96}N_{10}S_{16}Zn_3$	51.83 (44.8)	7.25 (5.64)	9.41 (8.17)	17.28 (29.9)		Zn, 13.64 (11.4)
23	$C_{68}H_{128}N_{14}O_4S_{16}Cu_3$	40.80 (42.8)	6.48 (6.6)	9.83 (10.3)	24.65 (26.8)		Cu, 12.80 (10.0)
24	$C_{36}H_{16}N_{10}S_{16}Cu_3$	32.98 (32.5)	4.11 (4.2)	9.60 (10.5)	30.36 (38.6)		Cu, 15.36 (14.3)
25	$C_{36}H_{56}N_{10}S_{16}Ni_3$	32.46 (32.8)	4.02 (4.3)	9.41 (10.6)	31.04 (38.9)		Ni, 5.14 (13.36)
26	$C_{40}H_{60}N_{10}S_{16}Zn_3$	37.39 (34.1)	7.58 (5.7)	8.77 (10.0)	31.79 (36.4)		Zn, 13.13 (13.9)

TABLE II (Continued)

Analysis*

Ex. No.	Empirical Formula	Analysis*				Halogen or Phosphorus	Metal
		C	H	N	S		
27	$C_{36}H_{56}N_{10}S_{16}Zn_3$	32.48 (32.3)	4.31 (4.2)	9.77 (10.5)	37.90 (38.3)		Zn, 14.31 (14.7)
28	$C_{48}H_{96}N_{10}S_{16}Zn_3$	40.64 (37.9)	6.77 (6.3)	8.54 (9.2)	30.60 (33.6)		Zn, 12.40 (12.8)
29	$C_{48}H_{96}N_{10}S_{16}Ni_3$	37.79 (38.4)	5.78 (6.4)	8.41 (9.3)	32.06 (34.1)		Ni, 10.96 (11.7)
30	$C_{48}H_{96}N_{10}S_{16}Cu_3$	41.87 (38.0)	6.53 (6.4)	7.92 (9.25)	26.60 (33.8)		Cu, 12.29 (12.5)
31	$C_{38}H_{52}N_{10}O_2S_{16}Mn_3$	27.31 (25.9)	5.00 (4.3)	11.00 (11.5)	38.63 (42.3)		Mn, 11.5 (13.6)
32	$C_{24}H_{48}N_{10}S_{16}Mn_3$	26.8 (25.0)	4.7 (4.2)	11.75 (12.1)	40.78 (44.4)		Mn, 11.7 (14.3)
33	$C_{28}H_{56}N_{10}S_{16}Zn_3$	24.46 (27.1)	4.76 (4.5)	10.50 (11.3)	37.91 (41.3)		Zn, 18.2 (15.7)
34	$C_{24}H_{48}N_{10}S_{16}Cd_3$	23.75 (21.7)	5.13 (3.6)	10.68 (10.6)	36.44 (38.6)		Cd, 24.46 (25.4)
35	$C_{24}H_{48}N_{10}S_{16}Co_3$	23.75 (24.7)	4.10 (4.1)	10.66 (12.0)	31.90 (44.0)		Co, 14.20 (15.2)
36	$C_{96}H_{200}Br_2N_{12}S_{16}Zn_3$	48.59 (48.2)	8.73 (8.43)	6.84 (7.05)	21.48 (21.45)	Br, 2.56 (6.68)	Zn, 8.06 (8.2)
37	$C_{60}H_{168}Br_2N_{12}S_{16}Zn_3$	44.99 (44.4)	7.76 (7.8)	7.52 (7.8)	22.24 (23.6)	Br, 6.26 (7.4)	Zn, 8.29 (9.1)
38	$C_{64}H_{136}I_2N_{12}S_{16}Zn_3$	36.14 (37.8)	6.59 (6.7)	8.65 (8.3)	24.93 (25.2)	I, 8.27 (12.5)	Zn, 10.46 (9.6)
39	$C_{56}H_{88}Cl_2N_{12}S_{16}Zn_3$	37.29 (39.4)	4.86 (5.2)	9.73 (9.8)	30.08 (30.0)	Cl, 2.09 (4.1)	Zn, 11.46 (11.5)

TABLE II (Continued)

Analysis*

Ex. No.	Empirical Formula	Analysis*				Halogen or Phosphorus	Metal
		C	H	N	S		
40	C ₃₆ H ₉₈ Cl ₄ N ₁₂ S ₁₆ Zn ₄	35.93 (36.4)	4.64 (4.8)	8.90 (9.1)	26.74 (27.7)	Cl, 8.37 (7.7)	Zn, 14.25 (14.2)
41	C ₃₄ H ₁₇₆ Br ₂ N ₁₂ S ₁₆ Zn ₃	42.36 (45.3)	7.73 (7.97)	6.98 (7.56)	22.80 (23.1)	Br, 4.13 (7.2)	Zn, 12.95 (8.8)
42	C ₈₀ H ₁₆₈ Br ₂ N ₁₂ S ₁₆ Cu ₃	45.55 (44.5)	7.85 (7.8)	8.40 (7.8)	24.74 (23.7)	Br, 1.21 (7.4)	Cu, 10.38 (8.8)
43	C ₈₀ H ₁₆₈ Br ₂ N ₁₂ S ₁₆ Ni ₃	43.71 (44.7)	7.35 (7.8)	8.25 (7.8)	25.97 (23.9)	Br, 3.60 (7.4)	Ni, 8.77 (8.2)
44	C ₂₈ H ₄₄ N ₆ S ₈ Mn	38.16 (43.3)	5.13 (5.7)	9.45 (10.8)	24.23 (33.1)		Mn, 7.50 (7.09)
45	C ₂₈ H ₄₄ N ₆ S ₈ Mn	38.76 (43.3)	5.04 (5.7)	9.65 (10.8)	27.96 (33.1)		Mn, 8.51 (7.09)
46	C ₁₈ H ₂₈ N ₅ S ₆ Fe	32.03 (34.6)	4.11 (4.5)	9.80 (11.2)	28.83 (41.0)		Fe, 7.83 (8.9)
47	C ₁₈ H ₂₈ N ₅ S ₆ Fe	32.38 (34.6)	4.41 (4.5)	8.83 (11.2)	30.28 (41.0)		Fe, 7.40 (8.9)
48	C ₈₀ H ₁₆₈ N ₁₆ P ₂ S ₁₆ Zn ₃	45.97 (45.3)	7.95 (7.9)	10.11 (10.6)	21.80 (24.1)	P, 3.08 (2.9)	Zn, 8.69 (9.2)
49	C ₇₂ H ₁₃₂ N ₁₂ P ₂ S ₁₆ Zn ₃	43.45 (44.7)	7.02 (6.8)	7.83 (8.7)	19.10 (26.4)	P, 3.5 (3.2)	Zn, 9.45 (10.1)
50	C ₈₂ H ₁₃₆ N ₁₂ P ₂ S ₁₆ Zn ₃	50.54 (47.9)	6.95 (6.6)	7.20 (8.2)	19.35 (24.9)	P, 3.06 (3.0)	Zn, 8.20 (9.5)
51	C ₉₂ H ₉₆ Cl ₂ N ₈ P ₄ S ₁₆ Zn ₃	44.56 (50.0)	4.03 (4.3)	5.12 (5.06)	23.07 (23.1)	P, 5.16 (5.6)	Zn, 11.05 (8.1)
						Cl, 3.52 (3.2)	
52	C ₂₄ H ₄₈ N ₁₀ S ₁₆ (Mn—Zn) ₃	26.70 (25.0)	4.95 (4.16)	11.85 (12.1)	40.79 (44.4)		Mn, 11.1; Zn, 0.7

TABLE II (Continued)

Ex. No.	Empirical Formula	Analysis*				Halogen or Phosphorus	Metal
		C	H	N	S		
53	$C_{26}H_{52}N_{10}O_2S_{16}(Mn-Zn)_3$	26.90 (25.9)	4.62 (4.3)	10.88 (11.5)	39.00 (42.3)		Mn, 10.5; Zn, 0.9
54	$C_{26}H_{52}N_{10}O_2S_{16}(Ni-Zn)_3$	22.24 (25.6)	3.54 (4.2)	10.54 (11.4)	40.24 (41.7)		Ni, 6.91; Zn, 3.11

Calculated values are in parentheses.

The onium metal chelates of the invention possess biocidal properties and in this respect are especially useful as agricultural fungicides. These biocidal preparations may be used as prepared in an essentially pure form from which water-soluble impurities have been leached or in their relatively crude form. When so used, it is usually desirable to reduce the particle size to a small diameter. A preferred range of particle size is from 0.5 to 3 microns.

For use as pesticides one or more of the onium metal chelates are usually present in compositions containing, apart from the active chelate(s), one or more of the following, namely another pesticide, a solid diluent, a liquid diluent, or a surface active agent, such as a wetting, dispersing or spreading agent. For example, the onium metal chelates may be formulated as wettable powders, dusts, granular formulations, aerosols, emulsifiable con-

centrates or flowable emulsion concentrates. In such formulations, suitable surfactants are usually incorporated.

Compounds of this invention may be dissolved in a water-miscible liquid such as dimethylformamide or dimethyl sulfoxide. Such solutions are easily extended with water. Some compounds of this invention can form up to 50% solutions by weight in these solvents. Such solutions are eminently suitable for low-volume spray applications.

The onium metal chelates may be taken up on or mixed with a finely particled solid carrier, as, for example, clays, inorganic silicates, carbonates, and silicas. Organic carriers may also be employed. Dust concentrates are commonly made wherein the onium metal chelates are present in the range of 20 to 80%. For ultimate application these concentrates are normally extended with additional solid from about 1 to 20%.

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Wettable powder formulations are made by incorporating the compounds of this invention in an inert, finely divided solid carrier along with a surfactant which may be one or more emulsifying, wetting, dispersing or spreading agents or a blend of these. The onium metal chelates are usually present in the range of 10 to 80% by weight and the surfactants in from 0.5 to 10% by weight.

Commonly used emulsifying and wetting agents include polyoxyethylated derivatives of alkylphenols, fatty alcohols, fatty acids, alkylamines, alkylarene sulfonates, and dialkyl sulfosuccinates. Spreading agents include such materials as glycerol mannitan laurate and a condensate of polyglycerol and oleic acid modified with phthalic anhydride. Dispersing agents include such materials as the sodium salt of the copolymer of maleic anhydride and an olefin such as diisobutylene, sodium lignin sulfonate and sodium formaldehydenaphthalene sulfonates.

Flowable emulsion concentrate formulations may be made by dispersing the onium metal chelates of this invention into water, which may optionally contain an agronomically acceptable organic solvent, and one or more surfactants such as an emulsifying, wetting or suspending agent. A suitable organic solvent is dimethylformamide. The surfactants useful for these formulations may constitute about 0.5% to 10% by weight of the flowable emulsion concentrate and may be anionic, cationic or nonionic in character. Anionic surfactants include alcohol sulfates or sulfonates, alkylarene sulfonates and sulfosuccinates. Cationic surfactants include fatty acid alkyl amine salts and fatty acid alkyl quaternaries. Nonionic emulsifying agents include ethylene oxide adducts of alkylphenols, fatty alcohols, mercaptans and fatty acids. The concentration of the active ingredients may vary from 10 to 80%, preferably in the range of 25 to 50%.

Ready-for-use compositions containing the chelates will usually contain an agronomically acceptable carrier by which is meant any substance which can be used to dissolve, dispense or diffuse the toxic agent to be used therein without impairing its effectiveness and which does no permanent damage to such environment as soil, equipment and agronomic crops. The most usual of such carriers are water or finely divided inert solids.

For use as pesticides, the chelate compounds should be applied in an effective amount sufficient to exert the desired biocidal activity by techniques well known in the art. These include conventional high gallonage hydraulic sprays, low-gallonage sprays, airblast sprays, aerial sprays and granular and dust applica-

tions. This includes the application of the quaternary metal chelates to the loci to be protected in an effective amount either alone or when incorporated in an agronomically acceptable carrier. Generally the chelate compounds will be applied so as to control the growth of fungi on crops yielding a vendible product.

Dilute sprays may be applied at concentrations of 0.05 to 20 pounds of the active ingredient per 100 gallons of spray (U.S. gallons are used throughout this specification). They are usually applied at 0.1 to 10 pounds per 100 gallons and preferably at 0.125 to 5 pounds per 100 gallons. In more concentrated sprays, the active ingredient is increased by a factor of 2 to 12. With dilute sprays, applications are usually made to the plants until run-off is achieved, whereas with more concentrated sprays the materials are applied as mists.

In general, the compounds of the invention are exceptionally easily dispersed. For fungicides of the dithiocarbamate class, it is usually desired to use a minimum of formulation aids in order to obtain maximum active ingredient levels. Thus, the ease of dispersion of the instant product is a particularly advantageous property.

The compounds of this invention may be used as the sole pesticidal agents or they may be used in conjunction with other fungicides or with insecticides, miticides and comparable pesticides, or with plant nutrients. For example they can be used with fungicides such as dinitro(1 - methylheptyl)phenyl crotonate, N - trichloromethylthiotetrahydrophthalimide, sulfur, N - dodecylguanidine acetate, fixed coppers, fungicidal oils and antibiotics. They can be used with insecticides, such as DDT, benzene hexachloride, phosphatics such as parathion and S - (1,2 - dicarboethoxyethyl)-O,O - dimethyldithiophosphate, rotenone, lead arsenate and 1 - naphthyl N - methylcarbamate, and with miticides, such as 1,1 - bis(p-chlorophenyl)2,2,2 - trichloroethanol and 2,4,4',5 - tetrachlorophenyl sulfone.

Initial fungicidal evaluations of the quaternary ammonium metal chelates were derived from the standard slide spore germination test [cf. *Phytopathology*, 33, 627 (1943)], utilizing spores of *Alternaria solani* (Alt.), *Sclerotinia fructicola* (Scl.) and *Stemphylium sarcinaeforme* (Stem.) or *Botrytis cinerea* (Bot.). Table III exhibits the results so obtained in terms of concentration in parts per million (ppm.) of the test compound which effectively controlled 50% of the spores (ED₅₀).

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TABLE III
Fungitoxicities of Onium Metal Chelates

Ex. No.	Alt.	Scl.	Stm. (Bot.)
1	<1	<1	<1 ^a
2	10—50	50—200	10—50
3	<1	<1	1—10 ^a
4	10—50	200—1000	50—200 ^a
5	>1000	>1000	>1000
6	<1	<1	1—10
7	<1	10—50	10—50 ^a
8	<1	10—50	1—10 ^a
9	1—10	10—50	1—10 ^a
10	1—10	10—50	10—50 ^a
11	<1	1—10	1—10 ^a
12	<1	<1	<1 ^a
13	<1	<1	1—10 ^a
14	<1	1—10	1—10 ^a
15	<1	<1	1—10 ^a
16	<1	<1	1—10 ^a
17	<1	<1	1—10 ^a
18	<1	10—50	1—10 ^a
19	<1	10—50	1—10
20	50—200	50—200	50—200 ^a
21	50—200	200—1000	10—50
22	200—1000	50—200	200—1000
23	10—50	50—200	1—10 ^a
24	<1	10—50	<1
25	1—10	50—200	10—50
26	200—1000	200—1000	50—200
27	1—10	1—10	1—10
28	10—50	50—200	10—50

TABLE III (Continued)

Ex. No.	Alt.	Scl.	Stm. (Bot.)
29	50—200	>1000	10—50
30	200—1000	200—1000	200—1000
31	50—200	200—1000	200—1000 ^a
32	<1	<1	1—10 ^a
33	>1000	>1000	10—50 ^a
34	10—50	10—50	10—50
35	200—1000	>1000	200—1000 ^a
36	200—1000	200—1000	50—200
37	1—10	50—200	1—10
38	50—200	200—1000	50—200
39	<1	10—50	1—10
40	<1	<1	1—10 ^a
41	<1	50	<1
42	50—200	50—200	10—50
43	10—50	50—200	10—50
44	<1	<1	<1
45	<1	<1	<1
46	<1	<1	<1
47	<1	<1	<1
48	<1	<1	<1
49	1—10	50—200	1—10 ^a
50	10—50	1—10	1—10 ^a
51	<1	<1	1—10 ^a
52	<1	<1	1—10 ^a
53	10—50	10—50	50—200 ^a
54	10—50	>1000	10—50 ^a

^a Means that *Botrytis cinerea* was the test fungus.

As shown in the slide spore data of Table III, the onium metal chelates disclosed herein possess exceptional biocidal characteristics. Because of these properties, they have proven to be particularly valuable for the control of fungicidal diseases on agronomic crops.

Specific control of *Peronospora parasitica*, the causal agent of downy mildew on broccoli and other crucifers, was exhibited by the compounds of Examples 2, 3, 18, 24, 25, 28, 30, 37 and 39. In this test, six-week old broccoli plants were sprayed with aqueous suspensions of the test chemicals, dried, then weathered in a fog chamber overnight. The dried plants were inoculated with an aqueous suspension of *Peronospora parasitica* sporangia containing 15,000 sporangia per milliliter and incubated at 53° F. for about 40 hours. Plants not treated with chemicals were included for check purposes. All plants were then placed on a greenhouse bench and stored at about 70° F. to allow disease lesions to develop and 6 to 8 days later the lesions were counted. Representative compounds of this invention gave good to excellent control of this disease.

In another greenhouse observation, several of the quaternary metal chelates were examined for their ability to control rice blast cause by *Piricularia oryzae*. In this examination, young rice plants at the 2 to 3 true leaf stage were sprayed until run-off with the test compounds dissolved in an appropriate solvent or suspended in water. After drying, the plants were placed in a fog chamber overnight. They were then removed from the fog chamber and allowed to remain on a greenhouse bench all day and night. On the third day, the plants were subjected to an artificial rain equivalent to 1.5 inches in about 7 minutes. After drying, the plants were inoculated with spore suspension of 25,000 to 30,000 conidia per ml. of *Piricularia oryzae*. Again, the plants were placed in a fog chamber overnight. Following their removal from the fog chamber, the plants were maintained in a humid environment for another day, after which time they were placed on a greenhouse bench until the disease lesions appeared. This usually occurred in about 4 to 6 days. At this point, the lesions were counted and the results compared with control plants. Those compounds described in Examples 1, 2, 12, 27, 28, 37, 39 and 40 exhibited fair to excellent control of rice blast.

Compounds of this invention, such as Example 3, have given good control of barley helminthosporium disease, *Helminthosporium teres*.

The molecular structure of the onium compounds of this invention appear to exert a considerable effect upon the fungicidal properties of these materials. For example, the onium compounds of the invention containing zinc

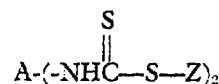
as the sole metal ion are effective as fungicides at significantly lower dosages than for zinc ethylenebisdithiocarbamate.

The structural formulas as given present one depiction of the structures of this invention, but they are not necessarily the only ones possible. This invention is intended to cover the products as made by the processes described irrespective of what the exact structures may be. Judging from the relatively low decomposition points of the compounds of this invention, the structures would appear to exist in a monomeric or in a low molecular weight form. The structural formulas exemplify a unit in the structure and are intended to embrace both the monomeric and polymeric structures.

WHAT WE CLAIM IS:—

1. A process for the preparation of onium metal bisdithiocarbamate chelates which comprises reacting in solution:

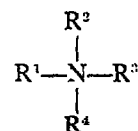
(1) a bisdithiocarbamate of the formula



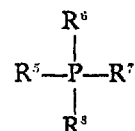
where A is a phenylene or C₂—C₆ alkylene group and Z is a cation,

(2) a source of one or more of the following metal ions, namely cadmium, cobalt, copper, iron, manganese, nickel and zinc ions, and

(3) an onium salt where the onium group is a morpholinium, imidazolium, (C₁—C₆)-alkyl imidazolium, 1 - (2 - hydroxyethyl)-2 - N - alkylcarbamoylimidazolium wherein the alkyl is 1 to 24 carbon atoms, N - (C₁—C₆)-alkyl pyridinium, alkylene-diammonium wherein the alkylene is 2 to 6 carbon atoms, the group



wherein R¹, R², R³ and R⁴ represent individually alkyl of 1 to 24 carbon atoms, cycloalkyl, aryl, benzyl, alkyl-substituted benzyl containing up to 12 alkyl carbon atoms hydroxy-alkyl of 1 to 4 carbon atoms, or hydrogen except that, when R¹, R² and R³ each represent hydrogen, R⁴ must be a group other than hydrogen or methyl; the group



wherein R⁵, R⁶, R⁷ and R⁸ represent, individually, alkyl of 1 to 24 carbon atoms, mono-



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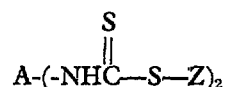
as the sole metal ion are effective as fungicides at significantly lower dosages than for zinc ethylenebisdithiocarbamate.

The structural formulas as given present one depiction of the structures of this invention, but they are not necessarily the only ones possible. This invention is intended to cover the products as made by the processes described irrespective of what the exact structures may be. Judging from the relatively low decomposition points of the compounds of this invention, the structures would appear to exist in a monomeric or in a low molecular weight form. The structural formulas exemplify a unit in the structure and are intended to embrace both the monomeric and polymeric structures.

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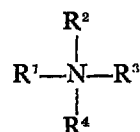
(1) a bisdithiocarbamate of the formula



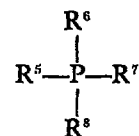
where A is a phenylene or C₂—C₆ alkylene group and Z is a cation,

(2) a source of one or more of the following metal ions, namely cadmium, cobalt, copper, iron, manganese, nickel and zinc ions, and

(3) an onium salt where the onium group is a morpholinium, imidazolium, (C₁—C₆)-alkyl imidazolium, 1 - (2 - hydroxyethyl)-2 - N - alkylcarbamoylimidazolium wherein the alkyl is 1 to 24 carbon atoms, N - (C₁—C₆ - alkyl pyridinium, alkylene-diammonium wherein the alkylene is 2 to 6 carbon atoms, the group



wherein R¹, R², R³ and R⁴ represent individually alkyl of 1 to 24 carbon atoms, cycloalkyl, aryl, benzyl, alkyl-substituted benzyl containing up to 12 alkyl carbon atoms hydroxy-alkyl of 1 to 4 carbon atoms, or hydrogen except that, when R¹, R² and R³ each represent hydrogen, R⁴ must be a group other than hydrogen or methyl; the group



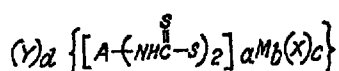
wherein R⁵, R⁶, R⁷ and R⁸ represent, individually, alkyl of 1 to 24 carbon atoms, mono-



alkylamino and dialkylamino groups wherein the alkyl radicals contain from 1 to 24 carbon atoms, or aryl, benzyl or alkyl-substituted benzyl containing up to 12 alkyl carbon atoms.

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2. A bis-dithiocarbamate of the formula



wherein A is a straight or branched chain alkylene group of 2 to 6 carbon atoms or phenylene;

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a is the integer 2 or 4;

M is at least one of cadmium, cobalt, copper, iron, manganese, nickel and zinc;

b is the integer 1, 3 or 4;

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X is at least one anion which complexes with metal M;

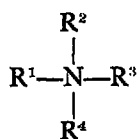
C is 0 or an integer from 1 to 4;

d is an integer from 1 to 4;

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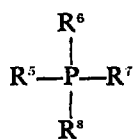
Y is an onium group which is a morpholinium, imidazolium, (C_1-C_6) -alkyl imidazolium, 1 - (2 - hydroxyethyl) - 2 - N - alkylcarbamoylimidazolium wherein the alkyl is 1 to 24 carbon atoms, (C_1-C_6) -alkyl pyridinium, (C_2-C_6) -alkylenediammonium, the group

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wherein R^1 , R^2 , R^3 and R^4 each represent a (C_1-C_{24}) -alkyl, cycloalkyl, phenyl, benzyl, alkyl-substituted benzyl having up to 12 alkyl carbon atoms or (C_1-C_4) -hydroxyalkyl group, or hydrogen except that, when R^1 , R^2 and R^3 each represent hydrogen, R^4 is a group other than hydrogen or methyl; the group

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wherein R^5 , R^6 , R^7 and R^8 each represent a (C_1-C_{24}) -alkyl, monoalkylamino and dialkylamino groups wherein the alkyl radicals contain from 1 to 24 carbon atoms, phenyl, benzyl and alkyl-substituted benzyl containing up to 12 alkyl carbon atoms.

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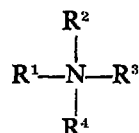
3. A bis-dithiocarbamate according to Claim 2, wherein X is halide.

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4. A bis-dithiocarbamate according to Claim 2, wherein M is at least one metal ion selected from the group cupric, ferric, manganous and zinc.

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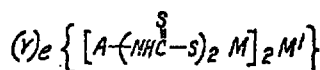
5. A bis-dithiocarbamate according to Claim 3, wherein Y is the group



wherein R^1 , R^2 , R^3 and R^4 each represent (C_1-C_{24}) - alkyl, (C_1-C_4) - hydroxyalkyl, benzyl or hydrogen with the proviso that when R^1 , R^2 and R^3 each represent hydrogen, R^4 is a group other than hydrogen or methyl.

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6. A bis-dithiocarbamate of the formula



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wherein A is (C_2-C_6) -alkylene or phenylene;

M and M' are at least one of cadmium, cobalt, copper, iron, manganese, nickel and zinc;

Y is as defined in Claim 2; and

e is 1 or 2

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7. A bis-dithiocarbamate according to Claim 6, wherein A is ethylene.

8. A bis-dithiocarbamate according to Claim 7, wherein Y is dimethylammonium, M and M' are zinc, and e is 2.

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9. A bis-dithiocarbamate according to Claim 7, wherein Y is trimethylammonium, M and M' are zinc, and e is 2.

10. A bis-dithiocarbamate according to Claim 7, wherein Y is tetramethylammonium, M and M' are zinc, and e is 2.

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11. A bis-dithiocarbamate according to Claim 7, wherein Y is (2-hydroxyethyl)trimethylammonium, M and M' are zinc, and e is 2.

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12. A bis-dithiocarbamate according to Claim 7, wherein Y is ethylene - 1,2 - bis-ammonium, M and M' are zinc, and e is 1.

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13. A bis-dithiocarbamate according to Claim 7, wherein Y is morpholinium, M and M' are zinc, and e is 2.

14. A bis-dithiocarbamate according to Claim 7, wherein Y is 1 - (2 - hydroxyethyl) - 2 - N - tert - octadecylcarbamoylimidazolium, M and M' are zinc, and e is 2.

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15. A bis-dithiocarbamate according to Claim 7, wherein Y is tetramethylammonium, M is manganese, M' is zinc, and e is 2.

16. A bis-dithiocarbamate according to Claim 7, wherein Y is tetra(2 - hydroxyethyl)-ammonium, M and M' are zinc, and e is 2.

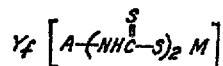
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17. A bis-dithiocarbamate according to Claim 7, wherein Y is tetra(tert - octylamino)-phosphonium, M and M' are zinc, and e is 2.

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18. A bis-dithiocarbamate of the formula



wherein Y, A and M are as defined in Claim 2 and f is 1 when M is trivalent and 2 when M is divalent.

19. A bis-dithiocarbamate according to Claim 18, wherein M is ferric or manganous.

20. A bis-dithiocarbamate according to Claim 18, wherein A is ethylene.

21. A bis-dithiocarbamate according to Claim 20, wherein Y is benzyltrimethylammonium and M is ferric.

22. A bis-dithiocarbamate according to Claim 20, wherein Y is benzyltrimethylammonium and M is manganous.

23. A process according to Claim 1 as applied to the preparation of a compound according to any one of Claims 2—22.

24. Onium metal chelates when prepared by a process according to Claim 1 or 23.

25. A fungicidal composition containing as active ingredient a chelate according to Claim 24.

26. A fungicidal composition containing as active ingredient a compound according to any one of Claims 2—22.

27. A composition according to Claim 25 or 26 containing another pesticide, a solid diluent, a liquid diluent or a surface active agent.

28. A method for the control of phytopathogenic fungi on a crop yielding a vendible product which comprises applying to the crop area a composition according to any one of Claims 25—27.

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