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## COMPLETE SPECIFICATION

### Metal Bisdithiocarbamate Complexes

5 We, ROHM & HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 222 West Washington Square, Philadelphia 5, Pennsylvania, 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:—

10 This invention is concerned with new complex metal salts of fungicidally active water-insoluble manganese alkylenebisdithiocarbamates, e.g. manganese ethylenebisdithiocarbamate, manganese propylenebisdithiocarbamate, and manganese trimethylene bisdithiocarbamate. The invention also concerns methods of inhibiting fungal disease in plants yielding a vendible crop by applying to the plant one or more of the new complex metal salts.

20 The most preferred aspect of this invention is concerned with new complex metal salts of maneb. Maneb is the given common name for the well-known relatively insoluble fungicide, manganese ethylene bisdithiocarbamate. As is known, there are several forms of manganese ethylenebisdithiocarbamate, one of which is soluble in water. The relatively insoluble version is formed as a precipitate when a soluble manganese salt and a soluble salt of ethylenebisdithiocarbamic acid are brought together in relatively concentrated solutions. When, on the other hand, dilute solutions of the two kinds of salts are brought together, no precipitate occurs since the resulting product is freely soluble. For example, when two to three pounds of manganese sulfate is added to 100 gallons of water containing an equivalent amount of disodium ethylenebisdithiocarbamate, no precipitate is formed, but, on the other hand, when the same amounts of reactants are added to three gallons of water or less, a precipitate rapidly forms and can be isolated. This separated precipitate is the type of manganese ethylenebisdithiocarbamate

which is identified herein as maneb.

In accordance with the present invention, there is provided a water-insoluble metal complexed manganese alkylenebisdithiocarbamate in which the complexing metal component comprises one or more of the metals: cobalt, copper, iron and zinc.

X-ray powder diffraction diagrams of the complex metal salts indicate the presence of the manganese alkylene bisdithiocarbamate skeleton as opposed to the presence of the skeleton of the alkylene bisdithiocarbamic acid salt of the complexing metal. From metal complexed maneb's there have been obtained X-ray powder diffraction diagrams with lines with relative intensities at 8.04 Å°(strong), 6.91 Å°(medium), 6.51 Å°(medium), 4.46 Å°(medium-strong), and 3.03 Å°(strong). In addition to the above-noted X-ray diffraction lines which are designated as medium to strong, there may be observed in some preparations very weak lines at 4.15 Å°, 4.04 Å°, 3.32 Å°, and 3.21 Å°. While the above X-ray data are also characteristic of the corresponding non-complexed maneb's, they differ from the X-ray data for zineb and this shows that the zinc in the compounds of the invention is not present as zineb.

The X-ray powder diffraction diagrams referred to in this specification are powder photographs giving lines corresponding to interplanar spacings in the crystal lattice of the values stated.

A preferred class of complex metal bisdithiocarbamates provided by the invention are those containing, per 20 parts by weight of manganese, at least 0.1 part by weight of complexing metal in the form of cobalt, copper, iron, zinc or mixtures thereof and not more than 13, 4, 50 and 10 parts by weight of cobalt, copper, iron and zinc respectively. Typical examples of such complex salts are: (a) a zinc complexed manganese salt containing 0.1 to 10 parts of zinc, (b) a cobalt complexed manganese salt containing 0.2 to 13

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parts of cobalt, (c) a copper complexed manganese salt containing 2.0 to 4.0 parts of copper, and (d) an iron complexed manganese salt containing 0.1 to 50 parts of iron. In the above listed typical complex salts, in which, the parts of the complexing metal are parts by weight per 20 parts by weight of maneb, the carbon disulfide content on analysis will usually be from 38% to 57.4% based on the weight of the complex salt and the man-

gane content will usually be from 13.8% to 20.7% based on the weight of the complexed salt.

Within the class of metal complexed maneb described above, the various complexed maneb tabulated below are of particular utility as fungicides. In the table, figures in parentheses indicate preferred amounts of complexing metal.

TABLE I

| Nature of Complex Salt. | Complexed Metal Mn Ratio* |
|-------------------------|---------------------------|
| Zinc complexed maneb    | 0.1-7 (0.2-3)             |
| Cobalt complexed maneb  | 0.25-10 (0.4-6)           |
| Copper complexed maneb  | 0.2-2.5 (0.5-1)           |
| Iron complexed maneb:   |                           |
| A. Ferric               | 0.1-10 (0.6-4)            |
| B. Ferrous              | 1-50 (10-30)              |

\*Parts by weight of complexed metal per 20 parts by weight of Mn.

It is the metal complexed maneb described in Table I above which are referred to herein after as being the preferred products of the invention.

The preferred metal complexed maneb described in Table I particularly the zinc complexed salts, generally exhibit one or more desirable properties as fungicides not displayed by their non-complexed maneb counterpart. These desirable properties are (a) greater fungicidal activity for a given quantity of applied active ingredient, (b) greater persistence, (c) reduced phytotoxicity towards the growing plants upon which the growth of fungus is to be controlled or prevented and (d) fungicidal activity over a wider spectrum of fungal diseases.

The zinc, ferric and cobaltous maneb appear of greatest utility and, rather surprisingly, the copper-complexed maneb are of somewhat lesser utility although they still exhibit improved properties in one or more of the respects indicated above.

If the quantities of complexed metal specified above in connection with the preferred products of the invention are exceeded, it is generally found that the improved properties of the preferred products are diminished or lost. Increasing the amount of complexing metal decreases the solubility of the complex product and there appears to be a certain minimum solubility for each type of metal complex product which should be exhibited for best performance of the product. Also, with amounts of complexing metal substantially

exceeding the limits set for the preferred products, the products may show a higher degree of phytotoxicity than would normally be desired, particularly when copper is the complexing metal. Nevertheless, the broader class of products provided by the invention all exhibit useful fungicidal activity and constitute a hitherto unknown group of fungicidally active compounds.

The complex metal salts of the invention are prepared by reacting, in an aqueous medium, a water-insoluble manganese alkylene bisdithiocarbamate with at least one water-soluble salt of cobalt, copper, iron and zinc to complex the metal(s) of the water-soluble salt(s) with the manganese bisdithiocarbamate. In this reaction, any salt of an inorganic or organic acid which has a solubility of at least 5 parts by weight in 100 parts by weight of cold water is suitable.

The amount of water-soluble salt(s) employed will, in general, be such as to provide a ratio of complexing metal to manganese not exceeding that in the desired complexed product.

The reaction to prepare metal complexed maneb is conveniently water, maneb and one or more water-soluble salts at a temperature between 10° and 50° C. Thus, for example, an aqueous slurry of maneb may be mixed with a metal salt or mixture of metal salts or an aqueous solution of the latter. Alternatively, powdered maneb may be mixed with aqueous metal salt solution.

The amount of water present during the

reaction is primarily a matter of convenience and practical handling. Where drying follows reaction, it is, of course, desirable to have present merely enough water to ensure adequate mixing of reactants and uniformity of product. With maneb as reactant, this minimum depends in part upon the particular nature or state of the maneb, which may be in the form of a slurry as obtained from its precipitation from reacting in water a soluble manganese salt, such as manganous sulfate, chloride, or nitrate and a water-soluble salt of ethylene bisdithiocarbamic acid, such as the lithium, sodium, potassium, calcium, magnesium, ammonium, or quaternary ammonium salts. As is known, such precipitation does not occur when the concentration of ethylenebisdithiocarbamate in water is less than about 2%, since the manganese salt which forms by interaction is a soluble salt, probably the cyclic salt, a monomeric form. At least 5% of slurry is necessary to ensure formation of a chain of manganese and acid ions. The maneb as thus obtained is in hydrated form. It may be used as such or it may be washed and it may be partially or completely dehydrated.

In general, the proportion of maneb, hydrated or dried, to water is 5:95 to 65:35 by weight and preferably 40:60 to 60:40.

Reaction between metal salt and maneb in water takes place in a relatively short time. In general, times from about ten minutes to about five hours allow for essential completion of the reaction. These times represent the period within which salt in solution is in contact with maneb in suspension before the reaction product is used, isolated, or dried. In a continuous process wherein salt, water, and maneb are continuously mixed and the resulting product is separated and/or dried, the residence time is within the stated time limits.

The reaction product may be separated as by filtering or centrifuging and may then be dried below decomposition temperatures. If desired, the filtered or centrifuged product may be washed before drying. On the other hand, the entire reaction mixture may be dried, leaving, of course, soluble salts in the product thus obtained.

Drying may be accomplished under normal or reduced pressure. Spray drying may be practiced or vacuum drum drying or tray drying. For example, the reaction product is desirably dried between 40° and 85°C. under reduced pressures, desirably at pressures of 5 to 30 mm. (Hg). In spray drying inlet gas temperatures up to about 315°C. may be used, but under these conditions the temperature of the drying particles remains well below the decomposition point. Under any of the drying conditions, the temperature of the product is below 90° C.

After the product has been dried, it may be desired to render the product more finely divided, as by grinding or sieving. For this

purpose, there may be used micropulverizing, micronizing, crushing, and screening, or other comminuting steps. To ensure finely divided products, there may be utilized at one or more stages of preparation a dispersing agent, such as sodium lignin sulfonate, sodium naphthalene - formaldehyde sulfonate, or sodium dioctylsulfosuccinate.

If desired, a stabilizing agent may be admixed with the metal-complexed manganese bisdithiocarbamate as by addition of hexamethylenetetramine to the slurry to be dried or to the dried product. The use of hexamethylenetetramine as a stabilizer for manganese salts of alkylenebisdithiocarbamic acid is claimed in our copending Application No. 28195/59 (Serial No. 929,210).

Soluble salts of the above-noted complexing metals include chlorides, nitrates, acetates, and sulfates. Convenient salts are zinc chloride, zinc sulfate, zinc nitrate, zinc acetate, ferrous sulfate, ferric chloride, ferric nitrate, ferric sulfate, cobalt chloride, cobalt sulfate, cobalt nitrate, cupric sulfate, cupric chloride, cupric acetate, and cupric nitrate. Salts may be used in any of the usual forms, including hydrated forms, and may be used as such or as solutions. As above indicated, mixtures of salts or solutions of several salts may be used, such as cobalt and zinc salts or copper and zinc salts.

When maneb and added metal salts are brought together in water under appropriate conditions, a reaction occurs whereby the metal ion is taken up by the maneb. The X-ray powder diffraction diagram for the reaction product has the medium and strong lines indicated above and lacks lines which would correspond to the ethylenebisdithiocarbamate of the added metal. Hence, the product is not a mixture of maneb and another ethylenebisdithiocarbamate. Furthermore, the new product has some properties differing from those of the salt or ethylenebisdithiocarbamic acid corresponding to that formed with the added metal salt and also from those of maneb.

The proportions of metal salts added to maneb and which provide the development of particularly desirable properties vary somewhat from metal to metal. Since there may be used any soluble salt of these metals, it is most convenient in defining steps of preparation to express the proportion of reacting salt to maneb in terms of the percent of metal ion by weight of maneb. The effect of zinc ions and development of new properties begins to be noticeable with about 0.1% of zinc ion based on weight of maneb and desirable properties of the complex are noticed up to about 7% of zinc ion. The preferred proportions of zinc, however, are 0.2% to 3% of zinc ion. The optimum proportion of zinc ion depends in minor degree upon the particular preparation of maneb and also upon whether it is in hydrated or dried form. In any case, the optimum proportions of metal ion will be those

providing enhanced disease control with minimum harm to plants. The optimum proportions for copper are from about 0.2% to about 2.5%, with 0.5% to 1.0% preferred, calculated as copper ion based on the weight of maneb. With ferric salts the optimum limits are from 0.1% to 10%, with 0.6% to 4.0% preferred. Ferrous salts appear to develop a complex at 1% to 50% of ferrous ion, preferably between 10% and 30%, but changes other than complex formation occur with the ferrous ion including its oxidation. With cobalt, the optimum limits are 0.25% to 10% of cobaltous ion, with 0.4% to 6% preferred.

The following examples present typical preparations of reaction products of this invention. Parts are by weight and meshes are U.S. Standard Sieve series unless otherwise designate.

#### EXAMPLE 1

There were reacted equimolar amounts of disodium ethylenebisdithiocarbamate and manganous chloride in concentrated aqueous solution. A precipitate formed which was washed by decantation three times to give an aqueous slurry containing 38% of hydrated manganese ethylenebisdithiocarbamate. A portion of 800 parts of this slurry was mixed with a separately prepared solution of 24.5 parts of zinc nitrate hexahydrate in 25 parts of water. The resulting mixture was stirred for one-half hour at 30°C. and was spray dried, the inlet gas temperature being 280°C. and the outlet temperature 125°C. The dry solid which formed was micronized. Product collected amounted to 272 parts.

By analysis this product contained 47.5% of carbon disulfide, 17.3% manganese, and 1.7% of zinc. It is a complex salt in which maneb is modified by reaction with zinc ions. It shows the typical medium and strong X-ray lines given earlier.

#### EXAMPLE 2

A slurry was prepared from 400 parts of a commercial maneb and 250 parts of water. This commercial material by carbon disulfide analysis contained 352 parts of manganous ethylenebisdithiocarbamate. To the agitated slurry were added 27.5 parts of zinc sulfate monohydrate and 50 parts of water. The mixture was stirred for an hour at 28° to 31° C. and then dried under reduced pressure. The maximum temperature reached was 80° C. while the pressure was reduced to 20 mm. The dried batch was cooled to about 40° C. and the drier was vented with nitrogen before discharge.

The dried product was micropulverized under a 0.02-inch herringbone screen with six hammers operating at 6,950 rpm. The product amounted to 367 parts and contained by analysis 46.9% of carbon disulfide, 18.9% of manganese, and 2.7% of zinc.

X-ray studies of the products prepared in the above examples show that the product is not a mixture of maneb and zineb. Infrared absorption curves have lines not occurring with pure zineb and mixtures of zineb and maneb. The products are complex zinc-containing manganese ethylenebisdithiocarbamates.

When zinc is used as the complexing metal, the water-insoluble product will usually contain from 19.2% to 20.7% of manganese. When the product as made contains non-manganese containing impurities such as water-soluble salts, the percent of manganese will, of course, appear proportionately less. The carbon disulfide content of the zinc complex as such will usually vary from 53% to 57.4%. When impurities are present, as when salts are not washed out, carbon disulfide analyses may be as low as 42%.

#### EXAMPLE 3

Manganese ethylenebisdithiocarbamate was prepared by mixing a concentrated aqueous solution of disodium ethylenebisdithiocarbamate and a concentrated aqueous solution of manganous sulfate, filtering off the resulting precipitate, washing it with water, washing it with methanol, and drying the resulting solid at ambient temperatures. There were mixed 635 parts of this solid, 650 parts of water, and a solution of 24.8 parts of cupric sulfate pentahydrate in 30 parts of water. This mixture was agitated for two hours at 27° to 30° C. Pressure on the reaction mixture was reduced to 12 mm. and later to 8 mm., while the temperature thereof was raised to 75° C. A solid product was thus obtained in an amount of 522 parts. It contained by analysis 48.3% of carbon disulfide, 19.9% of manganese, and 1.1% of copper.

The product is a complex copper-manganese salt of ethylenebisdithiocarbamic acid, as shown by infrared and X-ray data. The water-insoluble copper-complexed maneb usually yields 56% to 57.2% of carbon disulfide while the crude reaction product may yield from 44% upwards.

#### EXAMPLE 4

There were mixed 200 parts of a 50% slurry of precipitated manganese ethylenebisdithiocarbamate dihydrate in water and 5.5 parts of zinc sulfate monohydrate at 25° to 30° C. The mixture was agitated for two hours. It was then charged to a vacuum drier. Pressure was reduced to 28 mm. and the temperature of the batch was raised gradually to 76° C. The product was cooled to about 30° C. and then ground to pass a 325 mesh screen. The product contained 48.2% of carbon disulfide, 17.5% of manganese, and 1.9% of zinc. X-ray and infrared data show this product to be a complex zinc-manganese salt of ethylenebisdithiocarbamic acid.

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## EXAMPLE 5

A suspension was prepared from 5 parts of a commercial maneb containing 85% manganese ethylenebisdithiocarbamate (by analysis for carbon disulfide) and 95 parts of water. To this suspension was added one part of zinc sulfate heptahydrate. The mixture was stirred for two hours at 24° to 27° C. The reaction mixture was then spray dried with gas inlet temperatures of 280°—290° C. an outlet temperature of about 125° C. The product was a finely particled solid which was passed through a 325 mesh screen to give 4.2 parts of a complex zinc-manganese salt of ethylenebisdithiocarbamic acid. The product contained 4.3% of zinc and 48% of carbon disulfide.

The above procedure is repeated with the use of one-half part of zinc sulfate heptahydrate and one part of cobalt nitrate hexahydrate. The product is a complex containing 3.8% of cobalt, 2.1% of zinc, 16.1% of manganese, and 45% of carbon disulfide.

## EXAMPLE 6

Pure manganese ethylenebisdithiocarbamate dihydrate was suspended in aqueous 70% methanol to give a 37% slurry. There were mixed 100 parts of this slurry and 1.2 parts of aqueous 70% zinc chloride solution. The mixture was agitated at 30° C. for an hour. Water and methanol were removed by heating the mixture under reduced pressures, the temperature being about 75° C. and the pressure being reduced to 3 mm. The product was carefully leached of soluble salts and dried under reduced pressure at 50° C. The product was micropulverized. It was demonstrated to be essentially free of soluble zinc salt or zineb and was a complex salt of zinc and manganese ethylenebisdithiocarbamate. This product contained 0.9% of zinc, 20.4% of manganese, 56% of carbon disulfide, 17.8% of carbon, 2.2% of hydrogen, and 10.2% of nitrogen.

## EXAMPLE 7

Commercial maneb was used. By carbon disulfide analysis, it contained 81.4% of manganese ethylenebisdithiocarbamate. Over a period of one hour 4300 parts of this material were added with stirring to a solution of 231 parts of cobalt chloride hexahydrate in 5050 parts of water. The resulting suspension was stirred for two hours at 31°—33° C. It was spray dried with an average temperature of inlet gas of 286° C. and an average outlet temperature of 123° C. The dry product was pulverized in an air mill to give 3340 parts of a complex cobalt-containing manganese ethylenebisdithiocarbamate, containing by analysis 47.1% of carbon disulfide, 17.4% of manganese, and 1.3% of cobalt. This product is a complex cobalt-containing manganese ethylenebisdithiocarbamate.

When the starting maneb is of about 80% purity and the entire reaction mixture is dried,

the carbon disulfide content typically varies from 41.9% to 45.9%. When purified maneb is used and soluble salts are removed, the product typically contains 52.3% to 57.3% of carbon disulfide.

## EXAMPLE 8

Pure manganese ethylenebisdithiocarbamate dihydrate was heated at 63° to 67° C. in a vacuum tray dried at one to 1.5 mm. pressure for 8 hours and was thus converted to the anhydrous form. A portion of 10 parts of this dried maneb was slurried in a solution of 0.5 part of zinc sulfate in 10 parts of water. This slurry was stirred for an hour at 25° to 30° C. and then vacuum tray dried for 27 hours. The drier was heated with water maintained at 75° C. and the pressure therein was 6 to 15 mm. The dried material was passed through a 325 mesh screen to yield 9.1 parts of a complex zinc-containing manganese ethylenebisdithiocarbamate. This product was washed with water and with methanol and dried at 50° C. at 5 mm. pressure. This product contained 1.9% of zinc, 20.3% of manganese, 56% of carbon disulfide, 17.6% of carbon, 2.3% of hydrogen, and 10.2% of nitrogen.

## EXAMPLE 9

To an agitated slurry of 532 parts of commercial maneb (85% manganese ethylenebisdithiocarbamate) in 368 parts of water was added a solution of 37.2 parts of zinc sulfate monohydrate in 67 parts of water. The mixture was agitated for four hours at 28° to 33° C. The mixture was filtered on a vacuum filter, the collected solids were washed with water, and the filter cake was dried for eleven hours in a vacuum oven at 75° C. and 6 to 15 mm. pressure. The dry material was micropulverized in a hammer mill equipped with a 0.02 inch herringbone sieve, a corrugated dome, and six hammers operating at 6,950 rpm. The final product amounted to 493 parts. It gave by analysis 47.3% of carbon disulfide, 19.1% of manganese, and 2.4% of zinc. It gave the X-ray and infrared lines typical of the complex salts based on maneb.

## EXAMPLE 10

Freshly precipitated manganese ethylenebisdithiocarbamate dihydrate was washed with water and methanol and dried at room temperature. There was slurried a portion of 30 parts this material and 70 parts of water. Thereto was added 1.1 part of ferric nitrate hexahydrate. The mixture was stirred at 30°—35° C. for two hours. The solid was filtered off, washed, and dried in a vacuum oven at 70° C./5 mm. for ten hours. The product comprised 24.6 parts of iron-manganese complex salt of ethylenebisdithiocarbamic acid, containing 52.5% of carbon disulfide, 20.2% of manganese, and 0.6% of iron.

The carbon disulfide content of ferric-

- complexed maneb usually is 52.3% to 57.4%, while, when commercial maneb is used and the reaction product is dried, as by spray drying, the carbon disulfide content may be as low as 41%.
- When ferrous salts are used to complex maneb, typical products may vary in carbon disulfide content from 30.8% to 56.9%, because of the considerable range in proportions of ferrous ions which may be complexed to provide improved properties. When pure maneb is used and soluble salts are removed, the carbon disulfide usually varies from 38.5% to 56.9%.
- The unique nature of the preferred complex salts herein described may be most readily seen from biological data. The first biological test here discussed is the "persistence test", in which (1) test plants, here tomato plants, are sprayed to run-off with suspensions of agents under evaluation in a dosage series, (2) the sprayed plants are dried, (3) the dried plants are subjected to a flow of finely atomized water for 16 hours, (4) the plants are dried again, (5) the plants are illuminated for four days, (6) the plants are inoculated with a suspension of 30,000 spores per milliliter of *Phytophthora infestans*, (7) plants are held at 52°—55° F. and 100% relative humidity (to incubate spores) for about 22 hours, (8) plants are stored in light for 42 hours, and (9) counts of lesions are made. From the counts at the different dosages there are now calculated the ED<sub>50</sub> values; that is, the dosage in parts per million of agent giving 50% control.
- This method of evaluation was used with zineb, maneb, mixtures of maneb and zineb, and complex zinc-manganese ethylenebisdi-thiocarbamates, one made by reacting maneb with 7% of its weight of zinc sulfate monohydrate (A) and the other with 3.5% of its weight of the same zinc salt (B). Test data are summarized in Table II, using tomato plants.

TABLE II

ED<sub>50</sub> Values for Persistence Tests on Tomatoes with *Phytophthora Infestans*

| Compound         | Zineb | Maneb | Mixtures* | A   | B   |
|------------------|-------|-------|-----------|-----|-----|
| ED <sub>50</sub> | 1132  | 360   | 400       | 162 | 183 |

\*Mixtures were maneb containing zineb equivalent to the zinc used in preparing A & B, approximately the same value being found for the two mixtures.

- These tests show the complex salts to be much more effective against *Phytophthora infestans* on tomatoes than the single salts or a mixture of these salts.

In another set of persistence tests, ED<sub>50</sub> values were obtained for zineb, maneb, mechanical mixtures of zineb and maneb, and the complex salt formed by reacting maneb with 10% of its weight of zinc sulfate monohydrate (C). Results are summarized in Table III.

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TABLE III

ED<sub>rrr</sub> Values for Late Blight on Tomatoes

| Ratio of Zineb to Maneb | ED <sub>60</sub> |
|-------------------------|------------------|
| 1:0                     | 1109             |
| 4:1                     | 675              |
| 2:1                     | 417              |
| 1:1                     | 407              |
| 1:2                     | 356              |
| 1:4                     | 345              |
| 0:1                     | 322              |
| Complex C               | 179              |

- 5 Late blight persistency data were obtained on a complex cobalt-manganese ethylenebis-dithiocarbamate made by reacting mane b with 3% of its weight of cobalt nitrate hexahydrate (D), a complex copper-manganese ethylenebis-dithiocarbamate made by reacting mane b with 5% of its weight of cupric nitrate trihydrate (E), a complex iron-manganese ethylenebis-dithiocarbamate made by reacting mane b with 50% of its weight of ferrous sulfate hepta-hydrate (F), and a complex iron-manganese ethylenebisdithiocarbamate made by reacting mane b with 10% of its weight of ferric nitrate nonahydrate (G). The results are given in Table IIIA in terms of ED<sub>50</sub> values. In the same set of tests comparison was made with the same lot of mane b used for preparation of above metal complexes.

TABLE IIIA

ED<sub>50</sub> Values for Late Blight on Tomatoes

| Agent     | ED <sub>50</sub> |
|-----------|------------------|
| Complex D | 187              |
| Complex E | 217              |
| Complex F | 173              |
| Complex G | 172              |
| Maneb     | 244              |

- 20 Stability tests on foliage also establish differences for the complex salts formed from mane b by reaction with a metal salt such as shown above. In this test plants are sprayed with suspensions of the compounds under study, usually at several rates of application. The treated plants are stored under favourable conditions in a greenhouse with water applied only to the soil in which the plants are growing. A leaf is taken at each test date and a

disc cut therefrom, the disc being 20 mm. in diameter. The disc is placed in an agar plate with spores of *Endomycopsis* spp. The plate is incubated and the zone of inhibition measured. Results are summarized in Table IV.

TABLE IV

Zone of Inhibition, in mm.

| Compound  | Rate lb/100 gal.* | Days | on Tomatoes |    |    | on Cucumbers |    |    |
|-----------|-------------------|------|-------------|----|----|--------------|----|----|
|           |                   |      | 1           | 8  | 15 | 1            | 8  | 15 |
| Maneb     | 0.75              |      | 35          | 30 | 21 | 39           | 33 | 23 |
|           | 0.375             |      | 31          | 21 | 21 | 23           | 27 | 21 |
| Complex A | 0.75              |      | 34          | 33 | 30 | 34           | 35 | 31 |
|           | 0.375             |      | 31          | 28 | 27 | 32           | 33 | 26 |
| Complex B | 0.75              |      | 36          | 36 | 30 | 37           | 37 | 34 |
|           | 0.375             |      | 32          | 28 | 26 | 35           | 33 | 29 |

\*Gallons referred to herein are U.S. gallons.

These data show that although at the beginning of the test all compounds had about the same activity, Complex A and Complex B retained a greater degree of biological activity with passage of time and growth of the plant.

The above results are representative for the various metal complexes formed from maneb by reaction with zinc, iron, cobalt, and copper salts within the proportions set forth in Table I.

Stability tests were conducted by spraying plastic discs with aqueous dispersions of modified complexed maneb reacted with metal salts, drying the sprayed discs, subjecting them to ultra-violet illumination, and measuring the zone of inhibition in agar plates seeded with *Endomycopsis* spp. The data established markedly less deterioration in films of the

complexed maneb than in films from maneb itself.

Comparisons were also made for various complexes from maneb with iron, cobalt, copper, and zinc against a mixture of 30% of commercial maneb and 70% of zinc ethylene-bisdithiocarbamate, zineb. (Mix Z). The various complexes and compounds were applied in sprays to field grown cucumber plants for control of downy mildew (*Pseudoperonospora cubensis*). A four-day spray schedule was followed. Applications were made at 0.75 lb. and 1.5 lbs. per 100 gallons. Readings were made about one month after the start of the spray schedule, the number of lesions being counted for 20 leaves picked at random.

The average counts obtained are recorded in Table V.

TABLE V

Control of Downy Mildew on Cucumbers

| Agent     | Lesions per Leaves |              |            |
|-----------|--------------------|--------------|------------|
|           | At 0.75 lb.        | at 1.50 lbs. | Mean Value |
| Complex A | 28                 | 8            | 15         |
| Complex B | 32                 | 16           | 22         |
| Maneb     | 73                 | 22           | 45         |
| Mix Z     | 65                 | 20           | 42         |

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Essentially the same values as shown for Complex A and Complex B are obtained with a complex formed from maneb and other metal ions shown above.

- 5 The control obtained with Complex A is matched with complexes formed by reacting 1% to 3% of cobalt nitrate hexahydrate and maneb in a slurry according to methods shown in the examples, or 10% of ferric nitrate nonahydrate and maneb in a slurry, or 3% of cupric trihydrate and maneb in a slurry.

- 10 The effectiveness of some of the complexes was well demonstrated with tests for controlling *Cercospora apii* on celery plants. After about seven weeks from the time of setting out celery plants in the field, a nine-day spray schedule was followed with maneb, zineb, the complex formed by reacting maneb with 5% of its weight of zinc sulfate monohydrate in a slurry (H), and the complex formed by reacting maneb with 7% of its weight of copper sulfate pentahydrate (I). After 63 days of this spray schedule, counts of *Cercospora* lesions were made on leaflets selected at random. The counts here are based on the number of lesions on 25 leaflets. With maneb at 1.5 lbs. per 100 gallons, the number of lesions was 121; with zineb at 1.5 lbs. per 100 gallons, 109; with Complex H at 1.5 lbs. per 100 gallons, 56; and with Complex I at 1.5 lbs. per 100 gallons, 50.

- 30 Parallel with the above, test plots of celery plants were subjected to the same spray schedules, but natural rain-fall was supplemented with overhead sprinkler irrigation. Under these conditions, counts were as follows:—maneb, 134; zineb, 84; Complex H, 18; and Complex I, 24.

- 35 Favourable results are also obtained in combating *Septoria apii* on celery, *Botrytis spp.* on strawberries, *Colletotrichum Lindemuthianum* and *Uromyces phaseoli* on beans, *Helminthosporium maydis* or *turcicum* on corn, *Cercospora spp.* on such crops as bananas, cowpeas, peanuts, and sugar beet, *Stemphylium solani* on tomatoes, and *Alternaria solani* on tomatoes or potatoes and powdery mildew on such plants as apples, cucurbits, grapes and roses.

- 50 In greenhouse tests, the preferred complexes of this invention were found to be generally less phytotoxic than the conventional manganese salt of ethylenedisithiocarbamic acid. These tests were conducted with tender, succulent tomato plants about one month old at the three-true-leaf stage. Such plants in the greenhouse are particularly susceptible to damage from applied chemicals and similar differential phytotoxic responses have been observed in the field. With this test it has been found that maneb causes measurable injury when applied at 0.5 lb. per 100 gallons. The complex salts formed with zinc ion have produced no injury when applied at 0.5 lb., 1.0 lb., and 2.0 lbs. per 100 gallons.

- 65 The remarkable increased safety of the pre-

ferred zinc complexed maneb has been demonstrated in the field. Plots of apple trees, which included Rome varieties, were sprayed in the spring with commercial maneb and with zinc-complexed maneb prepared as in Example 2 at a concentration of 2 lb./100 gallon. In the plots in which commercial maneb was applied at the blossom stage, blossoms turned brown in a matter of a few hours. These blossoms no longer attracted pollinators and soon abscised. On the other hand, the application of the zinc-complexed maneb caused no change in appearance of the blossoms and pollination took place normally.

Application of commercial maneb to the more sensitive varieties of apples, such as varieties of Rome and Golden Delicious, causes phytotoxic responses which become evident from necrotic spotting of the leaves. In the most severe instances defoliation may result. In contrast, these same varieties sprayed with the zinc complexed maneb of Example 2 showed no evidence of phytotoxic responses even on a weekly to fortnightly spray schedule at concentrations as high as 2 lb./100 gallon.

A concentration of the zinc complexed maneb of Example 2 of about 1.5—2 lb./gallon was sufficient to control various apple diseases. The most important of these is apple scab caused by *Venturia inaequalis*. A normal spray schedule in which the zinc-complexed maneb was applied at 0.75 and 1.5 lb./100 gallon throughout the season produced fruit over 95% of which was marketable as U.S. No. 1 grade in contrast to 85%, for a regularly recommended treatment under the same conditions. Furthermore, these spray schedules controlled cedar apple rust (*Gymnosporangium juniperi-virginianae*), quince rust (*Gymnosporangium clavipes*), black rot of the fruit and frog-eye leaf spot (*Physalospora obtusa*) botryosphacria spot (*Botryosphacria ribis*), apple blotch (*Phyllostica solitaria*), Brooks spot (*Mycosphaella pomii*), bitter rot (*Glomerella cingulata*), and fly speck (*Leptothyrium pomii*).

During the tests for the control of apple diseases, it was observed that, when the zinc complexed maneb was applied to apple trees, there was an 80% suppression of the mite population as compared to the mite population of the control plots. Similarly, the zinc-complexed maneb suppress rust mite on citrus.

The metal-complexed manganese bisdithiocarbamates of the invention can be used in essentially pure form from which water-soluble impurities have been leached or in their relatively crude form. They can be used in conjunction with carriers, liquid or solid, in any manner comparable to the way in which maneb or zineb is presently used, such as conventional high-gallonage hydraulic sprays, low-gallonage sprays, airblast sprays, aerial sprays, and dusts. The dilution and rate of application

of the metal-complexed salt will depend upon the type of equipment employed, the method of application, and the diseases to be controlled, but the amount is usually one-half to five pounds per acre per application in aqueous sprays in volumes from five to 175 gallons. If desired, small amounts of wetting agents and/or sticking agents may be added to the spray mixtures as may other pesticidal agents.

Aqueous-spray compositions are conveniently formed by dispersing in water a concentrate comprising one or more of the complex metal salts with or without a wetting agent, dispersing agent, stabilizer or mixture of two or more such additives.

Dusts can be prepared by mixing one or more of the complex salts with a finely divided solid carrier which may be inert or may be a mixture of inert material and pesticidally active material. A typical dust is prepared by blending six parts of cobalt-complexed maneb containing 4% of cobalt with 24 parts of calcium carbonate and then mixing with 70 parts of micronized sulfur. In another formulation, 10 parts of zinc-complexed maneb containing 2.5% of zinc is thoroughly mixed with 90 parts of calcium carbonate.

The metal-complexed maneb can be used in conjunction with other pesticides and with nutritional sprays. They can be used with other fungicides such as dinitro(1-methylheptyl)phenyl crotonate, N-trichloromethylthiotetrahydrophthalimide (captan), sulfur, N-dodecylguanidine acetate (dodine), fixed coppers, fungicidal oils, and antibiotics. They can be used with insecticides, such as dicophane, benzene hexachloride, phosphatics such as parathion and O,O-dimethyl dithiophosphate of diethyl mercapto succinate 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.

In addition to providing new complex metal salts, the invention also provides a mixture comprising a water-insoluble manganese alkylene bisdithiocarbamate and at least one water-soluble salt of cobalt, copper, iron and zinc. Such a mixture on addition to water and, if necessary, heating to a temperature up to 50° C. will result in an aqueous fungicidal dispersion of a water-insoluble complex metal bisdithiocarbamate. A typical mixture of this sort would be a dry mixture of anhydrous maneb and zinc chloride or sulfate in an amount such as to provide 0.1 to 6.8, e.g. 2.5, parts by weight of zinc per 20 parts of manganese. Such a dry mixture could be mixed with water at the desired location and the resulting dispersion of zinc complexed maneb applied as a fungicide.

#### WHAT WE CLAIM IS:

1. A fungicidal water-insoluble metal complexed manganese alkylene bisdithiocarbamate in which the complexing metal component comprises one or more of the metals: cobalt, copper, iron and zinc. 65
2. O bisdithiocarbamate according to Claim 1, which is a metal complexed maneb. 70
3. A fungicidal metal complexed maneb containing, per 20 parts by weight of manganese, at least 0.1 part by weight of complexing metal or mixture of complexing metals and not more than 13, 4, 50 and 10 parts by weight of cobalt, copper, iron and zinc respectively. 75
4. A fungicidal zinc complexed maneb containing from 0.1 to 7 parts by weight of zinc per 20 parts by weight of manganese. 80
5. A fungicidal zinc complexed maneb according to Claim 3 containing from 0.2 to 3 parts by weight of zinc per 20 parts by weight of manganese. 85
6. A fungicidal cobalt complexed maneb according to Claim 3 containing from 0.25 to 10 parts by weight of cobalt per 20 parts by weight of manganese. 25
7. A fungicidal cobalt complexed maneb according to Claim 3 containing 0.4 to 6 parts by weight of cobalt per 20 parts by weight of manganese. 90
8. A fungicidal copper complexed maneb containing from 0.2 to 2.5 parts by weight of copper per 20 parts by weight of manganese. 95
9. A fungicidal copper complexed maneb containing 0.5 to 1 part by weight of copper per 20 parts by weight of manganese. 35
10. A fungicidal ferric iron complexed maneb containing 0.1 to 10 parts by weight of ferric iron per 20 parts by weight of manganese. 100
11. A fungicidal ferric iron complexed maneb containing from 0.6 to 4 parts by weight of ferric iron per 20 parts by weight of manganese. 105
12. A fungicidal ferrous iron complexed maneb containing from 1 to 50 parts by weight of ferrous iron per 20 parts by weight of manganese. 110
13. A fungicidal ferrous iron complexed maneb containing 10—30 parts by weight of ferrous iron per 20 parts by weight of manganese. 115
14. A process for preparing a compound according to Claim 1 which comprises reacting, in an aqueous medium, a water-insoluble manganese alkylene bisdithiocarbamate with at least one water-soluble salt of cobalt, copper, iron and zinc to complex the metal(s) of the water soluble salt(s) with the manganese bisdithiocarbamate. 120
15. A process according to Claim 14 as applied to the preparation of a metal com- 125

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of the metal-complexed salt will depend upon the type of equipment employed, the method of application, and the diseases to be controlled, but the amount is usually one-half to five pounds per acre per application in aqueous sprays in volumes from five to 175 gallons. If desired, small amounts of wetting agents and/or sticking agents may be added to the spray mixtures as may other pesticidal agents.

Aqueous-spray compositions are conveniently formed by dispersing in water a concentrate comprising one or more of the complex metal salts with or without a wetting agent, dispersing agent, stabilizer or mixture of two or more such additives.

Dusts can be prepared by mixing one or more of the complex salts with a finely divided solid carrier which may be inert or may be a mixture of inert material and pesticidally active material. A typical dust is prepared by blending six parts of cobalt-complexed maneb containing 4% of cobalt with 24 parts of calcium carbonate and then mixing with 70 parts of micronized sulfur. In another formulation, 10 parts of zinc-complexed maneb containing 2.5% of zinc is thoroughly mixed with 90 parts of calcium carbonate.

The metal-complexed manebes can be used in conjunction with other pesticides and with nutritional sprays. They can be used with other fungicides such as dinitro(1-methylheptyl)phenyl crotonate, N-trichloromethylthiotetrahydrophthalimide (captan), sulfur, N-dodecylguanidine acetate (dodine), fixed copers, fungicidal oils, and antibiotics. They can be used with insecticides, such as dicophane, benzene hexachloride, phosphatics such as parathion and O,O-dimethyl dithiophosphate of diethyl mercapto succinate 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.

In addition to providing new complex metal salts, the invention also provides a mixture comprising a water-insoluble manganese alkylene bisdithiocarbamate and at least one water-soluble salt of cobalt, copper, iron and zinc. Such a mixture on addition to water and, if necessary, heating to a temperature up to 50° C. will result in an aqueous fungicidal dispersion of a water-insoluble complex metal bisdithiocarbamate. A typical mixture of this sort would be a dry mixture of anhydrous maneb and zinc chloride or sulfate in an amount such as to provide 0.1 to 6.8, e.g. 2.5, parts by weight of zinc per 20 parts of manganese. Such a dry mixture could be mixed with water at the desired location and the resulting dispersion of zinc complexed maneb applied as a fungicide.

#### WHAT WE CLAIM IS:

1. A fungicidal water-insoluble metal complexed manganese alkylene bisdithiocarbamate in which the complexing metal component comprises one or more of the metals: cobalt, copper, iron and zinc.

2. O bisdithiocarbamate according to Claim 1, which is a metal complexed maneb.

3. A fungicidal metal complexed maneb containing, per 20 parts by weight of manganese, at least 0.1 part by weight of complexing metal or mixture of complexing metals and not more than 13, 4, 50 and 10 parts by weight of cobalt, copper, iron and zinc respectively.

4. A fungicidal zinc complexed maneb containing from 0.1 to 7 parts by weight of zinc per 20 parts by weight of manganese.

5. A fungicidal zinc complexed maneb according to Claim 3 containing from 0.2 to 3 parts by weight of zinc per 20 parts by weight of manganese.

6. A fungicidal cobalt complexed maneb according to Claim 3 containing from 0.25 to 10 parts by weight of cobalt per 20 parts by weight of manganese.

7. A fungicidal cobalt complexed maneb according to Claim 3 containing 0.4 to 6 parts by weight of cobalt per 20 parts by weight of manganese.

8. A fungicidal copper complexed maneb containing from 0.2 to 2.5 parts by weight of copper per 20 parts by weight of manganese.

9. A fungicidal copper complexed maneb containing 0.5 to 1 part by weight of copper per 20 parts by weight of manganese.

10. A fungicidal ferric iron complexed maneb containing 0.1 to 10 parts by weight of ferric iron per 20 parts by weight of manganese.

11. A fungicidal ferric iron complexed maneb containing from 0.6 to 4 parts by weight of ferric iron per 20 parts by weight of manganese.

12. A fungicidal ferrous iron complexed maneb containing from 1 to 50 parts by weight of ferrous iron per 20 parts by weight of manganese.

13. A fungicidal ferrous iron complexed maneb containing 10—30 parts by weight of ferrous iron per 20 parts by weight of manganese.

14. A process for preparing a compound according to Claim 1 which comprises reacting, in an aqueous medium, a water-insoluble manganese alkylene bisdithiocarbamate with at least one water-soluble salt of cobalt, copper, iron and zinc to complex the metal(s) of the water soluble salt(s) with the manganese bisdithiocarbamate.

15. A process according to Claim 14 as applied to the preparation of a metal com-



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plexed maneb according to any one of Claims 2—13.

16. A process according to Claim 14 as applied to the preparation of a bisdithiocarbamate according to any one of Claims 4—13 and in which the amount of water-soluble salt(s) in the reaction mixture is such as to provide a ratio of complexing metal to manganese not exceeding that in the desired complexed product.

17. A process according to Claim 14, which comprises mixing together water, maneb, and a water-soluble salt of cobalt, copper, iron, or zinc, and reacting the maneb and said salt between 10° and 50° C., the ratio of maneb to water being from 5:95 to 65:35 by weight and the amount of said water-soluble salt being such as to provide, based on the weight of maneb, from 0.25% to 10% of cobalt ion, 0.2% to 2.5% of copper ion, 0.1% to 10% of ferric ion, 1% to 50% of ferrous ion, or 0.1 to 7% of zinc ion.

18. A fungicidal mixture comprising a water-insoluble manganese alkylene bisdithiocarbamate and at least one water-soluble salt of cobalt, copper, iron and zinc.

19. A mixture according to Claim 18, comprising powdered maneb and a powdered water-soluble zinc salt.

20. A mixture according to Claim 19, wherein the maneb is anhydrous.

21. A mixture according to Claim 19 or 20, wherein the zinc salt is zinc sulfate or chloride.

22. A fungicidal composition comprising a metal complexed manganese bisdithiocarbamate according to Claim 1 and a carrier.

23. A composition according to Claim 22 in the form of a dispersion of the bisdithiocarbamate in water.

24. A composition according to Claim 22, wherein the carrier is a finely divided solid.

25. A composition according to any one of Claims 22—24, containing at least one other pesticide.

26. A composition according to any one of Claims 22—25 containing a bisdithiocarbamate according to Claim 2 or 3.

27. A composition according to any one of Claims 22—26, wherein the bisdithiocarbamate is a metal complexed maneb according to any one of Claims 4—13.

28. A concentrate for forming an aqueous fungicidal composition comprising a dry finely divided metal complexed manganese bisdithiocarbamate according to Claim 1, together with a wetting agent, a dispersing agent or stabilizer for the bisdithiocarbamate or mixture of two or more such additives.

29. A concentrate according to Claim 28, wherein there is included, as stabilizer, hexamethylenetetramine.

30. A concentrate according to Claim 28 or 29, containing a bisdithiocarbamate according to Claim 2 or 3.

31. A concentrate according to Claim 28 or 29, wherein the bisdithiocarbamate is a metal complexed maneb according to any one of Claims 4—13.

32. A process according to Claim 15, substantially as hereinbefore described with reference to any one of the foregoing Examples.

33. A metal complexed maneb according to Claim 2, substantially as hereinbefore described with reference to any one of the foregoing Examples.

34. A method of inhibiting fungal diseases in plants yielding a vendible crop which comprises applying to the plants a metal complexed manganese alkylene bisdithiocarbamate according to Claim 1.

35. A method according to Claim 34, wherein there is applied an alkylene bisdithiocarbamate according to Claim 2 or 3.

36. A method according to Claim 34, wherein there is applied a zinc complexed maneb according to Claim 4 or 5.

37. A method according to Claim 36 as applied to the control of apple scab.

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