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FUNGICIDAL COMPOSITIONS

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This invention relates to fungicidal compositions containing as the essential active ingredient the double salts of heavy metal salts and certain amine hydrohalides.

The novel compounds of the present invention comprise a carrier and an effective concentration of a double salt of a heavy metal salt and an amine hydrohalide, said amine having the formula RR'R'N, wherein R is an aliphatic hydrocarbon radical having from 8 to 20 carbon atoms and R' is either hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms.

The double salts which form a part of the compounds of this invention are produced, generally, by forming a solution containing an amine and a hydrogen halide gas such as hydrogen chloride and adding a solution containing a heavy metal salt. It is an important element of the invention that the reactants be added in such quantities that the proper ratios are present for forming the double salts rather than complexes or mixtures. In connection with the object of preparing the double salts, rather than complexes, we have made the following observations:

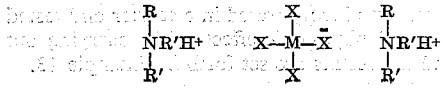
(1) When long-chain N-substituted amines are used with heavy metal salts, the resulting double salts or complexes in most cases involve 2 moles of the amine for each mole of heavy metal compound.

(2) When primary or secondary amines are mixed with heavy metal salts, complexes between the two substances are formed unless sufficient hydrogen halide is present to neutralize or block all the nitrogen atoms and thus prevent the formation of complexes or coordination compounds.

(3) Therefore, in order to prepare double salts of primary or secondary amines, it is necessary to add enough moles of hydrogen halide to neutralize or block all of the amino groups. In other words, for each mole of heavy metal salts, it is necessary to add 2 moles of hydrogen halide along with the 2 moles of amine. The double salt used in the present invention therefore involves a 2:2:1 molar ratio of amine:hydrogen halide:heavy metal salt.

Although in the foregoing description the carrying out of the reaction is described in terms of adding three ingredients, namely, the amine, the hydrogen halide, and the heavy metal salt, it will be understood that the invention also contemplates the use of equivalent procedures and materials such as, for example, the use of an amine hydrohalide instead of the amine and the hydrogen halide separately.

Structurally, the double salts used in the present invention are distinguished from complexes by reason of the fact that in the double salts the metal is not coordinated with amino nitrogen, whereas in the complex it is coordinated with amino nitrogen. Thus, as an illustration, one class of the double salts used in the present invention may be structurally portrayed as follows:



The structural formula for the above may be given as follows:

$$(RR'R'NH)_2^+(MX_4)^=$$

wherein R is an aliphatic hydrocarbon radical having from 8 to 20 carbon atoms and R' is either hydrogen or an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, X is halide, and M is a heavy metal.

As a further means of distinguishing the double salts of this invention, the color may be employed as an identifying factor in the case of some of the heavy metal compounds. Thus, for example, when copper is used as the heavy metal, the double salts of the present invention under normal conditions have a characteristic yellow color, as distinguished from the dark blue or purple color of secondary amine copper chloride complexes or the light blue color of primary amine copper chloride complexes.

Any suitable "heavy" metal may be used as a component of the double salts contemplated by the present invention. Such metals are to be found in groups I–B, II–B,VI–B, VII–B, and VIII of the periodic chart of the elements. As specific examples, we may use the salts of heavy metals such as copper, chromium, tin, zinc, cadmium, mercury, manganese, iron, cobalt, and nickel. The use of copper, cadmium, zinc, manganese, and iron salts is preferred. Although we prefer to use halides as the anionic portion of the heavy metal salts, it will be understood that other suitable anions such as acetate, sulphate, nitrate, and oxalate may also be used.

Any primary, secondary, or tertiary saturated or unsaturated amine, containing at least one long chain aliphatic group having from 8 to 20 carbon atoms, will serve as a starting material in forming the double salts used in the present invention. The amine starting material may be represented generally by the formula RR'R'N wherein R is an aliphatic hydrocarbon radical having from 8 to 20 carbon atoms and R' is either hydrogen or an aliphatic hydrocarbon radical of from 1 to 20 carbon atoms. As representative members of R in the above formula, the following may be mentioned: octyl, decyl, dodecyl, dodecenyl, tetradecyl, tetradecenyl, hexadecyl, hexadecenyl, octadecyl, octadecenyl, and octadecadienyl. The R may also constitute mixtures of long chain aliphatic radicals such as those found in natural fatty acid mixtures obtained from coconut oil, cottonseed oil, soybean oil, or lard oils. Thus, for example, there may be used tallow-amines (derived from tallow and in which "tallow" comprises a mixture of the following radicals: dodecyl, tetradecyl, tetradecenyl, hexadecyl, hexadecenyl, octadecyl, octadecenyl, octadecadienyl, and eicosyl); cocoamines (derived from coconut oil and in which "coco" comprises a mixture of hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl, and octadecadienyl radicals); and soya-amines (derived from soybean oil and in which "soya" comprises a mixture of hexadecyl, octadecyl, eicosyl, octadecenyl, octadecadienyl, and octadecatrienyl radicals). Hereinafter, the terms "tallow," "coco," and "soya" are meant to refer to the respective mixtures of radicals set forth above.

The R' in the above amine formula may be either hydrogen or an aliphatic hydrocarbon radical of from 1 to 20 carbon atoms. The aliphatic hydrocarbon radical may thus be any of the radicals falling under the definition of R given above and in addition may comprise members such as methyl, ethyl, propyl, butyl, hexyl, and mixtures thereof.

The reaction to form the double salts used in the present invention may be carried out without special apparatus. It may be conducted in any convenient vessel adapted to contain the reactants. The reaction proceeds spontaneously merely by mixing or contacting the reactants in the presence of moderate heat. To facilitate

contact it is desirable to dissolve the reactants in a suitable liquid solvent which is a mutual solvent for the reactants, i.e., a solvent which will dissolve each of the reactants. Preferably, the solvent should not enter into, or interfere with, the desired reaction. Generally, solvents having a minor proportion of water are suitable, as, for example, 95% aqueous ethanol. Various low molecular weight organic solvents will be suitable for the reaction, in particular the low alcohols and ketones and the lower homologs of toluene, and the like. Mixtures of such solvents may likewise be employed.

According to the preferred practice, the reaction is favored with a moderate amount of heat, although it is quite satisfactory to conduct the reaction at room temperature. Higher and lower temperatures may be employed, but at relatively high temperatures there is an undesirable tendency toward breakdown of the double salts. It is advisable to agitate and stir the reaction mixture until the reaction is substantially completed.

There is considerable variation in the length of time required for completion of the reaction. In some cases the reaction is completed almost instantaneously while in other cases several hours are required for completion. In any case, it will be clear that it is not necessary to react all of the reacting materials in order to obtain a satisfactory product. In other words, the reaction may be terminated as soon as the desired quantity of product is obtained.

Following the desired reaction the product may be isolated from the reaction zone by any suitable method. For example, the reaction mixture may be cooled so as to cause precipitation or crystallization of the product and the mixture then filtered or decanted to isolate the product. Also, it will be satisfactory to evaporate the solvent and thereby leave the desired product as a residue.

In the present invention, the double salts are used as an active ingredient in compositions for combating fungal attack. Such compositions can take the form of emulsions, solutions, powders, etc. When used on growing plants, the double salts are not applied in full strength, but instead are combined with an inert carrier so that a fungistatic but non-phytotoxic concentration of the double salts can be applied. It has been found that there is a considerable margin of safety between active and phytotoxic concentrations. For example, with most of the compounds falling within the scope of this invention, an effective fungistatic or fungitoxic action is obtained in concentrations ranging from 10 to 100 parts per million, whereas no phytotoxicity is exhibited in concentrations of 1,000 parts per million or more, and in the hardier plants concentrations as high as 5,000 and 6,000 parts per million produce no phytotoxicity. This permits the fungicidal composition of this invention to be sprayed or dusted on plants without danger of phytotoxicity due to over concentrations. It will be understood that the above concentrations are in terms of solutions or suspensions which are sprayed on plants and that such concentrations are subject to upward adjustment when used in connection with dry, powdered compositions which are applied by dusting on plants.

This invention is further illustrated and its value shown by the following specific examples:

EXAMPLE 1

Dioctylamine hydrochloride-cupric chloride double salt

A solution of 8.5 gms. (0.05 mole) of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 24.1 gm. (0.1 mole) of dioctylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$[(C_8H_{17})_2NH_2]_2^+(CuCl_4)=$$

Calculated: N, 4.07; Cl, 20.6; Cu, 9.2. Found: N, 3.53; Cl, 20.1; Cu, 9.7.

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 2

Octylamine hydrochloride-cupric chloride double salt

A solution of 8.5 gms. (0.05 mole) of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 12.9 gms. (0.1 mole) of octylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula:

$$(C_8H_{17}NH_3)_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such tests and the results are set forth in Example 13.

EXAMPLE 3

Dioctylamine hydrochloride-ferric chloride double salt

A solution of 8.1 gms. (0.05 mole) of ferric chloride in 100 mls. of isopropyl alcohol was added with stirring to 24.1 gms. (0.1 mole) of dioctylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$[(C_8H_{17})_2NH_2]_2^+(FeCl_5)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 4

Dodecylamine hydrochloride-cupric chloride double salt

A solution of 8.5 gms. (0.05 mole) of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 18.5 gms. (0.1 mole) of dodecylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$(C_{12}H_{25}NH_3)_2^+(CuCl_4)=$$

Calculated: N, 4.85; Cl, 24.6; Cu, 11.02. Found: N, 4.92; Cl, 24.4; Cu, 10.9.

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 5

Dodecylamine hydrochloride-cadmium chloride double salt

A solution of 9.2 gms. (0.05 mole) of cadmium chloride in 100 mls. of isopropyl alcohol was added with stirring to 18.5 gms. (0.1 mole) of dodecylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The double salt precipitated. Upon cooling, the double salt was filtered and dried. The white double salt had the formula

$$(C_{12}H_{25}NH_3)_2^+(CdCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 6

Dodecylamine hydrochloride-ferric chloride double salt

A solution of 8.1 gms. (0.05 mole) of ferric chloride in 100 mls. of isopropyl alcohol was added with stirring to 18.5 gms. (0.1 mole) of dodecylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated: Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$(C_{12}H_{25}NH_3)_2^+(FeCl_5)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 7

Dodecylamine hydrochloride-zinc chloride double salt

A solution of 6.8 gms. of zinc chloride (0.05 mole) in 100 mls. of isopropyl alcohol was added with stirring to 18.5 gms. (0.1 mole) of dodecylamine and 3.6 gms. (0.1 mole) of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The double salt precipitated. Upon cooling, the double salt was filtered and dried. The white double salt had the formula

$$(C_{12}H_{25}NH_3)_2^+(ZnCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 8

Hydrogenated tallow-amine hydrochloride-cupric chloride double salt

A solution of 0.05 mole of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 0.1 mole of a primary amine derived from hydrogenated tallow fatty acids and 0.1 mole of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$(\text{Tallow-}NH_3)_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 9

Hydrogenated di-tallow-amine hydrochloride-cupric chloride double salt

A solution of 0.05 mole of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 0.1 mole of a secondary amine derived from hydrogenated tallow fatty acids and 0.1 mole of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellow, and the double salt precipitated. Upon cooling, the double salt was filtered and dried. The yellow double salt had the formula

$$[(\text{Tallow})_2\text{-}NH_2]_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 10

Dimethylsoya-amine hydrochloride-cupric chloride double salt

A solution of 0.05 mole of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 0.1 mole of a tertiary amine, namely, dimethylsoya-amine, and 0.1 mole of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned light-green, and the resulting double salt had the formula

$$(\text{Soya-}NH(CH_3)_2]_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 11

Dimethylcoco-amine hydrochloride-cupric chloride double salt

A solution of 0.05 mole of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 0.1 mole of a tertiary amine, namely, dimethylcoco-amine, and 0.1 mole of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned yellowish-brown, and the resulting double salt had the formula

$$[\text{Coco-}NH\text{—}(CH_3)_2]_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 12

Methyl-dicoco-amine hydrochloride-cupric chloride double salt

A solution of 0.05 mole of $CuCl_2 \cdot 2H_2O$ in 100 mls. of isopropyl alcohol was added with stirring to 0.1 mole of a tertiary amine, namely, methyl-dicoco-amine, and 0.1 mole of hydrogen chloride dissolved in 250 mls. of isopropyl alcohol. The solution turned light-green, and the resulting double salt had the formula

$$[(\text{Coco})_2NHCH_3]_2^+(CuCl_4)=$$

The double salt was incorporated in a carrier and tested for its fungistatic and phytotoxic effect. The carrying out of such test and the results are set forth in Example 13.

EXAMPLE 13

The fungicidal activity and the phytotoxicity of the foregoing compounds were tested according to the following procedure:

Fungicidal activity

For this test, the Standard Fungicidal Test of the American Phytopathological Society was employed using the fungi: peach brown rot (*Monilinia fructicola*); apple bitter rot (*Glomerella cingulata*); and tomato early blight (*Alternaria oleracea*). Briefly described, this test involves subjecting the spores of various fungi to graded concentrations of the test compound and determining the extent of spore germination at the end of 24 hours. The calculated percentage of spore not germinated serves as an index of the fungistatic or fungicidal activity of the chemical. A check is kept on the viability of the culture.

Phytotoxicity tests

Young tomato, pepper, and bean plants contained in individual pots are placed on a slowly revolving stand and sprayed from above and below at 45 degree angles to the point of runoff. The materials are prepared as aqueous solutions with a wetting agent, or as emulsions, and applied to the plants by means of an atomizer at 12.5 p.s.i. As the plants are sprayed, they are tagged and returned to an artificially lighted plant table for observation.

Results

The compounds tested, concentrations used, the percentage of spore germination obtained for each organism,

and the phytotoxic response levels of tomato, pepper, and bean plants are presented in Table I below:

TABLE I

Compound	Organism	Percent Spore Germination at conc. in p.p.m.				LD_{50}, p.p.m.	Minimal Phytotoxic Dosage in p.p.m. for—		
		100	10	1.0	0.1		Tomato	Pepper	Bean
Dioctylamine hydrochloride-cupric chloride double salt (Example 1).	A.o.	0.0	0.0	74.7	91.4	1.7	5,000	5,000	
	G.c.	0.0	0.0	92.7	98.5	2.6			
	M.f.	0.0	0.0	54.7	95.7	1.1			
Octylamine hydrochloride-cupric chloride double salt (Example 2).	A.o.	0.0	65.8	95.2	99.0	14.5			1,000
	G.c.	0.0	85.9	98.0	99.0	22.0			
	M.f.	0.0	66.6	84.8	96.1	15.0			
Dioctylamine hydrochloride-ferric chloride double salt (Example 3).	A.o.	0.0	53.3	90.1	99.0	11.0			1,000
	G.c.	0.0	74.2	98.0	100.0	17.5			
	M.f.	0.0	55.8	93.2	99.5	11.5			
Dodecylamine hydrochloride-cupric chloride double salt (Example 4).	A.o.	0.0	0.0	53.3	98.5	1.1	5,000	5,000	
	G.c.	0.0	0.0	63.9	97.6	1.4			
	M.f.	0.0	18.7	91.3	99.5	4.0			
Dodecylamine hydrochloride-cadmium chloride double salt (Example 5).	A.o.	0.0	0.0	72.2	95.8	1.7			1,000
	G.c.	0.0	0.0	92.7	99.5	2.6			
	M.f.	0.0	0.0	56.3	92.2	1.2			
Dodecylamine hydrochloride-ferric chloride double salt (Example 6).	A.o.	0.0	0.0	56.1	85.5	1.2			1,000
	G.c.	0.0	0.0	85.9	99.5	2.2			
	M.f.	0.0	0.0	54.8	96.6	1.1			
Dodecylamine hydrochloride-zinc chloride double salt (Example 7)	A.o.	0.0	0.0	56.1	88.4	1.2			1,000
	G.c.	0.0	0.0	92.7	99.0	2.6			
	M.f.	0.0	0.0	76.2	96.5	1.8			
Hydrogenated tallow-amine hydrochloride-cupric chloride double salt (Example 8).	A.o.	0.0	53.4	88.4	97.1	11.0			1,000
	G.c.	0.0	37.4	87.8	98.6	6.0			
	M.f.	0.0	42.4	88.0	95.7	7.2			
Hydrogenated di-tallow-amine hydrochloride-cupric chloride double salt (Example 9).	A.o.	0.0	73.0	97.2	99.0	16.5			1,000
	G.c.	49.6	86.8	98.0	97.0	96.0			
	M.f.	0.0	92.2	98.6	100.0	26.0			
Dimethylsoya-amine hydrochloride-cupric chloride double salt (Example 10).	A.o.	0.0	36.6	96.2	99.0	7.2			1,000
	G.c.	0.0	48.6	91.2	97.6	9.4			
	M.f.	0.0	42.7	91.8	98.0	7.6			
Dimethylcoco-amine hydrochloride-cupric chloride double salt (Example 11).	A.o.	46.2	95.6	99.0	98.6	88.0			1,000
	G.c.	0.0	88.4	98.0	98.6	23.5			
	M.f.	0.0	0.0	76.2	99.5	1.85			
Methyl-dicoco-amine hydrochloride-cupric chloride double salt (Example 12).	A.o.	0.0	42.8	91.8	96.6	5.1			1,000
	G.c.	53.4	92.2	99.5	98.0	35.0			
	M.f.	0.0	0.0	0.0	0.0	0.03			

The term LD_{50} in the foregoing Table I means the lethal dose required to kill 50% of the test organisms.

EXAMPLE 14

(A) An emulsifiable concentrate consists of:

50% active chemical.
5–10% non-ionic emulsifier such as the coco acid or rosin fatty acid esters of polyethylene glycols.
45–40% aromatic or aliphatic solvent such as xylene or acetone.

This is diluted with water to give 1–2 lbs. active ingredient per 100 gals. water for the final spray.

(B) A wettable powder which may be used in the form of a water spray consists of:

50–75% active chemical.
5% non-ionic emulsifier such as the coco fatty acid or rosin fatty acid esters of polyethylene glycols.
45–20% inert diluent such as pyrophyllite, clays, celite, etc.

One to two pounds of this powder is placed in 100 gals. of water and sprayed in this form.

(C) A dust concentrate composition consists of:

50–75% active ingredient.
50–25% inert diluent such as pyrophyllite, clays, celite, etc.

The average particle size should not be greater than 30 microns. Efficiency appears to increase with the fineness of the dust.

It will be understood that any of the double salts described herein can be used in the specific formulations of this example.

While in the foregoing specification this invention has been described in relation to certain specific embodiments thereof, and details have been set forth for the purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible of other embodiments and many of the details set forth herein can be varied considerably without departing from the basic concept of the invention.

We claim:

1. A fungicidal composition comprising from about ten to about 6,000 parts per million of a double salt of a heavy metal salt and an amine hydrochloride, said double salt comprising a 2:2:1 molar ratio of amine:hydrogen halide:heavy metal salt, said amine having the formula RR'R'N, wherein R is an aliphatic hydrocarbon radical having from 8 to 20 carbon atoms and R' is selected from the group consisting of hydrogen and an aliphatic hydrocarbon radical having from 1 to 20 carbon atoms, and an inert adjuvant as a carrier therefor.

2. The fungicidal composition set forth in claim 1 wherein said heavy metal is copper.

3. The fungicidal composition set forth in claim 1 wherein said heavy metal is cadmium.

4. The fungicidal composition set forth in claim 1 wherein said heavy metal is zinc.

5. The fungicidal composition set forth in claim 1 wherein said heavy metal is iron.

6. The fungicidal composition set forth in claim 1 wherein said amine is dodecylamine.

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