Patented June 23, 1942

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UNITED STATES PATENT OFFICE

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PEST CONTROL

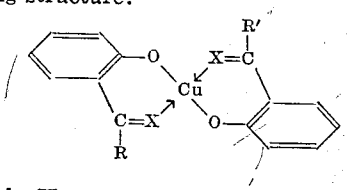
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No Drawing. Application June 27, 1940, Serial No. 342,684

24 Claims. (Cl. 167—30)

This invention relates to pest control and is particularly directed to methods and compositions for preventing, arresting, or eradicating infestations of fungi, bacteria, insects, molds and various other organisms economically harmful to man which infest organic matter, whether plant or animal or of plant or animal origin, either in its natural, fabricated or synthetic state, which methods and compositions distinguish from the processes and compositions heretofore known in the use of a cupric chelate of a compound selected from the class consisting of ortho-carbonyl phenols and ortho-carbimino phenols, especially those in which the aromatic nucleus is free of salt-forming groups and those in which the carbonyl and carbimino substituents constitute but a minor proportion of the mass of the molecule.

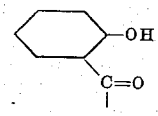
This application is related to application Serial No. 234,778 filed April 13, 1938, now Patent 2,208,253 of July 16, 1940, which is directed to the use of chelate cupric enolates in pest control compositions. We have now discovered a particular sub-group of cupric chelates having the same characteristic ring structure which has an effectiveness in the control of fungi of the same high order of the effectiveness of the preferred group of compounds described in the above mentioned pending application. The compounds described in the copending application are characterized by a spirane structure of two 6-membered rings, each of which contains an enol oxygen member, a keto oxygen member, a double bond conjugated with the keto linkage (this double bond is part of the enol group), and a copper member which is shared by both rings through covalent links with the enol oxygens and through coordinate links with the keto oxygens. The compounds to which the present invention is directed have essentially the same chelate structure and are particularly characterized in that a benzo group is associated with each of the 6-membered rings in the chelate structure. A double bond which is conjugated with the double bond of a carbonyl or carbimino group forms part of a benzene ring, as shown in the following structure:



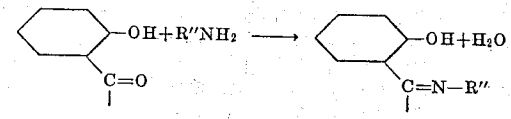
in which X represents oxygen or the group =NR''.

These copper chelates are, in general, readily obtained by reacting a copper salt with an ortho-hydroxy-benzaldehyde, an aliphatic ortho-hydroxyphenone, the corresponding carbimino compounds or an aliphatic ortho-hydroxy-benzoate. Thus R and R' in the above formula may be hydrogen or aliphatic radicals and may be the residue of an aldehyde, a ketone or an ester. The radicals R and R' may be different but usually are the same. The radical R'' may be hydrogen, hydroxy, alkyl or hydroxyalkyl. Preferably the radicals R, R' and R'' together constitute but a minor proportion of the mass of the molecule.

The aldehyde, ketones and esters from which the cupric chelates of this invention are derived are all characterized by the ortho-carbonyl phenol group,



The aldehyde and ketones react with a primary amine, ammonia, or hydroxylamine to yield ortho-carbimino phenols, thusly:



Both types may be reacted with cupric salts to form the cupric chelate. In some cases where a polyhydric amo compound (primary amine ammonia or hydroxylamine) is present an aldehyde or ketone may yield both carbonyl and carbimino chelates. For example, if 122 parts of salicylaldehyde is added to a solution of ammonical copper sulfate prepared by adding just enough concentrated ammonium hydroxide to a solution of 125 parts of copper sulfate pentahydrate in 700 parts of water to redissolve the precipitate initially formed, a mixture of the cupric chelates of salicylaldehyde and salicylaldimine separates as a green precipitate which after filtering, washing with water, dilute ammonium hydroxide, and finally cold acetone, and drying in vacuo, appears as 131 parts of a light green powder. Alternatively the reaction may be carried out in organic solvents, particularly in the lower aliphatic alcohols. Other copper salts may be used. Thus, if a solution of 22.4 parts of cupric acetate monohydrate in 204 parts of methanol and 45 parts of water is added with efficient stirring to a solution of 17.5 parts of 5-chloro-salicylaldehyde in 160 parts of methanol and allowed to stand overnight, the cupric chelate of 5-chloro-salicylaldehyde separates as a bronze colored crystalline product. This product is filtered off and combined with a second crop of crystals obtained by evaporating the filtrate. It is thoroughly washed in warm water until all soluble cupric salts are removed. It is then washed with methanol and dried in a vacuum. Seventeen

parts of yellow-green scales analyzing 15.75% copper are obtained. The cupric chelates of the aliphatic ortho-hydroxyphenones and the aliphatic esters of the ortho-hydroxybenzoic acids may be prepared by suitable variations of these processes.

The cupric chelates of the ortho-carbonyl and ortho-carbimino phenols are particularly effective in the control of micro-organisms, many of them showing fungicidal efficiency substantially greater than can be attributed to the copper content of the compounds. For high effectiveness the carbonyl and carbimino substituent should be of relatively low molecular weight and the chelate aromatic nucleus should be free of salt-forming groups such as hydroxy, amino, sulfo, carboxy and the like. We mean the term "salt-forming group" to include also the salts of such groups. The aromatic nucleus may be substituted, and in some instances the effectiveness of the compound can be increased by introducing nuclear substituents such as bromine. For example, the cupric chelate of 3,5-dibromo-2-hydroxybenzaldehyde is effective in concentrations of 1–16000 against Penicillium lumber molds and *Aspergillus niger*, whereas the unsubstituted compound is effective at 1–4000. Under the same conditions the usual copper fungicides are effective at from 1–250 to 1–500. Other groups, such as alkyl, acyl, alkyloxy, nitro, iodo, fluoro and the like, may also appear as ring substituents. Suitable compounds include the cupric chelates of salicylaldehyde, 3-chloro-2-hydroxybenzaldehyde, 3,5 - dibromo-2-hydroxybenzaldehyde, 3-allyl-2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde, 3-iodo-2-hydroxybenzaldehyde, 5-fluoro - 2 - hydroxy - benzaldehyde, 5-nitro - 2-hydroxybenzaldehyde, 3-methyl-2-hydroxybenzaldehyde, 5-acetyl - 2 - hydroxybenzaldehyde, ortho - hydroxyacetophenone, ortho-hydroxypropiophenone, ortho-hydroxybutyrophenone, methyl salicylate, ethyl salicylate, propyl salicylate, salicylaldimine, salicylaldoxime, N-amyl salicylaldimine and salicylalglycine.

The cupric chelates of the ortho-carbonyl and ortho-carbimino phenols may be used for such varied purposes as copper fungicides are commonly employed. Being more highly effective than the ordinary copper fungicides their range of usefulness is much wider. Thus they are useful as industrial fungicides for preserving and disinfecting proteinaceous materials, cellulosic materials and other fabricated organic products subject to the attack of fungi, bacteria and like micro-organisms, representative applications of which are set forth in the copending application above identified. More particularly, however, they are suitable for the control of mildew and other fungus diseases of living plants. A special field of application may be considered as that of a more active and less injurious substitute for Bordeaux mixture, Burgundy mixture and other copper-containing agricultural fungicides. The following examples illustrate compositions suitable for these purposes. The parts are by weight.

Example 1

A dry, free-flowing powder suitable for dusting or for dispersing in aqueous sprays is prepared by milling together 20 parts of the cupric chelate of salicylaldehyde, 20 parts of bentonite, 48 parts of Bancroft clay, 10 parts tricalcium phosphate, 1 part sulfite cellulose waste and 1 part n-dodecyl alcohol. This product is easily dispersible in water and in the proportions of 1 to 5 lbs. per 100 gallons produces spray suspensions capable of depositing heavy resistant loads on foliage. The product may also be diluted with a suitable dusting powder such as talc and applied as a dust.

The cupric chelate of salicylaldehyde has been observed to have insecticidal and repellent action for certain insects, which makes the materials of this invention particularly suitable as fungicides to be used in combination with insecticides.

Tank-mix chelate cupric fungicides may be prepared after the manner of preparing Bordeaux mixture or Burgundy mixture and offer advantages in that the gelatinous flocculent precipitate so obtained strongly adheres to foliage. Tank mixes of this type may be prepared as described in the following examples.

Example 2

The cupric chelate of salicylaldehyde may be prepared in the spray tank in suitable form for application to foliage by reaction of salicylaldehyde with lime and copper sulfate. The procedure is as follows: To a mixture of 2.3 parts of slaked lime in 2450 parts of water 2.54 parts of salicylaldehyde is added and stirred in. This is then followed by 26 parts of an aqueous solution containing 10% by weight of copper sulfate pentahydrate. The copper chelate separates as a gelatinous flocculent suspension, an ideal physical condition for spraying purposes.

Example 3

A dispersion of the copper chelate of salicylaldehyde may also be obtained by reacting salicylaldehyde with a freshly prepared Bordeaux mixture. The latter is obtained by adding 26 parts of a 10% solution of copper sulfate pentahydrate to a mixture of 2.3 parts of slaked lime in 2450 parts of water. With efficient agitation a 10% solution of 2.54 parts of salicylaldehyde in ethyl alcohol is slowly added. The conversion of the Bordeaux mixture into the suspension of the copper chelate of salicylaldehyde is accompanied by a change in the color of the precipitate from a light blue to the characteristic greenish blue of the copper chelate. As in Example 2, the copper chelate of salicylaldehyde is in the form of a gelatinous suspension that slowly flocks on standing.

The method described in Example 3 is of particular interest because Bordeaux mixture is a widely known and used fungicide. The operator need only to prepare the Bordeaux mixture according to practices which are well known and standardized and add a solution of salicylaldehyde or other ortho-carbonyl phenol in solution in a water-miscible solvent. Other than this he need only to adjust the concentration of the spray mixture in view of the more strongly fungicidal character of the cupric chelate.

While we have described our invention with reference to particular compounds and compositions thereof and particular applications, it is to be understood that the invention in its broadest aspects is not limited in any of these respects but is intended to cover such variation as may reasonably be made within the spirit and scope of the invention as described and as set forth in the appended claims.

We claim:

1. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a

cupric chelate of an ortho-carbonyl phenol in which the carbonyl substituent is selected from the class consisting of hydrogen and a monovalent aliphatic radical which characterizes the carbonyl group as a carbonyl group of a ketone or ester.

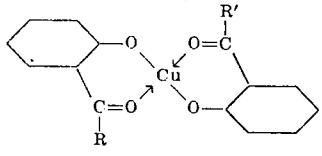
2. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of an ortho-carbonyl phenol in which the carbonyl substituent is selected from the class consisting of hydrogen and a monovalent aliphatic radical which characterizes the carbonyl group as a carbonyl group of a ketone or ester and in which the aromatic nucleus is free of salt-forming groups.

3. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of an ortho-carbonyl phenol in which the carbonyl substituents constitute but a minor proportion of the mass of the molecule and are selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester.

4. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of an ortho-carbonyl phenol in which the aromatic nucleus is free of salt-forming groups and in which the carbonyl substituents constitute but a minor proportion of the mass of the molecule and are selected from the group consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester.

5. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a chelate cupric compound characterized by a spirane structure of two 6-membered rings each of which contains a phenolic oxygen member, a carbonyl oxygen member, a double bond conjugated with the double bond of the carbonyl group and constituting a part of the phenolic nucleus, and a copper member which is shared by both rings through covalent links with the phenolic oxygens and through coordinate links with the carbonyl oxygens.

6. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient an organo-copper complex having the following structure



in which R and R′ are selected from the class consisting of hydrogen and a monovalent aliphatic radical which characterize the carbonyl group as a carbonyl group of a ketone or ester.

7. A pest control composition according to claim 6 in which R and R′ constitute a minor proportion of the mass of the molecule.

8. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of a compound selected from the class consisting of ortho-carbonyl phenols in which the carbonyl substituent is selected from the group consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester and the corresponding carbimino phenols.

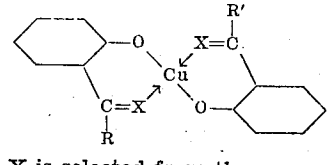
9. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of a compound selected from the class consisting of ortho-carbonyl phenols in which the aromatic nucleus is free of salt-forming groups in which the carbonyl substituent is selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester and the corresponding ortho-carbimino phenols.

10. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cuprice chelate of a compound selected from the class consisting of ortho-carbonyl phenols in which the carbonyl substituent is selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of an ester or ketone and the corresponding ortho-carbimino phenols and in which the carbonyl and carbimino substituents constitute but a minor proportion of the mass of the molecule.

11. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a cupric chelate of a compound selected from the class consisting of ortho-carbonyl phenols in which the carbonyl substituents are selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester and in which the aromatic nucleus is free of salt-forming groups, the carbonyl and carbimino substituents constituting but a minor proportion of the mass of the molecule.

12. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient a chelate cupric compound characterized by a spirane structure of two 6-membered rings each of which contains a phenolic oxygen member, a carbimino nitrogen member, a double bond conjugated with the double bond of the carbimino group and constituting a part of the phenolic nucleus and a copper member which is shared by both rings through covalent links with the phenolic oxygens and through coordinate links with the carbimino nitrogens.

13. A pest control composition useful for controlling fungi, insects, bacteria and like organisms which contains as an active ingredient an organo-copper complex having the following structure



in which X is selected from the group consisting of oxygen and the =NR″ residue of a polyhydric amo compound and R and R′ are selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize a carbonyl group as a carbonyl group of a ketone or ester.

14. A pest control composition according to

claim 13 in which R, R' and R'' constitute a minor proportion of the mass of the molecule.

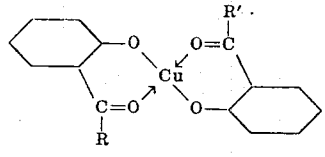
15. A pest control composition useful for controlling fungi, insects, bacteria, and like organisms, which contains as an essential active ingredient the cupric chelate of salicyl-aldehyde.

16. A pest control composition useful for controlling fungi, insects, bacteria, and like organisms, which contains as an essential active ingredient the cupric chelate of 3,5-dibromo-2-hydroxybenzaldehyde.

17. A pest control composition useful for controlling fungi, insects, bacteria, and like organisms, which contains as an essential active ingredient the cupric chelate of 3-allyl-2-hydroxybenzaldehyde.

18. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with a cupric chelate of an ortho-carbonyl phenol in which the carbonyl substituent is selected from the class consisting of hydrogen and a monovalent aliphatic radical which characterizes the carbonyl group as a carbonyl group of a ketone or ester.

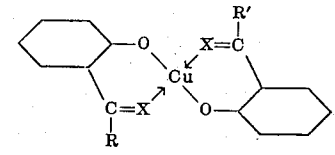
19. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with an organo-copper complex having the following structure



in which R and R' are selected from the class consisting of hydrogen and a monovalent aliphatic radical which characterize the carbonyl group as a carbonyl group of a ketone or ester and in which R and R' constitute a minor proportion of the mass of the molecule.

20. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with a cupric chelate of a compound selected from the class consisting of ortho-carbonyl phenols in which the carbonyl substituent is selected from the group consisting of hydrogen and monovalent aliphatic radicals which characterize the carbonyl group as a carbonyl group of a ketone or ester and the corresponding carbimino phenols.

21. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with an organo-copper complex having the following structure



in which X is selected from the group consisting of oxygen and the =NR'' residue of a polyhydric amo compound and R and R' are selected from the class consisting of hydrogen and monovalent aliphatic radicals which characterize a carbonyl group as a carbonyl group of a ketone or ester and in which R, R' and R'' constitute a minor proportion of the mass of the molecule.

22. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with the cupric chelate of salicylaldehyde.

23. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with the cupric chelate of 3,5-dibromo-2-hydroxybenzaldehyde.

24. The method of controlling infestations of pestiferous organisms, such as fungi, insects, bacteria and the like, in organic matter which comprises treating the organic matter with the cupric chelate of 3-allyl-2-hydroxybenzaldehyde.

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