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CUPROUS DERIVATIVES OF SUBSTITUTED THIOUREAS

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10 Claims. (Cl. 167—22)

This invention relates to copper-containing chemical compounds, compositions including the same, and to processes for the preparation and utilization of these compounds and compositions. More particularly, it relates to cuprous thione compounds and hydrohalide acid salts thereof, compositions including the same, and to processes for the preparation and utilization of these compounds and compositions as fungicides.

It is well known in the fungicide art that many copper compounds are active fungicides. However, in the field of plant pathology, it is recognized that the most active copper fungicidal compounds are those of appreciable water solubility. One disadvantage of water-soluble copper compounds is phytotoxicity. The more insoluble copper compounds have low phytotoxicity, but also are less fungitoxic. In the field of material preservation, such as for example, the protection of fabrics from fungi, copper compounds known to the art have the disadvantage of being colored.

According to the present invention, novel and useful copper compounds and compositions have been prepared that are highly fungitoxic, that have a low degree of phytotoxicity, and that have suitable solubility or dispersion properties. In addition, many compounds of this invention are white or a light color and are more useful in the field of material preservation than known copper fungicidal compounds.

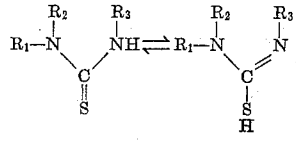
An object of this invention is a new class of compounds and compositions.

Another object is a process for the preparation of cuprous thione compounds and hydrohalide acid salts thereof.

An additional object is to provide compounds, compositions, and processes for inhibiting, preventing, and arresting the attack by fungus and similar growth on wood, cotton, leather, fruit, seeds, plants, and other articles.

Further objects and advantages of this invention will be readily seen and appreciated as the same become better known and understood by reference to the following detailed description when considered in conjunction with the specific examples and the claims.

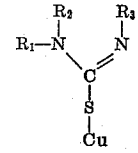
In the process of this invention, starting compounds having a functional group represented by a thiourea-type structural formula are used to obtain cuprous derivatives thereof, a restriction being that at least one nitrogen atom must have as one of its substituents a hydrogen atom to permit the isomerization



to occur. The nitrogen substituents, as represented by R_1, R_2, and R_3, may be selected from the group consisting of hydrogen, an alkyl radical having from 1 to

4 carbon atoms, and a substituted alkyl radical having from 1 to 4 carbon atoms having substituents selected from the group consisting of an amino radical, an imino radical, and a thio radical, with at least one of the said nitrogen substituents being selected from the group consisting of said alkyl radical and said substituted alkyl radical and with no more than one of the said nitrogen substituents being said substituted alkyl radical. Starting compounds and processes for preparing the same are known to those skilled in the art; and some starting compounds are available commercially.

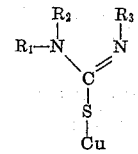
In the process of the invention, the aforesaid starting compounds, having a functional group represented by the thiourea-type structural formula, are treated with a cuprous ion solution to obtain products having a characteristic group represented by the formula



The cuprous ion solution may be prepared in situ with the starting compounds or may be prepared apart from the starting compounds. Where the cuprous ion solution is prepared apart from the starting compounds, the cuprous ion solution may be added to the starting compounds or the starting compounds may be added to the cuprous ion solution.

Cuprous ion solutions for the processes of this invention may be prepared from solutions of cuprous salts, or from solutions of cupric compounds by reduction with a reducing agent. Where the cuprous ion solution is prepared by reduction of a cupric compound, preferably the reducing agent should be an amount at least equal to the stoichiometric amount necessary to reduce the cupric compound, and the reducing agent should be of a type that will not react with the starting compound or product. The absence of cupric ions and reducing agents of a type that react with the starting compound or product assures the absence of undesirable side reactions. Where the cuprous solution is prepared from a cuprous salt, a small amount of a reducing agent may be included to assure the absence of cupric ions, for it is well known that cuprous salts frequently oxidize to cupric salt structure. The cuprous ion solution may be prepared in situ with the starting compound by the addition of a cupric compound to a solution containing the starting compound and a suitable reducing agent.

Where the cuprous ion solution is a hydrohalide acid solution, the product is a hydrohalide acid salt of a cuprous thione compound having an aforesaid characteristic group represented by the formula



A hydrohalide acid is an acid selected from the group consisting of hydrochloric, hydrobromic, hydriodic, and hydrofluoric.

Where the cuprous ion solution is an alkaline or neutral solution and, however, one of the nitrogen substituents of the starting compound is an aforesaid substituted alkyl radical, the product is a cuprous thione compound having an aforesaid characteristic group.

Accordingly, the products of the process of the invention consist of cuprous thione compounds and cuprous