United States Patent Office 2,890,150 Patented June 9, 1959

2,890,150

CUPROUS DERIVATIVES OF SUBSTITUTED CYCLIC THIOUREAS

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No Drawing. Application April 6, 1956
Serial No. 576,538

17 Claims. (Cl. 167—33)

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.

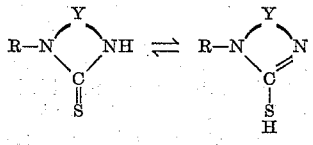
An object of this invention is a new class of compounds and compositions.

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.

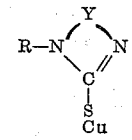
In the process of this invention starting compounds having a functional group represented by a thiourea-type structural formula are used to obtain the corresponding cuprous derivatives, a restriction being that at least one nitrogen atom must have as one of its substituents a hydrogen atom to permit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



to occur. A nitrogen substituent, as represented by R,

may be selected from the group consisting of hydrogen, alkyl radicals, substituted alkyl radicals and aryl radicals; and a nitrogen-linking substituent, as represented by Y, may be selected from the group consisting of a bivalent alkyl radical having at least two carbon atoms, a substituted bivalent alkyl radical having at least two carbon atoms, a bivalent aryl radical, and a substituted bivalent aryl radical. Starting compounds and processes for preparing the same are known to those skilled in the art; and some starting compounds, such as 2-imidazolidinethione or ethylenethiourea, are commercially available.

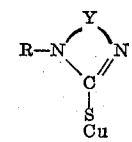
In the process of the invention, the aforesaid starting compounds, having a functional group represented by the thiourea-type structural formula, are treated with a cuprous ion solution to obtain products having a characteristic group represented by the formula



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 amount of reducing agent should be at least 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 reacts with the starting compound or product, assures the absence of undesirable side reactions. Where the cuprous ion 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 structures. 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 an alkaline or neutral solution, the product obtained is a cuprous compound of the aforesaid starting compounds and has the characteristic group represented by the formula



Where the cuprous ion solution is a hydrohalide acid solution, the product is a hydrohalide acid salt of the aforesaid cuprous compound having the characteristic group. A hydrohalide acid is an acid selected from the group consisting of hydrochloric, hydrobromic, hydriodic, and hydrofluoric.

Generally, upon treatment of the hydrohalide acid salt of the cuprous compound having the aforesaid characteristic group with excess alkali, the cuprous compound