

Synthesis of Copper oxychloride as Fungicide in bench scale

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Abstract

In one exemplar embodiment, the present invention comprises a method of making cupric hydroxide that comprises the steps of preparing a suspension of insoluble copper oxychloride in aqueous medium, mixing sodium lignosulfonate into the copper oxychloride suspension for more uniformly dispersing the copper oxychloride particles in the aqueous medium agitating the copper oxychloride suspension and added sodium lignosulfonate until a desired viscosity is obtained, adding sodium hydroxide to the copper oxychloride suspension for reacting with the copper oxychloride to form cupric hydroxide, and recovering the cupric hydroxide. This invention relates to a process for making a stable copper (cupric) hydroxide by means of reacting sodium hydroxide with copper oxychloride.

LITERATURE

There are numerous ways disclosed in the prior art for making cupric hydroxide. One technique uses a copper sulfate solution reacted with ammonia to form cupric hydroxide and a compound containing the sulfate radical for particular use in the preparation of a cuprammonium cellulose solution in making rayon as disclosed in U.S. Pat. No. 2,758,013. Others disclose use of a copper sulfate solution reacted with ammonia and then with an alkali metal hydroxide (such as sodium hydroxide) to precipitate non-soluble cupric hydroxide as shown in U.S. Pat. Nos. 1,800,828; and 1,867,357. Another variation of the ammonia reaction processes is the reaction under anhydrous conditions of an inorganic copper salt, ammonia and a lower alkanol solvent for the inorganic copper salt to form a resulting complex which is then reacted with an alkali metal hydroxide, with the resulting complex decomposed under vacuum to obtain cupric hydroxide as disclosed in U.S. Pat. No. 3,956,475. It is known that stable, separable cupric hydroxide cannot generally be made by direct reaction between copper sulphate and sodium hydroxide. The combination of these two chemicals results in the formation of blue cupric hydroxide in a sludge form but which rapidly decomposes to black cupric oxide. U.S. Pat. No. 1,920,053 discloses a process for making cupric hydroxide from copper sulfate and excess sodium hydroxide carried out at low temperatures (below 10° C.) to help overcome this problem. Another process for making cupric hydroxide is disclosed in U.S. Pat. No. Re. 24,324 in which trisodium phosphate is reacted with copper sulfate to form copper sodium phosphate which is in turn reacted with sodium hydroxide to precipitate cupric hydroxide. All of the prior art processes are too complex or expensive or fail to produce a stable form of cupric hydroxide suitable for large scale production, particularly for use as an agricultural fungicide and bactericide. The present invention remedies the problems of the prior art by providing a process or method of making cupric hydroxide that comprises the steps of preparing a suspension of insoluble copper oxychloride in an aqueous medium, mixing sodium lignosulfonate into the copper oxychloride suspension for more uniformly dispersing the copper oxychloride particles in the aqueous medium, agitating the copper oxychloride suspension and added sodium lignosulfonate until a desired viscosity is reached, adding sodium hydroxide to the copper oxychloride suspension for reacting with the copper oxychloride to precipitate cupric hydroxide, the sodium lignosulfonate further acting to stabilize the cupric hydroxide formed, and recovering the cupric hydroxide. The cupric hydroxide made according to this process is extremely stable, is the result of a one-reaction process, and enables a manufacturer to produce cupric hydroxide in large bulk quantities at lower prices than presently possible.

EXPERIMENTAL

The process for making stable cupric hydroxide, which is particularly suited for large scale production in manufacturing agricultural fungicides and bactericides, includes the following basic steps:

Step 1: Prepare a suspension of insoluble copper oxychloride ($\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$) in an aqueous medium of any convenient concentration and place in a suitable mixing vessel;

Step 2: Add sodium lignosulfonate (approximately 1% by weight) to the copper oxychloride suspension and agitate until the mixture achieves a desired viscosity as judged by when it takes on a "smooth" or "creamy" appearance as judged by eye;

Step 3: As rapidly as possible, add a sodium hydroxide solution (NaOH) of 50.0% concentration and containing an excess quantity of sodium hydroxide then stoichiometrically necessary to react with the copper oxychloride to form cupric hydroxide to the mixture of sodium lignosulfonate and copper oxychloride suspension and continue agitation until the resulting reaction slurry (comprising a suspension of cupric hydroxide in the resultant reaction) changes color from light blue or gray-blue to a dark blue (as judged by eye and memory);

Step 4: Stop agitation and collect the cupric hydroxide ($\text{Cu}(\text{OH})_2$) from the slurry by vacuum filtration. The above process is carried out at normal room temperatures. The collected cupric hydroxide filter cake is washed with fresh water until the pH is lowered to approximately 8. The washed dark blue filter cake may then be dried in any convenient manner to obtain a dried granular form of cupric hydroxide. The resultant aqueous filtrate or mother liquor, primarily a sodium chloride solution (NaCl) with remaining sodium lignosulfonate, is disposed of as waste.

In preparing large quantities of cupric hydroxide in the batch process, it has been found that certain preferred quantities and concentrations of starting materials yield the best results. For example, if it is desired for the above process to yield one ton of cupric hydroxide, then the copper oxychloride suspension in an aqueous medium should preferably be 9120 liters and have a concentration of 98 grams per liter. The pH range desired is 6-7. The quantity of sodium lignosulfonate added would be 11 kilograms. The sodium hydroxide solution should be a 50% concentration containing a maximum of 410 kilograms of the sodium hydroxide dry base. While varying percentages of excess sodium hydroxide than that necessary to stoichiometrically react with the copper oxychloride to form cupric hydroxide may be used, it has been found that large excess percentages, for example 80.0%, are preferable to accelerate the reaction rate and form the desired size of cupric hydroxide particles of crystals in suspension.

There is no exact formula for the starting material copper oxychloride, but it has been found convenient to use the following formulation: $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ which when reacted with the sodium hydroxide provides: $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2 + 2\text{NaOH} \rightarrow 4\text{Cu}(\text{OH})_2 + 2\text{NaCl}$

The dried granular cupric hydroxide is formulated for final use as an agricultural fungicide or bactericide by mixing with sodium lignosulfonate (7.0% by weight), a suitable wetting agent (such as nonyl phenol exohxilate or other suitable agent) (less than 1.0% by weight) and calcium carbonate (about 16% by weight). The calcium carbonate is used as a filler to reduce the copper concentration in the final product to a maximum of 50%. The above mixture is then pulverized in a hammer mill to a fine powder to form the final stable cupric hydroxide product.

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