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COPPER FUNGICIDE

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5 Claims. (Cl. 167—16)

This invention relates to a copper containing fungicide.

One of the objects of the present invention is the provision of a process for making a copper phosphate fungicide by electrolytic dissolution of metallic copper. A further object is the provision of a safe and efficient fungicide.

We have found that if a copper anode, together with a cathode made either of copper or an inert material be immersed in a solution containing sodium phosphate and sodium sulfate and a suitable direct current be passed through said electrodes, that a copper phosphate-sodium phosphate complex will be precipitated in the electrolyte in very finely divided form. This operation may be made continuous by continuously removing the precipitated copper-sodium phosphate complex from the solution and continuously replenishing the electrolyte. According to our invention it is possible to operate the cell without diaphrams, thus simplifying the operation considerably.

In previous work on the production of copper phosphate by electrolysis of copper anodes it has been proposed to utilize an electrolyte containing chlorine compounds, particularly sodium perchlorate (German Patent 91707). Furthermore it has hitherto been found necessary to utilize diaphrams surrounding the cathode. For continuous production by the electrolytic method we have found that chlorine compounds are undesirable in the electrolyte, particularly when preparing copper phosphate since the presence of such compounds causes the formation of a layer or coating over the anodes which in time increases the resistance of the cell. The use of chlorate in the electrolyte in a short time builds up a heavy layer of copper phosphate on the anode which strips off from time to time and peels back against the cathode, causing a short circuit.

For producing a copper phosphate-sodium phosphate complex suitable for use as a fungicide and for other purposes we have found that an electrolyte composed of sodium sulfate and sodium phosphates can be used continuously in a cell composed of copper electrodes or at least a copper anode together with an inert cathode and relatively high efficiencies obtained. For reasons already stated it is desirable that the chlorine content of the electrolyte either as chlorine ion or as chlorate ion be relatively low.

By way of example we give the following description of one method of carrying out our invention:

An electrolytic cell having copper anodes and cathodes is connected to a suitable source of direct current. The current density used may be varied between 15 and 70 amperes per sq. ft. of anode area, however, for most satisfactory operation, we prefer to operate in the neighborhood of 27 to 30 amperes per sq. ft.

The electrolyte is a dilute solution containing sodium sulfate, disodium phosphate and monosodium phosphate. We have obtained satisfactory results using a solution containing 4.5% of Na_2SO_4 and 0.5% of a mixture of Na_2HPO_4 and NaH_2P_4, the proportions of the latter two salts being such as to give a pH between 5.0 and 8.0. While the composition of the product is substantially unchanged between these last enumerated pH values, for most satisfactory operation we prefer to operate with an electrolyte containing the above mentioned salts, the sodium phosphates being therein proportioned so as to give a pH between the limits of 6.0 to 6.4, which electrolyte it will be recognized is somewhat on the acid side of neutrality. During operation the electrolyte tends to become more basic, which condition is corrected by the regulated addition of phosphoric acid to the electrolyte. During operation the temperature of the electrolyte is maintained at approximately 30° C.

The product of our process is a double salt of tribasic copper phosphate and disodium phosphate. The formation of this compound therefore withdraws sodium phosphate from the electrolyte which compound must be replaced. We find it necessary to add disodium phosphate in addition to the phosphoric acid already mentioned to the electrolyte in order to keep the sodium phosphate content of the electrolyte substantially constant.

The formation of a copper phosphate-sodium phosphate complex occurs as a light blue, very finely divided precipitate in the electrolyte. For continuous operation we therefore remove continuously a portion of the electrolyte containing the suspended product, pass the same through a filter press and return the filtrate to the electrolytic cell. The filtrate returned to the cell is caused to agitate the electrolyte to prevent the copper phosphate from settling out on the bottom. The filter cake in the press is washed, then removed from the press and dried. It may then be finely ground for use as a fungicide, or as an ingredient thereof.

The product as produced by our process has a composition corresponding to the formula: $3Cu_3(PO_4)_2.2Na_2HPO_4.XH_2O$, where X is in the

neighborhood of 6. It is a light blue powder insoluble in cold water and when ground to a size suitable for use in fungicidal preparations it has a particle size varying from 2 to 20 microns. The bulk density varies between 10 and 15 lbs. per cubic foot and usually is in the neighborhood of 12 to 13 lbs. per cubic foot. This is considerably less than the density of copper phosphate as produced by the reaction of copper oxide and phosphoric acid the latter having been found to have a bulk density of 50–53 lbs. per cubic foot when ground to the same degree of fineness as the product produced by the present process.

The electrolytic product as herein prepared consists of agglomerates of crystals of the copper phosphate complex, over 99 per cent of the agglomerates being smaller than 20 microns in size. The individual crystals making up the agglomerates are approximately 1 to 2 microns in size. It is distinguished from the product produced by precipitation of disodium phosphate and copper sulfate by being considerably more uniform and finer. The precipitated product consists of particles 63% of which are between 60 and 30 microns 17% between 30 and 12 microns and 20% less than 12 microns in size. The electrolytic product as herein produced is also distinguished from the product produced by the reaction of copper oxide and phosphoric acid in that the latter has bulk density approximately four times that of our product.

The copper phosphate-sodium phosphate complex as produced by our process normally carried in the neighborhood of 6 molecules of water of crystallization. By heating the complex we are able to lower the amount of contained water of crystallization to any desired degree and indeed we may make a substantially dehydrated product merely by heating to the dehydrating temperature.

We may also produce tribasic copper phosphate: $Cu_3(PO_4)_2$ by leaching the copper-sodium phosphate double salt with hot water. The sodium phosphate may be removed in whole or in part. The tribasic copper phosphate thus produced is of low bulk density and may be used as an ingredient of fungicides in the usual manner.

The sodium phosphate removed from the copper-sodium phosphate double salt may be returned to the electrolytic cell for reuse in the process.

The products as produced by our process may be employed as dusting powders in the customary manner, or they may be made into the form of a slurry with water, by the incorporation therewith of lime or colloidal clays. Other insecticides or fungicides may be incorporated with the normal copper phosphate or with the complex if desired. Our product being of extremely fine particle size and of low density is particularly useful when employed with the customary spreaders and adhesives.

Field experiments with our improved fungicide have indicated successful control of the various fungus diseases which attack peach and apple trees, with considerably less damage to the plant than commercial Bordeaux mixture.

This application is a division of Serial No. 85,886 filed June 18, 1936, now Patent Number 2,169,576, granted August 15, 1939.

What we claim is:

1. A copper fungicide comprising a double salt of tri basic copper phosphate and di sodium phosphate in the form of crystals of the order of 1 to 2 microns in size.

2. A copper fungicide comprising the compound: $3Cu_3(PO_4)_2.2Na_2HPO_4$ in the form of agglomerated crystals, said crystals being of the order of 1 to 2 microns in size.

3. A copper fungicide comprising the compound: $3Cu_2(PO_4)_2.2Na_2HPO_4.XH_2O$ where X is approximately 6 said compound being in the form of agglomerated crystals, the individual crystals being of the order of 1 to 2 microns in size.

4. A copper fungicide comprising the hydrated compound: $3Cu_3(PO_4)_2.2Na_2HPO_4$ in the form of agglomerates of very fine crystals, said agglomerates being smaller than 20 microns in size and the crystals being of the order of 1 to 2 microns in size.

5. A copper fungicide comprising the compound $3Cu_3(PO_4)_2.2Na_2HPO_4$ said compound having a bulk density in the neighborhood of 10 to 15 lbs. per cubic foot.

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