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[54] **PROCESS FOR APPLYING COPPER 8-QUINOLINOLATE TO CELLULOSICS FROM SOLVENT SYSTEM**
7 Claims, No Drawings

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ABSTRACT: Copper 8-quinolinolate was dissolved in acetic acid-xylene solvent mixtures and applied at room temperature (25° C.) to cotton fabrics by pad-dry-cure method to produce treated fabrics with excellent fungicidal properties from the in situ deposition of the fungicide in fine particle size for better uniformity and penetration of treatment.

PROCESS FOR APPLYING COPPER 8-QUINOLINOLATE TO CELLULOSICS FROM SOLVENT SYSTEM

This invention relates to a process for solubilizing a difficulty soluble fungicide for application to cellulosic textiles. Specifically, this invention relates to the direct solubilizing of copper 8-quinolinolate in acetic acid-xylene solvent mixtures. More specifically, this invention relates to a process of making this excellent fungicide easy to apply to cellulosic textiles from solution at room temperature, by conventional techniques, such as the pad-dry-cure method of treating fabrics, where the solvent evaporates and is capable of being reclaimed by condensation.

The main object of the instant invention is to provide a means of directly solubilizing copper 8-quinolinolate at room temperature for nondegrading cellulosic treatments.

A second object of the instant invention is to provide a means of applying the fungicide to fabrics, in order to impart to cellulosic fabrics better rot and weather resistance, through in situ deposition of the fungicide in fine particle size throughout the treated fabric.

A third object is to provide a practical method of quantitatively applying copper 8-quinolinolate from solution in organic solvents at room temperature.

A fourth object is to provide a novel solvent system for copper 8-quinolinolate and alkyd resins for application to cellulosic fabric from a single bath to produce a fungicidal coating.

A fifth object is to provide a novel solvent system for copper 8-quinolinolate and pinene polymer resins for application to cellulosic fabric from a single bath to produce a fungicidal coating with water resistance.

Another object includes the preparation of a solvent system for combined applications of paints or other coatings which require the inclusion of a good fungistatic agent.

The prior art teaches that copper 8-quinolinolate is a recognized fungicide useful in applications to cellulosic materials, but it is very difficulty soluble in organic solvents, demonstrating little or no direct solubilization, requiring that this fungicide be applied only from emulsion, double decomposition, or dispersion systems where maximum in situ deposition and minimum particle size have not been attained. Many emulsion and dispersion systems exist for the application of copper 8-quinolinolate to cellulosics. Although solubilized by mineral acids, the solutions thus produced degrade cellulose. The discovery of a suitable nondegrading organic solvent system for the application of copper 8-quinolinolate to cellulosics has several values relative to utility. The solvent can be reclaimed by condensation from the wet padded cellulosic fabric during drying, and again used in formulating more copper 8-quinolinolate solution. The solvent system, which is the instant invention, wets the entire cellulosic material uniformly, and results in a more uniform treatment. Waxes and resins can be incorporated into the solvent system to produce water resistant fungicidal treatments applicable from a single bath. While prior art has shown that copper 8-quinolinolate is soluble to the extent of about 5 percent in hot (110° C.) glacial acetic acid, we have learned that on cooling the solution to room temperature (25° C.) most of the compound separates from solution as crystals. This is impractical for fabric treatments, since as the solutions cool in a padding operation the deposition of crystals of copper 8-quinolinolate would produce an irregular and nonuniform treatment. The solution must be stable at what is commonly referred to as "room temperature," which is about 25° C. for utility in conventional processing of cellulosic fabrics.

In the process of investigative work which led to the instant invention, it was discovered that when the hot glacial acetic acid solubilized copper 8-quinolinolate, the solution could be stabilized by adding an equal volume of xylene containing a small quantity of acetic anhydride to remove a fractional percentage of water in the acetic acid, and that the solution of copper 8-quinolinolate could then be cooled to room temperature (25° C.) and used for periods of 8 hours without any indication of crystal formation or any other such phenomenon which would interfere with the application of the ingredients to cotton fabrics, paper, rope, and other cellulosic materials by conventional wetting and drying in air or oven. The fabrics and other cellulosic materials so treated were evaluated through outdoor weathering and soil burial (for rot resistance) and found to have very good fabric protection, as determined by tests.

Other preparations were formulated to include alkyd resins, polycoumarone-indene resins, and polypinene resins in the same bath with the copper 8-quinolinolate. These treatments were applied separately to cotton duck to give a copper 8-quinolinolate fungicide treatment with water resistance characteristics. By incorporating a ground pigment with the resin-copper 8-quinolinolate solution a paint was formulated to impart fungicidal characteristics with light screening pigment and resin binder.

In general, the invention can be best described as a novel direct solubilization and applicational process for applying copper 8-quinolinolate to cellulosics from an organic solvent system at room temperature, where other resins and paints are compatible, to produce good uniformity and maximum penetration of fungicide through in situ deposition of copper 8-quinolinolate within the treated cellulosic, on evaporation of the solvent. In solution, the fungicide is reduced to the ideal applicational state for maximum penetration and uniformity or treatment, while the cure-evaporated solvents can be reclaimed by condensation, to be used again to solubilize other copper 8-quinolinolate.

The following examples are presented to illustrate the invention and certain aspects of its usefulness. These are not to be interpreted as limiting the invention in any manner whatever.

The tests applicable to the treatments on cotton fabrics are the following:

Breaking Strength—Scott Tensile Test (ASTM D39–40).

Soil Burial—Compost, soil, sand—90° F. and 90 percent relative humidity.

Water Resistance—Bead test and pouring water across the treated fabric surface, followed by observation for wet-in and wet through.

EXAMPLE 1

Solubilizing Copper 8-Quinolinolate:

Fifty milliliter of glacial acetic acid (99.5 percent) were poured into a 300 ml. Erlenmeyer flask. A 2.0 gram sample of powdered copper-8 was added, and the mix gradually heated to a boil and boiled for 1 minute, while stirring. All of the solid dissolved and a dark green solution was produced. While the solution was almost boiling (100° C.), 50 ml. of xylene were added and mixed by stirring. A dark green solution resulted, which remained uniform when cooled to room temperature. After standing for 1 hour at room temperature, a little sediment of copper-8 was noted, and most of the copper-8 remained in solution.

EXAMPLE 2

Solubility of Copper-8 in the Cold (25° C.):

2.0 grams of copper-8, 50 ml. of glacial acetic acid (99.5 percent) and 50 ml. of xylene were mixed and stoppered in a flask. Solubility was observed over 24 hours. At the end of this time, the solid dissolved, and a deep green solution resulted.

EXAMPLE 3

Solubilizing Copper-8 with Acetic Acid, Acetic Anhydride and Xylene:

The presence of 0.5 percent water in 99.5 percent glacial acetic acid was eliminated by adding a small amount of acetic

anhydride, which reacted with this water to produce acetic acid:

$(CH_3CO)_2O+H_2O \rightarrow 2CH_3COOH$

The presence of water in the solvent system reduced the stability of the solution and caused some precipitation on standing. The use of acetic anhydride increased the stability and thus prevented precipitation of solid copper-8 . The following formulation was effectively prepared and demonstrated:

A. 3.0 grams copper 8-quinolinolate powder (18 percent Cu)

B. (45 ml. glacial acetic acid [99.5 percent] or 47.5 grams mixed (5 ml. acetic anhydride or 5.5 grams

C. 50 ml. xylene or 44.0 grams The copper-8 was weighed into a Pyrex Erlenmeyer flask. The mixture of glacial acetic acid and acetic anhydride added, and the flask heated just to a boil for 2 minutes. All of the copper-8 dissolved with the temperature at 110° C. The flask was then cooled to 90° C., when 50 ml. of xylene were added and stirred in to form a uniform solution (dark green). When cooled to room temperature (25° C.) complete solution of the copper-8 had been effected, and a dark green solution resulted (100 grams).

EXAMPLE 4

Padding with the Copper-8 Solution from Example 3:

A 1 yard × 8 inch piece of scoured army duck was wetted with the solution and padded twice through tight rolls to remove excess solution. The wet sample was then oven dried at 120° C./5 minutes. A deep yellow copper-8 fabric treatment was effected with the fabric. The solution represents 3 percent copper-8, the add-on was 0.37 percent copper as metal with a 70 percent wet pickup.

EXAMPLE 5

Poly α-pinene Resin (Piccoflex 120 Resin) Copper-8 Solubility:

Solution from example 2 was treated with 2 grams of Piccoflex 120 Resin, resulting in the solubility of the resin in the solution. A sample of 80×80 printcloth 6 inches ×6 inches was wetted with the solution, blotted, and allowed to air dry for 4 hours. The treated fabric was deep yellow, slightly stiff in hand, and showed water resistance characteristics when water was poured over it.

EXAMPLE 6

Poly-Coumarone-Indene (Nevillac Hard Resin) Copper-8 Solubility:

Solution from example 2 was treated with 1 gram of "Nevillac Hard" Resin, producing a solution of the resin and copper-8. This solution was applied to 80×80 cotton fabric 8 inches × 4 inches, blotted, and allowed to air dry for 4 hours. A yellow-brown fabric treatment was uniformly produced. Water resistance was demonstrated after 8 hours drying, by flowing water over the treated fabric surface.

EXAMPLE 7

Alkyd Resin—Copper-8 Miscibility:

Solution from example 2 was mixed with a liquid alkyd resin to produce a 10 percent solution of the alkyd resin in the copper-8 solution. Complete solubility (miscibility) was effected. A section of 80×80 printcloth 8 inches × 4 inches was treated with the solution and blotted. It was air dried for 24 hours, producing a brownish-yellow fabric, moderately stiff hand, and uniform in treatment. When the alkyd resin was mixed with ground pigment (ochre) and incorporated with the solution, a pigmented coating (paint) was produced on the fabric, along with the fungicide.

EXAMPLE 8

Soil Burial (Rot Resistance) Results with Copper-8 Solution:

The solution from example 2 was used to pad scoured 9 oz. duck. The wet padded and squeezed duck was oven dried at 120° C./5 minutes to give a 0.2 percent copper metal add-on. The fabric was soil buried for 6 weeks and examined after each week's exposure. A control (untreated) rotted in one week, while the treated duck showed 100 percent retained tensile strength through two weeks, 72 percent through three weeks, 28 percent through four weeks, 28 percent through five weeks, and 10.7 percent in 6 weeks.

EXAMPLE 9

Outdoor Weathering Results with Copper-8 Solution:

The solution from example 2 was used to pad scoured 9 oz. duck according to the procedures in example 8. The dry treated duck was exposed along with untreated duck on the weathering racks outdoors for 15 months. The untreated duck was completely covered with mildew and algae and showed 23 percent retained tensile strength after 15 months exposure. The treated duck showed some algae growths and negligible mildew after 15 months exposure, and retained 38 percent strength.

EXAMPLE 10

Demonstration of Effect of Solvent Copper-8 Treatment on Cotton 9 oz. Duck and 80×80 Printcloth:

Untreated cotton 9 oz. scoured duck, having an initial breaking strength of 137.0 pounds, and cotton 80×80 printcloth (untreated) having an initial breaking strength of 48.4 pounds, were treated with the copper-8 solution described in example 2, followed by squeezing out excess solution to give a 50 percent wet pickup, and oven drying at 130° C. for 4 minutes. The samples were then tested for percent retained tensile breaking strength. The 80×80 printcloth retained 100 percent strength, while the scoured duck retained 95 percent strength, demonstrating that the treatment did not adversely affect the fabrics for utility.

I claim:

1. A process for imparting water and rot resistance to a cellulosic material from a single-bath solution, comprising:
   a. forming a single bath solution by mixing (1) a resin selected from the group consisting of an alkyd resin, a polypinene resin, and a cumarone-indene resin, with (2) a solution containing about from 1.00 percent to 3.00 percent, by weight, of copper 8-quinolinolate fully dissolved in a water-free glacial acetic acid to xylene mixture in molar ratios, respectively, of about 1.5:1.0 to 2.0:1.00.
   b. impregnating the cellulosic material with the single-bath solution thus formed to about a 70 percent wet pickup, and
   c. drying the wet, impregnated cellulosic material for about 5 minutes at about from 120° to 130° C.

2. The process of claim 1 wherein the resin is an alkyd resin.

3. The process of claim 1 wherein the resin is a polypinene resin.

4. The process of claim 1 wherein the resin is a cumarone-indene resin.

5. A process for imparting fungicidal properties to a cellulosic textile comprising:
   a. impregnating the cellulosic textile with a water free glacial acetic acid to xylene mixture in molar ratios respectively of about from 1.5:1.0 to 2.0:1.0, containing about from 1.00 percent to 3.00 percent by weight of copper 8-quinolinolate fully dissolved therein, to obtain a wet pickup of about 70 percent, and
   b. drying the wet impregnated cellulosic textile for about 5 minutes at about from 120° to 130° C.

6. A process for imparting fungicidal properties to a cellulosic textile comprising:
   a. impregnating the cellulosic textile with a water free glacial acetic acid to xylene mixture in molar ratios respectively of about from 1.5:1.0 to 2.0:1.0, containing about from 1.00 percent to 3.00 percent by weight of copper 8-

quinolinolate fully dissolved therein, to obtain a wet pickup of about 70 percent, and

b. air drying the wet, impregnated cellulosic textile for about 4 hours at about 25° C.

7. A process for imparting water and rot resistance to a cellulosic material from a single-bath solution, comprising:

a. forming a single-bath solution by mixing (1) a resin selected from the group consisting of an alkyd resin, a polypinene resin, and a cumarone-indene resin, with (2) a solution containing about from 1.00 percent to 3.00 percent, by weight, of copper 8-quinolinolate fully dissolved in a water-free glacial acetic acid to xylene mixture in molar ratios, respectively, of about 1.5:1.0 to 2.0:1.0,

b. impregnating the cellulosic material with the single-bath solution thus formed to about a 70 percent wet pickup, and

c. air drying the wet, impregnated cellulosic material for about 4 hours at about 25° C.

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