Patented Aug. 14, 1945 2,381,863

UNITED STATES PATENT OFFICE

2,381,863

METHOD OF FUNGUSPROOFING TEXTILES

Paul George Benignus, Belleville, Ill., assignor to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application May 1, 1943, Serial No. 485,341

2 Claims. (Cl. 117—138.5)

This invention relates to fungicides for rendering textiles permanently resistant to fungus attack and more particularly to the fungus-proofing of textiles with copper salt derivatives of 8-hydroxy quinoline.

It is known that 8-hydroxy quinoline (oxy quinoline) and 8-hydroxy quinoline sulfate (quinosol) possess preservative properties. For example, United States Patent No. 575,978 issued to Ostermann disclosed this characteristic of 8-hydroxy quinoline. In addition, 8-hydroxyquinoline, its oil-soluble salts, such as the benzoate and palmitate, or groups substituted for the hydrogen atom, were suggested in United States Patent No. 2,021,137 issued to Stone for use in water-proof coatings for fibrous materials to render them antiseptic as well as water-proof. The preparation of the copper salt of 8-hydroxy quinoline as an analytical reagent has been disclosed in the art. Inorganic heavy metal salts have been employed in the treatment of cellulose fibers for various purposes, such as fire-proofing, water-proofing and preservation. A large ratio of heavy metal to treated fibrous material had to be established to provide even a moderate degree of preservative action. Moreover, the treatment was not enduring, apparently because the heavy metal impregnant lacked the stability and resistance to removal by water and aqueous solutions under conditions normally encountered in the atmospheric weathering of textiles.

One of the objects of the present invention is to provide textiles permanently fungicide-impregnated with copper salt derivatives of 8-hydroxy quinoline.

Another object is to provide fungus-proofed textiles characterized by improved resistance to removal of the fungicide agent by water and aqueous solutions in the normal weathering of the impregnated material.

A further object is to provide a method for permanently fungus-proofing fibrous organic materials with copper salt derivatives of 8-hydroxy quinoline.

A further object is to provide a fungus-proofing impregnating agent for textiles characterized by the property of imparting a permanently high degree of resistance to fungal growth together with a low ratio of heavy metal to textiles.

Further objects will become apparent from the following description of the invention.

According to the present invention generally stated, textiles, such as cotton fabrics, duck, osnaburg, twine and cord, are rendered fungus-proof by impregnation with copper salt derivatives of 8-hydroxy quinoline. This impregnation may be accomplished in several ways. For example, the textile, such as cotton duck or khaki, may be soaked in an aqueous solution of a copper salt, such as the acetate, sulfate or other water-soluble copper salt. After impregnation is accomplished to the desired extent, the textile may be removed from the solution, rendered free of excess salt solution, if desired, and transferred to a solution containing 8-hydroxy quinoline, desirably present as the acetate, sulfate, phosphate or other acid salt. Following this treatment, the textile is removed from the solution, excess solution is expelled from the textile by any suitable means, for example, pressure rollers, and the treated textile is dried or washed and dried, as desired. Textiles treated by this process have been found to resist fungus attack under drastic conditions, such as dampness, exposure to fungus attack, abrasion and repeated and prolonged washings with water and with soaps. It has been found unnecessary to dry the textile immediately upon its removal from the 8-hydroxy quinoline solution in order to fix or set the fungicide-impregnant in the textile. The textile may be washed with water or soap and water while still wet from the treating solution without danger of substantial removal of the fungicide from the textile.

As an alternative to the foregoing procedure, the textile may be treated in a single-stage with an aqueous solution of the copper salt derivatives of 8-hydroxy quinoline in which the salt derivatives are made soluble by reducing the pH of the aqueous solution to a pH within the range of 2.7 to 2.2, or lower. For example, a 0.1N hydrochloric acid solution, which has a pH of about 1.0 may be used to dissolve solid copper 8-hydroxy quinoline and the solution thus formed may be employed to impregnate the textile. Acid solutions having a pH value below that of 0.1N hydrochloric acid may be employed, care being taken, however, to avoid concentrations of acid which will impair the strength characteristics of the textile for a given purpose. This may be accomplished by mixing an acid, such as dilute hydrochloric acid, with a suspension of the copper salt derivatives of 8-hydroxy quinoline in water. The conditions under which impregnation is effected with the solubilized salt derivatives may be varied. For example, the impregnation may consist of a simple washing operation at room or elevated temperatures or, if desired, a boiling operation followed by a lowering of the

temperature of the impregnation solution to a point below the boiling point of the solution. After the impregnation has been effected to the desired extent, the pH of the solution is raised to a point above 2.7, for example, by adding ammonium hydroxide or any other suitable alkali or alkaline material, such as sodium hydroxide or sodium carbonate. It is to be understood that this elevation of the pH to a point above the pH of 2.7 is for the purpose of rendering the copper salt derivatives of 8-hydroxy quinoline present on the textile fibers and within the interstices of the fibers insoluble in water or aqueous solutions having a pH in the range of 2.8 to 13. For this purpose, it is only necessary to add sufficient alkali to neutralize sufficient of the acid present in the impregnating solution to raise the pH to a point above 2.7. After the copper salt derivatives of 8-hydroxy quinoline have been insolubilized within the interstices of the textile, the textile may be removed from the bath, excess liquid may then be expelled and the textile may be dried. The insolubilization treatment may be carried out in an alkaline bath apart from the impregnation bath.

As a further alternative method, analogous in part to the procedure first hereinbefore described, namely, the 2-stage procedure, in place of an acid salt solution of 8-hydroxy quinoline, the free-base 8-hydroxy quinoline may be employed by using an organic solvent for the base in place of water. The organic solvent selected may be miscible or immiscible with water. As an alternative, the free base may be emulsified with water at temperatures above 75°–76° C., the melting point of 8-hydroxy quinoline, and the fabric which has been impregnated with copper salt solution may be placed in the emulsion.

The process of the present invention may be employed in the treatment of textiles of many varieties, including twines and cords and fabrics of the close-mesh as well as loose-mesh types. The textiles may be composed of cotton, wool, silk, cellulose derivatives or mixtures of any of these. The treatment should be applied in a manner such as to insure uniform impregnation of the textile in order that isolated untreated portions of the textile may be avoided. The technique of impregnation, as practiced in the textile art and in the art of water-proofing and treating textiles for various purposes, is understood by those skilled in those arts.

The textiles to be treated by the method of the present invention to provide the permanently fungus-proof textiles of this invention are desirably treated in the unsized condition in order to insure sufficient impregnation of the fibers per se. The textiles may be dyed, bleached or in the natural state. Textiles rendered permanently fungus-proof by the process of the present invention may be subsequently dyed. The process of the present invention may be applied advantageously to textiles which are to be coated or impregnated subsequently, for example, with plastic compositions containing vinyl resins, styrene resins, cellulose esters or ethers or other plastic materials.

Textiles which are to be rendered permanently fungus-proof by the process of the present invention may be processed by either a batch or a continuous method. In a continuous method using the 2-stage process, the textile may be led first through the copper salt bath, thence through rollers to expel excess solution and thereafter into a bath continuing the acid salt of 8-hydroxy quinoline. From this bath, the textile may be led through wringer rollers to expel the excess solution, through a clear water bath, through wringer rollers and thereafter through drying rollers to dry the textile. Prior to immersion in the first bath, the textile may be pre-wetted by immersion in water or by spraying water upon the material. Various alternative procedures for treating textiles by the process of the present invention are contemplated as part of the present invention.

Textiles rendered fungus-proof by the process of the present invention are permanently fungus-proof under the most drastic conditions, such as contact with acid soils, the pH of which ranges from approximately 3.5 to 4 or even somewhat lower. This property is apparently unique with textiles containing the copper salt derivatives of 8-hydroxy quinoline, since none of the other metal salt derivatives, for example, the aluminum, cadmium, calcium, and magnesium salt derivatives of 8-hydroxy quinoline, were found to impart the combination of adequate fungus-proofing and permanency of fungus-proofing to textiles exposed to contact with moist or wet acid soils. At pH conditions from 2.8 to 4.0, these other salts were solubilized and leached from the textile, thereby exposing the textile to attack by fungus.

The fungus-proof textiles, and the process of rendering textiles permanently fungus-proof, of the present invention are further demonstrated in the following examples, which are to be construed merely as illustrative of the invention and not as limiting the invention.

Example I

An aqueous solution containing 2% of copper acetate was prepared and heated to 40° C. A test strip of osnaburg fabric measuring 6'' x 8'' was immersed in 400 cc. of this solution and allowed to soak for about 2–5 minutes with occasional agitation. The fabric was then removed from the solution and passed through a winger to remove excess solution. An aqueous solution containing 2.5% of 8-hydroxy quinoline acetate was prepared and heated to 40° C. The test strip previously impregnated with copper acetate solution was immersed in 400 cc. of 8-hydroxy quinoline acetate solution and allowed to soak for about 2–5 minutes. The fabric was then removed from the solution, rinsed with tap water and dried.

The treated fabric was scrubbed and washed vigorously and repeatedly with a soap containing powdered pumice until the suds remained white. After thorough washing in clear water, the fabric was dried and exposed to the textile rotter, *Chaetomium globosum*, for 14 days by the method given in Corps of Engineers, U. S. Army Tentative Specification No. T—1452—A, entitled "Processing Fabrics, Cordage and Threads for Mildew-Proofing," dated January 15, 1943, paragraphs F—3—*a* (3) to 3—*a* (8), inclusive. There was no evidence of fungus growth on the cloth. An untreated specimen exposed under similar conditions was heavily attacked by the fungus.

Another specimen of osnaburg fabric impregnated in the manner hereinbefore described was leached in running water for 90 hours, the rate of flow of water through the fabric being about 1 gallon per hour. After exposure of the specimen to *Chaetomium globosum* for 14 days, there was no evidence of fungus growth. The specimen was analyzed for copper and was found to contain

0.44% of the copper salt derivative of 8-hydroxy quinoline.

Example II

A cotton duck fabric was immersed in a 1% copper acetate solution at 80° C. for 5 minutes. The fabric was removed from the solution, drained to expel excess solution and immersed in a 1.6% solution of 8-hydroxy quinoline acetate solution at 70° C. for 5 minutes. The fabric was removed, washed with soap and finally with clear water and dried. After 14 days of exposure to *Chaetomium globosum* by the method of Example I, there was no evidence of fungus growth.

Example III

A khaki fabric was immersed in a 0.5% solution of copper acetate and the solution was heated to boiling and boiled for 20 minutes. Thereupon the solution was allowed to cool to 50° C. The fabric was removed, drained and immersed in an 0.8% solution of 8-hydroxy quinoline acetate for 5 minutes at 40° C. The fabric was removed from the solution, washed with soap and water and dried. After 14 hours exposure to *Chaetomium globosum* by the method of Example I, there was no sign of fungus growth.

Example IV

A piece of twisted cotton cord was immersed in a 0.25% solution of copper nitrate for 30 minutes at room temperature. The cord was removed, drained and immersed in a 0.4% solution of 8-hydroxy quinoline sulfate for 5 minutes. The treated cord was washed with water and dried. After 14 days exposure to *Chaetomium globosum* by the method of Example I, there was no evidence of fungus growth on the cord.

Example V

A cotton-wool fabric was first soaked in water, drained and then immersed in a 0.12% solution of copper sulfate at room temperature for 10 minutes. The fabric was drained and immersed in a 0.2% solution of 8-hydroxy quinoline acetate for 5 minutes. The fabric was removed from the solution, washed with water and dried. Analysis of a portion of the fabric revealed the presence of 0.25% of copper 8-hydroxy quinoline in the fabric. The remainder of the fabric was exposed to *Chaetomium globosum* for 14 days in the manner of Example I; there was no evidence of fungus growth in the fabric.

Example VI

A bag of the type used for sand was immersed in a 0.06% solution of copper acetate at 50° C. for 15 minutes. The bag was removed from the solution, passed through a wringer and immersed in a 0.1% solution of 8-hydroxy quinoline acetate at 50° C. for 15 minutes. The treated bag was removed from the solution, washed with water and dried. Analysis of a specimen of the bag revealed the presence of 0.1% of the copper salt derivative of 8-hydroxy quinoline in the fabric. The bag was then exposed to contact with a wet acid soil having a pH of approximately 3.5–4.0 for several weeks. The bag was thereupon washed with water and dried. After inoculation and incubation with *Chaetomium globosum* by the method of Example I, there was no evidence of fungus growth on the bag.

Example VII

An aqueous solution of the copper salt derivatives of 8-hydroxy quinoline was prepared by mixing 200 cc. of a 0.06% solution of copper acetate with 200 cc. of a 0.1% solution of 8-hydroxy quinoline acetate and adding sufficient hydrochloric acid to this mixture to lower the pH of the solution to 2.4, or until the precipitate which formed upon mixing the reactants became solubilized in the acidic solution. The solution was heated to 40° C. An osnaburg fabric was immersed in the solution for 10 minutes. After this time, sufficient ammonium hydroxide solution was added to raise the pH of the solution to 2.8. The fabric was removed from the solution, drained, washed with soap and water and dried. After inoculation and incubation with *Chaetomium globosum* by the method of Example I, there was no evidence of fungus growth on the fabric.

Example VIII

An aqueous solution of the copper salt derivatives of 8-hydroxy quinoline was prepared by mixing 200 cc. of an aqueous 2% copper acetate solution with 200 cc. of an aqueous 2.5% 8-hydroxy quinoline acetate solution and adding sufficient hydrochloric acid to lower the pH of the solution to 1.7, or until the precipitate which formed upon mixing the reactants became solubilized in the acidic solution. The solution was heated to 50° C. A cotton duck fabric was immersed in the solution for 10 minutes. After this time, the fabric was removed from the solution and drained free of aqueous solution. The fabric thus treated was immersed in a 5% solution of sodium carbonate for 2 minutes, removed, drained, washed with soap and water and dried. After exposure to *Chaetomium globosum* by the method of Example I, there was no evidence of fungus growth on the fabric.

It will be observed that the quantity of the copper salt derivative of 8-hydroxy quinoline present in the textiles treated and tested in the examples hereinbefore described is relatively small and yet there was no evidence of fungus growth when the textiles were subjected to abrasion, washing, leaching and finally to inoculation and incubation with *Chaetomium globosum* by the method of Example I. The permanence and effectiveness of the treatment are apparent from the drastic conditions under which the textiles were tested before inoculation.

In addition to the permanent fungus-proofing imparted by the treatment of the present invention, there is evidence that the treatment also imparts resistance to bacterial action and that this resistance is substantially of the same degree of permanence as the resistance to fungus attack.

The proportions of copper salt derivative of 8-hydroxy quinoline to textile may be varied widely, depending upon the extent of treatment desired and the type of service conditions for which the textile is intended. It is evidenced, however, that a minute quantity of the treating agent in the textile is sufficient under very drastic conditions.

The term "textile" as employed in describing the present invention is intended to embrace all forms of textile materials, including yarn, twine, cord, rope, fringes and fabrics of various types of weaves, from closely woven to loosely woven.

The term "copper salt derivatives of 8-hydroxy quinoline" as employed in describing the present invention is intended to embrace the compounds formed when a copper salt reacts with 8-hydroxy quinoline or its acid salt. These compounds are most likely to be of the type known as "chelate" compounds, in the structure of which secondary valances are involved. In the event that more

than one structure can result from the reaction in the practice of the present invention, the various structures thus formed are contemplated as being within the scope of this invention.

I claim:

1. A process of rendering a textile resistant to attack by mold organisms which comprises impregnating the textile with an aqueous solution of the copper salt derivatives of 8-hydroxy quinoline, said salt derivatives being solubilized at a pH in the range of 2.2–2.7, subsequently raising the pH of the impregnated textile to a pH above 2.7, and thereafter washing the treated textile to remove water soluble substances.

2. A process of rendering a textile resistant to attack by mold organisms which comprises impregnating the textile with an aqueous solution of the copper salt derivatives of 8-hydroxy quinoline, said salt derivatives being solubilized at a pH below 2.7, subsequently raising the pH of the impregnated textile to a pH above 2.7, and thereafter washing the treated textile to remove water soluble substances.

PAUL G. BENIGNUS.