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PROCESS FOR THE TREATMENT OF CELLULOSIC MATERIALS
TO PREVENT DETERIORATION AND DECAY

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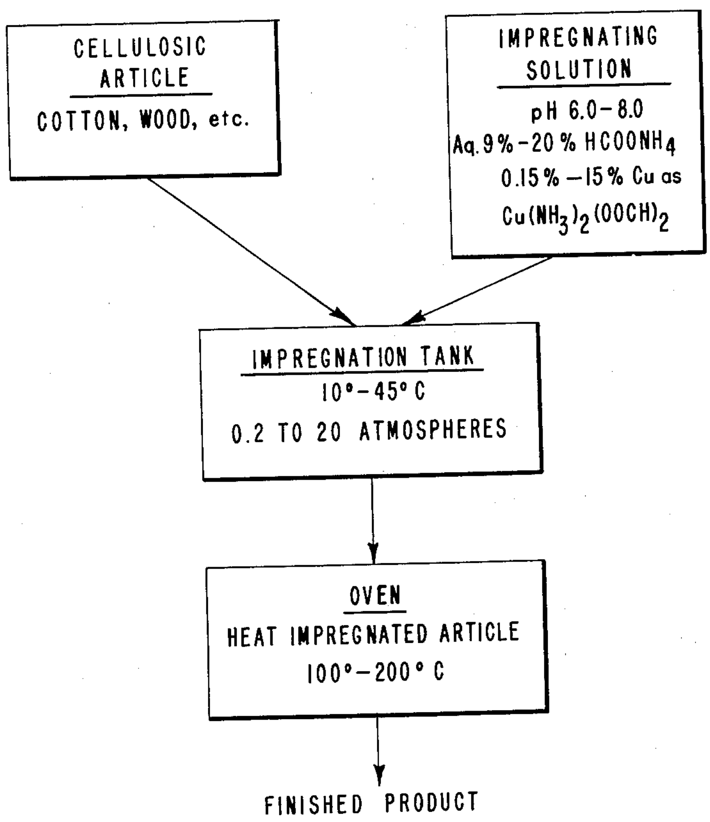

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PROCESS FOR THE TREATMENT OF CELLULOSIC MATERIALS TO PREVENT DETERIORATION AND DECAY

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This invention relates to a process for the treatment of cellulosic materials to prevent their deterioration and decay from the attack of biological organisms and cellulose-attacking insects, and more specifically, this invention relates to a process for impregnating such cellulosic materials with a high level of copper.

It has been known for some time that inclusion of the copper ion in a cellulosic material may impart a remarkable degree of preservation. More recently, as in United States Patent 2,749,256, issued on June 5, 1956, to Robert R. Bottoms, it has been disclosed that a cellulosic material could be made highly resistant to deterioration and decay by impregnation with an aqueous solution of copper formate followed by subsequent thermal decomposition in situ of the copper salt whereby some form of a chemical bond between the cellulose and the copper was obtained. However, in the past, the effectiveness of such treatment has been limited by the penetrating power and rate of absorption of the treating solutions and the high temperatures required to obtain chemical bonding to the cellulose, as well as by the corrosive nature of the copper formate, particularly in low-cost ferrous metal equipment.

Therefore, an object of the present invention is to provide an improved process for treating cellulosic materials to render them resistant to deterioration from biological attack. It is another object of this invention to provide a treating solution of superior penetrating power which, when absorbed within a cellulosic material, will undergo thermal decomposition within said cellulosic material at a relatively low temperature to provide a cellulose-copper compound having exceptionally good preservative properties. It is a further object of this invention to provide a treated cellulose containing a higher percentage of copper, both bound and unbound to the cellulose, than has heretofore been possible.

It has now been discovered that the objects of this invention can be achieved by the use of a process employing a treating solution for cellulosic materials comprising an aqueous solution consisting of from 9% to about 20% by weight ammonium formate and from 0.15% to about 15% by weight of copper in the form of cupric ammonium formate, said solution having a pH in the range of 6.0 to 8.0. The process of this invention involves treating the cellulosic materials by impregnating them by immersion in an aqueous solution as described hereinabove, containing ammonium formate and cupric ammonium formate, said aqueous solution being maintained at a temperature in the range of 10° C. to 45° C. and at a pressure between about atmospheric pressure and about 20 atmospheres, removing the cellulosic material from the impregnating solution, and fixing copper within the cellulosic material by heating said impregnated cellulosic material to temperatures in the range of 100° to 200° C. whereby from about 0.5% to about 8% by weight of copper, based on the dry weight of the cellulosic material, is deposited in said cellulosic material, and from about 0.3 to about 6% by weight of copper is chemically bound to cellulose so that it cannot be removed

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by heating the cellulosic material with aqueous ammonia. In a preferred embodiment of this invention, the treating solution employed consists of from 11–12% by weight of ammonium formate in water and from 2–5% by weight of copper in the form of cupric ammonium formate, and the aqueous solution is maintained at a temperature of 15–30° C. If maximum penetration into the cellulosic material is desired, the pH is adjusted to 8.0 by the addition of excess ammonia or other alkaline material. While either lower or higher temperatures for reacting the copper formate with the cellulose may be employed, as hereinabove disclosed, the preferred range is between about 135° and about 150° C.

The particular process details employed will vary depending upon the nature and state of division of the cellulosic material to be treated, as is well known to those skilled in the art. Bulky, woody products such as planks and beams are preferably impregnated after having been first subjected to a vacuum to de-aerate and dehydrate them so as to render them more penetrable by the aqueous treating solution. Finely-divided cellulosic materials such as sawdust, wood chips, cotton fibers, and cotton textiles, etc., are more readily penetrated and require less severe pretreatment and shorter immersion to obtain satisfactory penetration of the cupric ammonium formate solution.

The impregnating solution used in the process of this invention comprises a complex salt of the cupric ion and ammonia with the formic ion which salt is dissolved in a solution of ammonium formate. The copper compound may be approximated by the stoichiometric formula of cupric ammonium formate, $Cu(NH_3)_2(OOCH)_2$. This copper compound is soluble in aqueous ammonium formate solutions having concentrations greater than 9% at all levels of copper up to about 15% at room temperatures; an ammonium formate concentration of 11–12% by weight is preferred. Solutions of the complex formate in aqueous ammonium formate exhibit a nominal pH of 7.0±0.1, but the pH may be adjusted within the range of 6.0 to 8.0 without altering appreciably the properties of the solution as to solubility, copper absorption, or corrosive action on ferrous metals. However, a somewhat greater penetration and concentration and consequent higher copper fixation is obtained at the higher end of the pH range, probably due to swelling or partial solubility of some portions of the cellulose in the alkaline solution.

Some of the advantages to be obtained from the use of the novel treating solution of this invention, in the process of this invention, have been demonstrated by direct comparison with the use of the aqueous copper formate solutions of the prior art under similar conditions. Thus, controlled tests have shown that a solution of cupric ammonium formate in ammonium formate, as hereinabove disclosed, will penetrate into wood at a rate of about 1.5 times greater than the rate of penetration of aqueous copper formate of the same concentration. It has been found that cellulose treated in this manner will contain at least 1.2 times as much copper as cellulose which has been treated with aqueous copper formate solution. Furthermore, cellulose treated by the process of this invention with cupric ammonium formate in ammonium formate shows a greater percentage of bound or fixed copper after having been heated in the range of 135° C. to 150° C. than is shown by an equivalent cellulose impregnated in an equivalent manner with aqueous copper formate and heated to the same temperature range. Furthermore, a lower temperature of fixation of the copper may be employed with satisfactory results with cellulose treated by the process of this invention than with cellulose treated by prior art processes such as impregnation with aqueous copper formate.

Example 1

Two portions of white pine sawdust, after having been subjected to vacuum, were impregnated at room temperature with solutions containing copper. Two solutions were used; one, a control, was an aqueous cupric formate solution containing 2% by weight copper, and one was a cupric ammonium formate solution in 11–12% aqueous ammonium formate. This solution likewise contained 2% by weight copper, and it had a ph of 7.0. Fifty grams of sawdust (less than 16 mesh) was treated with 500 cc. of the aqueous copper formate control by stirring under vacuum, then at atmospheric pressure, for 5 minutes; after vacuum filtration and drying at 105° for 16 hours, the dry product contained 3.08% copper. After heating to 135° C. and subsequent leaching with 4% aqueous ammonia, this impregnated sawdust retained 1.62% copper, based on the dry weight of the sawdust. Another portion of this material was heated to 150° C. and after having been leached subsequently with 4% aqueous ammonia, retained 2.00% copper by weight. In contrast with the above, a second portion of the white pine sawdust was given parallel treatment using the copper ammonium formate solution in ammonium formate. The impregnated cellulose contained 3.51% by weight of copper based on the dry weight of the sawdust. After heating to 135° C., and leaching with aqueous 4% ammonia, the copper content of this sample of sawdust was 2.20%. Another portion treated with copper ammonium formate solution was heated to 150° C., leached as decribed above, after which there remained 2.85% bound copper.

Similar results can be achieved with the process of this invention in the treatment of cotton textiles, cotton duck, and in the treatment of wood chips and pulp used for paper making, whereby the paper, manufactured from the treated pulp or wood chips containing bound copper cellulose, is rendered highly resistant to biological and insect attack; good results are also achieved in the treatment of wood planks and beams for use in marine construction and in buildings where the wood is to be exposed to the action of biological organisms.

The particular method employed for preparing the solutions of cupric ammonium formate used in the process of this invention is not critical. Thus, a compound having a stoichiometric formula of cupric ammonium formate may be prepared, dried, and dissolved in aqueous ammonium formate to give any desired concentration of copper up to about 15%. The simplest mode of preparation of cupric ammonium formate is by the direct addition of aqueous ammonia to copper formate tetrahydrate and subsequent dehydration in a vacuum or by solvent precipitation. Other methods of preparation may be used, such as to dissolve anhydrous copper formate in water containing formic acid, followed by the addition of ammonia. Still another starting material which may be used is malachite, $CuCO_3.Cu(OH)_2$, which may be dissolved in water containing formic acid, and when effervescence ceases, aqueous ammonia may be added. It is also possible to start with copper metal powder in an aeration tower with water, aqueous ammonia and formic acid, and to convert this to soluble copper ammonium formate by sparging with air until all of the copper has been dissolved. Additional water and formic acid may be added to obtain solutions having concentrations suitable for use in the process of invention.

Another method in which malachite may be used as starting material for the preparation of solutions used in the process of this invention is to place the malachite in water in a boiler equipped with a reflux condenser, add aqueous ammonia and methyl formate, and heat to approximately 50° C. for a period of about one hour. While the resulting solution contains some methanol, it does not behave differently from methanol-free solutions; if desired, the bulk of the methanol may be removed along with any unreacted methyl formate by distillation, preferably under a slight vacuum. In all of these methods of preparation, the proportions may be varied, so as to give a product within the range of the solutions which is described hereinabove.

In the accompanying drawing a flow sheet of the process is set forth.

Examples illustrating quantitatively the aforementioned methods of preparing the cupric ammonium formate solutions for use in the process of this invention are as follows:

Example 2

Dissolve 7.2 g. of anhydrous copper formate in 145 ml. water containing 16.06 g. formic acid. Add 7.53 g. of ammonia as 31.4 ml. of 25% aqueous ammonia.

Example 3

Dissolve 10.6 g. copper formate tetrahydrate in 144 ml. water containing 15.8 g. formic acid. Add 31.0 ml. of 24% aqueous ammonia.

Example 4

To 5.21 g. of malachite, $CuCO_3.Cu(OH)_2$ in 145 ml. water, add 20.45 g. formic acid. When effervescence ceases, add 31.3 ml. of 24% aqueous ammonia.

Example 5

In a cylindrical aeration tower place 3.1 g. of copper metal powder, 100 ml. water, 32 ml. of 24% aqueous ammonia, and 16.06 g. formic acid. Sparge with air until solution of the copper is obtained. Add 48 ml. water and 4.4 g. formic acid.

Example 6

In a boiler fitted with reflux condenser place 132 ml. water, 5.2 g. malachite, $CuCO_3.Cu(OH)_2$, 31.2 ml. of 24% aqueous ammonia, and 26.6 g. of methyl formate. Hold at approximately 50° C. for one hour. The resulting solution contains about 7% methanol. The bulk of the methanol and any unreacted methyl formate may be removed by distillation, preferably under slight vacuum.

Cellulosic products treated by the process of this invention with a solution prepared by any of the above methods show superior resistance to the action of biological organisms and cellulose-attacking insects. It is presumed that this superior resistance, in comparison with the products obtained by prior art processes, is due to the higher level of copper obtained in the cellulose by the process of this invention. Thus, the prior art, as in 2,749,256 mentioned hereinabove, discloses that only about 1%±0.3% of copper based on the dry weight of the cellulose, can be bound to the cellulose, while the process of this invention provides a method for adding from 1.2 to 4 times as much copper to the cellulosic material. As a result, cellulosic products treated by the process of this invention appear to undergo no attack when buried in mud containing cellulose-attacking organisms, or when placed in the ground in a region highly infested with termites. Thus, the novelty of this invention consists in the use of a solution which will penetrate cellulosic materials to a high degree at a faster rate than those previously known to the art. As a result, it is possible to impregnate cellulose materials in a shorter time and at a lower cost than has been possible heretofore. Since copper formate solutions previously used are quite corrosive to mild steel and other ferrous materials normally used in equipment for treating wood, a sound economic advantage is obtained in the use of this solution in the process of this invention from the fact that the solution of cupric ammonium formate in ammonium formate is non-acidic and does not appear to attack at any appreciable rate the mild steels used in processing equipment for impregnation of wood.

I claim:

1. A process for treating cellulosic materials to render them highly resistant to the deterioration and decay caused

by the attack of biological organisms and cellulose-attacking insects which comprises impregnating a cellulosic material by contact with an aqueous solution having a pH between 6.0 and 8.0 and consisting essentially of from 9% to about 20% ammonium formate and from about 0.15% to about 15% by weight copper in the form of cupric ammonium formate, said aqueous solution being maintained in the range of 10° to 45° C. and at a pressure between 0.2 and 20 atmospheres, removing the impregnated cellulosic material from contact with the solution, and fixing the copper within the cellulosic material by heating to temperatures within the range of 100° C. to 200° C., and recovering a product having 0.5% to about 8% by weight of copper deposited in the cellulosic material including from about 0.3% to about 6% by weight of copper chemically bound to the cellulose as determined by the fact that the copper is insoluble when said cellulosic material is leached with 4% aqueous ammonia.

2. A process for treating cellulosic materials to render them highly resistant to the deterioration and decay caused by the attack of biological organisms and cellulose-attacking insects which comprises impregnating a cellulosic material by immersion in an aqueous solution having a pH of 7.0±0.1 and consisting essentially of from 11% to 12% by weight ammonium formate and from 2% to 5% by weight of copper in the form of cupric ammonium formate, said aqueous solution being maintained at a temperature of 15° to 30° C. at atmospheric pressure, removing the cellulosic material from the impregnating solution, and fixing the copper within the cellulosic material by heating said impregnated, cellulosic material to a temperature between about 135° C. and about 150° C., and recovering a product having at least 3.5% copper, based on the dry weight of the cellulosic material, deposited in said cellulosic material including at least 2% by weight of copper chemically-bound to the cellulose as determined by the fact that the copper is insoluble when said cellulosic material is leached with 4% aqueous ammonia.

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