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MODIFYING CELLULOSE TEXTILES WITH
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10 Claims. (Cl. 8—54.2)

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This invention relates to the treatment of cellulosic textile fibers and involves altering or modifying the properties of such fibers.

In the processing of cellulosic fibers, particularly in the form of yarn or cloth, it is customary to subject such materials to one or more operations such as bleaching, dyeing or mercerizing. Prior to these operations the fibers generally are treated with aqueous alkali or certain enzymes or other agents which will remove grease, waxes, sizing and/or other extraneous substances and thereby render the fibers more susceptible or amenable to the operations of dyeing, bleaching, mercerizing, etc. I have noted if cellulosic or vegetable fibers are treated with certain aqueous solutions of copper compounds subsequent to removal of sizing, grease, etc., then the properties of such fibers may be altered or modified to some degree and as a result they behave in an unexpected manner in the finishing operations which may be employed. I have noted also in some instances that the physical appearance of the treated yarn or cloth is altered or modified somewhat as compared with the original or untreated material. Thus, for example, the luster of the treated goods may be slightly less than that of the untreated goods, or the twist of yarn may be somewhat greater or the feel of yarn may be firmer due to the treatment described in this specification.

The copper compounds which I prefer to use are those water-soluble substances resulting from the interaction of an alkylolamine and a copper salt or oxide or hydroxide. More properly these water-soluble substances can be designated as alkylolamine-copper complexes. Interaction can be effected, for example, by dissolving a copper salt, such as the chloride, acetate or sulfate, in water and then adding an alkylolamine in sufficient quantity to give a clear blue solution. Addition of the alkylolamine to the aqueous solution of a copper salt apparently results in two reactions: first, the formation and precipitation of copper hydroxide with the simultaneous formation of a water-soluble salt of the alkylolamine; and second, on continued addition of the amine, interaction of the alkylolamine with copper hydroxide to give the water-soluble alkylolamine-copper complex.

Another method comprises dissolving the copper salt in water, adding a sufficient quantity of an aqueous alkali (e. g., an aqueous solution of sodium or potassium hydroxide) to precipitate the copper as its hydroxide or hydrated oxide, washing the insoluble material with water until

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it is substantially free of the alkaline precipitant, and then dissolving the copper hydroxide (or hydrated oxide) in an aqueous solution of alkylolamine. This method furnishes a solution of the alkylolamine-copper complex which is substantially devoid of dissolved alkylolamine salts.

Still another manner in which I may prepare solutions applicable for my purpose comprises mixing an aqueous solution of the copper salt with an aqueous solution of a salt, e. g., a sodium or potassium salt, of an organic (carboxylic) acid, filtering and washing the resulting water-insoluble copper compound, and dissolving the latter in an aqueous solution of an alkylolamine. As an alternative procedure, copper hydroxide (or oxide) is dissolved in an aqueous solution of an alkylolamine and to the copper solution is added a carboxylic acid in an amount equivalent to the copper content.

Aqueous solutions of the alkylolamine-copper complex prepared by any of the above-mentioned methods, or by any other convenient and equivalent procedure, are suitable for my purpose.

Cellulosic fibers can be treated in any convenient manner with the aqueous solutions of alkylolamine-copper complexes. For example, the fibers in the form of cloth or yarn are immersed in the solution, kept immersed for a sufficient period of time to obtain the desired effect, and afterwards are removed from the solution and washed with water. If washing with the latter liquid does not remove substantially all of the copper compound from the fibers, then they may be washed with a dilute aqueous solution of an acid which will form water-soluble copper salts, e. g., sulfuric, hydrochloric or acetic acid. After treatment with the acid, the fibers should be rinsed well with water. Instead of employing an aqueous solution of an acid for effecting removal of small quantities of the copper compound retained by the treated fibers, a water solution of a substance which forms water-soluble complex compounds with copper, for example, sodium thiosulfate, can be used.

Treatment of the cellulosic fibers is not to be limited merely to immersing the fibers in the solution of the alkylolamine-copper complex. To illustrate, after the fibers have been immersed sufficiently long so that they are completely saturated with the treating liquid, they may be removed from the latter, pressed to remove non-adsorbed or adhering liquid, and while still damp with the copper solution kept in a suitable container for the necessary period of time. Again, if the fibers are in the form of cloth, the solution

of alkylolamine-copper complex may be applied in the form of a spray to the fibers until the latter are thoroughly saturated.

In most instances it is suitable to effect treatment of the fibers at atmospheric or room temperature. However, I do not wish to be limited to such a temperature, as lower temperatures (for example, 0° C. or -10° C.) or higher temperatures (e. g., 60° C. or 100° C.) may prove to be more useful. The temperature and duration of treatment, as well as the concentration of the solution of alkylolamine-copper complex, are factors which can be readily determined for the particular material at hand.

The following examples will illustrate my invention though I do not wish to be limited only to them. It will be understood that in each case the textile material was freed of sizing, dirt, grease, etc., by a suitable operation prior to the treatment described.

Example 1.—An aqueous solution was prepared by dissolving copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in water, adding solid 2-amino-2-methyl-1,3-propanediol slowly until the precipitate which was formed at first had dissolved and a clear blue liquid was obtained, and then diluting with water until the concentration of the solution was equivalent to 2.5 g. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 cc.

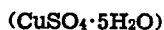
Bleached cotton yarn was immersed in this solution at room temperature for 30 minutes, using approximately by weight 8 parts of liquid to 1 part of yarn. Afterwards, the yarn was washed well with cold water and then dried.

A portion of the treated yarn as well as one of the original bleached untreated yarn were dyed in separate baths using by weight 100 parts of water per 1 part of yarn and 3 per cent (based on the weight of yarn) of a yellow substantive dye. In each case the baths (with the cotton goods therein) were kept at a temperature of 80-90° C. for 20 minutes and then allowed to cool for 20 minutes. The samples were removed from the respective baths, rinsed well with cold water and air-dried. It was noted that the cotton goods which was treated with the copper solution was lighter in color.

Example 2.—Portions of the copper-treated bleached cotton yarn from Example 1 and of the initial bleached yarn were mercerized in the following manner: The yarn was stretched on a wooden frame and the latter was immersed for 4 minutes in an aqueous solution of sodium hydroxide of sp. gr. 1.27. The frame then was removed from the alkaline liquid and the samples of yarn, while on the frame, were washed successively with water, dilute sulfuric acid and water. Afterwards, they were removed from the frame and dried.

The mercerized samples were dyed in separate baths in the manner described in Example 1 and the same dye was employed. It was noted that the yarn which had been pretreated with the copper solution was distinctly lighter in color and also did not exhibit as much luster or sheen as the other sample. Both samples, however, were much darker in color than the corresponding ones from Example 1.

Example 3.—Crystalline copper sulfate



was dissolved in water, then 2-amino-2-methyl-1-propanol was added slowly until a dark blue solution was obtained, and afterwards the latter was diluted with water until its concentration

was equivalent to 1.57 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per 100 cc. of solution. Bleached linen cloth was saturated with the solution of alkylolamine-copper complex and the damp cloth was placed on a frame and left exposed to the atmosphere for 18 hours. At the end of this period of time, the fabric was substantially dry to the touch and was blue in color. The linen was then washed successively with water, dilute aqueous sulfuric acid and water, and dried.

This portion of cloth as well as one of the bleached but untreated fabric were dyed as indicated in Example 1, with the exception that a blue substantive dye was used. It was noted that the copper-treated sample was much lighter in color.

The dyeing operation was repeated using the dyed samples but this time employing 4 per cent of dye (on basis of weight of cloth) in the case of the non-treated linen and 4.5 per cent dye in the case of the copper-treated sample. Although both samples were somewhat darker in color due to this second dyeing operation, the copper-treated sample was still lighter in color and did not exhibit a sheen or gloss to as great a degree as the other sample.

Example 4.—Crystalline copper chloride was dissolved in water, monoethanolamine was added slowly until a clear blue colored liquid was obtained, and the latter then diluted with water to give a solution whose concentration was equivalent to 5.0 g. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 cc. Unbleached cotton yarn was immersed in this solution for 1.5 hours, then removed and washed successively with water, dilute aqueous sodium thiosulfate and water. Afterwards the yarn was dried.

This sample and also one of the unbleached, untreated yarn were dyed (in separate baths) using 50 parts of water (by weight) to 1 part of yarn and 5 per cent (based on weight of yarn) of a red substantive dye. The dye baths containing the cotton goods were kept at a temperature of 80-90° C. for 30 minutes and then were allowed to cool for 30 minutes. The samples were removed, rinsed with cold water and air-dried. It was observed that the material which had been treated with the alkylolamine-copper complex was much darker in color than the other. Also, the copper-treated yarn had the appearance of being somewhat more tightly twisted than the untreated material.

Example 5.—Crystalline copper chloride was dissolved in water and to the solution was added monoethanolamine until a clear blue liquid was obtained and then an additional quantity of the amine, equal to 30 per cent of that initially used, was admixed with the blue liquid. The latter then was diluted with water to yield a solution whose concentration was equivalent to 7.5 g. of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per 100 cc.

Bleached cotton cloth was immersed in a portion of the solution of alkylolamine-copper complex for a few minutes, and then removed and pressed sufficiently to eliminate non-adsorbed liquid. The cloth saturated with liquid was placed in a container in which the temperature was maintained at 60° to 65° C. and kept there for 30 minutes. At the end of that time the fabric was substantially dry and blue in color. It was washed well with cold water and after wringing as dry as possible the textile material was saturated again with the solution of alkylolamine-copper complex and heated for 30 minutes at a temperature of 60° to 65° C. After this second heating operation, the sample was washed suc-

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cessively with water, dilute aqueous sulfuric acid and water.

This treated sample and also one of the original bleached but untreated cotton cloth were dyed separately, using 100 parts of water per 1 part of cloth and 10 per cent (based on weight of cloth) of a green substantive dye. In each instance the dye bath containing the cloth was kept at a temperature of 80° to 90° C. for 30 minutes and then allowed to cool for 30 minutes. The two portions of fabrics then were rinsed with cold water and air-dried.

It was noted that the copper-treated cloth was much lighter in color than the untreated cloth. Also, the copper-treated fabric had the appearance of being more closely woven than the non-treated fabric.

Example 6.—Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was dissolved in water and to the solution was added a quantity of aqueous sodium hydroxide slightly in excess of that required to precipitate all the copper as the hydroxide. The precipitate was permitted to settle and the supernatant liquid then separated. Afterwards, the precipitate was washed with cold water by mixing the insoluble material with the aqueous liquid, allowing it to settle and then withdrawing the supernatant layer of water. This operation was repeated until the wash water was neutral to litmus and substantially free of dissolved salts. During this washing the precipitate changed in color from a blue to a dark brown, indicating a partial conversion at least of the copper hydroxide into copper oxide. This brown colored material was filtered and as much water as possible was removed by draining. While still wet, a portion of the water-insoluble compound was mixed with a 30 per cent aqueous solution of triethanolamine, and the mixture allowed to stand for several hours with an occasional stirring. Finally, the liquid was separated by filtration from the undissolved material. This procedure yielded a blue solution which contained 0.90 g. of copper oxide per 100 cc. and a considerable excess of triethanolamine over that required to react with this quantity of copper oxide.

Example 7.—Unbleached linen cloth was saturated with some of the solution from Example 6, saturation in this instance being accomplished by allowing the solution of alkylolamine-copper complex to drop slowly onto the fabric. The latter was left exposed to the atmosphere for 3 hours, during which time some liquid evaporated from the textile material. The latter again was saturated with some of the solution from Example 6 and left exposed to the atmosphere for approximately 12 hours. The cloth, which was still wet to the touch, then was washed well with water.

This treated linen sample and also one of the original untreated linen were bleached (separately) using 15 parts of an aqueous solution of sodium hypochlorite (containing 0.42 g. of available chlorine per liter) to 1 part of cloth. Treatment with bleaching solution was continued for 1.25 hours, after which the samples were soured (separately) in dilute aqueous sulfuric acid, then washed successively with water, dilute aqueous sodium thiosulfate and water.

After they were dried, portions of each of the bleached samples (which were not completely decolorized and exhibited no appreciable difference in color between themselves) were dyed separately, using in each case 100 parts of water per 1 part of cloth and 5 per cent (on weight of

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cloth) of a yellow substantive dye. The baths containing the samples were kept at a temperature of 80° to 90° C. for 30 minutes and then allowed to cool for 30 minutes. The samples were removed from the baths, rinsed well with cold water and air-dried. It was noted that the copper-treated linen fabric was darker in color and also possessed a clearer and brighter color than the non-treated sample.

The remaining portions of undyed, bleached fabrics were boiled for 15 minutes with 1 per cent aqueous sodium carbonate, washed well with water, dried and again subjected to a bleaching operation with sodium hypochlorite as described above. Each of the twice-bleached samples were dyed, using the same procedure and dye as that just mentioned above. In this instance also the sample of linen fabric which had been pretreated with the solution of alkylolamine-copper complex was darker in color and also possessed a slight gloss or sheen as contrasted with the other sample.

Example 8.—To a portion of the solution from Example 6, oleic acid was added in an amount equivalent to the copper oxide dissolved in the liquid (i. e., in the ratio of 2 mols of acid to 1 mol of copper oxide). The mixture was stirred, at room temperature, until all of the acid was dissolved. Bleached cotton cloth was covered with some of the solution of alkylolamine-copper complex containing dissolved oleic acid and kept immersed therein for 1.5 hours. Next, the cloth was removed, pressed to eliminate adhering liquid and then washed successively with water, dilute aqueous sodium thiosulfate and water.

This sample of treated cotton fabric and also one of the original untreated fabric were dyed separately, using 100 parts of water per 1 part of cloth and 5 per cent (on weight of cloth) of a red substantive dye. In each case the bath was kept at a temperature of 80–90° C. for 30 minutes and then allowed to cool for 40 minutes. Afterwards, the samples of textile material were rinsed well with cold water and air-dried. In this case it was noted that the copper-treated sample was much darker in color and also possessed a softer feel than the other sample.

Example 9.—Dried flakes of a white commercial soap were dissolved in water in a sufficient amount to furnish approximately a 0.75 per cent solution. To the latter was added, at room temperature and with constant stirring, a dilute aqueous solution of copper sulfate, the quantity of copper salt slightly less than that required to react with all the soap. The resulting green precipitate of copper soap was allowed to settle, and the supernatant liquid withdrawn. After washing the precipitate once with water by decantation, it was filtered, washed well with water while on the filter, and permitted to drain.

A portion of the same precipitate was admixed with a small quantity of water and monoethanolamine was added slowly to the mixture, which became a blue jelly-like mass. The latter was mixed with a small quantity of water and warmed gently whereupon it became fluid. After adding sufficient monoethanolamine to obtain a clear blue liquid, the latter was cooled to room temperature. Analysis indicated the copper content of the solution of alkylolamine-copper complex was equivalent to 200 mg. of copper oxide per 100 cc.

Example 10.—Unbleached cotton cloth was covered with some of the solution from Example 9 and kept immersed therein for 48 hours. At the

end of this time the cloth was taken out, pressed to remove as much liquid as possible, and then washed successively with water, dilute aqueous sodium thiosulfate and water, and dried.

This treated sample and also one of the untreated unbleached cloth were dyed separately, using 75 parts of water to 1 part of cloth and 5 per cent (based on weight of cloth) of a yellow substantive dye. Dyeing was conducted for 30 minutes at a temperature of 80° to 90° C. for 30 minutes and then the baths (containing the samples) were allowed to cool for 30 minutes. The fabrics were removed, rinsed with cold water and air-dried. The copper-treated sample was slightly more yellow in color, was a brighter yellow color and possessed a somewhat softer feel than did the untreated sample.

From the foregoing description it will be seen that my invention comprises treating cellulosic fibers, such as those of cotton, linen, and the like, with an aqueous solution of an alkylolamine-copper complex and then removing substantially all of the alkylolamine-copper complex adsorbed or retained by the fibers. Treatment can be effected at atmospheric or room temperature or at somewhat higher or lower temperatures. Also, the cellulosic fibers may be treated with the solution of alkylolamine-copper complex either prior to or subsequent to such operations as bleaching or mercerizing.

The alkylolamines which are suitable for my purpose are not only water-soluble compounds but are either monohydroxy or polyhydroxy substances. In addition, they may be primary, secondary or tertiary amines. The following are examples of alkylolamines which are applicable: monoethanolamine, a monohydroxy primary amine; diethylethanolamine, a monohydroxy tertiary amine; diethanolamine, a polyhydroxy secondary amine; triethanolamine, a polyhydroxy tertiary amine; and methyldiethanolamine, a polyhydroxy tertiary amine. The proportion of alkylolamine employed in the solutions for treating cellulosic fibers may be just equal to that required to form the corresponding copper complex compound, or the alkylolamine may be present in excess of that proportion. I prefer that the alkylolamine be substantially the only alkaline compound (other, of course, than the copper hydroxide or copper oxide) present in solution and that the solution be substantially free of alkalies such as sodium or potassium hydroxide.

Any convenient method of treating the fibers may be employed. I have illustrated my invention by one method which comprised immersing the fibers in the solution of alkylolamine-copper complex and permitting them to remain therein for a period of time necessary to secure the desired effect. Another procedure described herein comprised saturating the fibers with the treating solution and then exposing them to the atmosphere whereby a slow evaporation of water occurred and fibers dry to the touch but impregnated with the alkylolamine-copper complex were obtained. Many variations of these methods or procedures are applicable. For example, the fibers can be saturated with a solution of alkylolamine-copper complex and afterwards exposed to the atmosphere for a sufficient period of time which allows only partial evaporation of water. Again, the fibers can be saturated with an aqueous solution of a copper salt and then covered with or immersed in an aqueous solution of an alkylolamine. In the latter instance, of course, the quantity of amine in the solution should be great

enough to form the corresponding copper complex. Neither do I wish to be limited to only one treatment of a particular sample of cellulosic fibers with a solution of alkylolamine-copper complex. In some instances two or more treatments may be necessary before effects of the desired degree are obtained.

The same solution of alkylolamine-copper complex may be employed in the treatment of two or more samples of cellulosic fibers. After using the solution once, it may be brought back to its original concentration (if desirable or necessary) by the addition of one or more of its components, i. e., by addition of water, alkylolamine or copper salt. The needed quantity of any one or more of these components can be determined readily by analysis of the solution which has been employed in the treatment of cellulosic fibers.

What I claim is:

1. The process which comprises treating undyed cellulose fibers with an aqueous solution of an alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present and removing substantially all adsorbed alkylolamine-copper complex from said cellulosic fibers by treatment with an aqueous solution of an agent forming water-soluble copper compounds.

2. The process which comprises treating undyed cellulose fibers with an aqueous solution of a monohydroxy alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, and removing substantially all adsorbed monohydroxy alkylolamine-copper complex from said fibers by treatment with an aqueous solution of an agent forming water-soluble copper compounds.

3. The process which comprises treating undyed cellulose fibers with an aqueous solution of a polyhydroxy alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, and removing substantially all adsorbed polyhydroxy alkylolamine-copper complex from said fibers by treatment with an aqueous solution of an agent forming water-soluble copper compounds.

4. The process according to claim 2 in which the monohydroxy alkylolamine-copper complex is ethanolamine-copper complex.

5. The process according to claim 3 in which the polyhydroxy alkylolamine-copper complex is triethanolamine-copper complex.

6. The process according to claim 3 in which the polyhydroxy alkylolamine-copper complex is diethanolamine-copper complex.

7. The process which comprises treating undyed cellulose fibers with an aqueous solution of an alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, maintaining the aqueous solution during treating at a temperature not exceeding about 100° C., and removing substantially all adsorbed alkylolamine-copper complex from said fibers by treatment with an aqueous solution of an agent forming water-soluble copper compounds.

8. The process which comprises treating undyed cellulose fibers with an aqueous solution of an alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, and removing substantially all adsorbed alkylolamine-copper complex from said cellulosic fibers with

an aqueous solution of an inorganic acid forming water-soluble copper compounds.

9. The process which comprises treating undyed cellulose fibers with an aqueous solution of an alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, removing substantially all adsorbed alkylolamine-copper complex from said cellulose fibers by treatment with an aqueous solution of an agent forming a water-soluble copper compound, and dyeing the treated fibers.

10. The process which comprises treating undyed cellulose fibers with an aqueous solution of an alkylolamine-copper complex as the essential treating agent, the alkylolamine being substantially the only alkaline substance present, maintaining the aqueous solution during treatment at a temperature not exceeding about 100° C., removing substantially all adsorbed alkylolamine-copper complex from said fibers by treatment with an aqueous solution of an agent forming water-

soluble copper compounds, and dyeing the treated fibers.

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