PROCESS OF HYDROPHILIZATION, PURIFICATION AND BLEACHING OF CELLULOSE FIBERS

ABSTRACT: Cellulosic materials, such as cotton fibers or mixtures of cotton and other cellulosic or synthetic fibers, are hydrophilized, purified and bleached by treating the cellulosic materials with a small amount of chlorine dioxide over a short period of time and then bleaching the treated cellulosic material with a peroxidized compound.
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BACKGROUND OF THE INVENTION

A high degree of hydrophilicity or water absorbency is desired in articles made from cellulose materials, such as cotton, in order to facilitate dyeing, notably in pad dying, printing, to facilitate the penetration of finishes and so forth. This high degree of water absorbency is also desired when the cellulose article is intended for surgical use, such as surgical gauze.

In addition, the dyeing of cellulose materials with dyes that react with the cellulose and the finishing techniques employing thermosetting resins require that the cellulose materials be quite purified and substantially free of noncellulosic matter that might interfere with the fixation of these dyes or reactive finishes such as the thermosetting resins.

The usual process of hydrophilization and purification of cellulose materials involves an alkaline cooking at elevated temperatures and at times above atmospheric pressure, followed by a bleaching of the cellulose material with a peroxide compound, such as hydrogen peroxide, sodium chlorite or sodium hypochlorite.

Even though such a process produces substantially purified and hydrophilic materials, the process has a number of disadvantages. For example, the alkaline cooking, which hitherto has been considered the most effective and most economical means of eliminating noncellulosic impurities, has the drawback of weakening the cotton fibers, altering its surface properties and sensitizing it to the oxidizing bleaching agents; moreover, after an alkaline treatment the bleached fibers often have mechanical properties inadequate for the application of certain finishes, which themselves further affect their strength. Furthermore, to be truly effective, alkaline cooking must be carried out at an elevated temperature and over a sufficient period of time, so that the fatty substances of the cotton can be saponified. Admittedly, this time can be shortened by working at high temperatures (130°C, for example), but this means that autoclave equipment must be available. Thus, one of the chief disadvantages of this process is the duration of the alkaline cooking and bleaching reactions which makes it difficult to treat (particularly by continuous application techniques) delicate fabrics, such as satins and poplins, which do not readily tolerate prolonged mechanical stress.

SUMMARY OF THE INVENTION

The present invention relates to a new process for treating cotton articles or mixtures of cotton and other natural or synthetic cellulose fibers that results in a cotton article having excellent hydrophilic properties, a high degree of purification and a high degree of whiteness without significantly affecting the cellulose in a very short period of time.

The process in accordance with the invention comprises treating the cellulose material with chlorine dioxide followed by bleaching with a peroxidized product, such as hydrogen peroxide, sodium peroxide, sodium chlorite or sodium hypochlorite.

The cellulose materials that can be treated according to this invention include cotton or mixtures of cotton with other cellulose materials, such as regenerated cellulose materials or mixtures with synthetic materials, such as polyester-cotton and viscose rayon-cotton mixtures. These cellulose materials may be in the form of flax, silver, lapis, yarn or cloth. The term cellulose materials are used herein is therefore intended to include mixtures of cellulose materials and the various forms thereof, such as set forth above.

If the cellulose materials, such as cloth, are sized, it is advantageous to first desize the cellulose material prior to treating the cellulose material in accordance with this invention. This desizing can be effected by a number of known processes, such as by diastases (amylolytic enzymes) alkali persulfate or alkali permanganate. If the cellulose material is to be continuously treated, the desizing operation could be effected by passing the cloth for a minute through the tank of a washing machine containing a concentrated solution of amylolytic diastase or enzyme followed by a vigorous washing to remove traces of hydrolyzed starch.

The pretreatment of the cellulose materials with chlorine dioxide prior to the bleaching operation constitutes an essential step of the invention. The treatment with chlorine dioxide involves contacting the cellulose material with a small amount of chlorine dioxide in the gaseous state or in solution for a very short period of time. If the chlorine dioxide is used in the gaseous state, it is advantageously diluted with air or inert gas, such as nitrogen, for example, and can be applied by passing the cellulose material which had been previously moistened with water through a chamber containing the gaseous medium in proportions so that the cellulose material picks up between about 0.05 to 0.5 percent by weight chlorine dioxide under the particular operating conditions employed.

The temperature and residence time of the cellulose material in the chamber containing the diluted chlorine dioxide gas can be varied, depending upon the particular concentration of the chlorine dioxide gas contained therein, the form of the cellulose material, as well as the type of cellulose material, as will be apparent to those skilled in the art. Generally, the temperature in the chamber when the diluted chlorine dioxide gas is used can be between about 10° and 130°C and the residence times can vary from between a few seconds to about 30 minutes.

The cellulose materials can also be treated according to this invention with an aqueous solution of chlorine dioxide by soaking the cellulose materials in an aqueous chlorine dioxide aqueous solution. Ordinary bleaching and dyeing equipment, such as vats, jiggers, washing machines, and so forth, can be used for treating the cellulose materials with chlorine dioxide in aqueous solutions. The chlorine dioxide aqueous solution can also be applied to the cellulose materials by impregnation with foulardage and then let the cellulose material stay in equipment of the J-box type, a pulp- and dye-maturation chamber, or any other suitable accumulation system. The chlorine dioxide to the cellulose material can also be carried out in an autoclave to permit heating to higher temperatures and pressures of from about 1 to 4 atmospheres if this ever becomes desirable.

When utilizing an aqueous solution of chlorine dioxide, the amount of chlorine dioxide used should result in a pickup on the cellulose material of from about 0.05 to 0.5 by weight of chlorine dioxide per 100 parts of the textile material during its passage through a residence in the chlorine dioxide containing aqueous solution under the particular operating conditions employed.

When using an aqueous solution of chlorine dioxide, the pH of the solution, the methods of bleaching, the pretreatment employed may be varied as will be apparent to those skilled in the art. It has been found to be advantageous, however, to use an aqueous solution of chlorine dioxide having a pH of between about 2 and 7 and to carry out the process at a temperature of between about 10° and 130° C. The cellulose material can be passed through a hot solution of chlorine dioxide or, if desired, it can be immersed in a cold solution of chlorine dioxide, and the temperature of the solution raised to the desired temperature. For example, in the pad processes the cellulose material can be impregnated with a cold solution of chlorine dioxide and after drying or removal of excess solution, the cellulose material can be heated with steam or some other heating system and placed in a J-box for a period of time which can vary from a few seconds to 30 minutes, depending upon the particular cellulose material being treated and the process conditions.

In general, since the amount of chlorine dioxide applied to the textile is very small, the reaction with the waxy substances of the cotton and the reducing substances is extremely rapid and it is possible to envisage very short treatments on ordinary equipment without fear of the drawbacks inherent in the application of current methods of bleaching with chlorine dioxide. In most cases amounts of chlorine dioxide of the order of
from 0.1 to 0.3 percent relative to the weight of the cotton are sufficient to prepare the fiber for bleeding. Such quantities are not enough to bleach natural cellulose fibers, but they are enough to oxidize the fatty substances and noncellulosic impurities which help to give these fibers their hypophilic character.

After pretreatment with chlorine dioxide the textile is treated, with or without intermediate washing, with the peroxide bleeding solution. Apart from peroxide, the latter contains the usual alkaline agents: caustic soda and sodium carbonate, the usual stabilizers: sodium silicate and magnesium silicate, and/or organic sequestants, such as, ethylenediamine tetracetic or diethylenetriamine pentacetic acid and their alkaline or alkaline-earth salts. Bleaching can be effected in ordinary equipment kiers with or without pressure, vats, jiggers, impregnation tanks and any thermal accumulation system of the J-box and pad-roll types or in equipment for pressure bleeding in a steam medium. The duration of bleeding with hydrogen peroxide can vary but generally takes between a few minutes and 30 minutes. The temperature at which bleeding is carried out can also vary and can generally lie between 80° and 140° C.

This peroxide bleeding following treatment with chlorine dioxide is another important step of the invention. In particular, it is the combination of the two treatments that make it possible to obtain the excellent hypophilic property of the cellulosic materials treated in accordance with the process.

The following examples illustrate the present invention. To avoid disturbing the hypophilic measurements no surface-active or wetting agent has been used in any of the operations.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE I

Combed cotton was plunged for 3 minutes into a solution containing 0.1 g. chlorine dioxide per liter and brought to pH 4 with acetic acid. The amount of solution represented 20 times the weight of the cotton and the temperature of the solution was 90° C.

The same cotton was then plunged into a solution containing 1 percent hydrogen peroxide, 1 percent caustic soda, and 1.5 percent liquid sodium silicate at 36° Be relative to the weight of the cotton.

The temperature of this solution was 90° C. and the ratio of material to bath 1:10. The temperature was kept at 95° C. for 30 minutes, after which the cotton was thoroughly rinsed with hot then cold water.

No wetting agent was used in the course of these operations. Once dry, the hypophilic or water absorbency of the cotton was checked by the method described in the Codex Francais. This method consists in carefully depositing on the free surface of a body of water contained in a 1-liter crystallizer a square of cotton measuring 2 cm. along the side and weighing about 0.25 g., and then measuring the time that the square of cotton takes to sink into the water. Cotton treated in accordance with the invention became soaked in 2 seconds, whereas another specimen that had only been bleached with hydrogen peroxide without a preliminary treatment with chlorine dioxide took 133 seconds to become soaked.

EXAMPLE II

An Egyptian cotton cloth, previously desized with malt diastase and washed in boiling water, was impregnated at the ambient temperature with a chlorine dioxide solution prepared by the action of sulfuric acid on a sodium chloride solution and containing 2 g. per liter of chlorine dioxide. The cloth was then dried by passing between the rolls of a pad so that it retained only its weight of liquid, after which its temperature was rapidly brought to 100° C. by passing it through a steam-heated chamber. It was then stored for 5 minutes in a thermally insulated J-Box. The cloth was then washed in cold water, then squeezed out and impregnated with a cold solution of hydrogen peroxide containing, in addition, caustic soda and sodium silicate. The concentration of this solution and the degree of bleaching (drying) of the cloth were so calculated that, after passing between the rolls of the foulard, there remained on the cloth 1 percent hydrogen peroxide, 0.5 percent caustic soda, and 2 percent sodium silicate at 36° Be relative to the weight of the cloth.

The J-Box was heated by passing through a steam-filled chamber and then kept for 10 minutes in the J-Box. Finally it was washed first in hot, then in cold water.

The hypophilic property of the cloth was checked by the ASA method No I 1415-1961 which consists in letting a drop of water fall from a buret fixed 1 cm. above the stretched surface of the cloth and in measuring the time taken by the textile to absorb the drop. Cloth treated as described above absorbs the water in 2 seconds (mean of 20 tests) whereas the same cloth which had only been desized before being treated with hydrogen peroxide only absorbed the water in 114 seconds (mean of 20 tests). By way of comparison a sample of the same cloth desized, boiled in soda, and then bleached with peroxide absorbs the water in 6 seconds.

The degree of whiteness, measured with the Zeiss Elrepho spectrophotometer using a 457 A filter, was 82.2 (relative to a magnesium oxide standard) for the cloth pretreated with chlorine dioxide and 80.1 for the nonpretreated cloth. The degree of polymerization of the cloth pretreated with chlorine dioxide was 1,830, that of the nonpretreated cloth 1,850.

EXAMPLE III

The operations described in example II were applied to the same type of cloth but in a high-temperature vaporizer in which the cloth stayed for 30 seconds at 130° C. for the pretreatment with chlorine dioxide and for 90 seconds at 130° C. for bleaching with hydrogen peroxide.

Hydrophilic tests gave a time of less than 1 second (mean of 20 tests) for the cloth pretreated with chlorine dioxide to absorb the drop of water, whereas the nonpretreated cloth took 8 seconds (mean of 20 tests).

The degree of whiteness of the pretreated cloth was 80.4 as against 78.6 for the nonpretreated cloth and the degrees of polymerization were 2,060 for the pretreated cotton and 2,040 for the nonpretreated cotton, respectively.

EXAMPLE IV

Raw wet carded cotton with a moisture content of 160 percent was placed in a heated chamber at 70° C. in which a stream of air containing 4.3 percent chlorine dioxide by volume was caused to circulate. The amount of chlorine dioxide introduced into the chamber was 0.18 percent relative to the weight of the dry cotton.

After 2 minutes all of the chlorine dioxide was found to have disappeared. The cotton was then impregnated with its own weight of a solution of hydrogen peroxide, like that used in example I, and placed in a chamber into which steam was injected to raise the temperature to 98° C. After heating for 30 minutes, the cotton was washed with water at 60° C., then with cold water, and dried. It was perfectly white and when tested by the Codex Francais method became soaked in 2 to 3 seconds.

I claim:

1. A process for obtaining cellulosic materials or mixtures of cellulosic materials and synthetic fibers characterized by improved hypophilic properties, purity and whiteness, comprising treating the cellulosic material with an amount of chlorine dioxide sufficient for and for a period of time long enough to hypophilize the cellulosic material but not to bleach the cellulosic material and then bleaching the cellulosic material with hydrogen peroxide, sodium chloride, sodium hypochlorite or sodium persulfate.

2. The process of claim 1 in which the chlorine dioxide is used in an amount of from about 0.1 to 0.3 percent by weight of the cellulosic material to be treated.
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3. The process of claim 1 in which the chlorine dioxide is used in the form of an aqueous solution having a pH between about 2 and 7.

4. The process of claim 1 in which the chlorine dioxide is used in gaseous form, diluted with air or an inert gas.

5. The process of claim 1 in which the treatment with chlorine dioxide is effected under conditions, such that from about 0.05 to 0.5 percent of the chlorine dioxide is fixed on the cellulosic material.

6. The process of claim 1 in which the treatment with chlorine dioxide is effected at temperatures in the range from 10°C to 130°C.

7. The process of claim 1 in which the reaction time of the chlorine dioxide treatment varies between a few seconds and 30 minutes.