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(54) **Method for bleaching fibrous articles**

Verfahren zum Bleichen von Fasergut

Procédé pour le blanchiment d'articles fibreux

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DescriptionTECHNICAL FIELD

5 **[0001]** This invention relates to a method for bleaching fibrous articles using oxidizing or reducing agents and light energy, e.g. from low-intensity light sources of ultraviolet and/or visible light.

BACKGROUND

10 **[0002]** Bleaching of fibrous articles including those of natural fibers such as cotton and wool and regenerated fibers such as viscose rayon and polynosic is generally carried out by treating colored compounds adsorbed on the fibrous articles with oxidizing or reducing agents by the cleavage of conjugated π -electron systems that is responsible for the generation of color. One industrial typical method for bleaching includes boiling for about 0.5 to 2 hours in the presence of oxidizing or reducing agents and successive washing. Another method involves using solutions of such chemical agents (oxidizing or reducing agents) in appropriate concentrations, padding so as to cause the agent to be absorbed on the fibrous article in an amount of 80 to 110% by weight of the fibrous article, and heating in a steam atmosphere (i.e., steaming) at about 95°C for about 0.5 to 1 hour. Generally stated, oxidizing agents are often used for vegetable fibers such as cotton and linen, while reducing agents are often used for silk and wool. Household bleaching is conducted by adding bleaching agents to washing water.

20 **[0003]** In these prior art bleaching methods, the reactions between the oxidizing or reducing agents and the colored compounds on the fibers takes place by the application of thermal energy given by heating water as the medium. This method needs a substantial amount of energy because water having a substantial heat capacity must be heated to its boiling point and kept at the temperature for a time necessary for the reactions. Undesirably a reaction tower of larger size is thus necessary.

25 **[0004]** Since these industrial bleaching methods are carried out at high temperatures, they are mass-consumption processes requiring large quantities of energy, leaving the additional problem of discharging large amounts of carbon dioxide.

[0005] Most currently available methods use halogenated agents such as chlorites and hypochlorites as the oxidizing agents. Undesirably such chemical agents having halogen atoms impose substantial loads to the environment.

30 **[0006]** Therefore, hydrogen peroxide is used as a non-halogenated oxidizing agent. Since hydrogen peroxide may make fibers brittle due to a rapid decomposition of the reagent, decomposition inhibitors must be added to suppress the decomposition of hydrogen peroxide so that slow reaction may take place over time. This, in turn, requires the use of steam heat for a long period of time. An additional problem is that the thus finished fibers become hard.

35 **[0007]** On the other hand, hydrosulfites such as $\text{Na}_2\text{S}_2\text{O}_4$ and sulfur dioxide (SO_2) gas are used as reducing agents. However, they have weak bleaching power, often failing to achieve satisfactory bleaching.

40 **[0008]** The above-discussed problems can be solved by the combined use of oxidizing or reducing agents and irradiation of light including laser as disclosed in JP-A 11-43861 and JP-A 11-43862. Irradiating light having low intensity from inexpensive light sources for a long time, as compared with irradiation of high-intensity light, raises the problems that fibrous articles are dried during light irradiation and once dried, bleaching reaction does not proceed even under light irradiation, so that the whiteness degree is no longer improved.

SUMMARY OF THE INVENTION

45 **[0009]** The present invention addresses the bleaching of a fibrous article using oxidizing or reducing agents and ultraviolet and/or visible photon energy. A preferred embodiment of the invention may provide an environmentally-friendly bleaching method capable of preventing drying of a fibrous article during light irradiation and thus achieving a satisfactory bleaching effect, and having advantages including minimized environmental loads, safety operation, resource saving, and energy saving.

50 **[0010]** The inventors have discovered that the problems associated with fabric bleaching can be solved by the combination of organic photochemical findings, characteristics of photoreactions with ultraviolet/visible light, and mechanistic findings regarding bleaching apparatus.

55 **[0011]** Specifically, because prior art bleaching methods using oxidizing or reducing agents with either thermo-chemical or photochemical methods often suffer from the embrittlement of fibrous articles due to reactive species generated by the decomposition of the oxidizing or reducing agents, various chemicals have been used for restraining the embrittlement of fibrous articles. It has been found that when colored compounds are activated by the irradiation of ultraviolet and/or visible light under treating conditions where no reactive species are generated by the photo-decomposition of the oxidizing or reducing agents, and when the activated compounds are effectively reacted with the oxidizing or reducing agents under the conditions where the fibrous articles impregnated with oxidizing agent or reducing agent solutions are not

dried, then the colored compounds are decomposed or decolored, and the bleaching of the fibrous articles is accomplished with restraining the fibrous articles from embrittling or hardening, and preserving their strength.

[0012] Accordingly, the present invention provides a method for bleaching fibrous articles, comprising the steps of impregnating fibrous articles with oxidizing or reducing agent solutions, irradiating the impregnated fibrous articles with ultraviolet and/or visible light, and adding at least once again oxidizing or reducing agent solutions to the fibrous articles while they are being irradiated with ultraviolet and/or visible light.

[0013] The oxidizing agent is typically selected from among peroxides, percarboxylic acids, percarbonate salts, perborate salts, peroxide salts, persulfate salts, and superperoxide salts. The reducing agent is typically selected from among sulfite salts, hydrogensulfite salts, borohydrides, dithionite salts, and thiourea dioxide.

[0014] In a preferred embodiment, the oxidizing or reducing agent solutions used in the impregnating step has a concentration of 0.01 to 40% by weight, and the oxidizing or reducing agent solutions used in the re-adding step has a concentration of 0.01 to 40% by weight.

[0015] The fibrous articles are typically woven fabrics, knitted fabrics or nonwoven fabrics.

[0016] The method of bleaching fibrous articles according to the invention achieves a satisfactory bleaching effect while restraining the fibrous articles from embrittling or hardening and preserving the hand or feel thereof and without losing the strength thereof. It is an environmentally-friendly bleaching method having advantages including a minimized environmental load, safety operation, resource saving, and energy saving.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The method for bleaching fibrous articles according to the present invention involves the steps of impregnating fibrous articles with oxidizing or reducing agent solutions, irradiating the impregnated fibrous article with ultraviolet and/or visible light, and adding at least once again the oxidizing or reducing agent solutions to the fibrous articles while they are being irradiated with the ultraviolet and/or visible light.

[0018] The oxidizing or reducing agents used herein may be any compounds including organic compounds, inorganic compounds and organic-inorganic complexes which are relatively stable in the solvent used herein. Suitable oxidizing agents include peroxides such as hydrogen peroxide and benzoyl peroxide, percarboxylic acids such as performic acid, peracetic acid and perlactic acid, percarbonates such as sodium peroxocarbonate, perborates such as sodium peroxoborate, peroxide salts such as sodium peroxide, persulfates such as sodium persulfate, and superperoxide salts such as potassium superperoxide. Suitable reducing agents include sulfites such as sodium sulfite and sodium hydrogen sulfite, hydrogensulfites, borohydrides such as sodium borohydride, dithionites such as sodium dithionite, and thiourea dioxide.

[0019] Of these, hydrogen peroxide, sodium peroxocarbonate and sodium peroxoborate are preferred as the oxidizing agents. Sodium borohydride, sodium dithionite, and thiourea dioxide are preferred as the reducing agents.

[0020] The oxidizing or reducing agents are used after they are dissolved in solvents which are transparent to ultraviolet and visible light, for example, water, alcohols such as methyl alcohol and ethyl alcohol, linear or cyclic alkanes such as heptane and cyclohexane, ethers such as ethyl ether and methyl ethyl ether, and mixtures thereof. Of these, water or solvent mixtures containing water are preferred herein.

[0021] The concentration of the oxidizing or reducing agents in the solution is not particularly limited as long as it is equal to or below the saturation concentration thereof in the solvent. The concentration is preferably 0.01 to 40% by weight, more preferably 0.1 to 20% by weight. Too low a concentration may result in an insufficient whiteness degree. Too high a concentration may be uneconomical because the resulting whiteness degree does not compensate for such an increment.

[0022] The fibrous articles which are used herein are not particularly limited and include woven fabrics, knitted fabrics and nonwoven fabrics, and more specifically, shirt textiles, skirt textiles, cloth textiles, underwear textiles, sheet textiles and the like. Also the fibers of which the fibrous articles are made are not particularly limited and include natural cellulose fibers, for example, seed fibers such as cotton and kapok, bast fibers such as flax, hemp, jute, ramie, kenaph and Musaliukiensis makino, nerve fibers such as abaca, sisal and henequen, fruit fibers such as coir, pulp and the like; regenerated cellulose fibers such as viscose rayon, cuprammonium rayon, and polynosic, refined cellulose fibers such as tencel (TM); semi-regenerated fibers such as cellulose acetate; and animal fibers such as wool and silk. Use may be made of fibers of one type or mixtures of fibers of two or more types. In the practice of the invention, cellulose fibers including natural fibers such as cotton and regenerated cellulose fibers such as rayon are preferred, with natural cellulose fibers such as cotton being more preferred. Of these, articles of fibers comprising at least 25% by weight, especially at least 50% by weight of cotton are most preferred for appropriate moisture absorption, water absorption and hand or feel.

[0023] The fibrous articles to be bleached by the inventive method may or may not have been bleached. Suitable fibrous articles include, but are not limited to, colored fabrics such as grey fabrics, desized fabrics, scoured fabrics, desized/scoured fabrics, fabrics colored during use after bleaching, and dyed fabrics.

[0024] In the bleaching method of the invention, fibrous articles are first impregnated with a solution of the oxidizing

or reducing agents. The impregnation may be carried out by techniques of dipping the fibrous articles in the solution, or techniques of coating, padding, spraying or otherwise applying the solution to the fibrous articles. Of these, padding or spraying techniques are advantageously used in terms of productivity.

[0025] Next, the fibrous articles impregnated with the oxidizing or reducing agents are irradiated with ultraviolet and/or visible light. Light irradiation may be done while the fibrous article is kept stationary or moving.

[0026] The ultraviolet and/or visible light sources used for light irradiation including low-intensity light sources are not particularly limited although light sources of 0.1 milliwatts to 10 kilowatts are appropriate. Examples of suitable light sources include conventional light sources such as low-pressure mercury lamps, blacklight lamps, high-pressure mercury lamps and xenon lamps, and various excimer lamps. Of these, low-pressure mercury lamps, blacklight lamps and excimer lamps are preferred in terms of efficient conversion from electricity to light. However, the light source used herein is not limited to these as long as effective bleaching is accomplished.

[0027] For ultraviolet and/or visible light sources including low-intensity light sources, laser beams expanded by optical components such as lenses and mirrors can be used. The laser light source is not particularly limited. The laser light may be either pulsed laser light or continuous-wave laser light. Suitable lasers include excimer lasers (e.g., ArF excimer laser, KrF excimer laser, XeCl excimer laser and XeF excimer laser), argon ion lasers, krypton ion lasers, and YAG lasers (e.g., second and third harmonics). The laser light may be suitably expanded by optical components before irradiation. Any of these light sources may be used alone or in a combination of two or more. It is desired to use light in the wavelength region of 180 nm to 600 nm.

[0028] The intensity of laser light irradiated is not particularly limited, but is typically in the range of 0.1 mJ/cm² per pulse to 1 kJ/cm² per pulse for the pulsed lasers and in the range of 0.1 mW/cm² to 10 kW/cm² for the continuous-wave lasers.

[0029] The temperature during light irradiation is not particularly limited as long as it is between the freezing point and the boiling point of the solvents used. The temperature is preferably from -80°C to 100°C, more preferably from 0° C to 50° C. The time for light irradiation is suitably determined depending on various factors including the degree of coloring of the fibrous articles, the type of oxidizing or reducing agents used, the type of solvents, and solution concentrations, as well as the type and intensity of ultraviolet and/or visible light irradiated. The time is preferably 1 to 60 minutes, more preferably 3 to 40 minutes although light irradiation can be continued over 60 minutes if necessary.

[0030] According to the invention, oxidizing or reducing agent solutions are added at least once again to the fibrous articles during the light irradiation. Although the point of time when the oxidizing or reducing agent solutions are re-added is not particularly limited, re-addition is preferably done within 30 minutes from the initial impregnation of the fibrous articles with the oxidizing or reducing agent solutions. More preferably, first re-addition is done within 10 minutes from the initial impregnation because this prevents the fibrous articles from drying. Where re-addition is repeated two or more times, a certain re-addition is done preferably within 30 minutes, more preferably within 10 minutes from the last addition.

[0031] The oxidizing or reducing agent solutions for re-addition may have any desired concentration, preferably of 0.01 to 40% by weight, more preferably 0.1 to 20% by weight of the oxidizing or reducing agents. Too low a concentration may result in an insufficient whiteness degree. Too high a concentration may be uneconomical because the resulting whiteness degree does not compensate for such an increment.

[0032] The re-addition may be conducted by various techniques such as dipping, coating, padding and spraying. Padding or spraying techniques are preferred for productivity.

[0033] The number of re-additions may be more than 10 times if the fibrous articles tend to dry during the processing, and is more preferably 1 to 10 times, and even more preferably 1 to 5 times. Without re-addition, the whiteness degree is insufficient. Excess re-additions may be uneconomical because the resulting whiteness degree does not compensate for such an extra amount of the chemical liquid used.

[0034] After oxidizing or reducing agent solution is re-added to the fibrous articles, a light source as exemplified above may be used under similar irradiating conditions including light intensity, temperature and time for continuing bleaching process. After the bleaching process, the fibrous articles are washed and dried in a conventional manner, obtaining bleached fibrous articles.

[0035] The method of the invention involving at least one re-addition of oxidizing or reducing agent solutions during light irradiation ensures efficient bleaching even with light irradiation using low-intensity light sources.

EXAMPLE

[0036] Examples of the invention are given below by way of illustration and not by way of limitation.

Example 1

[0037] A 50-count plain weave fabric of 100% cotton (warp density 58 yarns/cm (148 yarns/inch) weft density 31 yarns/cm (80 yarns/inch)) was desized and scoured in an ordinary way and then padded with a 6% sodium peroxocar-

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bonate aqueous solution (nip rate 100%). Using a XeF excimer laser (351 nm) of 2 mJ/cm² per pulse, 20 Hz, the fabric was irradiated with light for 10 minutes. At this point, the sodium peroxocarbonate aqueous solution was added once again by padding, and light irradiation from the XeF excimer laser was continued for another 10 minutes. The fabric was then washed and dried in an ordinary way. Using Macbeth Color Eye 7000, the thus bleached cotton fabric was measured for whiteness (JIS Z-8715, 1991) and yellow index (JIS K-7103, 1997), which were 81.7 and 2.2, respectively. The cotton fabric was also determined for weftwise tensile strength (JIS L-1096A, raveled strip test), which was 463.54 N.

Example 2

[0038] The same fabric as used in Example 1 was treated as in Example 1 except that the initial padding was followed by 5 minutes of light irradiation with an XeF excimer laser, one re-addition of the reagent solution (6% sodium peroxocarbonate aqueous solution) by padding, and 5 minutes of light irradiation, and the re-addition and light irradiation were repeated two more times. The total number of padding steps was 4 and the total time of XeF excimer laser irradiation was 20 minutes. The bleached cotton fabric was colorimetrically analyzed as in Example 1, to find a whiteness of 82.8 and a yellow index of 1.6. Also the cotton fabric had a weftwise tensile strength of 442.96 N.

Example 3

[0039] The same fabric as used in Example 1 was treated as in Example 1 except that an appropriate amount of sodium peroxocarbonate aqueous solution was re-added once by spraying. The bleached cotton fabric was colorimetrically analyzed as in Example 1, to find a whiteness of 81.6 and a yellow index of 2.2. Also the cotton fabric had a weftwise tensile strength of 466.48 N.

Comparative Example 1

[0040] A 50-count plain weave fabric of 100% cotton (warp density 58 yarns/cm (148 yarns/inch), weft density 31 yarns/cm (80 yarns/inch)) was desized and scoured in an ordinary way and then padded with a 6% sodium peroxocarbonate aqueous solution (nip rate 100%). Using a XeF excimer laser (351 nm) of 2 mJ/cm² per pulse, 20 Hz, the fabric was irradiated with light for 20 minutes. The fabric was then washed and dried in an ordinary way. The bleached cotton fabric was colorimetrically analyzed as in Example 1, to find a whiteness of 77.5 and a yellow index of 2.8. Also the cotton fabric had a weftwise tensile strength of 465.5 N.

[0041] Table 1 summarizes the bleaching conditions and the results of Examples 1-3 and Comparative Example 1.

Table 1

	Bleaching conditions				Evaluation		
	Oxidizing or reducing agent	Total number of padding steps	Light irradiation	Total irradiation time	Whiteness	Yellow index	Tensile strength (N)
Example 1	6% sodium peroxocarbonate aqueous solution	2	XeF excimer laser (351 nm)	10 min × min 2	81.7	2.2	463.54
Example 2	6% sodium peroxocarbonate aqueous solution	4	XeF excimer laser (351 nm)	5 min × 4	82.8	1.6	442.96
Example 3	6% sodium peroxocarbonate aqueous solution	2 (including one spraying)	XeF excimer laser (351 nm)	10 min × 2	81.6	2.2	466.48
Comparative Example 1	6% sodium peroxocarbonate aqueous solution	1	XeF excimer laser (351 nm)	20 min × 1	77.5	2.8	465.5

Claims

1. A method for bleaching fibrous articles, comprising the steps of
 5 impregnating fibrous articles with oxidizing or reducing agent solutions,
 irradiating the impregnated fibrous articles with ultraviolet and/or visible light, and
 re-adding at least once oxidizing or reducing agent solutions to the fibrous articles while they are being irradiated
 with ultraviolet and/or visible light.
2. The method of claim 1, wherein the oxidizing agent is selected from the group consisting of peroxides, percarboxylic
 10 acids, percarbonates, perborates, peroxide salts, persulfates, and superperoxide salts.
3. The method of claim 1, wherein the reducing agent is selected from the group consisting of sulfites, hydrogensulfites,
 borohydrides, dithionites, and thiourea dioxide.
- 15 4. The method of any one of claims 1 to 3, wherein the oxidizing or reducing agent solutions used in the impregnating
 step has a concentration of 0.01 to 40% by weight, and the oxidizing or reducing agent solutions used in the re-
 adding step has a concentration of 0.01 to 40% by weight.
- 20 5. The method of any one of claims 1 to 4, wherein the fibrous articles are woven fabrics, knitted fabrics or nonwoven
 fabrics.

Patentansprüche

- 25 1. Verfahren zum Bleichen von Fasergut, umfassend die Schritte
 des Imprägnierens des Faserguts mit Oxidations- oder Reduktionsmittellösungen,
 des Bestrahls des imprägnierten Faserguts mit ultraviolettem und/oder sichtbarem Licht und
 der erneuten, zumindest einmaligen Zugabe von Oxidations- oder Reduktionsmittellösungen zu dem Fasergut,
 während dieses mit ultraviolettem und/oder sichtbarem Licht bestrahlt wird.
- 30 2. Verfahren nach Anspruch 1, worin das Oxidationsmittel aus der aus Peroxiden, Percarbonsäure, Percarbonaten,
 Perboraten, Peroxidsalzen, Persulfaten und Hyperoxidsalzen bestehenden Gruppe ausgewählt ist.
- 35 3. Verfahren nach Anspruch 1, worin das Reduktionsmittel aus der aus Sulfiten, Hydrogensulfiten, Borhydriden, Dithio-
 niten und Thioharnstoffdioxid bestehenden Gruppe ausgewählt ist.
- 40 4. Verfahren nach einem der Ansprüche 1 bis 3, worin die Oxidations- oder Reduktionsmittellösungen, die im Imprä-
 gnationsschritt eingesetzt werden, eine Konzentration von 0,01 bis 40 Gew.-% aufweisen und die Oxidations- oder
 Reduktionsmittellösungen, die im Schritt der erneuten Zugabe eingesetzt werden, eine Konzentration von 0,01 bis
 40 Gew.-% aufweisen.
5. Verfahren nach einem der Ansprüche 1 bis 4, worin das Fasergut ein Gewebe, Gewirke oder Faservlies ist.

Revendications

1. Procédé pour blanchir des articles fibreux, comprenant les étapes consistant à
 50 imprégner des articles fibreux avec des solutions d'agent oxydant ou réducteur,
 irradier les articles fibreux imprégnés avec une lumière ultraviolette et/ou visible, et
 ré-ajouter au moins une fois des solutions d'agent oxydant ou réducteur aux articles fibreux pendant qu'ils sont
 irradiés avec une lumière ultraviolette et/ou visible.
2. Procédé selon la revendication 1, dans lequel l'agent oxydant est choisi dans le groupe constitué par les peroxydes,
 les acides percarboxyliques, les percarbonates, les perborates, les sels de peroxyde, les persulfates et les sels de
 55 superperoxyde.
3. Procédé selon la revendication 1, dans lequel l'agent réducteur est choisi dans le groupe constitué par les sulfites,
 les hydrogénosulfites, les borohydrures, les dithionites et le dioxyde de thiourée.

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4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel les solutions d'agent oxydant ou réducteur utilisées dans l'étape d'imprégnation ont une concentration de 0,01 à 40 % en poids, et les solutions d'agent oxydant ou réducteur utilisées dans l'étape de ré-addition ont une concentration de 0,01 à 40 % en poids.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel les articles fibreux sont des étoffes tissées, des étoffes tricotées ou des étoffes non tissées.

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REFERENCES CITED IN THE DESCRIPTION

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