(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number
WO 01/07709 A1

(51) International Patent Classification[7]: D06M 13/33, 13/35

(21) International Application Number: PCT/US00/18995

(22) International Filing Date: 13 July 2000 (13.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/361,876 27 July 1999 (27.07.1999) US

(71) Applicant: MILLIKEN & COMPANY [US/US]; 920 Milliken Road, Spartanburg, SC 29303 (US).

(72) Inventor: LI, Shulong; 204 Woodgrove Trace, Spartanburg, SC 29301 (US).

(74) Agent: PARKS, William, S.; P.O. Box 1927, Spartanburg, SC 29304 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TEXTILE SUBSTRATE EXHIBITING ANTIMICROBIAL PROPERTIES WITH LOW DELETERIOUS ODOR AND SKIN IRRITATION EFFECTS

(57) Abstract: This invention relates to antimicrobial fabrics which are treated with a specific durable and regenerable halamine/chlorine system and methods of removing residual active chlorine from the target textile surface without reducing the antimicrobial activity of the textile. Such methods comprise contacting an amine-treated fabric first with a halogen-based bleach (or other halogenated liquid) to produce halamines at the fabric surface, and subsequently washing the resultant halogenated fabric with a reducing agent which removes the residual, unbonded halogen (such as chlorine) from the fabric surface but does not, surprisingly, remove the halamine halogen. The remaining halamine halogen thus provides the desired antimicrobial activity. As a result, a method of substantially reducing fabric discoloration, odor, and potential skin irritation due to the presence of amounts of residual unbonded halogen (such as chlorine) on the target fabric surface is provided which simultaneously permits sufficient amounts of halamine halogen (such as chloramine chlorine) to remain on the target fabric for optimum microbiocidal properties. A fabric treated in accordance with this method is also provided.

WO 01/07709 A1

Disclosure

TEXTILE SUBSTRATE EXHIBITING ANTIMICROBIAL PROPERTIES WITH LOW DELETERIOUS ODOR AND SKIN IRRITATION EFFECTS

Technical Field

This invention relates to antimicrobial fabrics which are treated with a specific durable and regenerable halamine/chlorine system and methods of removing residual active chlorine from the target textile surface without reducing the antimicrobial activity of the textile. Such methods comprise contacting an amine-treated fabric first with a halogen-based bleach (or other halogenated liquid) to produce halamines at the fabric surface, and subsequently washing the resultant halogenated fabric with a reducing agent which removes the residual, unbonded halogen (such as chlorine) from the fabric surface but does not, surprisingly, remove the halamine halogen. The remaining halamine halogen thus provides the desired antimicrobial activity. As a result, a method of substantially reducing fabric discoloration, odor, and potential skin irritation due to the presence of amounts of residual unbonded halogen (such as chlorine) on the target fabric surface is provided which simultaneously permits sufficient amounts of halamine halogen (such as chloramine chlorine) to remain on the target fabric for optimum microbiocidal properties. A fabric treated in accordance with this method is also provided.

Background of the Prior Art

There has been a great deal of attention in recent years given to the hazards of antimicrobial contamination from potential everyday exposure. Noteworthy examples of such concern include the fatal consequences of food poisoning due to certain strains of *Eschericia coli* being found within undercooked beef in fast food restaurants; *Salmonella* contamination causing sicknesses from undercooked and unwashed poultry food products; and illnesses and skin infections attributed to *Staphylococcus aureus*, yeast, and other unicellular organisms. With such an increased consumer interest in this area, manufacturers have begun introducing antimicrobial agents, such as Triclosan, available from Ciba-Geigy under the tradename Irgasan®, within various household products. For instance, certain brands of polypropylene cutting boards, liquid soaps, etc., all contain this very effective antimicrobial compound. Generally, the incorporation of triclosan within liquid or polymeric media has been relatively simple. However, there is a long-felt need to provide effective, durable, and long-lasting antimicrobial characteristics within textiles, in particular apparel fabrics, which is extremely difficult to accomplish with triclosan. There are commercially available textile products comprising acrylic and/or acetate fibers co-extruded with triclosan (for example Hoechst Celanese markets such acetate fabrics under the name Microsafe™ and Courtaulds markets such acrylic polymer fabrics under the name Amicor™). However, such an application is limited to those types of fibers; it does not work specifically for and within polyester, polyamide, cotton, lycra, etc., fabrics.

Very recently, work has been undertaken to provide antimicrobial finishes to fabrics through the covalent bonding of certain nitrogen-containing groups, such as hydantoin, as merely one example, to individual fibers (such as cellulose fibers). Such nitrogen-containing groups (which may also include imines, amides, amines, imides, and the like) provide sites for the bonding and retention of chlorines (or other halogens) which ultimately provide the desired N-halamines which produce the desired antimicrobial characteristics. Such chlorines, and the like, are easily introduced to the textile surface through a washing process (such as with a chlorine bleach) during which some of the chlorines become bonded with the free accessible nitrogens on the hydantoins bonded to the fabric surface to produce N-halamines. Such N-halamines are, as noted above, very strong oxidants and are very effective against microorganisms. These halamines, this process, and the fabrics made thereby are more thoroughly discussed in U.S. Patent 5,882,357 to Sun et al., herein entirely incorporated by reference and fabrics treated with certain nitrogen-containing compounds (again such as hydantoin, imines, imides, amides, and the like) are herewith denoted by the term "amine-treated fabric." This term is intended to encompass all fabrics which are treated with nitrogen-containing compounds which ultimately form of N-halamines upon contact with halogen bleaches (or other halogenated liquids, including solid bleach-containing detergents which dissolve in water to form a liquid). Such fabrics are formed in accordance with the Sun et al. patent, noted above, as an example, and the nitrogen-containing compounds include those which include triazine, hydantoin, imidazolidinone groups, and the like. The

term "halamine-treated fabric" thus is intended to encompass any amine-treated fabric which has been contacted with and has retained halogens within the nitrogen-containing groups on the amine-treated fabric surface. Such halamine-treated fabric provides long-term wearability and also allows for replenishment of any removed or used antimicrobial halalamine halogen (such as chloramine chlorine). Subsequent washes with bleach, for example, will create halamines by reacting with "vacant" hydantoin groups. Thus, although the chlorine (or other halogen) may be removed or rendered unusable for antimicrobial activity, fresh supplies of chlorine, and the like, may be introduced and bonded with the hydantoin surface treatment over time to regenerate the microbiocidal capability of the target fabric.

This halamine treatment unfortunately also results in a substantial amount of adsorbed active chlorine (or other halogens) remaining on the surface of the fabric in addition to covalently bonded halamines, after each bleach (or similar halogen-containing liquid) wash. Such residual adsorbed halogen (chlorine, for instance), as is well known, produces an highly unpleasant odor, discolors fabrics, particularly those with dyes and colorants therein, and can cause irritation to a wearer's skin (if the target fabric is incorporated within apparel, for instance). Such circumstances associated with this halamine antimicrobial system have proven problematic for the incorporation of such a promising antimicrobial system and process within apparel and other textile applications in which human contact occurs. Thus, there has been noticed a necessity for providing a subsequent treatment for readily removing substantially all of the unbonded residual active chlorine (or other halogen) from the target fabric surface while also permitting the continued bonding of the antimicrobial

chlorine within the halamine. Such a procedure would reduce the deleterious odor and skin irritation prevalent in the fabrics now produced with this method. However, the prior art has not provided such an improvement for halamine antimicrobial systems to date.

Description of the Invention

It is thus an object of the invention to provide a safe, effective procedure of removing residual adsorbed active chlorine from a halamine-treated fabric surface to substantially reduce halogen-created odors, discolorations of fabric, and potential skin irritation. Another object of the invention is to provide a process which facilitates the production of an antimicrobial fabric finish while also permitting reductions in deleterious effects related to the presence of free chlorine or other halogen molecules, and the like, on a fabric surface. Yet another object of this invention is to provide a relatively inexpensive and quick post-wash rinsing of target halamine-treated fabric which renders the fabric wearable and usable.

Accordingly, this invention encompasses a method of removing substantial amounts of residual free halogen from a halamine-treated fabric surface comprising the steps of washing an amine-treated fabric with a halogen-containing liquid and subsequently rinsing the resultant halamine-treated fabric with a reducing agent solution having a pH of from about 3 to about 12 and having an instant reactivity with the target active halogen in a standard rinsing liquid, at a temperature from about 0 to about 70°C, wherein said reducing agent does not remove an appreciable amount of active halogen molecules bonded within said halamines, thereby permitting the

halamine-treated fabric to retain its antimicrobial properties. The term "antimicrobial properties" is intended to mean the ability to at least control the growth of bacteria. Thus, this term may also include a bactericide (which actually destroys bacteria). Considering the highly oxidative and reactive nature of active chlorine and other active halogen molecules, it is highly unlikely that the presence of such a reducing agent would only affect (in an appreciable manner) the free adsorbed halogens and not every oxidative halogen moiety (such as chlorine at a +1 or 0 valence state) present, whether bonded as in halamine or not, on the target fabric surface. In fact, it is well known that halamines possess similar oxidative potentials and/or reactivities with free active halogens (such as chlorines) and are used as chlorine, etc., substitutes in certain applications (such as fabric, etc., bleaches). Thus, it would be expected that since reducing agents generally react instantly (and at times violently) with highly oxidative and reactive compounds, such as free active halogens and active halamine halogens, such halogens would be removed through a rinsing step with such a reducing agent. Thus, a reducing agent rinse would theoretically render the target fabric surface antimicrobially inactive; again, unexpectedly, just the opposite appears to occur. There is no teaching nor fair suggestion within any of the prior art which would lead one of ordinary skill in the art to uncover such a phenomenon.

The proper selection of a reducing agent is made through the two parameters noted above, namely pH levels between 3 and 12, preferably from about 5 to 9, and most preferably from about 6 to about 8, and the ability to appreciable remove only free active halogens and not active halamine halogens. Any reducing agent which meets this limitation is considered to be within the scope of this inventive process.

Preferably, however, specific reducing agents include sodium bisulfite, sodium thiosulfate, sodium hydrosulfide, thiourea, sodium borohydride, sodium sulfite, ascorbic acid, and the like. Of these, sodium bisulfite, being the most readily available and the least costly, has proven to be the most preferred. The reactivity of the reducing agent is generally related to the concentration of reducing agent as well. A relatively high concentration of reducing agent will remove the bonded halogens which will subsequently substantially reduce the antimicrobial activity of the target halamine-treated fabric. Thus an aqueous reducing agent solution having a concentration of from about 0.1 to about 100, preferably from about 1 to about 10 grams per gallon should be utilized in the method. Furthermore, the pH levels may be adjusted through the inclusion of a pH buffer solution (such as sodium phosphate, dibasic, as merely one possible selection) and will not affect the performance of the reducing agent in removing only unbonded active halogens (such as chlorine, bromine, iodine, and the like) from the target fabric surface.

Other additives may also be used, such as low amounts of surfactants, perfumes, antistatic agents, and the like, in order to provide other desired properties to the target fabric through a rinsing step.

Any fabric can be utilized in this invention as the important requirement is that the reducing agent be utilized in a controlled amount and concentration to effectively remove the free, potentially damaging and/or deleterious active halogens from the target fabric surface. Polyester/cotton blends are most preferred; however, any natural fibers, such as cotton, ramie, and the like; any synthetic fibers, such as polyamides, lycra, and the like; and any blends thereof of any natural and/or synthetic fibers may

be utilized within the inventive fabric. Furthermore, woven fabrics are preferred; however, knitted and non-woven forms may also be utilized as well as combinations of any types of these forms. Of course, the desired fabric must be able to withstand washes with highly basic halogenated liquids (in order to regenerate the antimicrobial activity, as noted above). Thus, white and bleach-resistant colored fabrics are preferred.

Description of the Preferred Embodiment

The following example is indicative of the preferred embodiment of this invention and is compared with those found within the prior art:

EXAMPLE 1

A 65/35 polyester/cotton blend woven fabric was first impregnated with an aqueous solution containing about 4% by weight of 1,3-dimethylol-5,5-dimethylhydantoin and 1% by weight of magnesium chloride as a catalyst (as disclosed in U.S. Pat.5,882,357 to Sun et al., noted and incorporated herein previously). The wet fabric was then dried at 250°F for 1 minute and at 380°F for 2 minutes. The fabric gained about 3.5% of its previous weight after this treatment. The treated fabric was then machine-washed in a regular washing cycle, followed by a bleach rinse at about 0.01% sodium hypochlorite solution (diluted commercially and available under the tradename Clorox®-brand bleach from The Clorox Company). The fabric was then rinsed with a reducing agent comprising about 0.035% sodium bisulfite in aqueous solution. The resultant fabric was then dried in a regular clothes

dryer for about 40 minutes. The washed and dried fabric had no chlorine smell. Samples of this dried fabric were then tested for their antimicrobial properties against *Staphylococcus aureus* (ATCC 5368) and *Klebsiella pneumoniae* (ATCC 4352) using AATCC Test Method 100. The results were tabulated as follows with bacteria contact time measured at 20 hours for each:

TABLE 1

Bacteria Type	Log reduction in bacteria	Chlorine Smell
Staphylococcus aureus	>4.3	Minimal
Klebsiella pneumoniae	>5.5	Minimal

These results were then compared with other untreated and treated fabrics as follows:

EXAMPLE 2 (Comparative)

The same type of fabric as in EXAMPLE 1, above, was machine-washed with the same type of bleach without first treating with an hydantoin. The washed fabric had a minimal chlorine smell.

EXAMPLE 3 (Comparative)

The same type of fabric as in EXAMPLE 1, above, was impregnated with the same hydantoin (1,3-dimethylol-5,5-dimethylhydantoin) as in the same EXAMPLE, and found to have the same approximately weight gain after treatment. The fabric was then bleach rinsed with the same Clorox®-brand bleach as in EXAMPLEs 1 and 2, and dried. The resultant fabric exhibited a very strong chlorine smell.

EXAMPLE 4 (Comparative)

The resultant fabric of EXAMPLE 2 was then rinsed with a reducing agent (the same as in EXAMPLE 1) and dried in the same manner as in EXAMPLE 2. The chlorine smell was substantially reduced.

Each of the Comparative fabrics were then made into individual samples for testing of antimicrobial activity as in TABLE 1, above (for the same types of bacteria). The results are tabulated below as follows, for contact times of about 20 hours:

TABLE 2

A. EXAMPLE 2

Bacteria Type	Log reduction in bacteria	Chlorine Smell
Staphylococcus aureus	-0.22	Minimal
Klebsiella pneumoniae	0.52	Minimal

B. EXAMPLE 3

Bacteria Type	Log reduction in bacteria	Chlorine Smell
Staphylococcus aureus	>4.3	Strong
Klebsiella pneumoniae	>5.5	Strong

C. EXAMPLE 4

Bacteria Type	Log reduction in bacteria	Chlorine Smell
Staphylococcus aureus	0.28	None
Klebsiella pneumoniae	0.46	None

Clearly, the inventive procedure accords the same antimicrobial activity as in EXAMPLE 3 (which does not incorporate the reducing agent rinse) and also substantially reduces the undesirable chlorine odors associated with this EXAMPLE 3. Furthermore, the non-halamine treated fabrics do not exhibit any appreciable antimicrobial activity although the chlorine smell is lowered substantially for both.

Thus, the inventive method provides a superior final product in both antimicrobial activity and unpleasant odor.

Test samples were then made to measure empirically the potential damage and/or discoloration to fabric due to the retention of free chlorines on the surface due to chlorine bleaching in accordance with AATCC Test Method 114-1971, "Chlorine Retention and Scorch." Strips of white polyester/cotton blend (65/35) fabric were cut (14 inches by 1-1/4 inches each) and treated in accordance with Examples 1 and 3, above. The Example 3 strip exhibited an extremely strong chlorine smell while the Example 1 strip was essentially odor-free. Two heating plates were then pre-heated to about 365°F. Each strip was then placed between the two plates for 30 seconds after which the strips were removed and viewed empirically for the resultant condition of the fabric. The Example 1 strip exhibited very little discoloration; the Example 3 strip exhibited extensive browning of the fabric. Clearly, the fabric treated by the inventive process produced a more favorable result.

There are, of course, many alternative embodiments and modifications of the present invention which are intended to be included within the spirit and scope of the following claims.

Claims

What we claim is:

1. A method of removing substantial amounts of residual free halogen from a halamine-treated fabric surface comprising the steps of washing an amine-treated fabric with a halogen-containing liquid and subsequently rinsing the resultant halamine-treated fabric with a reducing agent solution having a pH of from about 3 to about 12 and having an instant reactivity with the target active halogen in a standard rinsing liquid, at a temperature from about 0 to about 70°C, wherein said reducing agent does not remove an appreciable amount of active halogen molecules bonded within said halamines, thereby permitting the halamine-treated fabric to retain its antimicrobial properties.

2. The method of Claim 1 wherein said reducing agent is present as an aqueous solution in a concentration of from about 0.1 to about 100 grams per gallon.

3. The method of Claim 2 wherein said reducing agent has a pH of from about 5 to about 9 and is present as an aqueous solution in a concentration of from about 1 to about 10 grams per gallon.

4. The method of Claim 2 wherein said reducing agent has a pH of from about 6 to about 8.

5. The method of Claim 1 wherein said reducing agent is selected from the group consisting of sodium bisulfite, sodium thiosulfate, sodium hydrosulfide, thiourea, sodium borohydride, sodium sulfite, ascorbic acid, and any mixtures thereof.

6. The method of Claim 5 wherein said reducing agent is sodium bisulfite.

7. A fabric produced in accordance with the method of Claim 1.

8. A fabric produced in accordance with the method of Claim 2.

9. A fabric produced in accordance with the method of Claim 3.

10. A fabric produced in accordance with the method of Claim 4.

11. A fabric produced in accordance with the method of Claim 1.

12. A fabric produced in accordance with the method of Claim 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/18995

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :D06M 13/33, 13/35
US CL :8/115.69; 442/123
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/115.51,115.54,115.69,147; 442/123

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,490,983 A (WORLEY et al) 13 February 1996, see entire document.	1-6
Y	US 5,882,357 A (SUN et al) 16 March 1999, see entire document.	1-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 OCTOBER 2000	27 NOV 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ULA C. RUDDOCK Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/18995

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7-12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

these claims are unexaminable because the fabric claims are dependent upon a method of removing residual free halogen.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

WEST 2.0
search terms: halamine, fabric, textile, amine, halogen, reducing agent, chlorine, sequestering, scavenging, antibacterial, microbiocidal, sodium thiosulfate