

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 098 029 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

09.05.2001 Bulletin 2001/19

(51) Int. Cl.⁷: **D06L 3/10**

(21) Application number: **00309523.9**

(22) Date of filing: **27.10.2000**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **04.11.1999 US 163493 P**

(71) Applicant: **ROHM AND HAAS COMPANY**

Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:

- **Schoots, Harrie Peter**
Boston, Massachusetts 02116 (US)
- **Ko, Jeremy Tong-Chau**
Chestnut Hill, Massachusetts 02467 (US)

(74) Representative:

Buckley, Guy Julian
ROHM AND HAAS (UK) LTD.
European Operations Patent Department
Lennig House
2 Mason's Avenue
Croydon CR9 3NB (GB)

(54) **Method and composition for whitening textiles**

(57) Disclosed is a system for bleaching greige fabric using a two component reducing solution, wherein the first component of the reducing solution is added to the second component just prior to treatment of the greige fabric. The first component of the reducing solution comprises 0.1 to 0.3 wt % borohydride and the second component of the reducing solution comprises bisulfite in water, wherein there is a stoichiometric excess of the bisulfite relative to the borohydride.

EP 1 098 029 A1

Description**BACKGROUND OF THE INVENTION**

5 [0001] The present invention relates to a method and composition for whitening textiles. In particular, the present invention relates to a method and composition for whitening textiles where oxidative bleaching is not desirable.

[0002] Wet processing of fabrics is a multi-step process, generally including at least: scouring, bleaching and finishing. Where the fabric is a stretch or elastomeric fabric, the process also typically involves heat-setting prior to wet-processing. Selection of the steps in processing a particular fabric depends upon several factors, including desired
10 appearance and performance of the finished fabric.

[0003] Bleaching is a typical part of the wet-processing because traditional fabrics made with natural fibers are typically buff or off-white in color, not "blue-white" that is, white without a yellow cast. On the other hand, synthetic fibers developed over the recent decades are typically white, either because the material itself is white, or because whitener is added to the fiber; however, during processing of fabric made from such fibers, yellowing may occur. This yellowing
15 occurs during heat setting, a high temperature process wherein various properties such as resiliency, elasticity and wrinkle-resistance are imparted to the fabric. When yellowing occurs, such fabrics may also be subjected to reductive bleaching.

[0004] For the majority of fabrics, bleaching is typically accomplished with strong oxidizing agents such as: hydrogen peroxide and other peroxide generators, or chlorine-containing bleaches including sodium hypochlorite, calcium hypochlorite or sodium chlorite. With certain fabrics, however, it is not desirable to use such strong bleaching agents,
20 as such agents could degrade the fabric.

[0005] Where fabrics are not suitable to bleaching with an oxidizing agent, a reducing scour or reducing bleach (collectively, "reducing bath") can be used. The reducing agent in such reducing baths is generally sodium dithionite (usually referred to as sodium hydrosulfite or hydro) or thioureadioxide (also known as formamidinesulfonic acid or FAS). Sodium hydrosulfite is very unstable, especially when it comes into contact with even small amounts of water, and often spontaneously combusts. Sodium hydrosulfite is typically provided as a powder containing 70-90 wt % active hydro,
25 sodium carbonate as a fire retardant, and a chelating or sequestering agent such as EDTA or STPP. Hydro is also now available as an aqueous solution; however, such solutions are prone to oxidation and must be stored under an inert atmosphere (and refrigerated for longer term storage). Although hydro is widely used in the textile industry, there are severe limitations to the use of this reducing agent. The most severe limitations include: the high fail rate, even with multiple passes through the reducing bath; the low amount of resultant whitening; the strong sulfur smell (caused by emission of SO₂); and the high flammability of hydro powder.
30

[0006] A typical conventional reducing bath contains sodium hydrosulfite, defoamer and wetting agents. Other chemicals useful in the reducing bath include, without limitation: other surfactants, sequestrants, caustic (usually soda ash or NaOH) and optical brighteners. The amount and type of chemicals used in the reducing baths will depend on the fabric being treated, method of treatment and end use of goods. In general, about 3% hydro is added to the reducing bath at the beginning of the process, and then a second dose of about 3% is added about halfway through the treatment (over about 10 mm), so that the typical residence time of fabric in a conventional reducing bath is about 1 - 1.5 hrs. Wet-processing of grey fabric usually takes about 6-9 hrs, and multiple treatments may be used. Sometimes the reducing
35 bath step is repeated in order to increase whitening. This can occur immediately after the first reducing bath step, or the whole wet-processing procedure can be repeated. Even after such treatments, the differences in whitening between the treated and untreated fabric will not be readily discernible to the naked eye, and can only be determined by spectral analysis.

[0007] There is therefore a need for a reducing bleach for fabrics which is safe, easy to use, cost-effective, and
45 highly efficacious. As detailed below, the present invention accomplishes all of these objectives.

STATEMENT OF THE INVENTION

[0008] The present invention is directed to a system for bleaching fabric comprising greige fabric to be treated, a
50 two component reducing solution, and means for heating said reducing solution to 70 to 110 °C; wherein said first component of the reducing solution comprises between 0.1 and 0.6 % owg borohydride and said second component of the reducing solution comprises bisulfite in water said bisulfite being present in a stoichiometric excess relative to the borohydride, and wherein the first component of the reducing solution is added to the second component just prior to treatment of the greige fabric.

55 [0009] The present invention is also directed to a method for bleaching greige fabric, comprising the steps of contacting greige fabric with a two-part reducing solution for a time sufficient to cause bleaching of the greige fabric to occur, wherein: such two-part reducing solution comprises a first component comprising between 0.1 and 0.6 % owg borohydride and a second component comprising bisulfite in water, said bisulfite being present in a stoichiometric

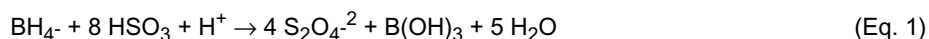
excess relative to the borohydride; and the first component of the reducing solution is added to the second component just prior to contacting the greige fabric with the reducing solution; and the two part reducing solution is maintained at a temperature between 70 and 110 °C during bleaching of the greige fabric.

5 DETAILED DESCRIPTION OF THE INVENTION

[0010] As used in this specification, the following terms have the following definitions, unless the context clearly indicates otherwise. "Greige" or "grey" fabrics are those just off the loom or knitting machine and which have only been partially finished (e.g., not yet dyed). "Fabric" or "textile" means, without limitation, yarns in skein or package form, and all woven, non-woven or knitted goods made from spun fibers, filamentary fibers or yarn and selected from natural and synthetic materials. Such natural and synthetic materials include but are not limited to: cellulosic acetates such as cellulose acetate and cellulose triacetate; silk, wool, and other protein fibers, flax and other bast fibers; nylon and other polyamide fibers; elastomeric or rubber fibers; acrylics; polyethylene terephthalate; and cotton and rayon fibers. "Spandex" fibers are elastomeric fibers in which the fiber forming substance is a long-chain synthetic polymer of at least 85% of a segmented polyurethane, and generically included both polyether- and polyester-segmented polyurethanes. "Yarn" means a continuous strand of fibers, filaments or other material in a form suitable for knitting weaving or otherwise inter-twining to form a textile fabric. "Elastomeric" fibers or yarn are those which at room temperature can be stretched repeatedly to at least twice their original length, and which, upon immediate release of the stretch, will return with force to approximately the original length. "Elastomeric fabrics" are fabrics comprising some elastomeric yarn in either the warp or weft (filling) orientation of the fabric. The following abbreviations are used throughout the specification: min = minutes; hr = hours; % owg = percent of the textile weight (on the weight of the goods) % owb = percent on weight of bath; wt % = percent by weight; g = grams; L = liters; g/L = grams per liter. Unless otherwise specified, temperatures are in degrees centigrade (°C) and ranges specified are to be read as inclusive.

[0011] The reducing bleach solution of the present invention is a two-component solution, typically aqueous. The first component contains a borohydride, and the second component contains a bisulfite in aqueous medium. The first component is added to the second component just prior to fabric treatment. In general, the reducing bath will also contain defoamer and wetting agent, usually added to the second component. Other chemicals useful in the reducing bath include, without limitation: other surfactants, sequestrants, caustic (usually soda ash) and optical brighteners. Such ingredients and their amounts are known to those skilled in the textile arts.

[0012] Borohydride and bisulfite react in water (at about pH 5-8) to produce hydrosulfite *in situ* according to the following equation 1:



In addition, it has been suggested that the radical anion $\cdot\text{SO}_2^-$, also a strong reducing agent, is a possible intermediate in this reaction. See, for example, Cook, M. M. in *Environmental Chemistry of Dyes and Pigments*, pp 33-41 (Reife et al., ed; J. Wiley, 1996). Although the exact mechanism of this reaction has not been fully characterized and this invention is in no way limited by any particular theory or mechanism of action, it is believed that this radical anion also contributes to the reducing ability of the reducing bleach of the present invention.

[0013] The amount of borohydride useful in the system of the present invention is between 0.1 and 0.6 % owg, preferably between 0.1 and 0.5 % owg, and most preferably between 0.1 and 0.3 % owg. Any borohydride may be used so long as the counterion does not interfere with fabric wet-processing. It is preferred to use a borohydride of formula $\text{T(BH}_4)_y$, wherein T is an alkaline metal, alkali earth metal or ammonium, and y is 1 or 2, depending on the valence of T. It is particularly preferred to use sodium or potassium borohydride. Borohydride is readily available as an aqueous alkaline solution containing 12 wt % sodium borohydride and 40 wt % sodium hydroxide. Such aqueous solution is available as COLORSTRIP™ 2000 from Rohm and Haas Company (N. Andover, MA). If such an aqueous borohydride solution is used, the amount suitable for purposes of the present invention is between 10 to 30 wt %, preferably no more than about 25 wt %, of the amount of 70% active anhydrous hydrosulfite recommended for conventional reducing bleaches, which will depend on the fabric to be treated.

[0014] The amount of bisulfite used in the present invention will depend in part on the amount of borohydride. As shown above in Eq. 1, 8 moles of bisulfite are required for each mole of borohydride; however, it is desired to use a stoichiometric excess, particularly a molar excess of at least 10 %. In general, the bisulfite will be of formula $\text{M(HSO}_3)_x$, wherein M is an alkaline metal, alkali earth metal or ammonium, and x is 1 or 2, depending on the valence of M. It is preferred to use sodium or potassium bisulfite. Where the borohydride is used in the form of an aqueous alkaline solution, a greater amount of bisulfite is needed. For example, such a borohydride solution containing 40 wt % caustic such as sodium hydroxide requires an additional 3.2 mole of bisulfite; thus in this case it is preferable to use up to about 12 moles of bisulfite per mole of borohydride. If the borohydride solution includes caustic, up to 40 wt % of caustic can be used. Such caustic is generally selected from Q(OH)_2 , wherein Q is an alkaline metal, alkali earth metal or ammonium,

and z is 1 or 2, depending on the valence of Q. It is preferred to use sodium hydroxide.

[0015] A typical wet-processing of elastomeric fabric using the system of the present invention includes the steps of: scouring, reducing bleach, whitening (optical brightening), dyeing, and acid washes. A typical amount and type of fabric used in such processing is as follows:

Weight of Goods → 275 kg of 80% nylon/20% Lycra® warp knit fabric.

[0016] The initial step consists of contacting the fabric with a scouring bath (scouring agent and wetting agent) for about 1 to 2.5 hrs.

[0017] The second step consists of contacting the fabric with the reducing bath such as detailed in Table 1 below for about 30 to 90 min at a temperature between 70 and 110 °C.

Table 1

<i>Sample Reducing Bath</i>	
Ingredient	Amount in bath
Defoamer	0.4 %owb
Surfactant/Scouring Agent	1.0 % owg
Optical Brightener	1.5 % owg
Bisulfite	16 % owg
12% Liquid Borohydride	4.0 % owg

[0018] The third step consists of contacting the fabric with the whitening bath such as detailed below in Table 2 for about an hour at about 70 - 110 °C.

Table 2

<i>Whitening Bath</i>	
Ingredient	Amount in bath
Citric Acid	0.35 % owb
Leveling Agent*	1.0 % owg
Ammonium Sulfate	1.0 % owb
Acetic Acid (56%)	0.25 % owb
Optical Brightener	0.5 % owg
Violet Acid Dye	0.001 % owg

* Dye Auxiliary

[0019] This step may be followed by at least one dyeing step, followed by several washing baths, the first of which contains 0.35% owb citric acid (or any mild acid). After the last such bath, the fabric is checked for shade.

[0020] The method of contacting the fabric with the baths in the above steps can be done at any point during wet processing of the grey fabric, using any of a number of methods known to those skilled in the art. Such methods include, without limitation: producer dyeing; stock dyeing; yarn dyeing; and piece or garment dyeing such as by pad baths, jigs, becks (pressurized and non) and jets. It is not required that the same method be used for each such bath.

[0021] The following examples are presented to illustrate further various aspects of the present invention, but are not intended to limit the scope of the invention in any respect. In the examples, the color evaluation readings are abbreviated as follows.

Color value**Scale**

L = Lightness (greyscale)

white = 100; black = 0

a = red/green

+ values are red; - values are green

b = yellow/blue

+ values are yellow; - values are blue

WI = whiteness index

100 = most white (natural); 0 = least white;
>100 = optical brightener added ΔE (total color difference) = Square root of $(L^2 + a^2 + b^2)$

[0022] The a and b values determine hue, and shifts of either of these values impact on the chroma (depth of hue). For purposes of the present invention, changes in L and WI are most significant in determining whitening of the treated fabric. Shifts in the value of b are also important, however, as white is often translated to mean a blue-white.

Example 1

[0023] The following example demonstrates the bleaching capability of a reducing solution of the present invention.

[0024] Warp knit fabric (21.5 g of 80% nylon and 20% Lycra fabric) was added to about 500 mL of water in a bath vessel. To this bath was added 1% owg of surfactant, with stirring. The bath was heated to boiling (about 95 °C) with stirring.

[0025] In a separate container, 0.67 g (3.11% owg) of sodium metabisulfite was mixed with about 10 g of water, and 0.18 g (0.83% owg) of 12% liquid sodium borohydride added to the mixture. Immediately upon addition of the borohydride to the bisulfite, that mixture was added to the fabric bath containing surfactant. The fabric was treated in this reducing bleach for up to about a half hour. Results are detailed in Table 3, below.

Table 3

Color Evaluation of warp knit fabric			
Color Value	Standard (pretreatment)	15 Minute Reduction	22 Minute Reduction
L	94.48	94.80	94.46
ΔL	---	0.32	-0.02
a	-1.78	-1.82	-1.60
Δa	---	-0.04	0.17
b	8.27	6.76	6.36
Δb	---	-1.50	-1.92
WI	44.03	52.27	53.72
ΔWI	---	8.25	9.69
ΔE	---	1.54	1.93

[0026] The results demonstrate that the reducing bleach of the present invention significantly whitens fabric subjected to such treatment. In fact, there is a difference in whiteness between the untreated and treated fabric can be seen by the naked eye when the reducing bleach of the present invention is used, whereas use of conventional reducing bleaches results in such slight differences in whiteness that no noticeable difference can be observed unaided.

Example 2

[0027] The following example further illustrates the whitening ability of the reducing bleach of the present invention.

[0028] The procedure of Example 1 was followed, except that the reducing bath contained a total of 1.0% surfactant, 1.0% owg 12% liquid sodium borohydride and 3.66% owg of sodium metabisulfite. In addition, the fabric was treated for up to about 1 hour in the reducing bath.

Table 4

<i>Color Evaluation of Warp Knit Fabric</i>			
Color Value	Standard (pretreatment)	30 Minute Reduction	60 Minute Reduction
L	94.48	94.94	94.59
ΔL	---	0.46	0.11
a	-1.78	-1.74	-1.61
Δa	---	0.04	0.17
b	8.27	7.01	6.81
Δb	---	-1.26	-1.46
WI	44.03	51.20	51.58
ΔWI	---	7.18	7.55
ΔE	---	1.34	1.48

[0029] The results further demonstrate the whitening ability of the reducing bleach of the present invention.

Claims

1. A system for bleaching fabric comprising greige fabric to be treated, a two component reducing solution, and means for heating said reducing solution to 70 to 110 °C; wherein said first component of the reducing solution comprises between 0.1 and 0.6 % owg borohydride and said second component of the reducing solution comprises bisulfite in water said bisulfite being present in a stoichiometric excess relative to the borohydride, and wherein the first component of the reducing solution is added to the second component just prior to treatment of the greige fabric.
2. The system of claim 1, wherein the bisulfite is of formula $M(HSO_3)_x$, wherein M is an alkaline metal, alkali earth metal or ammonium, and x is 1 or 2, depending on the valence of M.
3. The system of claim 1, wherein the first component of the reducing solution comprises between 0.1 and 0.5 % owg borohydride.
4. The system of claim 1, wherein the first component of the reducing solution comprises between 0.1 and 0.3 % owg borohydride.
5. The system of claim 1, wherein the borohydride is of formula $T(BH_4)_y$, wherein T is an alkaline metal, alkali earth metal or ammonium, and y is 1 or 2, depending on the valence of T.
6. The system of claim 1, wherein the reducing solution is maintained at a temperature between 70 and 110 °C while said reducing solution is in contact with the fabric to be treated.
7. A method for bleaching greige fabric, comprising the steps of contacting greige fabric with a two-part reducing solution for a time sufficient to cause bleaching of the greige fabric to occur, wherein:

such two-part reducing solution comprises a first component comprising between 0.1 and 0.6 % owg borohydride and a second component comprising bisulfite in water, said bisulfite being present in a stoichiometric

excess relative to the borohydride; and

the first component of the reducing solution is added to the second component just prior to contacting the greige fabric with the reducing solution; and

the two part reducing solution is maintained at a temperature between 70 and 110 °C during bleaching of the greige fabric.

8. The method of claim 7, wherein the first component of the reducing solution comprises between 0.1 and 0.5 % owg borohydride.

9. The method of claim 7, wherein the bisulfite is of formula $M(\text{HSO}_3)_x$, wherein M is an alkaline metal, alkali earth metal or ammonium, and x is 1 or 2, depending on the valence of M.

10. The method of claim 7, wherein the borohydride is of formula $T(\text{BH}_4)_y$, wherein T is an alkaline metal, alkali earth metal or ammonium, and y is 1 or 2, depending on the valence of T.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 9523

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	DATABASE WPI Section Ch, Week 198032 Derwent Publications Ltd., London, GB; Class E34, AN 1980-56092C XP002160549 & JP 55 084484 A (NISSO BENTORON KK), 25 June 1980 (1980-06-25)	1,2,5	D06L3/10
A	* abstract *	3,4	
A	WO 88 10334 A (EKA NOBEL AB) 29 December 1988 (1988-12-29) * column 5, line 28 - line 35; claims 1,5 *	1-6	
A	US 3 250 587 A (FMC CORPORATION) 10 May 1966 (1966-05-10) * example 1 *	1-6	
A	US 3 954 652 A (SCHMIDT OSWALD) 4 May 1976 (1976-05-04) * abstract; tables 1,2 *	1,2,6	
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 03, 31 March 1999 (1999-03-31) & JP 10 317274 A (SANDO IRON WORKS CO LTD), 2 December 1998 (1998-12-02) * abstract *	1,5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 February 2001	Examiner Saunders, T
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 9523

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

16-02-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 55084484 A	25-06-1980	NONE	
WO 8810334 A	29-12-1988	SE 457647 B	16-01-1989
		AT 68023 T	15-10-1991
		CA 1295440 A	11-02-1992
		DE 3865298 A	07-11-1991
		DE 3865298 D	07-11-1991
		EP 0319563 A	14-06-1989
		FI 890772 A,B,	17-02-1989
		NO 890764 A,B,	22-02-1989
		SE 8702616 A	25-12-1988
		US 4919755 A	24-04-1990
US 3250587 A	10-05-1966	BE 656375 A	16-03-1965
		CH 441214 B	29-04-1967
		CH 1569164 A	
		DE 1469224 A	02-04-1970
		FI 41640 B	30-09-1969
		FR 1420646 A	25-02-1966
		GB 1036540 A	
		NL 6414231 A	11-06-1965
US 3954652 A	04-05-1976	DE 2243330 A	28-03-1974
		AU 5969473 A	06-03-1975
		IT 990449 B	20-06-1975
JP 10317274 A	02-12-1998	JP 2815347 B	27-10-1998

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82