

Sequential Oxidative and Reductive Bleaching of Wool in a Single Bath

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ABSTRACT

A new bleaching process applicable to wool was developed in which an oxidative step (hydrogen peroxide) is combined with a subsequent reductive step (thiourea, thiourea dioxide, or sodium hydroxymethanesulfinate) in a single-bath process. Oxidative followed by reductive bleaching is normally a two- or three-step treatment done in separate baths. Effective bleaching with reduced time and equipment use is achieved by the new single-bath process with a specific order of reagent addition. Although the reductive stage of such a single-bath process may be achieved by the complete decomposition of unspent hydrogen peroxide and then addition of reductive substances such as thiourea dioxide or sodium hydroxymethanesulfinate with necessary pH adjustment, one may take advantage of the unspent hydrogen peroxide to form a reductive substance *in situ* by reaction with thiourea followed by an appropriate pH adjustment to 7–8. In all the cases above, greatly superior bleaching with less physical damage is achieved with the new process compared with conventional single- or multi-bath processes.

Scoured wool varies in shade from the light cream of wools considered to have good color to discolored, urine-stained wools and the near blacks of heavily pigmented wool. Bleaching is common with all of these wools, either for a specific color requirement or to increase the value of the fiber. The amount of wool bleached depends very much on current fashions; as long as pastel shades remain in fashion, wool bleaching will remain an important process, since the background natural color of wool interferes with such shades. There has been a great deal of work on bleaching of wool, which has been reviewed well in recent years [5, 8, 9, 14].

The conditions of any bleaching process will be determined to some extent by the nature of the substrate and the desired color, but even for wools of similar origin and color, bleaching conditions may vary. A recent survey [8] indicated that there was great disparity in the duration of bleaching processes adopted by the industry. More than 60% of wool was bleached using processes longer than three hours, indicating some potential for improvements. Traditionally, wool is bleached by oxidative processes (alkaline and acidic hydrogen peroxide) [6, 17, 24], reductive processes (sodium dithionate, sodium and zinc hydroxymeth-

anesulfinate, and thiourea dioxide) [10, 11, 25], or combinations of these.

Reductive bleaching is rarely practiced alone, but rather to further improve whiteness and lightfastness after peroxide bleaching [12, 16, 27]. Conventional combination bleaching involves treatment with warm alkaline peroxide followed by a second treatment with a reducing agent. It is common practice to include a fluorescent whitening agent with the second (reductive) stage of a combination bleaching. Alternatively, a third, reductive stage incorporating a fluorescent whitener is sometimes added, despite the risk of photosensitized yellowing that exists with such whiteners, particularly with wet wool.

A recent article by the International Wool Secretariat [12] on progress in wool bleaching deals with optimized use of hydrogen peroxide and thiourea dioxide. It emphasizes the trend towards short processing times; a one-hour process at 60°C is recommended using hydrogen peroxide (35% w/w) (22 ml/l) and tetrasodium pyrophosphate (6 g/l).

This paper presents two approaches for rapid and efficient bleaching of wool. Both are based on a combined oxidative/reductive bleaching in a single-bath. The first is oxidative hydrogen peroxide bleaching (alkaline or acidic), followed by addition of thiourea directly to the same bath so as to produce a reductive substance *in situ* after pH adjustment to pH 7–8. The second approach is oxidative hydrogen peroxide bleaching (alkaline or acidic), followed by decompo-

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sition of the remaining active hydrogen peroxide, and finally addition of a reductive agent (sodium hydroxymethanesulfinate or thiourea dioxide) directly to the bath with necessary pH adjustment.

Regarding the first approach, there is a vast amount of information available on thiourea in the literature [2, 4, 18, 22, 23]. In 1910, Barnett investigated the action of hydrogen peroxide on thiourea [2] and concluded that the resultant product depends very much on the pH and conditions of the reaction medium. Under closely controlled neutral conditions, he succeeded in synthesizing thiourea dioxide, $\text{HN}=(\text{NH}_2)\text{C}-\text{SO}_2\text{H}$, when he added finely powdered thiourea to an aqueous solution of hydrogen peroxide surrounded by ice [2]. On the other hand, Storch [20] obtained a salt of the disulfide, $\text{NH}=(\text{NH}_2)\text{C}-\text{S}-\text{S}-\text{C}(\text{NH}_2)=\text{NH}$, by oxidation of thiourea by hydrogen peroxide under acidic conditions. Thiourea dioxide is a strong reducing agent, and Weiss studied its chemistry in detail [26]. He mentioned that thiourea dioxide, in its pure form, is neither reductive nor oxidative. In a heated aqueous alkaline solution, however, thiourea dioxide realizes an extremely high reduction potential and is quite stable over a long period of time, unlike sodium hydroxysulfite. Thiourea dioxide gradually decomposes in aqueous solution to form a reductive substance. Although it is stable in acidic solutions, thiourea dioxide decomposes in heated alkaline solution to form urea and sulfinate anion. The latter is itself a reducing agent, which oxidizes to form sulfate anion.

In the second approach, adding a reductive substance directly into a hydrogen peroxide bath after completed peroxide bleaching is avoided because it wastes considerable reductive agent due to the large excess of hydrogen peroxide usually left in the bleach bath. A solution to this excess is to use an inorganic catalyst that decomposes hydrogen peroxide under conditions similar to those in bleaching. There are many inorganic catalysts that readily decompose hydrogen peroxide [7], but some (Fe^{3+} , Fe^{2+} , Cu^{2+} , Mn^{2+}) tend to cause excessive damage as well as discoloration to wool [3]. Co^{2+} is the only metal cation reported to cause no damage or discoloration [3]. Masri *et al.* [15] studied metal cation uptake by native wool contacted with salt solutions. They showed that Co^{2+} , among others, was the metal cation taken up the least by native wool. Hence, Co^{2+} should not interfere with further processing of wool such as dyeing.

Experimental

The wool we used for laboratory trials was a flannel fabric (20.60–26.39 microns, 233 g/m^2) with black

hair and yellow wool, kindly supplied by Forstmann and Co. Inc.,³ Dublin, GA. For industrial scale trials, we also used a wool flannel fabric (22.5 microns, 237 g/m^2 , whiteness index = 30.91, yellowness index = 14.21). The hydrogen peroxide was a 30% (w/w) aqueous solution. The nonionic wetting agent Triton X-100 was provided by Rohm and Haas Co., Philadelphia, PA. Thiourea dioxide, thiourea, and tetrasodium pyrophosphate decahydrate were obtained from Aldrich Chemicals Co., Inc., Milwaukee, WI. Sodium hydroxymethanesulfinate (Bleachit D) and activator Prestogen NB-W were supplied by BASF Chemicals Division, Charlotte, NC. All other chemicals used were of ACS grade.

BLEACHING TREATMENTS

The wool fabric was bleached using an Ahiba Texomat (Ahiba Inc., Charlotte, NC) laboratory dyeing apparatus. Oxidation potential was monitored on a voltmeter using a Corning platinum redox combination electrode (a high quality platinum sensing element and a sealed Ag/AgCl reference element, Fisher Scientific Co., Springfield, NJ); pH was monitored on an E & K pH meter (E & K Scientific Products, Saratoga, CA) using a combination glass electrode (Cole-Parmer International, Chicago, IL). All laboratory bleaching trials were done at a liquor to wool ratio of 30:1. Wool samples (10 g) were bleached in various bath compositions and conditions. Oxidative alkaline and acidic hydrogen peroxide bleach bath compositions are outlined here: Alkaline bleach bath composition: 20.0 ml/l hydrogen peroxide (30% w/w), 10.0 g/l tetrasodium pyrophosphate decahydrate, 1.0 g/l Triton X-100, initial pH of solution = 9.5. Acidic bleach bath composition: 20 ml/l hydrogen peroxide (30% w/w), 3.43 g/l Prestogen NB-W, 1.0 g/l Triton X-100, initial pH of solution = 5.6.

Approach 1

Use of thiourea⁴: Preliminary experiments were done in solution to investigate the reaction between hydrogen peroxide and thiourea under the conditions normally used for bleaching. The bleach bath solutions described above (alkaline or acidic, 300 ml) were first heated to 60°C while monitoring the pH and the solution potential. Thiourea (2.16 g) was then added to the solution, at which point there was a vigorous reaction

³ Reference to a brand or firm does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

⁴ Although thiourea is a cancer-suspect agent, it is easily handled with care and is consumed upon contact with hydrogen peroxide.

with a drop in pH and an increase in temperature. The pH of the solution was then adjusted to 7–8 with dilute sodium hydroxide. There was a marked change in the potential to negative values with this adjustment. This procedure was then applied to wool bleaching, and the method was repeated under the same conditions. Wool was first given an oxidative peroxide bleaching, followed by thiourea addition and the appropriate pH adjustment. Many variables were investigated such as thiourea concentration, thiourea and hydrogen peroxide treatment times, and bleaching temperature.

Industrial scale bleaching of a similar wool flannel fabric was done at Forstmann and Company, Inc., Louisville, GA, using the following bleach recipe: 6 lbs ammonium persulfate, 9 lbs Pomoco TLPP (concentrated aqueous tetrasodium pyrophosphate), 9 lbs Pomoco BL17 (sequestering agent), 1.5 lbs Kieralon JET (wetting agent), 38 lbs hydrogen peroxide (35% w/w), and 7.5 lbs ammonia. Wool flannel fabric (123 lbs) was bleached at a liquor to wool ratio of 14:1. The bleach bath was set at 37°C (pH = 9.5) and wool flannel fabric was then introduced. The temperature of the bath was raised to 60°C, and bleaching was continued at this temperature for 60 minutes. The pH at the end of the bleaching stage was 8.75. Thiourea (10 lbs) was then added to the bath, and there was a rapid drop in pH to 2–3 and a temperature rise of 5–7°C. Dilute sodium carbonate solution was then added slowly until the pH of the bath reached 7–8; at this point a high reduction potential was achieved. Treatment continued for 30 minutes, and the fabric was rinsed well and dried.

Approach 2

Use of thiourea dioxide or Bleachit D: Preliminary experiments were done in solution to decompose hydrogen peroxide in the temperature and pH range normally used for bleaching. The alkaline bleach bath solution described above (300 ml) was heated to 60°C (pH = 8.9), and the initial amount of active hydrogen peroxide present in the bath was determined by titration against acidified potassium permanganate. CoSO_4 (7.5 mg) was then added to the solution and a rapid evolution of oxygen was very evident. Aliquots (5 ml) were titrated to determine the amount of hydrogen peroxide remaining in the bath over time. When all the hydrogen peroxide was successfully decomposed, various amounts of thiourea dioxide or Bleachit D were then added while monitoring the reduction potential. Appropriate pH adjustments were made to obtain optimum reduction potentials under the conditions. This approach was then applied to wool bleaching under the same experimental conditions, and the effect of such bleaching was assessed.

Measurements of Wool Properties

Whiteness (ASTM E-313) and yellowness (ASTM D-1925) indices were measured with a Colorgard System 1000 tristimulus colorimeter (Pacific Scientific Co., Gardner Neotec Division, Silver Spring, MD). Samples were illuminated with a quartz halogen lamp at a color temperature of 2854 K with 360° circumferential illumination (CIE Source C, 1931 standard observer illuminant) at a 45° angle from the sample's normal direction, with sample viewing at 0°. The equations used in the Colorgard System for calculating whiteness and yellowness indices are

$$WI = 3.387Z - 3Y$$

and

$$YI = [100(1.277X - 1.06Z)]/Y$$

where X , Y , and Z are the measured tristimulus values.

The extent of degradation of the wool caused by bleaching was determined by measuring the weight loss of the sample after immersion in 0.1 M sodium hydroxide for 1 hour at $65 \pm 0.5^\circ\text{C}$ [13].

Wet tensile strength of the wool flannel, bleached and treated under various conditions, was measured according to the standard method [1]: the fabric was cut into ten equal strips 140 mm long and 13 mm wide, five strips oriented along the warp axis (18 yarns) and the other five along the weft (14 yarns). These samples were then soaked for 24 hours in an aqueous solution containing Triton X-100 (0.5 g/l). An Instron tensile testing machine (Instron Corp., Canton, MA) with a 90 mm gauge length was used to measure breaking load and elongation. The wetted-out samples were secured between the clamps and a constant load rate was applied along the warp or weft directions until the fabric strips broke.

Residual cobalt was determined indirectly using a Perkin Elmer 1100 B atomic absorption spectrophotometer at 240.7 nm with an air-acetylene flame. The cobalt content of the bath was measured and the uptake calculated by the difference from the original cobalt concentration.

Results and Discussion

APPROACH 1

Use of thiourea: In the preliminary experiments, we studied the reaction of hydrogen peroxide with thiourea in solution. The solution composition and the reaction conditions were closely related to those of bleaching. Alkaline or acidic hydrogen peroxide solution was titrated at 60°C with thiourea solution. The pH and the potential of the solution mixture were monitored con-

tinuously. In all cases there was a marked drop in the pH (pH = 2-3) and a temperature increase (by 5-7°C) of the solution along with the appearance of incipient turbidity. The solution was then adjusted to pH = 7-8 with dilute sodium hydroxide, at which point its potential changed markedly from a positive to a very negative value, indicating the complete consumption of hydrogen peroxide. We believe that the initial sudden drop in pH of the solution is due to the formation of acidic sulfur species. When the solution is later adjusted to pH = 7-8, reductive substances (sulfenic and sulfinic acid derivatives) that may have formed during the reaction become activated, as evident from the surge in reduction potential. The reaction was very fast (1-2 minutes) at the temperatures normally used in bleaching. The stoichiometric ratio of hydrogen peroxide to thiourea was 2:1. An exact amount of thiourea may therefore be calculated based

on the amount of hydrogen peroxide remaining after a bleaching process, and that amount may be added to the bleach bath for maximum efficiency.

Using the findings of the preliminary study in solution, we conducted bleaching trials to investigate the effectiveness of the reaction product on bleaching efficiency. The wool flannel fabric to be bleached was first given an oxidative peroxide bleaching, which was then followed by an addition of sufficient thiourea to fully consume the hydrogen peroxide, and finally an adjustment of the pH to 7-8 to attain a high reduction potential, which forms the reductive bleaching part of the process. We investigated variables such as thiourea concentration, oxidative peroxide bleaching time, reductive bleaching time, and temperatures to optimize bleaching efficiency. The results are shown in Tables I-IV and depicted graphically in Figures 1-4. Note that below a certain thiourea concentration, there is no im-

TABLE I. The effect of thiourea concentration on the oxidative/reductive bleaching of wool flannel.^a

Thiourea, g/l	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d	Warp ^e		Weft ^e		Solution potential, mV ^f
				Breaking load, N	Elongation, %	Breaking load, N	Elongation, %	
Unbleached	11.42 ± 0.45	23.71 ± 0.20	11.60 ± 0.43	35.62 ± 1.41	56.64 ± 1.92	24.72 ± 1.26	60.57 ± 2.79	-
- ^g	35.85 ± 0.54	12.38 ± 0.17	22.43 ± 1.09	35.18 ± 2.58	55.32 ± 2.44	27.87 ± 0.83	55.51 ± 1.72	+201
3.07	34.24 ± 0.48	13.16 ± 0.26	24.48 ± 0.49	-	-	-	-	+226
3.85	38.09 ± 0.07	11.49 ± 0.03	-	-	-	-	-	-170
4.61	43.15 ± 0.28	9.55 ± 0.03	22.14 ± 0.69	-	-	-	-	-663
5.38	43.83 ± 0.09	9.23 ± 0.04	23.53 ± 0.37	32.43 ± 1.06	55.13 ± 1.90	22.99 ± 0.63	51.25 ± 1.88	-698
6.15	43.52 ± 0.26	9.17 ± 0.16	24.00 ± 0.24	-	-	-	-	-692
7.69	43.62 ± 0.05	9.23 ± 0.08	24.44 ± 0.22	32.74 ± 1.73	53.58 ± 2.37	22.39 ± 1.59	50.48 ± 2.80	-680
5.38 ^h	31.84 ± 0.40	14.51 ± 0.22	-	43.30 ± 0.78	57.46 ± 1.72	27.82 ± 0.58	53.26 ± 0.99	-14
5.38 ⁱ	37.14 ± 0.42	12.11 ± 0.14	-	-	-	-	-	-242

^a Alkaline hydrogen peroxide bleaching, 60°C, 1 hour, followed by thiourea addition, pH adjustment with NaOH to pH 7.4-7.6 unless indicated, and continued bleaching, 60°C, 25 minutes. ^b As per ASTM E-313; mean value ± standard deviation of three samples, each having eight measurements. ^c As per ASTM D-1925; mean value ± standard deviation of three samples, each having eight measurements. ^d As per IWTO-4-60; mean value ± standard deviation of three samples. ^e As per ASTM D-1682-64; mean value ± standard deviation of five determinations. ^f Measured immediately after thiourea addition and pH adjustment. ^g Alkaline hydrogen peroxide bleaching for 1 hour and 25 minutes with no pH adjustment at 1 hour. ^h pH of the solution is not adjusted after the addition of thiourea (pH = 3.6). ⁱ Solution was buffered (pH = 6.8) before thiourea addition so that the reaction is done under neutral conditions.

TABLE II. The effect of thiourea bleaching time on the oxidative/reductive bleaching of wool flannel.^a

Bleaching time after thiourea addition, min	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d	Warp ^e		Weft ^e	
				Breaking load, N	Elongation, %	Breaking load, N	Elongation, %
- ^f	34.23 ± 0.66	13.15 ± 0.31	19.04 ± 0.33	35.32 ± 1.02	55.88 ± 1.70	28.25 ± 0.75	56.51 ± 1.03
15	43.69 ± 0.18	9.18 ± 0.07	22.05 ± 0.26	-	-	-	-
25	43.83 ± 0.09	9.23 ± 0.04	23.53 ± 0.37	32.43 ± 1.06	55.13 ± 1.90	22.99 ± 0.63	51.25 ± 1.88
35	44.75 ± 0.07	8.87 ± 0.07	-	31.17 ± 1.70	54.68 ± 2.82	21.97 ± 0.99	52.44 ± 1.47
45	43.61 ± 0.24	9.31 ± 0.08	22.54 ± 0.72	-	-	-	-
25 ^g	44.42 ± 0.05	9.03 ± 0.01	20.63 ± 0.44	37.36 ± 1.56	58.77 ± 2.17	26.58 ± 1.36	58.04 ± 1.85
25 ^h	44.63 ± 0.63	8.93 ± 0.25	21.45 ± 0.67	36.29 ± 2.02	57.49 ± 3.41	23.57 ± 1.44	54.33 ± 3.78

^a As per Table I, except 5.38 g/l thiourea was used for various bleaching times. ^b As per Table I. ^c As per Table I. ^d As per Table I. ^e As per Table I. ^f Alkaline hydrogen peroxide bleaching for 60 minutes, with neither subsequent pH adjustment nor addition of thiourea. ^g pH was adjusted to 7.1 (6 ml of 30% w/v Na₂CO₃ solution) after thiourea addition. ^h pH was adjusted to 7.4 (7.5 g NaHCO₃) after thiourea addition.

TABLE III. The effect of varying the hydrogen peroxide bleaching time on the oxidative/reductive bleaching of wool flannel.^a

Bleaching time, min		Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d	Warp ^e		Weft ^e	
Oxidative	Reductive				Breaking load, N	Elongation, %	Breaking load, N	Elongation, %
0 ^f	25	31.84 ± 0.19	13.98 ± 0.02	-	-	-	-	-
0 ^f	60	33.89 ± 0.94	13.51 ± 0.35	-	-	-	-	-
20	25	39.43 ± 0.38	10.97 ± 0.16	-	-	-	-	-
40	25	42.46 ± 0.15	9.69 ± 0.06	20.12 ± 0.34	-	-	-	-
60	25	43.52 ± 0.26	9.38 ± 0.04	24.00 ± 0.24	32.56 ± 1.51	54.90 ± 2.05	22.60 ± 1.20	50.95 ± 1.30
80	25	46.82 ± 0.16	8.04 ± 0.04	24.29 ± 0.13	30.91 ± 1.30	56.31 ± 1.35	19.20 ± 1.28	48.44 ± 1.22
65	0 ^g	34.23 ± 0.66	13.15 ± 0.31	19.04 ± 0.33	-	-	-	-
85	0 ^g	35.85 ± 0.54	12.38 ± 0.17	22.43 ± 1.09	35.18 ± 2.58	55.32 ± 2.44	27.87 ± 0.83	55.51 ± 1.71

^a As per Table I, except 6.15 g/l thiourea is used. ^b As per Table I. ^c As per Table I. ^d As per Table I. ^e As per Table I. ^f Reductive bleaching only; thiourea mixed with hydrogen peroxide and pH adjusted with no prior time for oxidative bleaching. ^g Oxidative bleaching only.

TABLE IV. The effect of bleaching temperature on the oxidative/reductive bleaching of wool flannel.^a

Treatment temperature, °C	Thiourea addition	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d
55	no	32.76 ± 0.39	13.77 ± 0.16	-
55	yes	40.11 ± 0.33	10.73 ± 0.15	-
60	no	34.23 ± 0.66	13.15 ± 0.31	19.04 ± 0.33
60	yes	42.46 ± 0.15	9.69 ± 0.06	20.12 ± 0.34
65	no	37.63 ± 0.33	11.57 ± 0.13	28.23 ± 0.63
65	yes	44.05 ± 0.31	9.00 ± 0.18	25.15 ± 0.52
70	no	39.36 ± 0.28	10.96 ± 0.11	32.61 ± 0.99
70	yes	45.43 ± 0.23	8.46 ± 0.14	28.88 ± 0.37

^a Alkaline hydrogen peroxide bleaching at different temperatures for 40 minutes, followed by thiourea addition (6.15 g/l; pH adjustment with NaOH to pH 7.4-7.6 only in the thiourea cases), and continued bleaching for 25 minutes. ^b As per Table I. ^c As per Table I. ^d As per Table I.

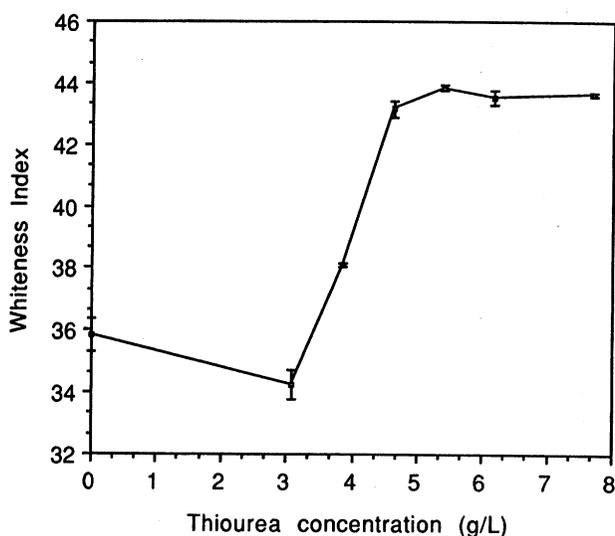


FIGURE 1. Dependence of whiteness index on thiourea concentration in the oxidative/reductive bleaching of wool flannel. Conditions as per Table I. Error bars denote standard deviation.

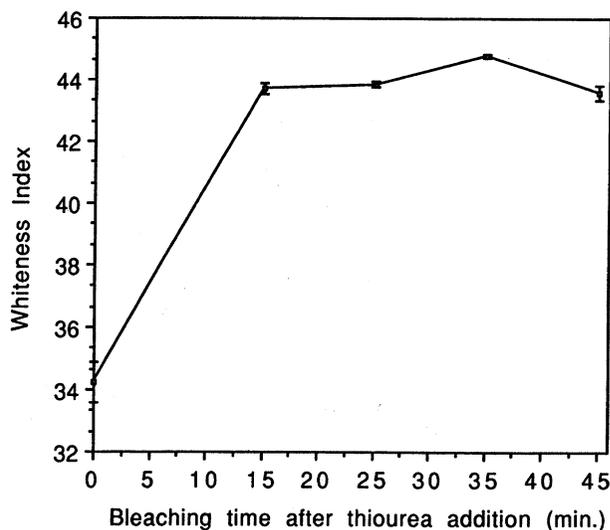


FIGURE 2. Dependence of whiteness index on the bleaching time after thiourea addition in the oxidative/reductive bleaching of wool flannel. Conditions as per Table II. Error bars denote standard deviation.

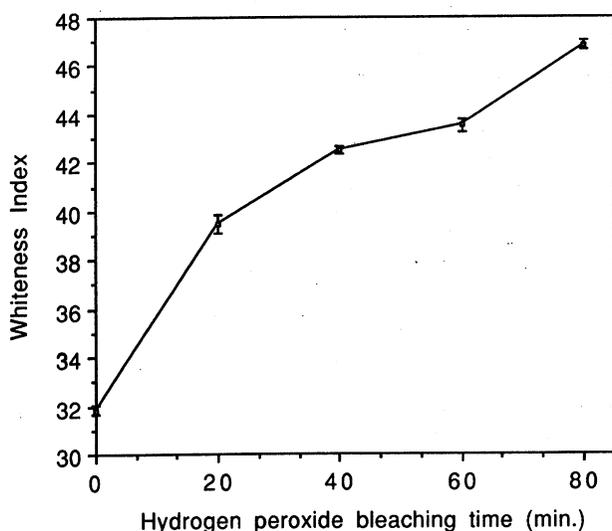


FIGURE 3. Dependence of whiteness index on the oxidative bleaching time in the oxidative/reductive bleaching of wool flannel. Conditions as per Table III. Error bars denote standard deviation.

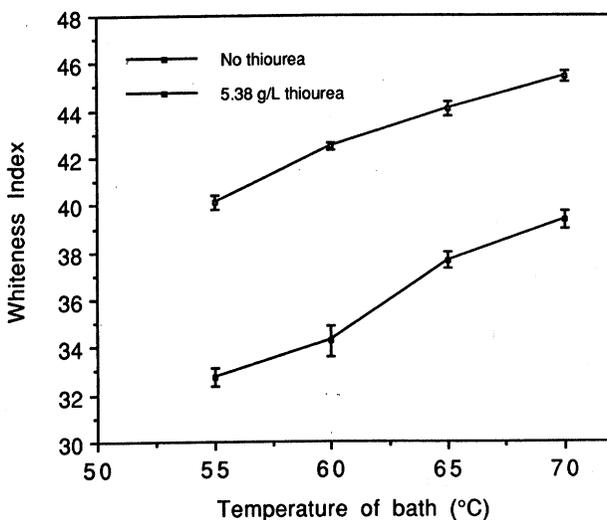


FIGURE 4. Dependence of whiteness index on the bath temperature in the oxidative/reductive bleaching of wool flannel. Conditions as per Table IV. Error bars denote standard deviation.

provement in whiteness of the wool flannel fabric; this is because under these conditions a reductive substance is not formed. There is not sufficient thiourea to react with all the residual hydrogen peroxide. We therefore suggest that excess thiourea be added to insure that all the hydrogen peroxide is consumed. Above a certain thiourea concentration, there is no further improvement in whiteness of the wool flannel. It is also apparent from the results in Table I that the pH adjustment to

7–8 is very critical for attaining a high reduction potential and improved whiteness. The results in Table II show that the bleaching time after the thiourea addition is not too critical in the time range studied (15–45 minutes). Bleaching times of 25–35 minutes after thiourea addition are considered to be reasonable.

The importance of hydrogen peroxide bleaching time prior to thiourea addition is highlighted in Table III. Clearly, the longer the hydrogen peroxide bleaching part of the process, the whiter the wool flannel fabric becomes. Although the total bleaching treatment given to wool flannel is different in each case, the differences in the whiteness values are far greater than would be expected on the basis of the peroxide bleaching time difference alone. Here we must emphasize that the wool flannel fabric to be bleached must first be given an oxidative peroxide bleaching before the thiourea addition. This is simply demonstrated by the results in Table III, where the wool flannel was not given an initial peroxide bleach. Hydrogen peroxide, thiourea, and all the other additives were mixed at the start of the bleaching treatment, and bleaching was allowed to proceed for 20 minutes. The importance of initial hydrogen peroxide bleaching becomes more apparent when the whiteness index values of wool bleached for 60 minutes (all chemicals are mixed at the start) are compared with those of wool bleached for 65 minutes (40 minutes alkaline peroxide bleach followed by thiourea addition and bleaching for 25 minutes after pH adjustment). Although in both cases there was a high reduction potential, it seems that the initial oxidative hydrogen peroxide bleaching somehow modifies wool sufficiently so that a following reductive bleach further whitens the wool effectively.

The effect of bleaching temperature on the efficiency of bleaching is shown in Table IV and depicted graphically in Figure 4. The whiteness index increases with bleaching temperature as expected. It is noteworthy that the same level of whiteness is reached at a bleaching temperature of 55°C with the hydrogen peroxide/thiourea bleaching system (oxidative/reductive) as at 70°C with the hydrogen peroxide system alone. Furthermore, the former process is less damaging to the wool, as evidenced by lower alkali solubilities.

The effectiveness of the hydrogen peroxide/thiourea system on the bleaching efficiency was also demonstrated under acidic oxidative bleaching with hydrogen peroxide followed by thiourea. The results are shown in Table V, and from them, we see that the bleaching efficiency is markedly improved with the hydrogen peroxide/thiourea system compared to an oxidative acidic hydrogen peroxide bleaching alone. We do not understand the decrease in breaking load and elonga-

TABLE V. The effect of thiourea on the oxidative/reductive bleaching of wool flannel.^a

Bleaching time, min		Thiourea, g/l	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d	Warp ^e		Weft ^e	
Acidic oxidative	Reductive					Breaking load, N	Elongation %	Breaking load, N	Elongation %
65	0	—	29.12 ± 0.12	16.24 ± 0.30	28.49 ± 0.30	37.25 ± 2.04	66.15 ± 2.48	24.39 ± 0.47	59.33 ± 2.00
40	25	5.38	42.56 ± 0.29	10.13 ± 0.14	21.72 ± 0.84	27.97 ± 1.83	56.82 ± 3.11	17.99 ± 1.26	51.88 ± 2.84
85	0	—	29.26 ± 0.33	16.03 ± 0.12	—	34.06 ± 0.31	63.11 ± 2.32	26.88 ± 1.85	63.75 ± 4.48
60	25	5.38	43.60 ± 0.21	9.51 ± 0.28	—	24.53 ± 0.83	53.46 ± 3.18	19.72 ± 0.88	56.22 ± 1.63

^a Acidic hydrogen peroxide bleaching (as per experimental) at 80°C, followed, when indicated, by thiourea addition (pH adjustment with NaOH to pH 7.4–7.6), and continued bleaching at 80°C for 25 minutes. ^b As per Table I. ^c As per Table I. ^d As per Table I. ^e As per Table I.

tion noted in Table V for acidic oxidative/reductive bleaching, but it is inconsistent with the alkali solubility results.

We compared the results of industrial scale bleaching with the new process to that of a conventional 3-hour alkaline hydrogen peroxide bleaching. For combined hydrogen peroxide/thiourea bleaching, the whiteness index = 51.77 and the yellowness index = 6.55; for the 3-hour alkaline hydrogen peroxide bleaching, the whiteness index = 43.62 and the yellowness index = 9.75. The results of the industrial trials show that the new combined hydrogen peroxide/thiourea bleaching system is superior to the conventional alkaline hydrogen peroxide bleaching.

APPROACH 2

Use of Bleachit D or thiourea dioxide: Preliminary results emphasized the need for removing residual hydrogen peroxide prior to reductive bleaching. Complete decomposition of residual hydrogen peroxide present in a typical bleach bath is possible over 10–15 minutes with 25 mg/l CoSO₄ at 60°C at a solution pH of 8.8–

9.0. In the case of acidic hydrogen peroxide bleaching (80°C, pH = 5.6), it is possible to raise the pH of the solution to 7.8–8.0 to successfully decompose hydrogen peroxide. Following the decomposition process, reductive bleaching agents (thiourea dioxide and Bleachit D) were added and the pH adjusted for optimal reductive bleaching.

The results of the oxidative alkaline hydrogen peroxide bleaching followed by reductive bleaching (thiourea dioxide, Bleachit D) are given in Table VI and depicted graphically in Figures 5 and 6. The decomposition of residual hydrogen peroxide is essential; preliminary experiments showed that large amounts of reductive agents (thiourea dioxide, Bleachit D) were needed to consume all the residual hydrogen peroxide before a high reduction potential could be attained with the addition of the reductive agent. Note also that thiourea dioxide, unlike Bleachit D, does not produce a high reduction potential under acidic conditions; runs with thiourea dioxide are therefore done at pH 6.5–7.0. For approach 2 to be of any economical value, all active, remaining hydrogen peroxide after an oxidative bleaching must be completely decomposed so that the

TABLE VI. The effect of reductive agent aftertreatment [Bleachit D (sodium hydroxymethanesulfinate), thiourea dioxide] on the oxidative/reductive bleaching of wool flannel.^a

Bath temperature, °C	Hydrogen peroxide, ml/l	Bleachit D, g/l	Thiourea dioxide, g/l	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d
60	20 ^e	—	—	35.85 ± 0.54	12.38 ± 0.17	22.43 ± 1.09
60	20 ^f	1.0	—	39.84 ± 0.42	10.66 ± 0.21	24.58 ± 0.47
60	20 ^f	2.0	—	39.93 ± 0.27	10.58 ± 0.07	—
60	20 ^f	4.0	—	40.80 ± 0.07	10.60 ± 0.03	24.59 ± 0.69
70	20 ^e	—	—	39.33 ± 0.36	10.94 ± 0.17	30.73 ± 0.78
70	20 ^e	—	1.0	35.75 ± 0.66	12.51 ± 0.24	22.65 ± 0.67
70	20 ^e	—	2.0	41.21 ± 0.13	10.26 ± 0.19	—
70	20 ^e	—	3.0	42.14 ± 0.28	9.69 ± 0.08	22.51 ± 0.32
70	20 ^e	—	5.0	43.26 ± 0.52	9.24 ± 0.19	—

^a As per Experimental; residual hydrogen peroxide quenched using CoSO₄ prior to reductive bleaching. ^b As per Table I. ^c As per Table I. ^d As per Table I. ^e Alkaline hydrogen peroxide bleaching for 1 hour and 25 minutes, as per Table I, note g. ^f As per e, but for 50 minutes, followed by peroxide decomposition with CoSO₄ for the next 10 minutes at pH 8.8, and finally reductive bleaching (Bleachit D, pH adjusted to 2.5) at the same temperature for 25 minutes. ^g As per f, except for reductive bleaching agent (thiourea dioxide, pH adjusted to 6.5–7.0).

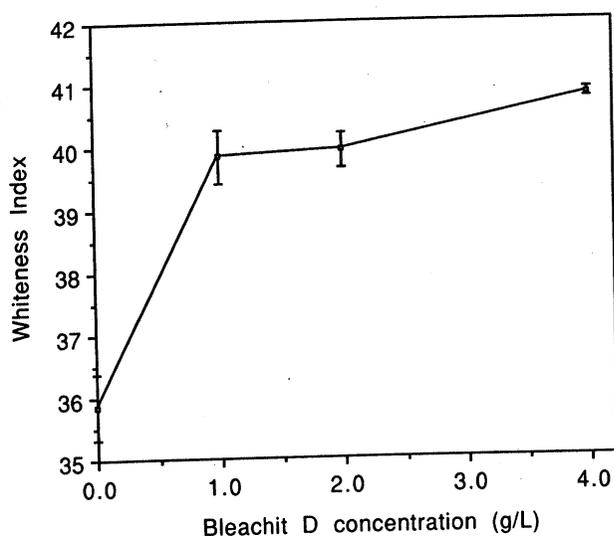


FIGURE 5. Dependence of whiteness index on Bleachit D (sodium hydroxymethanesulfinate) concentration in the oxidative/reductive bleaching of wool flannel. Conditions as per Table VI. Error bars denote standard deviation.

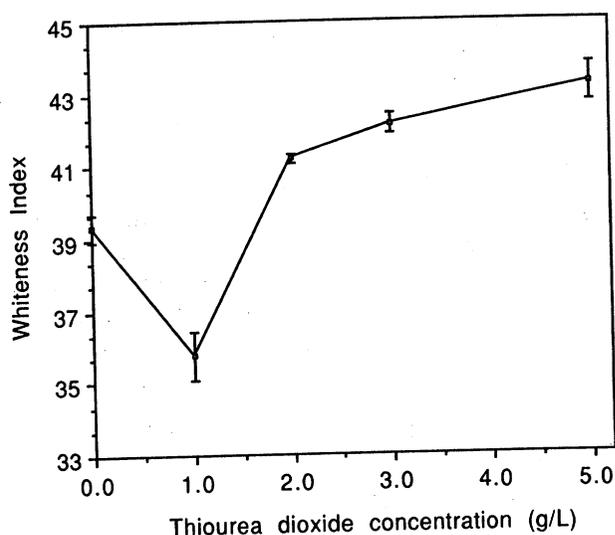


FIGURE 6. Dependence of whiteness index on thiourea dioxide concentration in the oxidative/reductive bleaching of wool flannel. Conditions as per Table VI. Error bars denote standard deviation.

addition of a small amount of reductive substance will create the reduction potential needed for the latter part of the process.

Atomic absorption spectroscopy was used to estimate the amount of residual cobalt on wool following the use of cobalt to quench unspent hydrogen peroxide.

Immediately upon addition of cobalt, the bath contained 2.85 mg cobalt per 300 ml. Following quenching and subsequent reductive bleaching (Bleachit D or thiourea dioxide), the bath contained 2.40–2.50 mg cobalt. The loss of 0.35–0.45 mg cobalt to the 10.0 g wool sample reveals a low propensity for cobalt adsorption by wool. Consequences to later dyeing could be estimated as follows: a pastel shade might equate to 0.3% dyeing on the weight of fiber (owf), or 3 mg dye per gram of wool. Based on a molar ratio of 1:1 cobalt to dye and a molecular weight ratio of 1:10 cobalt to dye, approximately 3 mg dye would coordinate with 0.3 mg cobalt. Our cobalt analysis shows that an order of magnitude less cobalt is available. The true significance of even these trace amounts of cobalt on dyeing would have to be assessed for any particular dye choice and concentration.

There have been a number of patents on new bleaching processes, but two are particularly noteworthy since they are related to the new processes mentioned in this paper. A Japanese patent [19] mentions a process whereby thiourea and hydrogen peroxide are mixed at the start of the bleaching process, and there is no prescribed pH adjustment. Optimal bleaching conditions are said to be 2.91 g/l hydrogen peroxide (30% w/w) and 2.0 g/l thiourea at 95°C for 20 minutes. A German patent [21] mentions a single-bath process whereby a reductive bleaching with thiourea dioxide precedes an oxidative hydrogen peroxide bleaching. In that patent, two processes—with and without thiourea dioxide—were compared and the conclusion was that the process with thiourea dioxide was more favorable than the one without. The optimal bleaching conditions were said to be a reductive bleaching with a 4 g/l buffer mixture (pH = 7.8) containing 0.36 g/l thiourea dioxide for 20 minutes at 80°C, followed by a direct addition of hydrogen peroxide (20 ml/l of 35% w/w solution) and further bleaching for 60 minutes at the same temperature.

We repeated both these processes in the exact manner mentioned in the patents for direct comparison purposes; the results are outlined in Table VII. Clearly our processes (A, B, E and F) give more effective bleaching than either of the other processes (C or D). Process C (Table VII, reductive/oxidative) with thiourea dioxide is a near reverse of our processes A, B, E and F (oxidative/reductive). We would therefore expect similar results. The differences we observed must be a function of the process sequence, since there were high reduction potentials in all four processes. We may therefore conclude that in a single-bath bleaching process, an oxidative hydrogen peroxide bleaching must be done first followed by a reductive bleach.

TABLE VII. Comparison of different bleaching processes.

Process type ^a	Treatment temperature, °C	Hydrogen peroxide, g/l	Thiourea, g/l	Thiourea dioxide, g/l	Bleachit D, g/l	Whiteness index ^b	Yellowness index ^c	Alkali solubility, % ^d
A	60	20	5.38	—	—	43.83 ± 0.09	9.23 ± 0.04	23.53 ± 0.37
B	80	20	5.38	—	—	42.56 ± 0.29	9.51 ± 0.28	21.72 ± 0.84
C	80	20	—	0.36	—	35.31 ± 0.07	13.29 ± 0.02	27.40 ± 0.64
C	80	20	—	—	—	32.59 ± 0.21	14.36 ± 0.07	—
D	95	2.91	2.0	—	—	20.33 ± 0.50	18.87 ± 0.15	—
E	60	20	—	—	4.0	40.80 ± 0.07	10.60 ± 0.03	24.59 ± 0.69
F	70	20	—	5.0	—	43.26 ± 0.52	9.24 ± 0.19	—

^a A (our process): alkaline hydrogen peroxide bleaching followed by thiourea, as per Table I, note a. B (our process): acidic hydrogen peroxide bleaching followed by thiourea, as per Table V, note a. C (German patent): Reductive bleaching with thiourea dioxide at pH 7.8 for 25 minutes, followed by hydrogen peroxide bleaching for 60 minutes [21]. D (Japanese patent): hydrogen peroxide and thiourea mixed at start of bleaching process with no pH adjustment [23]. E (our process): alkaline hydrogen peroxide bleaching followed by quenching, then reductive bleaching with Bleachit D, as per Table VI, note f. F (our process): as described for E, but with thiourea dioxide instead of Bleachit D, as per Table VI, note g. ^b As per Table I. ^c As per Table I. ^d As per Table I.

Conclusions

We have developed a combined oxidative/reductive single-bath bleaching process for wool as an improved alternative to conventional oxidative bleaching or two-bath oxidative/reductive bleaching processes. Of the variations presented here, alkaline hydrogen peroxide bleaching at 60°C for 60 minutes followed by an addition of thiourea, pH adjustment, and subsequent reductive bleaching at 60°C for 25 minutes offers excellent results at a low temperature (60°C) and reasonable time. A longer bleaching time, especially in the oxidative step, leads to even more effective bleaching. A shorter bleaching time at a higher temperature (70°C) is also effective, but it causes some damage to the wool. The new process in all its variations is the subject of a patent application.

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