

Single Bath Full Bleaching of Wool Using Sodium Trithiocyanurate in Place of Thiourea

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R eccently, a patented approach to full bleaching (oxidative followed by reductive) has been reported that integrates all the processes into a single bath procedure.¹⁻¹⁶ In this process, re-

ABSTRACT

A single bath full bleaching procedure for textile materials has been developed. In this procedure, following oxidative bleaching using hydrogen peroxide, the peroxide bath is converted to a reductive bath by addition of thiourea and bleaching continues without the need for a fresh bath for the reductive step. Such full bleaching is easy, economical and very effective in inducing improved whiteness. One drawback is the toxic nature of thiourea. Thiourea, though easily handled and thoroughly consumed in this procedure, is classified as a carcinogen unlike its oxidized counterpart, thiourea dioxide (formamidinesulfinic acid). This work presents how thiourea may be replaced by sodium trithiocyanurate (Na₃TTCA), which is not classified as a carcinogen. Full bleaching with the modified protocol is just as effective as the procedure using thiourea, but Na, TTCA was found to be most effective at 90% of the stoichiometric weight to peroxide, as opposed to 70% for thiourea; the Na TTCA process was more sensitive to the pH of the rinse bath than the thiourea process; and the Na₃TTCA reagent is more expensive than thiourea. Nevertheless, the attractiveness of using Na, TTCA is the avoidance of a potential carcinogen and achievement of exceptional whiteness over conventional peroxide bleaching.

KEY TERMS

Bleaching Hydrogen Peroxide Sodium Trithiocyanurate Thiourea Wool sidual H_2O_2 from the initial oxidative bleaching step is utilized in a 10minute chemical reaction that converts the bath into a reductive medium. When thiourea is added to the peroxide bath under controlled conditions, thiourea dioxide is produced *in situ* and reductive bleaching occurs (Fig. 1).¹⁷

The reaction proceeds by the interaction of thiourea with two moles of H₂O₂ under acidic conditions to form formamidinesulfinic acid (thiourea dioxide; Eq. 1 in Fig. 1). Subsequent hydrolysis under neutral or alkaline conditions then yields urea and the reducing species, the sulfinate ion (Eqs. 2 and 3 in Fig. 1). The course of this reaction is followed by measurement of the redox potential. The residual peroxide bath measures +200 to +400 mV. After addition of thiourea and a 10-minute residence time at pH 4.5, the pH is adjusted to above 7. Only then is there a sharp drop in redox potential to -600 to -700 mV.

 13 C NMR spectroscopy and empirical observations led to using less than the stoichiometric amount of thiourea to H₂O₂ (0.31:1.0 molar instead of 0.50:1.0), and later studies showed that whiteness was still vastly superior to peroxide bleaching even when about 30% of the residual H₂O₂ is discarded before addition of thiourea.^{4,6-8} The process, relative to conventional peroxide bleaching, showed insignificant losses in tensile strength and extension at break (extensibility) and no change in elastic modulus (resistance to elongation). Fabric handle of wool challis fabric was assessed using the Kawabata Evaluation System (KES).⁸ Results indicated that the single bath bleaching process produced fabric with a softer, more flexible and smoother feel than obtained with conventional bleaching.

Despite the advantages of using thiourea to induce *in situ* reductive bleaching, some potential users of the single bath process hesitated to use it due to a safety issue—although thiourea is an easily handled crystalline solid that is completely converted to less noxious compounds in the bleach bath, its classification as a carcinogen mandates careful handling. The bath may be monitored colorimetrically to assure the complete consumption of thiourea.¹⁸

Trithiocyanuric acid (TTCA; s-triazine-2,4,6-trithiol) is a cyclic analog of thiourea (Fig. 2—the literature reports no isolated oxidized analogs of thiourea dioxide such as TTCA hexoxide). It is most readily usable as the trisodium salt (Na₃TTCA; CAS No. 177766-26-6) in a 15% aqueous solution. It is marketed as a heavy metal precipitation agent for wastewater treatment and as a vulcanization agent for rubber. The present research investigates

REACTION MECHANISM

1	Formation of Thiourea Dioxide: H₂N-C(=NH)-SH + 2H₂O₂ → <u>PH 4.5-5.5</u> thiourea	H₂N-C(=N thiourea o	H)-SO ₂ H + 2H ₂ O lioxide	Eq. 1
2	Formation of Reductive Species: $H_2N-C(=NH)-SO_2H + 2OH^- \xrightarrow{pH 7-8}$ thiourea dioxide	H₂N-C(=N urea	H)-OH + SO ₂ ⁻ sulfinate ion	Eq. 2
3	Reductive Bleaching: $SO_2^- + [chromophore] \longrightarrow SO_4^{2-} + [reduction of a second strength of a second strength$	educed chro	mophore]	
1	sulfinate ion sulfate ior	7		Eq. 3

Fig. 1. Reaction mechanism for single-bath full-bleaching.



thiourea Na salt of trithiocyanuric acid

Fig. 2. Structures of thiourea and trithiocyanuric acid (TTCA).

the possibility that thiourea may be substituted in the original single bath bleaching process by an alternative, chemically related compound.

Experimental

Fabric

Wool flannel fabric (Style 188, fabric weight 11.9 oz/yd^2) was supplied by Carleton Woolen Mills,^{*a*} Eastland, Maine and was cut into 10 g rectangles measuring 184 mm x 171 mm (warp and weft respectively). The samples were mixed together to obtain a randomly selected representation of areas from the supplier's roll. These samples were then labelled and divided into sets containing six samples each. The samples were then soaked in deionized water for 15 minutes prior to use.

Equipment

Bleaching runs were carried out in an Ahiba Texomat apparatus (Ahiba AG) in 400mL beakers, with automatic temperature programming and agitation. A pH meter (E&K Scientific Products) was used with a combination glass electrode (Corning). Oxidation potential was measured on a multimeter (Fluke) using a redox combination electrode (Pt and sealed Ag/AgCl reference element; Corning).

Color analysis was done on The Color Machine (Byk-Gardner; 360° circumferential illumination, with tungsten source at color temperature of 2854K filtered to approximate illuminant CIE Source C; 1931 2° standard observer; illumination 45° from sample's normal direction with 0° viewing by detector). Whiteness Index was determined according to ASTM-E313 and Yellowness Index according to ASTM-D1925. The fabric samples were read by folding them into quarters and reading each quarter of the 4ply fabric once on each side. The average of the eight readings was then reaveraged with the rest of the samples for each set of six and the mean for whiteness and vellowness of the *n* sets was reported (Table I). Means above the 10% coefficient of variation were rejected.

Mechanical testing was done on an Instron Model 1122 Analyzer using an Instron 2511-302 load cell (500 kg) with full load-scale capacity of 50 kg and cross head speed of 200 mm/min. Data were processed using Instron Series IX Automated Materials Testing System software, version 5. Analyses were done according to ASTM 1682-64 ravelled strip method for wet specimens (section 17.2). Breaking load was expressed in N/yarn to normalize for dimensional changes. Data are given in Table II.

Reagents

Hydrogen peroxide (30% aqueous; Fluka), trisodium pyrophosphate decahydrate (Aldrich), Avolan UL 75 amphoteric wetting agent (Mobay), thiourea^b (Aldrich, 99%), trisodium trithiocyanurate (15% aqueous colution, pH 11.3; Fluka, practical grade) and sodium ethylenediaminetetraacetate (EDTA; 98%; Aldrich) were used as received.

Typical Bleaching Regimen

All bleachings were carried out at a 30:1 liquor/fabric ratio (vol./wt.) at 60C.

Oxidative Step

The oxidative bleach bath solution for samples 16/16, 16/16T and 16/ 16TTCA (2L for each set of fabrics) was prepared by addition 28.8 mL of 30% H_2O_2 , 8.0 g of tetrasodium pyrophosphate decahydrate (TSPP) and 0.668 g of Avolan UL 75 to deionized water. The resulting solution (300 mL) was introduced to each of six bath tubes. The bath temperature was adjusted to 40C and then a fabric sample was introduced to each tube. At this point, agitation was begun and the bath temperature was raised to 60C at a rate of 3C/min. The temperature, pH and redox potential $(m\bar{V})$ of each bath were measured every 15 minutes. The pH in the baths stayed between 8.5-9.5 with a redox potential between +100 mV to +200 mV. Oxidative bleaching was carried out for 60 minutes from the time the fabric was introduced into the bath. After 60 minutes, oxidative bleaching

^aMention of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Thiourea, a suspect carcinogen, must be handled with care. It is an easily handled crystalline solid that is completely consumed in the ARS process upon reaction with hydrogen peroxide.

		Tab	ole I. Bleach	ning and Co	lor Experiment	S			
	Fabric As Received	Unbleached Control	d Oxidatively Bleached		Bleached with Thiourea	Bleached with Na ₃ TTCA			
Run Codes	-	0/0	16/16	22/22	16/16T 70%	16/16TTCA 70%	16/16TTCA 80%	16/16TTCA 90%	16/16TTCA 100%
Run Conditions									
H ₂ O ₂ , 1st step (a/L 30% ag) 60 min, 60C	-	0	16	22	16	16	16	16	16
Residual H ₂ O ₂ , second step (g/L 30% ag) 25 min, 60C	-	0	16	22	16	16	16	16	16
Thio species, second step	-	none	none	none	thiourea	Na ₃ TTCA	Na ₃ TTCA	Na₃TTCA	Na ₃ TTCA
Thio species, % of true stoichiometry to H ₂	- 2O2	-	-	-	70	70	80	90	100
			Effect of	Bleaching or	Whiteness				
WI:Mean	5.15	7.79	19.24	22.69	26.24	10.58	19.07	25.38	23.45
Std Dev	0.41	0.33	1.22	0.25	1.04	1.61	1.25	0.90	1.05
n sets of 6	5	2	2	6	5	2	6	3	10
95% Conf.	±0.51	±2.77	±10.35	±0.26	±1.29	±13.66	±1.32	±2.23	±0.75
			Effect of I	Bleaching on	Yellowness				
YI:Mean	27.80	26.04	22.18	21.00	19.31	25.15	21.76	19.53	20.17
Std Dev	0.17	0.25	0.23	0.12	0.35	0.79	0.48	0.25	0.29
n sets of 6	5	2	2	6	5	2	6	3	10
95% Conf	±0.22	±2.11	±1.93	±0.13	±0.44	±6.74	±0.50	±0.61	±0.20

Table II. Effect of Bleaching on Wet Tensile Strength

	Fabric As Received	Unbleached Controls Thiourea Procedure	Unbleached Controls Na ₃ TTCA Procedure	Bleached with Thiourea 70%	Bleached with Na₃TTCA 90%
Run Codes Fabric sets n sets of 6	- 1	0/0 2	0/0 2	16/16T 2	16/16TTCA 2
Break Load:	2.45	2.46	2.46	2.33	2.34
Mean (N/yarn)		2.46	2.48	2.31	2.25
Normalized to	100%	101%	100%	95%	92%
Fabric as received		100%	101%	94%	95%
Standard	0.23	0.27	0.36	0.29	0.24
Deviation		0.26	0.29	0.19	0.20
Coefficient of	2.37%	2.77%	3.70%	3.15%	2.70%
Variation		2.67%	2.96%	2.08%	2.16%
Number of	20	13	13	19	6
samples per set		20	19	16	20
Bonferroni T	а	a	a	b,c	b
Test groupingsª		a	a	b,c	c

^aMeans with no letter in common are significantly different (p<0.05) by Bonferroni Least Significant Difference test.¹⁹

was continued for another 25 minutes (as in sample 16/16) or the residual peroxide was converted by thiourea or TTCA to reductive species and reductive bleaching was allowed to proceed for an additional 25 minutes (as in samples 16/16T or 16/16TTCA).

Reductive Bleaching with Thiourea

Converting the oxidative bath to a reductive bath with thiourea (16/16T samples) required only 70% of the stoichiometric weight of thiourea to initial H_2O_2 . Thiourea (1.1g) was added to each 300 mL bleach bath after oxidative bleaching had proceeded for one hour. Then the pH was adjusted to 4.5 using dilute acetic acid. After 10 minutes, the pH measured 3.0-3.5 and the redox potential +400 mV. At this time, the pH was adjusted to 7-8 with dilute aqueous ammonia, at which time there was a plunge in redox potential to -600 to -700 mV. Reductive bleaching then proceeded for 25 minutes.

Reductive Bleaching with Trisodium Trithiocyanurate

Conversion of the oxidative bath to a reductive bath with trisodium trithiocyanurate (Na₃TTCA) for samples 16/ 16TTCA used aqueous Na₃TTCA (15% wt./vol.; pH 11.3) as received. In this reaction, each 1 mole of thio group should react with 2 moles of H_2O_2 . Stoichiometrically, 1 mole of Na₃TTCA should react with 6 moles of H_2O_2 ; empirically, 90% of the stoichiometric amount of TTCA was sufficient.

In a typical run 9.2 mL of Na_3TTCA solution was added to each peroxide bath. The addition caused the pH to drop to 6.0-7.3, similar to the drop experienced by addition of thiourea, and the solution turned yellow—it had remained colorless in thiourea runs. Acetic acid was used to lower the pH to 4.5-5.0, at which time the solution turned colorless. It should be noted that Na₃TTCA yields an insoluble precipitate if added to an acidic medium. Only its reaction product with H₂O₂ is soluble at lower pH values; thiourea forms no such precipitate.

The reaction then was allowed to proceed as with thiourea. After 10 minutes residence time, the redox potential had dropped to -400 mV (with thiourea, the potential had remained positive). The TTCA system at this negative potential remained ineffective as a reductive bleaching medium. As with thiourea, only bringing the bath back to pH 7-8 with ammonia (*ca.* 7 mL 30% aq) allowed reductive bleaching, and a redox potential of -600 to -700 was achieved. Reductive bleaching then proceeded for the next 25 minutes.

Final Rinsing

At the end of the bleaching runs, the fabric samples were removed from the bath tubes and thoroughly rinsed with deionized water since the whiteness and yellowness of the samples bleached by the Na₃TTCA process seemed particularly sensitive to tap water. A series of experiments was conducted to assess the influence of tap water in the bleach bath and in the rinse step-baths for each were prepared from deionized water, tap water (22.1 ppm Ca, 13.9 ppm Mg), 0.1% or 0.3% ÊDTA in tap water, or tap water acidified with acetic acid to pH 5. Results are presented in Table IIÎ. The tap water was drawn in bulk at one time and the same batch was used for all runs and ion analysis. Ion content was determined by atomic absorption analysis, using a Perkin-Elmer Model 3300 atomic absorption spectrophotometer in the flame mode (air/acetylene). The samples were then laid flat to dry overnight. The reactions were replicated as per Table I.

Results and Discussion

The results of multiple bleaching runs are given in Table I. The most significant observation is that effective bleaching may be achieved using Na_3TTCA in place of thiourea. Nevertheless, no loss in bleaching efficiency was noticed when the weight of thiourea was trimmed to only 70% of the stoichiometric amount to hydrogen peroxide. Such economies were not realized using Na_3TTCA at 70% stoichiometry—in fact final fabric whiteness is not much improved from unbleached fabric. Nevertheless, use of

Table III. Effect of Tap Water¹ on Bleaching Efficiency²

Bleach bath	Rinse water	Rinse pH	Δ WI ³	∆ YI³	
Тар	Tap, acidified with acetic acid	5.2	17.21 ^A	-7.70 ^F	
Тар	Tap with 0.3% EDTA	4.9	16.24 ^{AB}	-7.15 ^{EF}	
Тар	Tap, acidified with acetic acid	5.0	15.36 ^B	-6.66 ^{DE}	
Тар	Deionized	7.0	15.15 ^B	-6.09 ^{CD}	
Deionized	Deionized	7.0	15.11 ^B	-6.17 ^D	
Тар	Tap with 0.1% EDTA	5.2	14.62 ^B	-6.25 ^D	
Tap with 0.1% EDTA	Tap with 0.1% EDTA	5.2	12.15 ^C	-5.32 ^{BC}	
Deionized	Тар	8.5	11.42 ^C	-4.97 ^{AB}	
Tap with 0.3% EDTA	Tap with 0.3% EDTA	4.9	10.57 ^C	-4.74 ^{AB}	
Тар	Tap⁴	8.5	10.49 ^C	-4.40 ^A	
Тар	Tap, 2nd rinse ⁴	7.2	11.03	-4.75	
Тар	Tap, 3rd rinse ⁴	5.0	14,32	-5.84	

¹Tap water containing 22.1 ppm Ca and 13.9 ppm Mg. One set of six fabric samples per run condition. ²Conditions: 16/16TTCA(90%) as per Table I. ³Means within the same column with no letter in common are significantly different (p<0.05) by Bonferroni Least Significant Difference test.¹⁹ ⁴The dried fabrics were subjected to a second rinse at pH 7.2 and then a third rinse at pH 5.0. Resultant corrected values for Δ WI and Δ YI are given. Na₃TTCA in 90% of stoichiometry produced very effective bleaching.

There were added complications using Na₃TTCA. One was its insolubility in neutral to acidic medium, though this was overcome by charging the bath with the trisodium salt instead of the free acid (TTCA). In the initial period after addition of Na₃TTCA, there was sufficient chemical reaction with hydrogen peroxide to obviate precipitation on subsequent acidification. Another complication was the formation of colored species, probably from chelation of Na₃TTCA with hard metal ions. The initial reductive bath turned vellow, but that color dissipated immediately during the souring step with acetic acid. Most importantly, results showed a yellowing of the final bleached fabric when tap water was used in the rinsing step, resulting in diminished effective bleaching. Data resulting from an investigation of this phenomenon are shown in Table III. No significant detrimental effect upon whiteness or yellowness was seen by using tap water in place of deionized water in the bleach bath. The effects were only significant for the rinsing step. At first it was believed that the problem was associated with hard water ions, so EDTA was incorporated in the tap water. Indeed, 0.1%-0.3% EDTA in the rinse water seemed to obviate the problem, but later analysis of the tap water showed it was relatively soft (about 40 ppm hardness). However, the relative alkalinity of the tap water (pH 8.5) and the acidification to pH 5 caused by addition of EDTA was noted. Indeed, rinsing in acidified tap water without EDTA obviated the problem as well as did EDTA. Thus, it was concluded that the rinse water should be acidified for best whiteness.

Wet tensile strength measurements (Table II) were measured on a per-yarn basis. There was a slight loss in strength relative to the control samples, and this was seen both for the thiourea system as well as the TTCA system, but losses were only in the 5 to 8% range.

Conclusion

The advantages of using the single bath process including excellent whiteness, full bleaching in a single bath, use of thiourea instead of more expensive thiourea dioxide, removal of residual iron (orange cast) when bleaching for pigmentation, strength retention, soft handle and potential for subsequent dveing in the same bath were discussed in previous publications. Substitution of Na₃TTCA for thiourea offers advantages of safety, though not yet economy. Use of TTCA also requires some attention to pH at the point of addition to the system, because it is only soluble in water in its salt form (Na₃TTCA). Prevention of fabric discoloration during the rinse stage is achieved by acidification of the rinse water. Nevertheless, the exceptional whiteness achievable by using Na₃TTCA in this single bath full bleaching far exceeds what can be obtained by conventional peroxide bleaching.

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