Bleaching of Wool with Sodium Borohydride

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ABSTRACT

An untreated wool fabric was bleached both with sodium borohydride (SBH) in the presence of sodium bisulphite (SBS) solution and with a commercial H_2O_2 bleaching method. The concentration effects of SBH and SBS, bleaching time, pH and temperature on SBH bleaching process were investigated. Whiteness, yellowness and alkali solubility results were assessed for both bleaching methods. The results showed that whiteness degrees obtained with SBH bleaching was comparable with that of H_2O_2 bleaching method; whereas the alkali solubility values of the SBH bleaching was superior to the H_2O_2 bleaching.

INTRODUCTION

The bleaching of wool may be carried out with either oxidation, or reduction, or both of the bleaching methods. Since hydrogen peroxide (H_2O_2) is liquid, odourless, easily manageable and available in convenient and safe forms, it is commonly used as bleaching agent [1, 2]. However, hydrogen peroxide and peroxy compounds damage wool fibres, due to progressive oxidation of disulphide bond ultimately forming cysteic acid [3]. This chemical damage can lead to adverse effects on the fibres mechanical properties [1].

The traditional textile reducing agents such as hydosulphite, thiourea, tiourea dioxide, formamidine sulphinic acid, zinc formaldehyde sulphoxylate and sodium formaldehyde sulphoxylate are problematic, since, even during minimal storage times, they lose strength through oxidation and generates environmentally hazardous by-products, using certain of those procedures [4]. Furthermore, they also have dosage, storage, and odour and dust problems [5].

Sodium borohydride ($NaBH_4$, SBH) is a mild reducing agent exhibiting unique properties in organic synthesis, such as reduction of aldehydes, ketones, acid chlorides and anhydrides, acid/ester and for dehalogenations [6, 7]. Increase of the hydrogen evolution (eq 1) from SBH is due to a decrease in the pH of the solution [7, 8].

$$NaBH_4 + 4\,H_2O \longrightarrow NaB(OH)_4 + 4H_2 \qquad (1)$$

SBH solution is stable in basic solutions; therefore the complete hydrolysis of the borohydride can be achieved rapidly by rise of temperature or by the addition of acids in aqueous solution [8]. In addition, the presence of metal cation, ligands of complex hydride and compounds of tetravalent sulphur increases the reactivity of sodium borohydride [6, 9-11]. The reaction between SBH and sodium bisulphite (SBS) has been proposed as follows [12]:

$$NaBH_4 + 8NaHSO_3 \rightarrow NaBO_2 + 6H_2O + 4Na_2S_2O_4 \qquad (2)$$

Except for the patent literature, there is only limited literature for SBH usage in textile finishing processes. The advantages of a commercial product based on SBH formulation in textile dyeing, reduction clearing, effluent discoloration and colour striping have been outlined in a recent literature [5]. In a conference paper, the use of SBH for bleaching of wool and wool/cotton blend has been compared against 5 practiced technologies currently used in industry. In this investigation, improved whiteness was reported without being detrimental to the fibre [13]. A technical bulletin has published bleaching methods for wool and wool blends with sodium borohydride and sodium metabisulphite, and it gives technical application details [14]. A few authors have reported to use SBH in vat dyeing of cellulosic fibres, textile waste water treatment and cotton bleaching. All of the literatures published so far report the advantages of SBH in terms of technical and environmental benefits [15-20].

In this study, the effects of SBH bleaching on whiteness, chemical damage and yellowing tendency of wool have been investigated. In order to optimize SBH bleaching process, the effects of temperature, time and pH with varying SBH and SBS concentrations were also investigated using wool fabric. All the results obtained with SBH bleaching were discussed with the conventional H_2O_2 bleaching.

EXPERIMENTAL

Materials

An untreated wool fabric used in this study was kindly supplied by Bahariye Mensucat A.S., Istanbul (Turkey). The characteristics of the fabric are given as follows: twill 2/1, 153 g/m^2, 41 ends/cm, 28 picks/cm.

The stabiliser (Stabiliser SOF Liq.), non-ionic wetting agent (Sandozin MRN Liq. TR), catalase enzyme (Bactosol SAP Liq.) and wetting-cleaning agent (Sandoclean PC) were obtained from Clariant, and crease inhibitor (Rucolin CS), anionic washing agent (Rucogen DFL) and buffer solution (Rucoacid ABS) were obtained from Rudolf-Duraner. Hydrogen peroxide (H_2O_2, 50 %), sodium tripolyphosphate ($Na_5P_3O_{10}$) and acetic acid (CH_3COOH, 98%) were commercial grade. Sodium bisulphite solution ($NaHSO_3$, %39) and sodium hydroxide (NaOH) were analytical reagent grade and supplied by Merck. Sodium borohydride ($NaBH_4$, %99) was provided by National Boron Research Institute/Turkey. A stabilized sodium borohydride (SBH) solution containing 12% $NaBH_4$ and 40% NaOH was prepared according to reference 4 and used throughout the study.

Procedures

All the scouring and bleaching processes were carried out by exhaustion technique on a beaker dyeing machine (Labotay HT10, Thailand) with the liquor ratio of 10:1. After each scouring or bleaching processes, the samples were rinsed at 60 ^oC with warm water and cold water respectively for 10 minutes with the liquor ratio of 30:1, and then washed samples were dried at 40 ^oC in a drying oven (Nüve FN 500).

Scouring

Before bleaching, the untreated wool fabric was scoured at 50 ^oC for 30 minutes with 1 g/l Rucolin CS and 2 g/l Rucogen DFL.

Hydrogen peroxide bleaching

The peroxide bleaching was carried out at 70 ^oC for 1 hour with 20 ml/l H_2O_2, 1 g/l Sandozin MRN Liq. TR, 1 ml/l Stabilizer SOF Liq. and the pH was adjusted to 7.5 with sodium tripolyphosphate. After bleaching, the wool fabrics were treated with 0.5 % Bactosol SAP Liq. at 50 ^oC for 20 minutes for removing of the peroxide residues.

Sodium borohydride bleaching

For the purpose of process optimization, SBH and catalyst (SBS) concentrations, bleaching temperature, bleaching time and pH value have been investigated as main bleaching parameters. The parameters investigated and the ranges used for SBH bleaching are listed in *Table I*. Except the recipes in *Table I*, 1 g/l wetting-cleaning agent (Sandoclean PC) was added to all bleaching liquors.

TABLE I. The parameters investigated and the related recipes used for SBH bleaching

Optimisation Parameters	SBH conc (g/l)	SBS conc. (g/l)	Temperature (^oC)	pH	Time (min)
SBH concentration	0, 0.5, 1.0, 1.5, 2.0, 2.5	20	90	6.0-6.7*	45
SBS concentration	2	0, 5, 10, 15, 20, 25	90	6.7-11.8*	45
Temperature	2	15	40, 50, 60, 70, 80, 90, 100	6.8	45
pH	2	15	60	4, 5, 6, 7, 8, 9, 10	45
Time	2	15	60	7	15, 30, 45, 60, 90

**) Changes within the ranges depending on the SBH or SBS concentration*

Testing and measurements

The whiteness (Berger 76) and yellowness (ASTM D1925) index values were measured using a Macbeth Colour Eye MS 2020 spectrophotometer under D65 illuminant, 10^{o} standard observer with specular and UV components included. The wool damage (alkali solubility, %) due to bleaching processes was determined according to ISO 3072 1975(E).

The yellowing tendency (i.e. photoyellowing) of bleached wool fibres with light exposure was tested by EN ISO 105 B02:1994 test method using an ATLAS Xenotest 150-S Weatherometer, and the yellowing results were evaluated by using the gray scale.

RESULT AND DISCUSSION

Hydrogen peroxide bleaching results

An individual peroxide bleaching process was included in this study only for comparison of the SBH bleaching results. The whiteness index, yellowness index and alkali solubility results are summarised in *Table II*.

TABLE II. Whiteness and yellowness index and alkali solubility values for untreated and H_2O_2-bleached wool.

Fabric	Whiteness index (Berger 76)	Yellowness Index (ASTM D1925)	Alkali solubility (%)
Untreated wool	17.21	24.32	10.31
H_2O_2-bleached wool	33.4	17.56	25.84

According to the values listed in *Table II*, a considerable increase in whiteness index and accordingly a decrease in yellowness index has occurred by the peroxide bleaching. This whiteness result however, shows that a slightly yellowish-white can be obtained using a regular peroxide bleaching process at pH 7.5 on this fabric. Normally, for further whiteness degrees (i.e. full-bleach) a second bleaching step, preferably a reduction bleaching, is required as in the case of the industry [2]. The alkali solubility result points out that considerable wool damage was occurred due to the peroxide bleaching when compared to the alkali solubility value of the untreated wool fabric. Since hydrogen peroxide and peroxy compounds damage wool fibres, especially in alkaline medium due to progressive oxidation of disulphide bonds, that result is expected [2, 3].

Effect of SBH concentration on bleaching of wool

In this experiment, bleaching of wool at six different SBH concentrations was carried out. The concentration of SBS was kept constant to change the ratio of SBS:SBH, and it was chosen as 20 g/l (%39) by considering the recommendations on a technical bulletin [23]. The effect of SBH concentration on whiteness values are shown in *Figure 1*. The results indicate a linear relationship between the SBH concentrations and the whiteness values. This also means that whiteness increases and yellowness decreases with increasing the SBH concentration. Maximum whiteness index (30.82) and minimum yellowness index values (17.49) were obtained with 2 g/l SBH, and there is no considerable difference between the whiteness and the yellowness indices with 2 g/l and 2.5 g/l. These results show that the maximum whiteness degree which can be reached by SBH bleaching is slightly lower than that of H_2O_2 bleaching. This difference is acceptable and whiteness degree with 2 g/l SBH is comparable with H_2O_2.

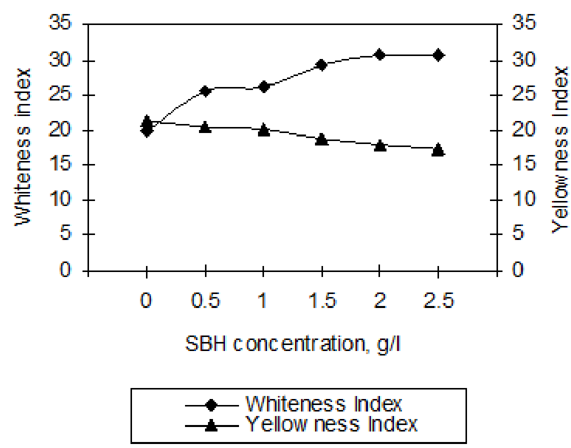

FIGURE 1. Effect of bleaching of wool with SBH on whiteness (Berger 76) and yellowness (ASTM D1925) indexes.

Effect of SBS concentration on bleaching of wool

To determine the effect of SBS concentration on bleaching of wool fibres, a series of trials were performed using six different SBS concentrations. The whiteness and yellowness results are shown in *Figure 2*. As seen by the result, when no SBS is used, the samples are not bleached, but yellowed [2]. This result can be attributed to the high pH value of SBH bleaching as the pH value of the bleaching liquor with without SBS was measured at 11.8. Because, it is not possible to generate H from $NaBH_4$ at higher

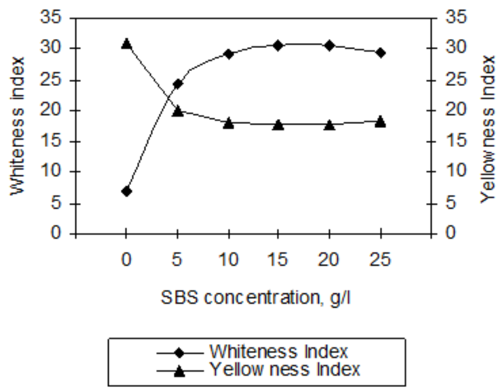

FIGURE 2. Effect of bleaching of wool with SBS on whiteness (Berger 76) and yellowness (ASTM D1925) indexes

pH values [8, 11]. However, fibre damage is possible, and the yellowing should be occurring due to this possible alkaline damage [2]. The whiteness and alkali solubility values at higher pH in *Figure 4* confirm this conclusion.

In *Figure 2*, a sharp increase in the whiteness indices is observed between 0 and 10 g/l SBS concentrations, but after 10 g/l the slope of the curve is decreased. With 15 g/l SBS concentration, the whiteness index values reach about a maximum, and then there is no significant increase for both SBS concentrations of 20 g/l and 25 g/l. Further, as seen from *Figure 2*, raising the SBS concentration from 0 to 10 g/l causes a dramatic decrease in yellowness, and the yellowness value with 15 g/l SBS lowers to a minimum. These results show that optimum SBS concentration is 15 g/l in tested conditions. However, SBH is more expensive than SBS and in practice, a slight excess of SBS can be used to ensure complete utilisation of the sodium borohydride.

Effect of bleaching temperature on whiteness and alkali solubility

In the light of the results obtained from the previous steps, 2 g/l SBH and 15 g/l SBS were used for investigating the effects of temperature on bleaching of wool. *Figure 3* shows the relationship between the whiteness and temperature for bleaching conditions of 45 minutes and pH 7. It can be seen from the figure that higher whiteness values were obtained at 50, 60 and 70 °C. The maximum whiteness value was obtained at 60 °C and it was closer to the H_2O_2 bleaching results.

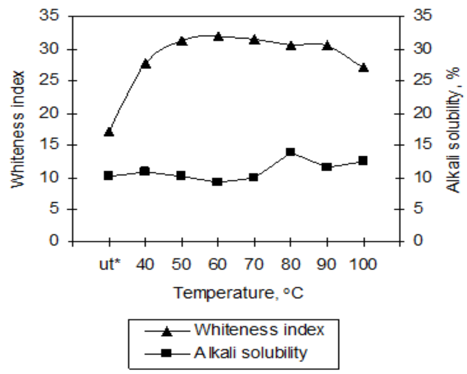

FIGURE 3. Effect of bleaching temperature on whiteness index (Berger 76) and alkali solubility.

Figure 3 shows a relationship between alkali solubility and temperature in SBH bleaching. It can be concluded that the bleaching temperatures up to 100 °C has no clear effect on the alkali solubility, but there is a tendency for slight increase after 70 °C. Furthermore, alkali solubility with SBH bleaching is much lower than that of peroxide bleaching even at 100 °C. According to this result it is possible to say that SBH bleaching has an important advantage over peroxide bleaching in terms of wool damage.

Effect of bleaching pH on whiteness and alkali solubility

The changes in whiteness index and alkali solubility versus varying pH values are shown in *Figure 4*. The highest whiteness value was obtained at pH 5-7 by the treatment of wool with 2 g/l SBH, 15 g/l SBS at 60 °C for 45 minutes. By increasing the pH, especially after pH 8, a tendency for a decrease appears. This can be attributed to a reduced H release due to higher hydrolysis stability of SBH in the alkali medium [8]

Alkali solubility values from *Figure 4* reveal that the pH value in SBH bleaching does not have a significant effect on the alkali solubility. All the alkali solubility values are around the solubility of the untreated wool, but the result shows a tendency for an increase between pH 7-10. When considering the alkaline degradation due to alkali attack to the disulphide bonds it is possible to say that this tendency for an increase in the solubility should be due to the alkaline pH [21, 22]. As a result, SBH bleaching can be carried out safely at pH 5-7 intervals in terms of whiteness index and alkali solubility.

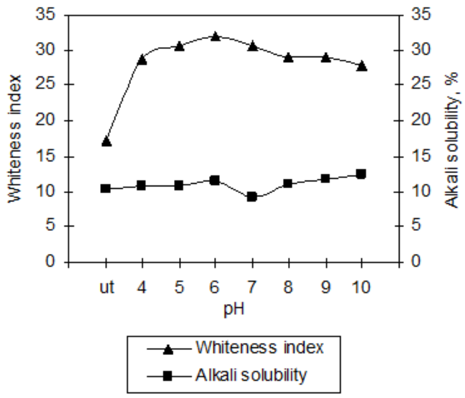

FIGURE 4. Effect of bleaching pH on whiteness index (Berger 76) and alkali solubility

Effect of bleaching time on whiteness and alkali solubility

The effect of bleaching time on whiteness indices and alkali solubility of SBH bleaching were investigated with 2 g/l SBH and 15 g/l SBS at 60 °C and pH 7. The results are summarised in *Figure 5.* According to the whiteness indices 15 minutes and 30 minutes are insufficient and 45 minutes seems optimum for obtaining maximum whiteness degrees. After 45 minutes (i.e. 60 and 90 minutes) whiteness index decreases slightly. This may be from yellowing slightly due to the longer treatment in hot liquor [2].

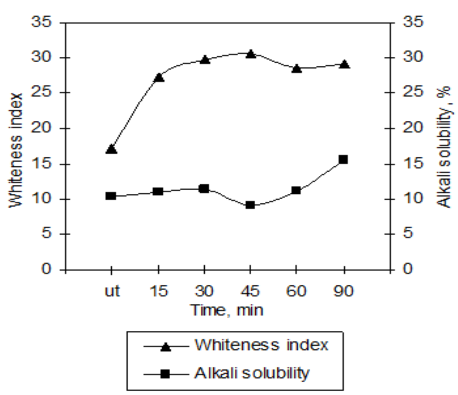

FIGURE 5. Effect of bleaching time on whiteness index (Berger 76) and alkali solubility

It can be seen from *Figure 5* that alkali solubility rates are not changed until 45 minutes significantly, but there is an increase after 60 minutes. This increase should be arising due to the heat damage from longer treatment time as in the case of the decrease in the whiteness values. Even though, maximum alkali solubility obtained for 90 minutes (i.e. 15.53 %) is much lower than that of hydrogen peroxide bleaching.

Yellowing tendency of wool after bleaching

It is known that, bleaching with peroxide above pH 7 makes wool more sensitive to chemical attacks. Thus peroxide bleaching has a negative effect on photo-stability of wool, i.e. yellowing of white wool (24). To compare yellowing tendency of SBH bleaching method, the peroxide bleached with 20 ml/l H_2O_2, 1 ml/l stabilizer and 1 g/l wetting agent at pH 7.5 and 70 °C for 60 minutes, and SBH bleached, with 2 g/l SBH and 15 g/l SBS at pH 7 and 60 °C for 30 minutes, samples were exposed to light according to EN ISO 105 B02:1994 test method and the yellowing degrees were evaluated by using the gray scale. The results have been summarized in *Table III.*

TABLE III. Light fastness values for untreated, H_2O_2 and SBH bleached wool

Fabric	Light Fastness
Untreated wool	5
H_2O_2 bleached wool	4-5
SBH bleached wool	4-5

It is concluded from *Table 3* that there is a slight yellowing for both SBH- and peroxide-bleached wool when compared to untreated wool. However, it was anticipated more yellowing with the peroxide bleaching than that of the SBH bleaching, and it can be attributed to the neutral pH used in the study for peroxide bleaching. When working with alkali peroxide bleaching bath such as in some practical applications, higher yellowing tendency than SBH bleaching can be expected.

CONCLUSIONS

The results presented in this study demonstrate that SBH could be used for bleaching of wool. Although SBH-bleached wool fabric samples exhibited very similar whiteness degrees with the ones bleached by hydrogen peroxide, wool damage (alkali solubility) with SBH was very low compared to the peroxide results. Furthermore, the results can be obtained at lower temperature, time and pH which have advantages in terms of wool quality and the environment.

The first stage of this study has shown that the SBH usage for bleaching of wool has considerable potential, especially for preservation of the wool quality. Compared to the conventional wool bleaching methods, further studies are needed in order to quantify the economical and environmental benefits of the SBH bleaching.

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