Bleaching of Cotton Fabrics by Hydrogen Peroxide in Milder Condition

M. Tahara[a], S . Yang[b] and M. Maekawa[c]

[a] Technology Research Institute of Osaka Prefecture, Osaka, 594-1157, Japan
[b] Graduate School of Human Culture, Nara Women's University, Nara, 630-8506, Japan
[c] Faculty of Human Life and Environment, Nara Women's University, Nara, 630-8506, Japan

Abstract:

In order to establish the bleaching method for cotton fabrics under a mild condition, we attempted to treat the fabrics in various concentration of ferrous sulfate solution prior to hydrogen peroxide bleaching. The whiteness index (WI) and tensile strength for cotton were measured and compared with those of alkaline bleaching. It was observed that the pH for the bleaching solution has changed during bleaching depending on the pretreatment conditions such as ferrous sulfate concentration and immersion period. In addition, the WI and tensile strength for cotton were determined by the pH of the bleaching solution after bleaching. Furthermore, we have studied the effects of an addition of NaOH into hydrogen peroxide bleaching bath, on white index of fabrics and tensile strength of yarns when the pre-treatment was carried out with copper vitriol.

Keywords: Bleaching; Hydrogen peroxide; White index; Tensile strength; Cotton fabrics; Iron (II) sulfate

1. Introduction

Recently, fiber processing with low impact onto ecological environment has been requested. In the bleaching of cotton fabrics, lots of studies have been reported. Some were studies of the biological methods with enzymes［1,2］, however, the method with enzymes has not been established satisfactorily in the view point of cost performance yet. On the other hand, absorbable organic halogen(AOX) free process has been realizing using mainly peroxide instead of chlorine–based bleaching agents［3］. Although bleaching process using hydrogen peroxide in alkaline condition at high temperature is effective to attain high whiteness for the fabrics, this method has faults to require lots of energy cost and washing water. Therefore, hydrogen peroxide bleaching using activators such as urea［4］, some kinds of amide ［5］or cationic activator［6］has been reported. In our previous work［7］, we attempted to treat in ferrous sulfate solution prior to hydrogen peroxide bleaching. Although some decrease in tensile strength of the bleached fabrics was observed, considerably high whiteness was attained. Metal ions have been applied to darkly pigmented wools containing melanin but not natural wool or cellulose fibers［8］. It is known that the decomposition of hydrogen peroxide may be catalyzed by contact with solid metal or metal ions in solution. In addition ferrous ions used in conjunction with peroxide give hydroxyl radicals which are capable of attacking cellulose［8］. Then, metal ions have been removing from solution by forming chelate compound in the bleaching［9］. In addition, there is a report that an addition of hydroxyl radical catcher like tertiary butyl alcohol is useful to prevent fibers from degradation［10］.

In our previous work［7］, however, we observed that the pH of the bleaching solution is a key factor for bleaching of cotton fabrics and it changes depending on the pretreatment condition. Therefore, in the present work, we attempted to probe a possibility to bleach cotton fabrics using hydrogen peroxide with ferrous ions. An optimal condition to treat cotton fabrics with ferrous sulfate prior to bleaching in order to get higher whiteness without loss of tensile strength for fabrics was investigated.

2. Experimental

2.1 Materials

Plain-woven cotton fabrics scoured with enzymes were supplied by Kurabo Co. Ltd. Commercial ferrous sulfate hepta-hydrated and hydrogen peroxide (35%, Kishida Chemicals Co. Ltd.) of extra pure grade reagents were used for experiments. Scourol 100 (non-ionic surfactant) supplied by Kao Co. Ltd. was used to stimulate chemicals to permeate into cotton fabrics through experiments.

2.2 Pretreatment and bleaching

Cotton fabrics were immersed in aqueous solutions of ferrous sulfate hepta-hydrated with the concentration of 0.005~0.1 g/l at a liquor to good ratio of 60:1 for 5~180 min at ca.25℃. Then the cotton fabrics were wrung into 100% water content and bleached in the hydrogen peroxide solution of 20ml(35% H2O2)/l at the liquor to goods ratio of 60:1 for 2h at 70℃. Then the bleached fabrics were rinsed with distilled water and dried at room temperature. The pH of the solutions before and after bleaching was measured. In addition, bleaching under alkaline condition at pH 10 was also carried out under the same condition as mentioned above except pretreatment with ferrous sulfate. The concentration of Scourol 100 used was 0.5g/l through experiment.

2.3 Evaluation of whiteness and strength

To obtain the whiteness index (WI) for the cotton fabrics, the values of Y and Z were measured using a spectrophotometer (Nippon Denshyoku Co. Ltd. SE-2000C) with standard illuminant C and 2°viewing angle, then WI was calculated according to Equation 1 by ASTM.

$$WI = 3.388Z - 3Y \qquad (1)$$

Tensile strength at break for warps picked from fabrics was

measured using Autograph (Shimazu AG-20kNG) with the tensile speed of 10cm/min. Average values for 30 yarns were obtained.

3. Results and discussion

Fig.1 represents the effects of the pretreatment conditions i.e. the concentration of ferrous sulfate and immersion time, on the WI for the bleached cotton fabrics.

The WI for the untreated fabrics was 23.2. It was revealed that the WI became large as both concentration of ferrous sulfate and immersion time increase. In particular, the effects of the concentration of ferrous sulfate on the WI were remarkable. To get WI more than 60, the concentration more than 0.03 g/l of ferrous sulfate is needed. The values of WI are more than 70 when ferrous sulfate is 0.1 g/l and immersion time is more than 1 h where the WI is higher than that of alkaline bleaching (67.8).

Fig.2 represents the effects of pretreated conditions on the tensile strength for the warps picked from bleached cotton fabrics. It is apparent that the concentration of ferrous sulfate affects the tensile strength for the warps definitely. Although the decrease of the strength is not so large when the concentration of ferrous sulfate is less than 0.03g/l, the drop is getting large with increasing time, when the concentration of ferrous sulfate is more than 0.05 g/l. By the way, the pH for bleaching solutions was not controlled arbitrarily in the present work, because we found that the pH of the solution settled into 3 during bleaching in our previous work, where the given concentration of ferrous sulfate was more than 0.1g/l［7］

Fig 3 represents the pH for the solutions after. bleaching versus pretreatment time for various concentrations of ferrous sulfate. It is apparent pH of solutions after bleaching depends on the conditions of pretreatment solution in both concentration of ferrous sulfate and immersion time. The pH at the beginning of bleaching was 5.5. When the concentration of ferrous sulfate was less than 0.01g/l, the pH became higher for the 5 min immersion samples and then decreases with increasing immersion time. On the other hand, it is getting lower with increasing time when the concentrations of ferrous sulfate were more than 0.03 g/l. It has been described about the reactions with ferrous sulfate and hydrogen peroxide as follows［8, 11, 12］.

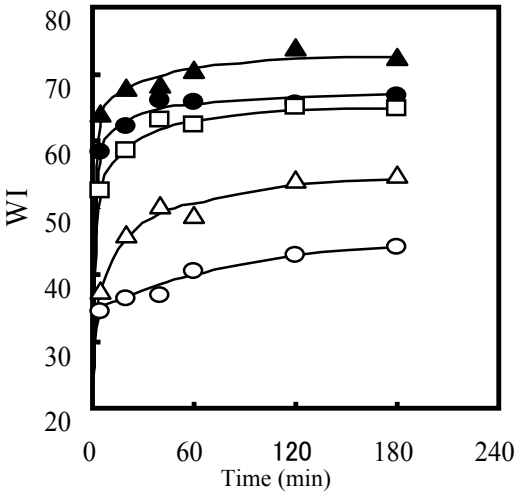

Fig.1 Effects of concentration of ferrous sulfate and immersion time at pretreatment on WI for bleached cotton fabrics. (FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

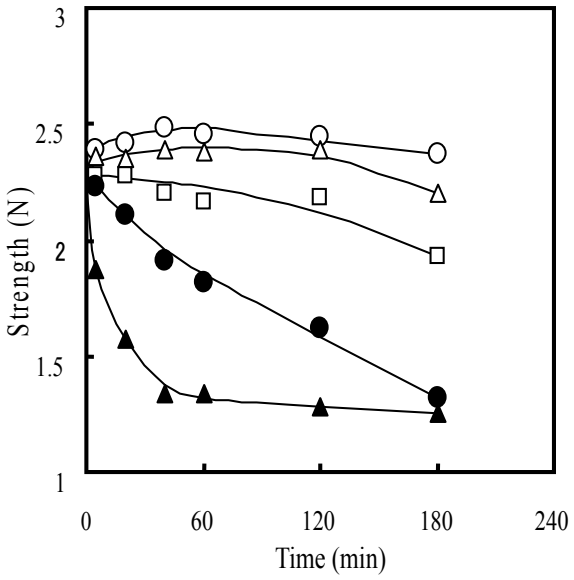

Fig.2 Effects of concentration of ferrous sulfate and immersion time at pretreatment on tensile strength of bleached cotton. (FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

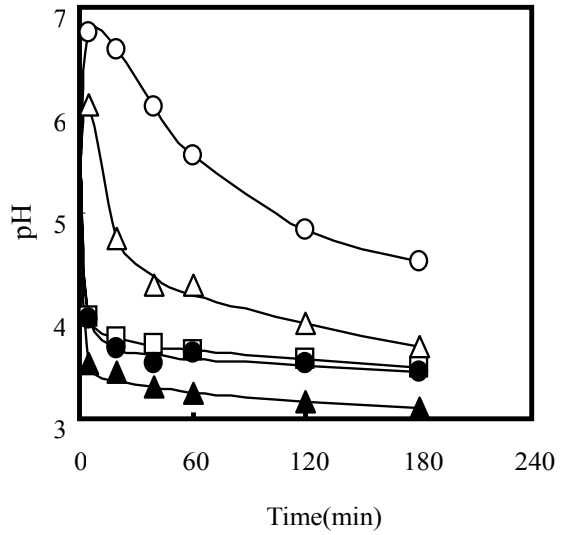

Fig . 3 Effects of immersion time and ferrous sulfate concentration on pH of bleaching solution after bleaching. (FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

$$Fe2+ + H2O2 \rightarrow Fe3+ + OH\cdot + OH- \quad (2)$$

$$Fe2+ + OH\cdot \rightarrow Fe3+ + OH- \quad (3)$$

$$H2O2 + OH\cdot \rightarrow HOO\cdot + H2O \quad (4)$$

$$Fe2+ + HOO\cdot \rightarrow Fe3+ + HOO- \quad (5)$$

$$Fe3+ + HOO\cdot \rightarrow Fe2+ + O2 + H+ \quad (6)$$

In this reaction scheme, an oxidation-reduction cycle is set up which produces radicals capable of attacking cellulose, and which

also gives rise to gaseous oxygen［8］.Catalysis in the presence of ferric ion proceeds similarly once the ion is reduced to ferrous by the peroxide ion,

$$Fe3+ + HOO- \rightarrow Fe2+ + HOO\cdot \quad (7)$$

As is apparent above reactions, the pH of the solution changes with procession of reaction.

Equation 2 shows production of hydroxyl ions as well as hydroxyl radicals at the beginning of reaction. On the other hand, the concentration of hydrogen ions increases with procession of the chain reaction (Equation 6). When immersion time of cotton fabrics in the ferrous sulfate solution is getting longer and/or the concentration of ferrous sulfate is getting higher, the amounts of ferrous ions on the fiber increase and the reactions described above progress.

Fig.4 represents the relation between the WI for the bleached fabrics and the pH for the bleaching solution after bleaching. It was revealed that the WI is in relation to the pH for the solution. The WI is getting higher as the pH of the solution is getting to higher acidity. When the concentration of ferrous sulfate at pretreatment is higher, the value of WI is higher, vice versa, the concentration of ferrous sulfate is getting lower, the values of WI are getting lower. This tendency is similar to that described elsewhere［8, 13］.

Fig.5 represents the relation between the tensile strength at break for the warps and the pH for the bleaching solution after bleaching. The strength for the untreated fabric was 2.24N. The strength is almost constant when the pH of solution is more than about 3.8. It was observed that the strength is getting smaller with decreasing pH less than 3.8, in which the concentration of ferrous sulfate is higher.

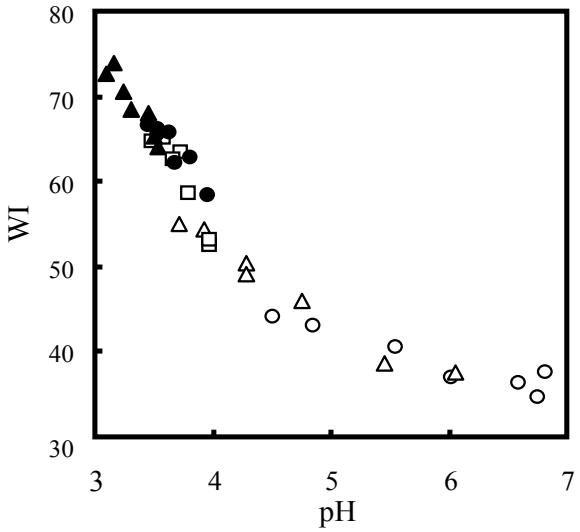

Fig.4.Relation between WI of bleached cotton fabrics and pH of bleaching solution after bleaching. (FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

As is apparent from Figs. 4 and 5, the relation between pH of the solution and the WI or the tensile strength is the contrary. Fig. 6 then represents the relation between the WI and the tensile strength of the samples prepared by various conditions.

The strength for warps keeps almost a constant value in the range where the WI is less than 65, which is as large as that of untreated warps. However it is getting smaller where the WI is more than 65. Then we considered that it is possible to bleach the cotton fabrics to attain 65 for the WI without drop of tensile strengths. On the other hand, the strength and the WI for the cotton bleached in alkaline condition are also plotted in Fig.6. Alkaline bleaching makes it impossible to reach higher WI without significant drop of tensile strength. Although the mechanism by which the colors is removed in unknown in alkaline bleaching, it has been assumed the species to work for bleach is the perhydroxyl ions that dissociated from hydrogen peroxide according to Equation 8［14］, while formation of oxygen also occurs.

$$H2O2 \rightarrow H+ + HOO- \quad (8)$$

$$2H2O2 \rightarrow 2H2O + O2 \quad (9)$$

The production of perhydroxyl ions is very small when pH is under the acid or neutral condition. An addition of alkaline promotes dissociation of perhydroxyl ions from hydrogen peroxide［15］.

$$H2O2 + OH- \rightarrow H2O + HOO- \quad (10)$$

The damage of cotton fabrics by perhydroxyl ions is seemed to be relatively small due to the electrical repulsion between the charged cotton and the ions. The damage of cotton might occur by formed oxygen, but it seems to be smaller than that by radicals. As is shown in Equation 6, this chain reaction produces hydrogen ions that make the pH of solutions lower. The concentration of hydrogen ions in the solution might depend on the concentration of ferrous ions on the fiber. Since the cellulose has negative charge, an action of perhydroxyl ions onto the cotton fabrics seems to be a little, however, neutral hydroxyl radical may attack both the cellulose fibers and impurities in the fiber. The tolerance of cellulose fibers on acid seems to be weaker than protein fibers, however, the tensile strength of cotton fabrics treated in acidic aqueous solution with pH 3 without hydrogen peroxide didn't drop significantly. Then the drop of the tensile strength must be introduced by an attack of hydroxyl radical produced by the reaction.

On the other hand, when pre-treatment was carried out with copper vitriol, the white index was low as 40~50 at pH 2~6. It refers that copper ion has little effect to activate hydrogen peroxide under the acidic condition. As shown in Fig. 5, an addition of NaOH into hydrogen peroxide bleaching bath introduced considerable high WI value as well as ferrous sulfate. However, tensile strength under this condition was decreased more than that using ferrous sulfate. It is supposed that an addition of NaOH has improved the bleaching effects and control the fiber strength, because that NaOH produce HOO· and O2 even under neutral or acidic condition.

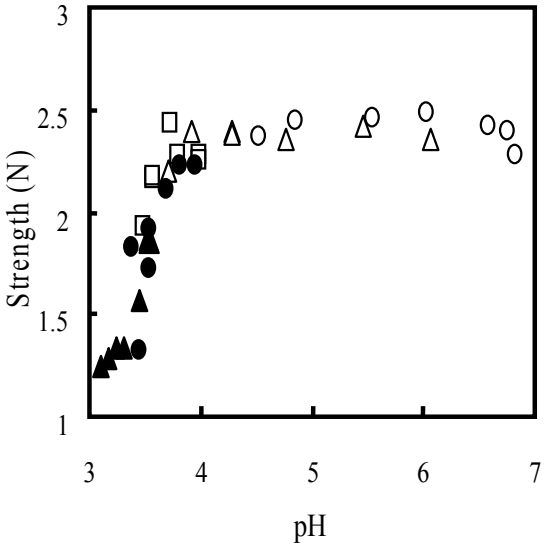

Fig.5 Relation between tensile strength of warps for bleached cotton and pH of bleaching solution after bleaching. (FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

4. Conclusion

We have studied bleaching of cotton fabrics using hydrogen peroxide after pretreatment in various concentrations of ferrous sulfate solutions for various periods. The effects of pretreatment conditions on the white index (WI) and tensile strength for cotton were investigated. The pH for the solution changed definitely during bleaching process depending on the pretreatment conditions. The WI for the bleached fabrics decreased with increasing pH for the bleaching solutions, in contrast, the tensile strength for cotton decreased definitely when the pH for the solutions is smaller than 3.8. Although the WI for the cotton treated in the present work was a little lower than that of alkaline bleaching fabrics, considerably high extent of whiteness could be attained without a drop of tensile strength when the concentration of ferrous sulfate and immersion time at pretreatment are selected properly. An addition of sodium hydroxide into bleaching bath showed the possibility to decrease damage of cotton fabrics.

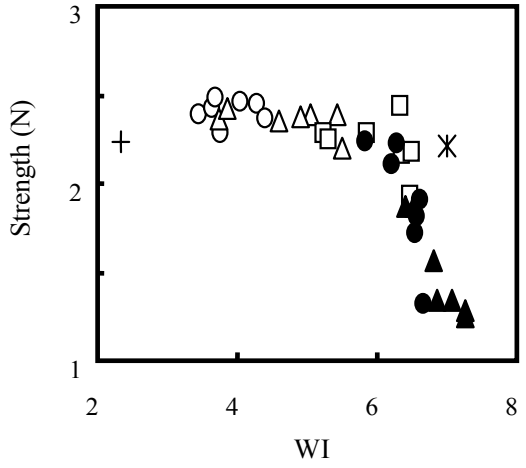

Fig.6 Relation between tensile strength and WI for bleached cotton. (＋untreated cotton, ＊alkaline bleached cotton , FeSO4(g/l) : ○ 0.005, △ 0.01, □ 0.03, ● 0.05, ▲ 0.1)

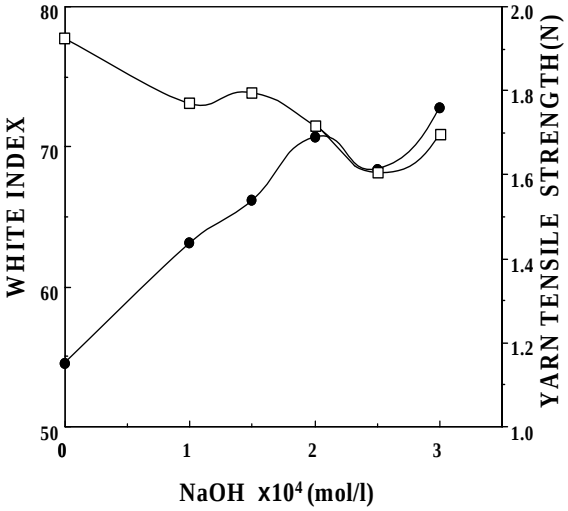

Fig.7 Effects of an addition of NaOH into hydrogen peroxide bleaching bath (20 mℓ/ℓ) at 70℃, on white index of fabrics and tensile strength of yarns when pre-treatment was carried out with copper vitriol.

□: Tensile strength of yarns

●: White index of fabrics

Acknowledgements

This work has been supported by the Nara Women's University Intramural Grant for Project Research.

References

［1］ H. Schacht, W. Kesting, and E. Schollmeyer, Perspektiven enzymatischer Prozesse in der Textilveredlung, Textilveedlr-ung, 30, 237-243 (1995)

［2］G.. Buschle – Diller, X. D. Yang, and R. Yamamoto, Enzymatic Bleaching of Cotton Fabric with Glucose Oxidase, Text. Res. J., 71, 388-394 (2001).

［3］J. Dannacher, and W. Schlenker, The Mechanism of Hydrogen Peroxide Bleaching, Text. Chem. Color. 28, 24-28 (1996)

［4］M. H. EI-Rafile, A. Higazy, and A. Hebeish, Bleaching of Linen Fabrics Using A Hydrogen Peroxide/Urea System, Am. Dyes. Reptr, 81, 49-54 (1992)

［5］ T. K. Das, A. K. Mandawalla, and S. K., Datta, Amid Activated Bleaching Processes, Text. Dyer Printer, 19, 21-28 (1986)

［6］N. C. Gursoy, A.El-Shafei, P. Hauser, and D. Hinks, Cationic Bleach Activators for Improving Cotton Bleaching, AATCC Review, 37-40 (2004)

［7］M. Tahara, O. Nezu, I. Suzuki, and M. Maekawa, Bleaching by Hydrogen Peroxide at Acid Area, Preprints, Jpn, 59(1), 138 (2004)

［8］ R. H. Peters, "Textile Chemistry", Bleaching of Cotton with Peroxide, 2, Elsevier, London, 211-232 (1967)

［9］ J. L. Colodette, S. Rothenbce, and C. W. Denerg, Factors Affecting Hydrogen Peroxide Stability in the Brightening of Mechanical and Chemimechanical Pulps. Part 1: Hydrogen Peroxide Stability in the Absence of Stabilizing Systems, J. Pulp

Paper Sci., 14(6), J126 (1998)
［10］ K. Poulakis, E. Bach, and E. Schollmeyer, Peressigsaure in der Textilveredlung Teil 3: Einsatz von Na2CO3 als Alkaliquelle fur die Peressigsaurrebleiche, Textilveredlung, 31, 55-60 (1996)
［11］W. G. Barb, J. H. Baxendale, P. George, and K.R. Hergrave, Reactions of Ferrous and Ferric ions with hydrogen peroxide. Part.I. The Ferrous Ion Reaction, Trans. Faraday Soc., 47, 462 (1951)
［12］ W. G. Barb, J. H. Baxendale, P. George, and K. R. Hergrave, Reactions of Ferrous and Ferric ions with hydrogen peroxide. Part II. The Ferric Ion Reaction, Trans. Faraday Soc., 47, 591-616 (1951)
［13］ E. Elod, and F. Vogel, Zer Kenntnis der Chlorbleiche I, Melliland Textilber., 18, 64-68 (1937)
［14］D. M. Coons, Bleach: Facts, Fantasy, and Fundamentals, J. Am. Oil Chem. Soc., 55, 104-108 (1978)
［15］N. Kitoh, and K. Katoh, The Mechanism of the Decoloring Agent and the Destaining Agent, and the Latest Developme- nt Trend, Fragrance Journal, 29(8), 46-54 (2001)