

# Retardation of Degradation in Accelerated Aging of Cotton Cellulose Using Borohydride Reduction

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**Abstract** : Degradation of cellulose during prolonged exposure in atmospheric conditions has been recognized as one of main problems in preserving cellulose-made products. The purpose of this research was therefore to study effects of borohydride reduction in improving both the color and strength retention of cotton fabrics artificially aged at temperatures ranging from 100°C to 150°C. Results indicated that the fabrics treated with either sodium or tetramethylammonium borohydrides (TMA) were degraded at rates about one-half that of water-washed cotton. These results were consistent over the temperature range. Calculation of the activation energy ( $E_a$ ) by different methods showed  $E_a = 25.5 \pm 1.5$  Kcal, in keeping with measurements made by others at lower temperatures. The TMA-treatment was effective in minimizing discoloration of the fabrics with pre-baking, but not of the un-prebaked fabrics.

**Key Words** : Borohydride, reduction, degradation, cellulose, activation energy

## I. Introduction

Sodium borohydride (SB), first used as a reducing agent for carbonyl groups in 1949 (Zeynizadeh & Behyar, 2005), was shown to be an effective reducing agent for the aldehyde groups in polysaccharides (Cao *et al.*, 2005). It was also reported that SB was efficient in stabilizing oxycellulose (Kolar, 1998). The use of SB on both oxycellulose and hydrocellulose in a dilute, unbuffered solution was highly effective in removing aldehydes and stabilizing the materials (Head, 1955). In addition to SB, other borohydrides are also useful in bleaching and stabilizing pulps against both alkaline and acidic treatments (Tang *et al.*, 1981). These borohydrides are therefore effective in paper conservation (Kolar, 1998; Kongruang *et al.*, 2004; Castellan *et al.*, 1992; Kongruang & Penner 2004).

However, the use of borohydride has mainly been limited to bleaching methods in the conservation of cellulosic textiles and paper. To some extent, the delay in studying the use of a reduction process was due to the belief that carboxylic acids, formed during the oxidation of cellulose, were a major cause of its decay. However, Block (1982) demonstrated that although deacidification and buffering with an alkaline material were useful in extending the lifetime of new cellulosic materials, the treatment was no more effective than rinsing in deionized water for protecting aged textiles.

That carboxylic acid groups on the cellulosic chain play a minor role in the decay of the material is not surprising. As the previous studies showed, acidic oxycelluloses are unstable because the carboxylic acids are converted to water-soluble, low molecular weight species (Kerr *et al.*, 1979; Hackney & Hedley, 1984).

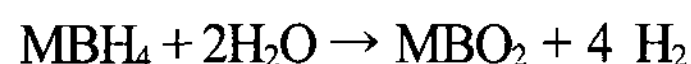
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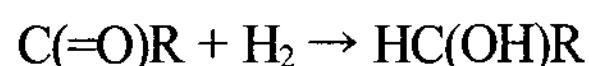
Thus, in old cellulosic textiles, the acidic species are removed from the fabric upon washing, and deacidification is not necessary. Paper that has been subjected to sulfite pulping or that contains alum or rosin, which may form acids, responds well to deacidification because the additives are being neutralized.

If the carboxylic acids on the cellulosic chain are not the major cause of the thermooxidative decay of old cellulosic textiles, one must consider the carbonyl species, particularly the aldehydes on the C<sub>2</sub> and C<sub>3</sub> carbons. It was noted that the primary autooxidation process was a reaction of molecular oxygen with aldehyde groups, which initiated a chain reaction resulting in more profound changes and decomposition of the molecule (Graminski *et al.*, 1979). Thus, the reduction of the aldehyde groups should lead to improved stability of degraded cellulose.

In aqueous solution, borohydrides decompose as follows:



whereas the carbonyl species in cellulose are reduced according to the following reaction:



Therefore, the purpose of this research was to study effect of borohydride reduction in improving both the color and strength retention of cotton fabric artificially aged at temperatures ranging from 100°C to 150°C.

## II. Experimental

### 1. Materials

A plain weave cotton print fabric (80 × 80 threads in warp and weft, respectively), weighing about 100 g/m<sup>2</sup> (Test fabrics, No. 400, USA), was used throughout the study. The fabric was twice laundered and dried according to the AATCC Test method No 124-2002.

### 2. Borohydride Treatment and Accelerated Aging

Both 98% pure sodium borohydride (SB, NaBH<sub>4</sub>) and 95%-pure tetramethylammonium borohydride (TMA, (CH<sub>3</sub>)<sub>4</sub>N(BH<sub>4</sub>)) were supplied by Aldrich. Aqueous solutions of SB and TMA (0.03 M) were made and transferred to a shallow glass tray maintained at 25°C in a water bath. Nine specimens of cotton fabric cut to 10 × 10 cm and weighing about 9 g *in toto* were placed in the tray and allowed to float in the solution. Preliminary experiments showed that the results of the testing were not changed by soaking for periods longer than 20 min, nor was prewetting in water necessary. All samples were treated for 20 min. Control samples were soaked in deionized water at 25°C for 20 min. At the same time, a water-washed sample was also prepared in the absence of borohydride. To investigate the effect of pre-baking on cotton fabric, some samples were pre-baked at 130°C before application of TMA.

Following soaking, samples were rinsed with deionized water, squeezed gently, and allowed to air dry overnight on glass-fiber screens. All samples were stored in desiccators over silica gel prior to the accelerated aging. Samples were removed from the desiccators and placed on glass-fiber screens in a forced-draft oven at the required temperature. Upon removal from the oven, samples were collected in desiccators and were then transferred to a conditioned laboratory for testing.

Because changes in the relative humidity of the oven could affect the results, a study of the change in the degradation rate as function of relative humidity was conducted. Moisture was added to the air in the oven by permitting de-ionized water to seep through eight tubes perforated by 1-mm diameter holes along their length, into a large shallow reservoir at the bottom of the oven. By adjusting the rate of water flow, the relative humidity could be controlled. The relative humidity was measured by use of wet-and-dry bulb thermometers and a psychrometric chart.

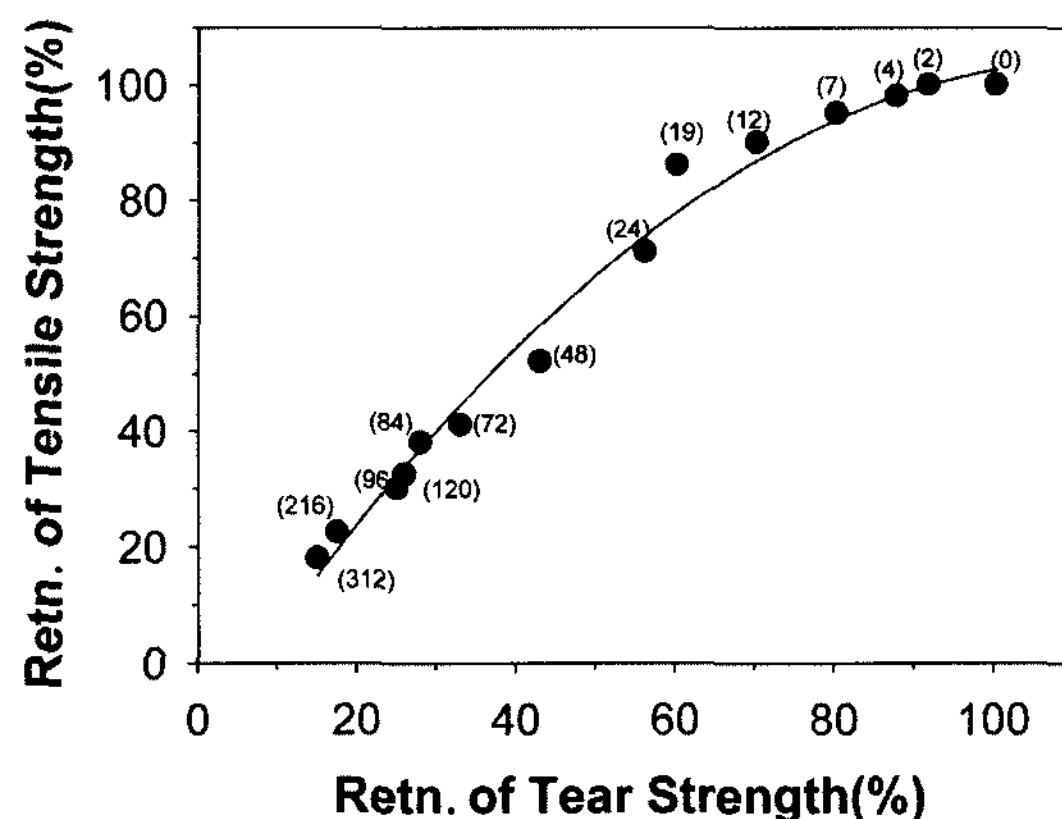
### 3. Fabric Evaluation

Tensile strength tests were performed with an Instron tensile tester as per the ASTM D-1682, and tear strength testing was done with an Elmendorf apparatus as per ASTM D-1424, at 21°C and 65% RH. Prior to the testing, the specimens were placed in the standard condition for at least 24 hrs. Results reported are the average of three tests. Color measurements were made on the samples with a Hunterlab model D25D2 colorimeter (USA) after conditioning, with D65 light source and 10° angle vision. A white standard plate was used as a backing. Both fronts and backs of the fabrics were measured three times, and the results were averaged. Color differences are reported in the LAB system and  $\Delta E$  value was calculated.

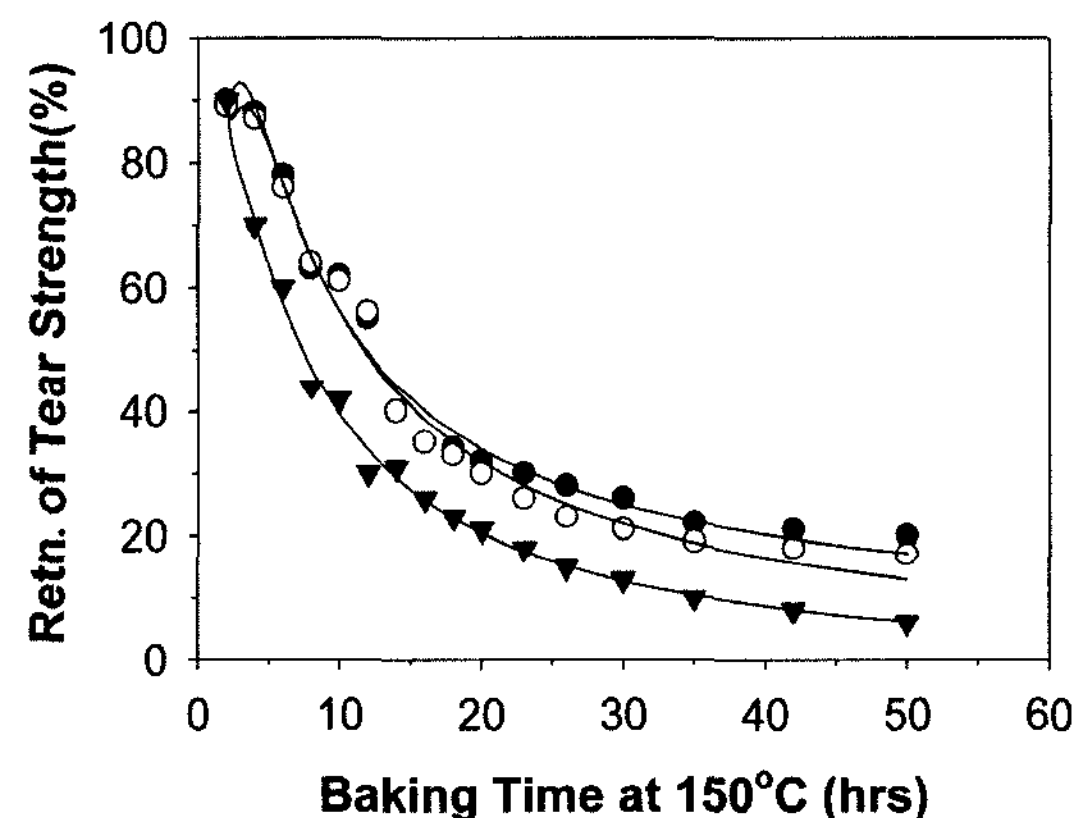
## III. Results and Discussion

### 1. Tensile Strength vs. Tear Strength

Initial measurements of tensile strength and extension at break were erratic, as were calculations of energy to break. This problem led the researcher to investigate the correlation between tensile and tear testing; the results are shown in <Figure 1>. This figure demonstrates that the tensile strength of the fabrics is not sensitive to baking time until tear strength has dropped below about 70% of the initial value. For the fabrics degraded beyond this point, a linear relationship exists between tensile and tear strengths. These results are analogous to those in the previous study (Graminski *et al.*, 1979) for the tensile strength and folding endurance of paper. This previous study showed that folding endurance was a more accurate measure of the degradation of the material. Furthermore, it was noted that tear strength was more directly involved in the assessment of serviceability of cotton fabrics than tensile strength (Block, 1984). Since tear strength is more closely related to the performance of the fabric in actual use, and it proved to be more



<Figure 1> Comparison of tear and tensile strengths. Numbers in parentheses refer to baking time at 150°C.



<Figure 2> Percent strength retention of cotton fabric baked at 150°C at different baking times and relative humidities. ●: 1% RH, ○: 2% RH, ▼: 10% RH.

sensitive to treatment of the fabric than tensile strength, mechanical testing is reported in terms of this parameter.

### 2. Effect of Relative Humidity

<Figure 2> shows effect of relative humidity on tear strength retention of the water-washed cotton fabrics at 150°C. The results revealed that a small humidity change (from 1% to 2% RH) did not affect cotton strength much. However, a certain decrease in tear strength was observed at higher humidity (10%), *i.e.*, about 15 to 20% tear strength reduction occurred with 10% RH and 10 hrs baking time. Such a decrease was

relatively independent of baking time, which was indicated by consistent tear strength reduction at 50 hrs baking time.

### 3. Effect of TMA-treatment on Cotton

To investigate effects of borohydride treatment on pre-baked fabrics, TMA was applied onto unbaked cotton fabrics, and the fabrics previously baked for 8 to 48 hrs. Experimental results are listed in <Table 1>, which show percent strength retention ratios of TMA-treated and water-washed fabrics. <Table 1> revealed that the reduction treatment with TMA significantly improved strength retention for older, pre-baked fabrics, and was also useful for new, unbaked ones. Especially, the TMA-reduction was highly effective in slowing the rate of strength loss of the pre-baked fabrics with a long baking time following the TMA treatment. For example, the ratios at the same pre-baking time were generally greater

at a longer baking time than that at a shorter one. In some cases, it was effective even for the fabrics that had been artificially degraded to less than 60% strength retention.

Effects of TMA-treatment on color change of cotton fabrics are shown in <Table 2>. The TMA treatment does little to affect the change in color of the fabrics without pre-baking or with slight degradation (pre-baking), but it is quite effective for those fabrics that have been pre-baked significantly. In general, the more degraded the fabric was, the greater the improvement in color. However, the color improvement effect became smaller for those fabrics with extremely great pre-baking times (48 hrs) at prolonged baking, such as 64 hrs.

### 4. Effect of SB-treatment on Cotton

Treatment with SB shows a similar pattern. The rates of degradation of new fabrics (previously unbaked) at

<Table 1> Percent strength retention ratio of TMA-treated and water-washed fabrics<sup>a</sup>

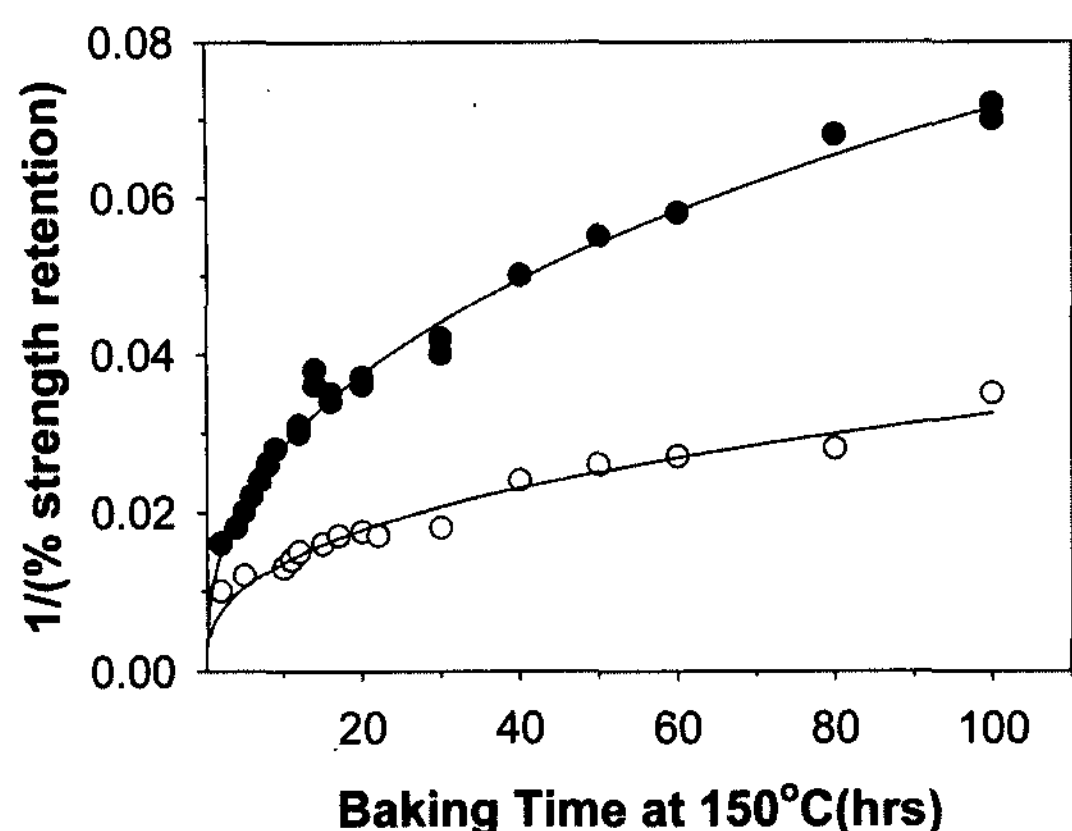
Pre-bake time (hrs)	Total baking time (hrs)										
	0	8	16	24	32	40	48	56	64	72	96
0	1.03	1.12	1.21	1.18	--	--	1.15	--	--	--	--
8	--	1.01	1.23	1.18	1.26	--	--	1.33	--	--	--
16	--	--	1.05	1.09	1.12	1.04	--	--	1.24	--	--
24	--	--	--	1.10	1.16	1.15	1.20	--	--	1.35	--
48	--	--	--	--	--	--	1.07	1.02	0.94	1.19	1.30

<sup>a</sup> Values are the percent strength retention ratios at 150°C of cotton fabric treated with TMA and water-washed.

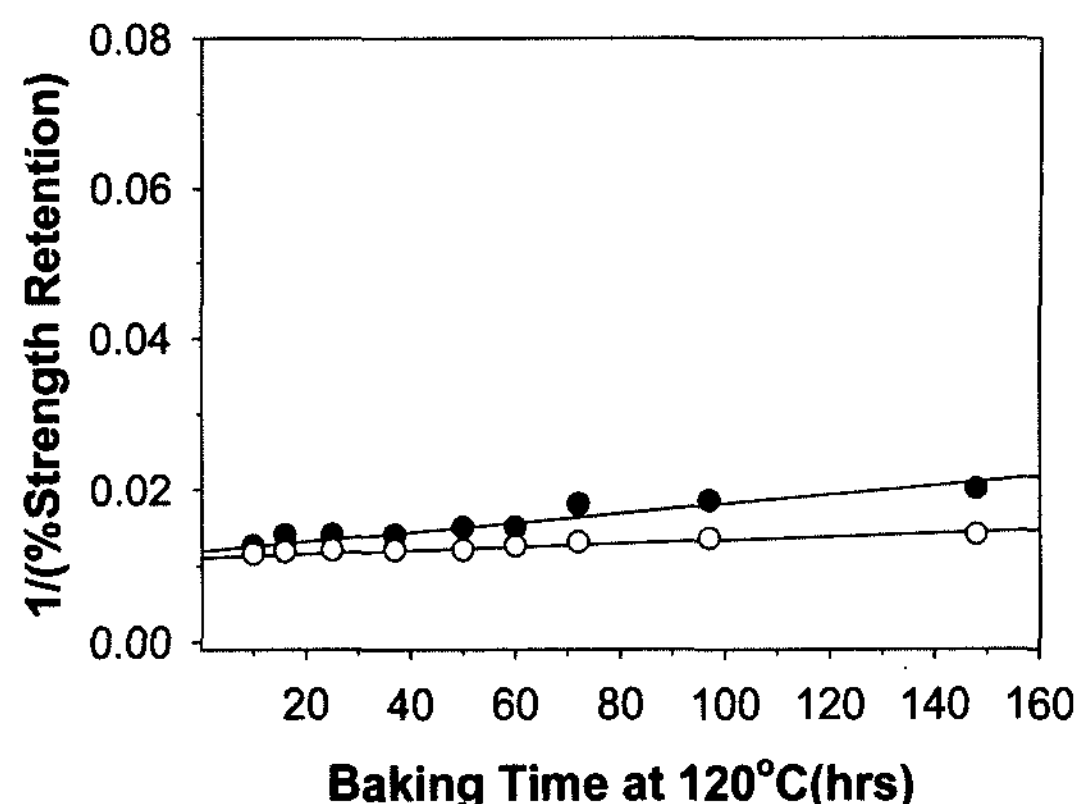
<Table 2> Color change of TMA-treated and water-washed fabrics<sup>a</sup>

Prebake time (hrs)	Total baking time (hrs)										
	0	8	16	24	32	40	48	56	64	72	96
0	0.2	-0.8	-0.8	-3.7	--	--	-1.8	--	--	--	--
8	--	1.6	1.0	1.0	-1.0	--	--	-1.0	--	--	--
16	--	--	0.3	2.5	2.7	1.9	--	--	1.6	--	--
24	--	--	--	3.6	3.8	3.7	4.3	--	--	1.5	--
48	--	--	--	--	--	--	5.0	3.0	1.0	1.0	1.0

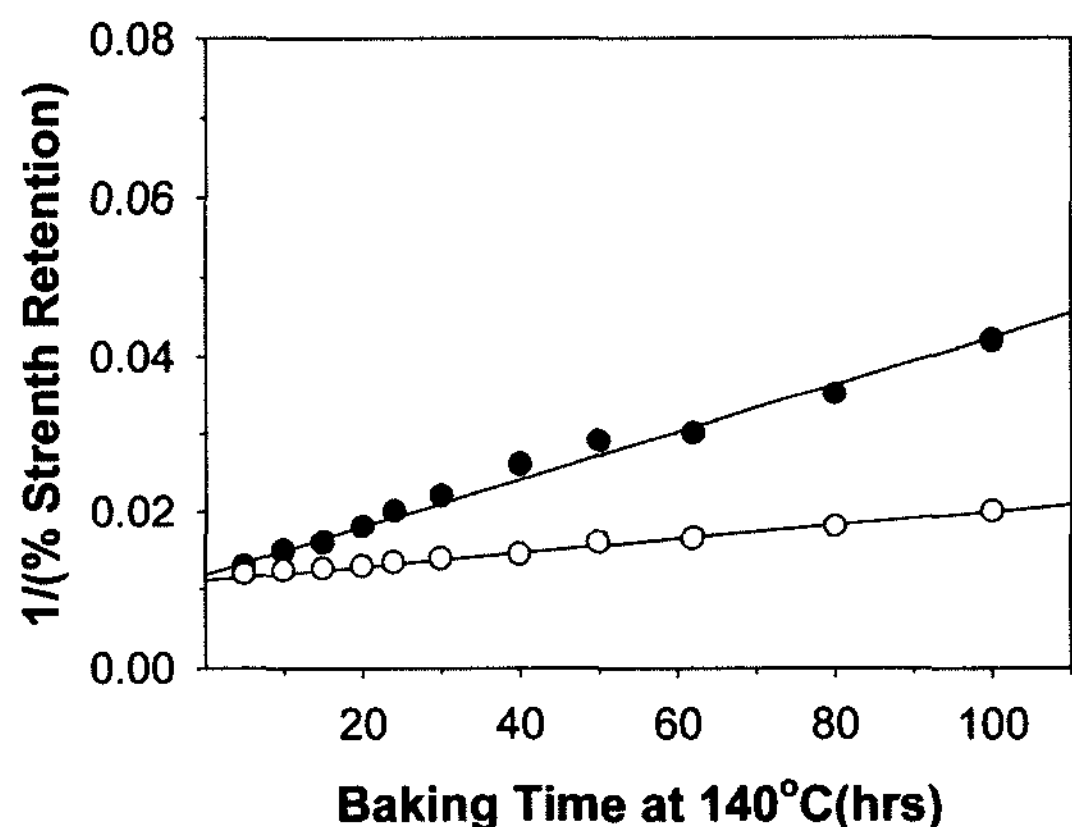
<sup>a</sup> Values are the differences in color change at 150°C between water-washed and TMA-treated cotton fabrics. Negative values mean that the water-washed fabric was less discolored than the TMA-treated fabric.



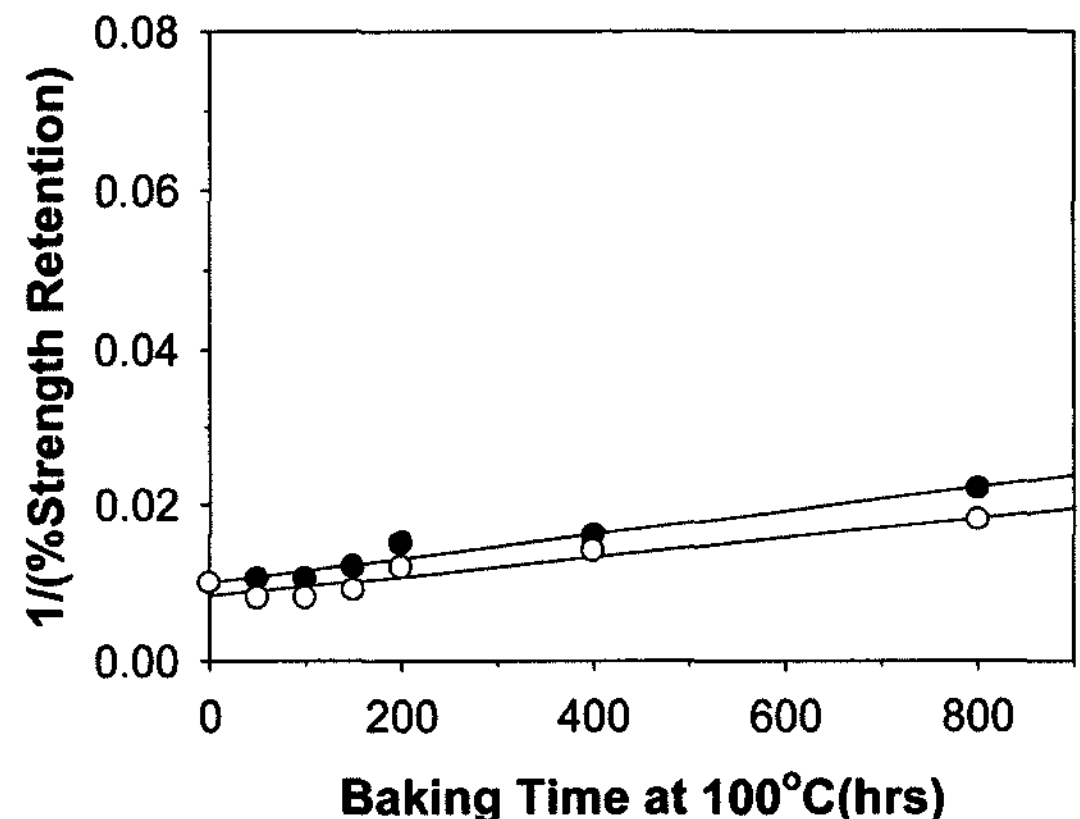
<Figure 3> Aging of cotton fabrics baked at 150°C. ●: water-washed, ○: treated with 0.05% SB.



<Figure 5> Aging of cotton fabrics baked at 120°C. ●: water-washed, ○: treated with 0.05% SB.



<Figure 4> Aging of cotton fabrics baked at 140°C. ●: water-washed, ○: treated with 0.05% SB.



<Figure 6> Aging of cotton fabrics baked at 100°C. ●: water-washed, ○: treated with 0.05% SB.

temperatures ranging from 150 to 100°C are shown in <Figures 3-6>. No experiment was carried out for pre-baked samples with SB. These plots are based on a statistical model that assumes first-order kinetics for depolymerization (Jellinek, 1978). They show that, in all cases, the SB-treatment was effective in protecting cotton fabrics against thermo-oxidative degradation. Furthermore, that the curves exhibit a linear portion indicates that strength loss is following first-order kinetics, and may mean that changes in the mechanical properties are directly proportional to changes in the chemical state of the system.

Examination of <Figure 3> shows that degradation in the early stages is linear with time, but occurs at a rate

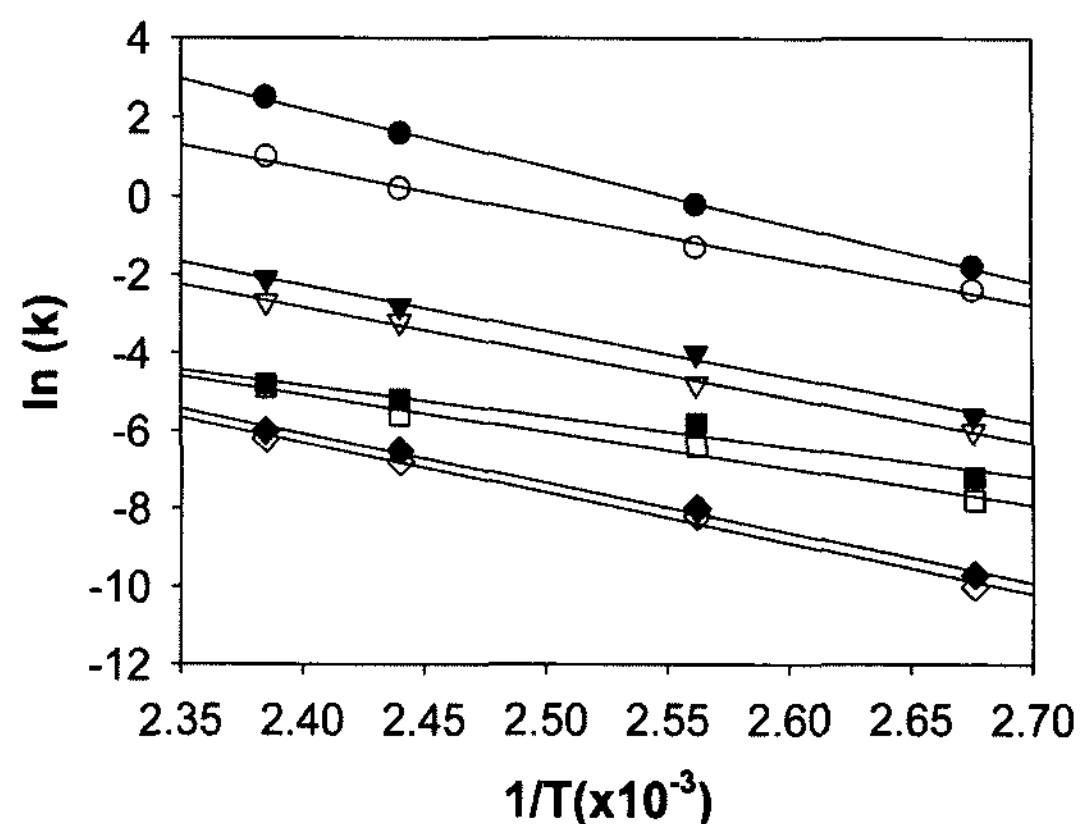
somewhat higher than the rate of degradation found later. This phenomenon is observed at temperatures down to 120°C <Figure 5>. Apparently we are observing at least two phenomena, one in which the cellulosic chains are readily broken, and one in which the chains are more resistant to thermo-oxidative attack. It is not necessarily true that these results indicate different chemical mechanisms at work. Considering somewhat defective crystal nature of cellulose comprised of many disordered regions (Richards, 1984), we can postulate that the same chemical mechanisms are at work, but that they proceed at a much faster pace in the disordered regions than in the well-ordered regions. If this hypothesis is true, then as cellulosic fabrics age, their



rate of degradation should continually decrease as less and less disordered material is available for reaction. Thus we should find that cellulosic fabrics degrade to some point, and in the absence of mechanical forces, such as handling and rapid changes in humidity, they should hardly seem to degrade further. This situation may account for the longevity of ancient cloths, such as Egyptian burial garments, and may also indicate that very ancient cellulosic textiles do not require chemical treatment. A second consequence of this model- that old cellulosic textiles should be more crystalline than new ones- is well documented (Block, 1984).

In <Figure 6> we see another phenomenon occurring that was not evident in the work done at higher temperatures. The time scale here is much extended. In the beginning, the fabric seems to increase in tear strength before undergoing any losses. Once again the SB-treated material performs better than the water-washed material. We are likely observing a slow rearrangement of the morphology of the cellulosic chains within the fiber that leads to a reduction in internal stress and a concomitant increase in tear strength, although a restructuring of the yarns during thermal treatment is not impossible. This stress reduction occurs along with degradation, and in the early life of the fabric it leads to some improvement in mechanical properties. It is, however, soon surpassed by the deteriorating effects of depolymerization, thus only at the lower temperatures is the phenomenon observed. At ambient conditions the molecular rearrangement is likely to be so slow that depolymerization is the overwhelming process.

<Figure 7> is an Arrhenius plot of the results for the accelerated aging of the fabrics (without pre-baking) at different temperatures. Regardless of the properties measured, long-term (> 30 hrs) strength retention and short-term ( $\leq 30$  hrs) strength retention or color change (the slopes) for both-SB-treated and water-washed fabrics fell within the range of  $25.5 \pm 1.5$  Kcal/mol; no statistically significant difference between the highest and lowest values at the 0.05 or the 0.1 confidence levels



<Figure 7> Arrhenius plot for cotton fabrics. Filled symbol: water-washed, unfilled: SB-treated.  
 ● & ○: 1/(percent strength retention), ▼ & ▽: short-term strength retention, ■ & □: long-term strength retention, ◆ & ◇ : color change.

was found. These results are in excellent agreement with the literature (Block 1984) and show that the reaction mechanisms do not change over the temperature range from 100 to 150°C.

### 5. Comparison between TMA- and SB-treated Cotton

From the preceding results in <Table 1> and <Figure 3>, percent strength retentions for borohydride-treated cotton fabrics baked 16, 24, and 48 hrs at 150°C were 1.21, 1.18, 1.15 for TMA-treated, and 1.67, 2.05, 2.12 for SB-treated fabrics, respectively. Results indicate that the reduction treatment improves strength retention for the cotton fabrics without pre-baking, and SB may be more beneficial than TMA.

Similarly, color difference values in <Tables 2 and 3> for borohydride-treated cotton fabrics (no pre-baking) indicate that both the TMA and SB treatment do little to hinder discoloration of the fabrics at different baking temperatures. Rather, SB treatment caused substantial yellowing on the fabrics baked at 150°C. However, it should be noted that considerable color improvement occurred on the pre-baked cotton fabrics with TMA-treatment, as discussed previously.

<Table 3> Color changes of NaBH<sub>4</sub>-treated and water-washed fabrics<sup>a</sup>

Baking temperature (°C)	Baking time (hrs)	Color change difference. <sup>a</sup>
150	4	-5.6
	10	-8.7
	16	-6.9
	24	-7.0
	48	-11.0
140	8	0.0
	16	-0.9
	24	-1.3
	48	-1.0
	96	-2.4
	144	-2.6
120	16	1.1
	24	1.0
	96	0.0
	144	0.0
100	200	0.0
	400	-0.1
	800	-0.1

<sup>a</sup> Values are the differences in color change between SB-treated and water-washed fabrics. Negative values mean that discoloration in the water-washed fabric was less than that of the treated fabric.

#### IV. Conclusions

Borohydride reduction (TMA and SB) of cellulosic textiles improves strength retention of the fabrics with or without pre-baking. SB appears to give better strength retention in general. On the other hand, both TMA and SB treatments are ineffective in minimizing discoloration of the baked cotton fabrics in the absence of pre-baking. The TMA treatment, however, significantly hinders yellowing of the pre-baked cotton. Further study is underway to confirm effects of various reducing agents (SB and others) on the color improvement of the pre-baked fabrics.

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