Effect of neutralizers and silicone softeners on phenolic yellowing phenomenon of OBA treated cotton knitted fabric

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1. Introduction

Clothing is the second basic need of humans. Commercially, different types of textile products such as domestic textiles, technical textiles, smart textiles, and functional textiles are available in the market [1, 2]. These products are categorized by fibrous and nonfibrous materials. In fibrous materials, it is divided into natural and man-made fibers. Natural fibers are known as cotton, jute, silk, hemp, ramie, and so on [3, 4]. Among all fibers, cotton is used to fulfill half of the clothing demand around the globe. Cotton cellulose is composed of D-anhydroglucopyranose units, also known as anhydroglucose, joined together by β-1, 4-glycosidic bonds. The repeating unit is generally 5000 [5, 6]. It is widely used due to its excellent wearability, superior wearing comfort, excellent moisture permeability, and outstanding breathability [7]. However, there have been some major drawbacks to the cotton fabric. Phenolic yellowing is one of them [8, 9].

Phenolic yellowing of textiles is the outcome of the phenolic compound present in the surrounding atmosphere and the reaction triggered by suitable pH conditions. These dependent variables are collectively responsible for phenolic yellowing. Butyl-hydroxytoluene (BHT) is the main phenolic compound that can react with the nitrogen oxides (NOx) in the air and forms nitrobenzene or quinone, which is a yellow chemical substance in a slightly alkaline medium [10, 11]. None of the nitrous oxides or BHT alone causes yellowing in contrast when they conjugate yellowing product forms. Optically brightened articles or pale shades that are processed with inappropriate core neutralizers always have a
propensity to cause yellowing. Slightly acidic core pH of the finished goods must have to ensure to avoid this problem. To prevent the aging of olefin, BHT is often added to the production of polyethylene and polypropylene bags. Besides, the impregnation of BHT as an antioxidant can increase the shelf life of packaging bags and avoid air oxidation. BHT is good for packaging material when reacts with textile material causes yellowing. So, textile materials are often advised not to be placed in poly bags which have antioxidants like BHT. BHT is a volatile compound having low vapor pressure thus can be easily transferred to textile goods when comes in contact [12, 13]. The interaction produces a compound named 2, 6-di-tert-butyl-4 - nitrophenol (DTNP), which is the main source of phenolic yellowing [14].

During optical brightening treatment (OBA) on cotton fabric, there are possible causes that create phenolic yellowing problems. In some cases, excess OBA is utilized due to oversight or wrong computation. Increasing the centralization of OBA past an immersion limit prompts dulling and yellowing [15]. The presence of metal particles, especially zinc can prompt the dulling of OBA for cotton. Zinc concentration could be expected to unreacted zinc in zinc formaldehyde sulphoxylate in a reductive fade, or zinc salt creates in phenolic yellowing up [16, 17]. Excess drying temperature can likely lead to yellowing. While cotton is dried and completed at 120–140 °C, and polyester and polyester mixes at 170–190 °C, excess temperature and additional contact time at raised temperature can decrease whiteness [18]. pH can create a problem during OBA treatment. This generally occurs with high-liking OBAs for cotton that are not stable in less than pH 5.0. Along with these lines in the ensuing balance after OBA treatment and/or during finishing, if pH is highly acidic, the whiteness index is reduce [19, 20].

To overcome this problem, several researchers have performed on it. Certain natural conditioners and silicone conditioners tend to prompt yellowing to the subsequent finishing process. Some of the softeners for whiteness that are non-yellowing such as Gamasoft KA, Sarasoft-SNY, Sarasoft-1367, Sarasoft-GA, Sarasoft-UK, or Supercone-2100, are suggested particularly for complete whiteness on the fabric [9, 21]. Only Sarasoft-1367, Sarasoft-GA, Sarasoft-UK, or Supercone-2100, are sug-

2. Experimental details

2.1. Materials

Grey cotton (100%) single jersey knitted fabric (160 g/m²) having 25 wales/inch and 40 courses/inch were obtained from SQUARE Textile Mills Ltd, Gazipur, Bangladesh. Commercial nonionic silicone softener (alkyl alcohol polyglycol ether) and complex acid (sulfuric acid, mono (2-Ethylhexyl) ester, and sodium salt) obtained from Zschimmer & Schwarz, Germany. Moreover, amino-functional cationic silicone (alkyl polyoxy-

2.2. Instrumentation

A 300ml bath capacity, suitable for the 10 gm of cotton fabric processing in the laboratory dyeing machine (Ahiba infrared dyeing machine, UK) used for bleaching, neutralizing, and softening. Similarly, an oven (James heal, UK) was used with a maximum heating capacity of 100 °C for drying. Phenolic yellowing testing apparatus named perspirometer also from James heal, UK. Digital pH meter for pH measurement from Mettler Toledo, USA. All the phenolic yellowing testing consumables such as Impregnated test paper, Butyl hydroxytoluene (BHT) free poly-

2.3. Methodology

Ahiba infrared exhaust machine (SDL, UK) was used in this study for all chemical processing. A 300 ml bath capacity pot is prepared for the scouring-bleaching. To make such happening 10 gm grey fabric was cut and weighed correctly using the digital balance (Ohaus, USA) having a measurement precision capacity of 0.001 gm. The M: L (material: liquor) ratio at 1:10 was maintained throughout the experiment. Sodium hydroxide (NaOH)-3 g/l, hydrogen peroxide (H₂O₂)- 6 g/l, sequestering agent- 1 g/l, detergent- 1 g/l, peroxide stabilizer- 1 g/l, and 1% optical brightening agent (OBA) added to the scouring-bleaching bath. Stock solution prepared for all chemicals for the precision of measurement. The required amount of chemical solution was taken using a digital pipette (Rainin, USA). Scouring-bleaching was carried out for 60 min at 100 °C with the machine at 40 rpm. Once the bleaching is completed the samples are washed with hot water for 10 min at 80 °C to remove the natural oil, wax, and impurities that come out from the grey cotton. Thorough rinsing is followed by hot washing to clean the extracted impurities. The neutralization conditions were optimized using different concentrations (0.5 g/l, 1 g/l, and 1.5 g/l) of the acids (acetic acid, citric acid, and complex acid) at 50 °C for 20 min. Once the neutralization was completed, different concentrations (1 g/l, 2 g/l, and 3 g/l) of both sil-

Appendix
3. Result and discussion

3.1. Mechanism of phenolic yellowing

Phenolic yellowing is a complex phenomenon and time-consuming physicochemical process. This chemical reaction is a conjugation process of oxidation and nitration. Quinone and nitrophenol are the outcomes of such chemical mechanisms in the presence of nitrous oxide. 2,6-ditert-4-nitrophenol is formed from 2,6-di-tert-butyl p-cresol in the presence of NOX which is a nitration reaction. Quinone forms in the presence of NOX. This is a visible yellow compound. Moreover, these nitrophenols and quinines are colorless in an acidic medium. By contrast, these become bright yellow in an alkaline medium. The mechanism of phenolic yellowing is represented in Figure 2.

3.2. FT-IR analysis

The presence of chemical compounds on the surface of treated cotton fabric is investigated by using Fourier Transform Infrared spectroscopy. The analysis is represented in Figure 3. Where Figure 3a is the non-treated cotton fabric and Figure 3 (b-g) is the treated cotton fabric using different types and amounts of softener and acid. The characteristic peaks of cotton fabric due to cellulose structure were observed at 3330 cm⁻¹ for O–H stretching, 2900 cm⁻¹ for C–H stretching, 1430 cm⁻¹ for C–H wagging, 1314 cm⁻¹ for C–H bending, and 1026 cm⁻¹ for C–O stretching. When the cotton fabric is treated with acid and softener, then the peak intensity is slightly decreased. In some cases, the peaks appear in the same band with different wavelengths because the same stretching and bending are possible for useable acid and softener. For complex acid, there is an interaction between acid and cellulosic cotton which can form sulfoxides. The peaks at 1050 cm⁻¹ for S=O stretching give the evidence in Figure 3 (b-c). In addition, the peak at 1010 cm⁻¹ for C–O stretching ensures the interactions of citric acid on cotton fabric Figure 3 (d-e). Moreover, the peaks at 3276 cm⁻¹ for O–H stretching and 1025 cm⁻¹ for C–O stretching also provide the interactions of acetic acid on cotton fabric Figure 3 (f-g). Therefore, the overall analysis of FTIR spectra indicates that cotton fabrics are made interactions with the chemicals.

3.3. CIE whiteness index

The CIE whiteness index is determined with the help of a reflectance spectrophotometer (Datacolor 650, USA). The instrument was calibrated accordingly with the setup of 10° viewing angle, a specular component included and larger aperture size. The fabric CIE whiteness index analysis is represented in Figure 4. Nonionic softener treated samples show a better whiteness index for all three types of acid. In contrast, cationic softener shows a lower whiteness index rating for all cases. Positive amino group nuclei of cationic softener negatively affect the whiteness index because of yellowing caused by the same. The positive charge reacts with the cellulose in an aqueous medium and causes yellowing in the presence of a suitable condition. Since the nonionic softener does not pose any active charge, therefore it does not react with the cellulose to affect the whiteness index. One more reason behind the lower whiteness rating by cationic softener may be the lower pH (4.7) value of the product as compared to the nonionic softener (pH = 6.1). Major OBAs are not stable in acidic pH, thus appearing yellower to greener because of reflectance value negatively impacted by the acidic pH, showing a lower
The samples were again tested after one-month conditioning in ambient conditions to determine the impact of the atmospheric condition on the whiteness index. Test results depict that nonionic softener and complex acid have outstanding whiteness indexes of 146.05 and 145.86, respectively for immediate testing and after one month of conditioning. Besides the cationic softener with complex acid has some

Figure 3. FTIR spectra (a) Non-treated cotton fabric, treated cotton using (b) 1.5 g/l complex acid & 3 g/l nonionic softener, (c) 1.5 g/l complex acid & 3 g/l cationic softener (d) 1.5 g/l citric acid & 3 g/l nonionic softener (e) 1.5 g/l citric acid & 3 g/l cationic softener (f) 1.5 g/l acetic acid & 3 g/l non-ionic softener, (g) 1.5 g/l acetic acid & 3 g/l cationic softener.

Figure 4. Fabric CIE whiteness Index analysis with 1.5 g/l Acid & 3 g/l Softener treatment.
influence on the whiteness index the reading is 144.67 and 140.1 for immediate and after conditioning. Similarly, citric acid and nonionic softener show a similar whiteness index of 145.69 and 140.5, respectively. While citric acid with the cationic softener the value was found to be 140.93 and 120.3, respectively. Moreover, acetic acid and nonionic softener give a whiteness index of 151 and 137.16, respectively. While acetic acid with cationic softener gives 145.61 and 125.85 whiteness index, respectively. The reason behind the lower CIE whiteness indexes after 30 days for all samples is due to the phenolic yellowing phenomenon. The oxides of nitrogen react with the fabric sample in a complex way to undergo yellowing. This complex chemical compound is yellow on a slightly higher pH medium. Under the atmospheric condition, pH slightly increases in the presence of moisture which accelerates the reaction. Since the yellow compound forms CIE whiteness rating which also goes down.

3.4. pH analysis

Fabric core pH was analyzed with the standard AATCC 81 (2012) test method. The samples were cut into small pieces according to the method and boiled at 80 °C in distilled water to have an aqueous extraction for the pH measurement. The results are shown in Figure 5. Acetic acid has the least neutralization performance means more pH reading as compared to all three dosages. In contrast, the complex acid has the lowest pH reading in all concentrations which is the outcome of better neutralization. Similarly, citric acid also shows a good neutralization behavior. The core pH of the fabrics with 1.5 g/l acid treatment was found to be 6.68, 6.15, and 5.13, respectively for acetic acid, citric acid, and complex acid. The samples were stored for one month in atmospheric conditions to analyze the pH variation effect. Repeated testing after one month depicted a slightly increased pH reading for all samples meaning that atmospheric conditions had some impact on the sample which was mainly caused by humidity. Under the atmospheric conditions, the presence of humidity caused slightly increased pH. This happens due to the presence of residual alkali in the fabric reacting with the acids in the presence of moisture and produces sodium salt of that respective acid which is the main reason for the increased pH. The acetic acid reacts with caustic soda produces sodium acetate, similarly citric acid produces sodium citrates, and commercial acid produces sodium sulfate. Since all these three salts have slightly alkaline pH, hence the fabric pH increases accordingly. After conditioning of the sample, complex acid-treated fabric shows a pH value of 5.25, citric acid shows a pH value of 6.61, and acetic acid shows a pH value of 7.20. Analyzed data depicts that acetic acid-treated samples have a slightly increased pH phenomenon while complex acid has the least.

3.5. Phenolic yellowing test

Assessment of phenolic yellowing of the treated samples were carried out according to the standard method of ISO 105- X18 (2007). According to the testing method, a maximum of six samples can test once at a time. Due to the number of samples, several tests were needed
for complete testing. Standard testing conditions of 50 °C for 16 h were maintained accordingly. Once the testing was completed, the samples were assessed using the greyscale (James heal, UK), and specific ratings had done separately. All the test results are represented in Figure 6, Figure 7, Figure 8, and Figure 9. Nonionic softener & complex acid gives the best (4–5) rating in all concentration of acid. While acetic acid and cationic softener have the worst rating of 2 for even maximum dosage of acid and minimum dosage of softener. However, citric acid performs a good rating (4–5) with nonionic softener and moderate for cationic softener in all concentrations. One common phenomenon found for all samples that better phenolic yellowing rating with the increased acid concentration was the outcome of proper core neutralization. Repeated testing after conditioning for one month gave a lower rating in all cases.

Acetic acid is a volatile substance and comparatively weak organic acid. In contrast, citric acid is not a volatile one like the commercial complex acid. The volatility of acetic acid leaves the fabric surface in insufficient neutralization compared to the citric and complex acid. Besides, the cationic softener would create a yellow complex reacting group with the BHT which be visible after testing. pH act as a catalyst for any
of any colorant to resist fading under specific wavelengths and leads to yellowing. Lightfastness is the photo-chemical process that resists the chemical reaction, here also higher pH accelerated the yellowing phenomenon. On the other hand, the nonionic softener does not have an active positive site, so it cannot create a yellow complex by reacting with the BHT. Since the complex acid is an inorganic sulfuric acid complex that gives the best core neutralization and least yellowing, the phenolic yellowing testing was repeated once after the conditioning time was completed. Test results showed that all the samples had a slightly lower rating compared to the immediate one. Such phenomenon found severe for cationic softener in contrast to nonionic.

### 3.6. Bursting strength test

Bursting strength is a tensile testing phenomenon to test the capability of fabric to withstand rupture against applied pneumatic pressure. Under the subjected pressure load, the fabric begins to expand in all directions when the limit exceeds getting to be burst. Bursting strength tested for 1.5 g/l acid and 3 g/l for softener treated samples. In Table 1, the results depict that all the three acids have almost similar readings means the neutralization and finishing process does not affect the tensile strength phenomenon. All the tests were repeated five times and the average is taken as the result is calculated automatically by the machine.

### 3.7. Lightfastness test

The unsaturated structure of OBA absorbs ultraviolet and violet radiation at 340–370 nm and it re-emits the absorbed light (shorter wavelength) to visible blue light (longer wavelength) at 420–470 nm. This unsaturation is very sensitive to sunlight and loses its ability to work and leads to yellowing. Lightfastness is the photo-chemical process of any colorant to resist fading under specific light exposure. The samples were exposed for a specified time according to the standard method and results were assessed with the help of greyscale. In Table 2, a similar lightness rating was found for all three types of acid treatment (1.5 g/l). So, it can be concluded that neutralization & softening does not adversely impact the lightfastness rating of the samples.

### 4. Conclusion

Processing chemicals and finishing auxiliaries play a vital role in the phenolic yellowing phenomenon. In addition, atmospheric pollutant also has a major influence on such types of yellowing. Such types of yellowing are the synergistic outcome of these factors. Similarly, core pH and CIE whiteness index were also influenced by these variables. With the increase of acid dosing, core pH consistently goes down. Non-volatile inorganic complex acid gives the best core neutralization while volatile organic acetic acid performs the least. Cationic softener greatly impacts the CIE whiteness index and phenolic yellowing for both cases of testing in contrast nonionic softener performs the best rating. FT-IR spectrum reveals the characteristic chemical functional groups for all sample types. Lightfastness rating & bursting strength are not greatly affected by these chemical treatments. Finally, we found that nonionic softener & commercial complex acid has good performance considering the variables.

### Table 1. Bursting strength test.

| Sample types                      | Bursting strength (kPa) |
|-----------------------------------|-------------------------|
| Complex acid & cationic softener  | 360.5                   |
| Citric acid & cationic softener   | 363.8                   |
| Acetic acid & cationic softener   | 365.9                   |
| Complex acid & nonionic softener  | 360.1                   |
| Citric acid & nonionic softener   | 363.4                   |
| Acetic acid & nonionic softener   | 365.2                   |

### Table 2. Lightfastness test.

| Sample types                      | Lightfastness rating |
|-----------------------------------|----------------------|
| Complex acid & cationic softener  | 3.4                  |
| Citric acid & cationic softener   | 3.4                  |
| Acetic acid & cationic softener   | 3.4                  |
| Complex acid & nonionic softener  | 3.4                  |
| Citric acid & nonionic softener   | 3.4                  |
| Acetic acid & nonionic softener   | 3.4                  |

### Declarations

**Author contribution statement**

Md. Salauddin Sk: Conceived and designed the experiments; Performed the experiments; Wrote the paper and address reviewer comments.

Rony Mia: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Bulbul Ahmed: Analyzed and interpreted the data; Wrote the paper.

Atiqur Rahman: Performed the experiments; Analyzed and interpreted the data.

Md. Mostafizur Rahman Palash: Performed the experiments.

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**Data availability statement**

Data included in article supp. material/referenced in article.

**Declaration of interests statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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