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An Approach towards a Single Pretreatment Recipe for Different Types of Cotton

Abstract
Pre-treatment (preparation) of cotton fabrics constructed from different grade cotton fibres with variable physicochemical properties using a single recipe to yield single results was investigated. The differences in fabric whiteness index and the reactive colour strength arising from these different grade cotton fibres were also examined. Thus, five cotton substrates with different characteristic properties were individually subjected to various pre-treatments processes followed by H_2O_2 bleaching. These pre-treatments include conventional scouring, reductive scouring (using D-glucose in a scouring bath), oxidative scouring, acidic pectinase scouring, alkaline pectinase scouring, and acidic demineralisation after scouring, or in combination with desizing (using D-gluconic acid) and grey mercerisation. For the other set of samples, mercerisation and cationisation were carried out after peroxide bleaching. The latter was conducted using the pad-steam technique. The fabrics were monitored for W.I after bleaching, K/S after dyeing, the degree of polymerisation, Eisenhute's tendering factor, the residual wax content as well as the tensile strength and elongation at break. The results obtained show that the most effective pre-treatment processes which reduce the differences in both the whiteness index and the depth of colour (upon reactive dyeing) among bleached and dyed cotton are the following: reductive scouring of cotton fabric using D-glucose along with sodium hydroxide, acidic demineralisation with D-gluconic acid and acidic pectinase scouring. It was also found that pre-treating the cotton fabrics with reductive scouring largely reduces the oxidation of cotton cellulose when boiling off the alkalis.

Key words: *bleaching, cationization, cotton fabric, dyeing, pectinase, pre-treatments, scouring.*

■ Introduction

Cotton cellulose has excellent properties such as higher water absorbency and moisture, and is comfortable to wear and easy to dye. For these reasons, the apparel industry is predominantly cotton-based, and the share of cotton in total fibre consumption is about 50% [1]. In the last two decades, and thanks to the GATT agreement and the open market, cotton and textile mills, in particular the pre-treatment, dyeing and finishing sectors, find themselves dealing with cotton fabric made of different cotton fibres of different origins and with different qualities, physical and chemical properties. After pre-treatment, bleaching and/or dyeing, problems of uneven whiteness or colour shade arise. This imposes great demands on the pre-treatment manager in a textile finishing plant. The latter has neither the possibility nor the time to classify the fabrics according to the fibre characteristics and then to handle each category in accordance with a specially adopted pre-treatment process. Such difficulty is observed irrespective of the production line, batchwise or continuous line, but the problem is undoubtedly much more difficult to handle in a continuous line compared with a batchwise line.

The aim, and indeed the need, is to prepare these different grades of cotton at low cost and with environmentally safe processes using (as far as possible) a single formulation to produce identical results and achieve the goal of 'Right first time, Right every time and Right on time'.

Cotton is composed almost entirely of cellulose (88.0 – 96.0%, based on weight of fibres). Impurities in cotton fibre range from 4 to 12% (owf). The overall composition of raw cotton fibres depends on the type, origin, fibre maturity, weathering and agricultural conditions [1 - 6]. Impurities include protein (1.0 – 1.9%), wax (0.4 – 1.2%), ash (inorganic salts) (0.7 – 1.6%), pectin (0.4 – 1.2%) and others (resins, pigments, hemi-cellulose) (0.5 – 0.8%) [3 - 8]. In addition to this, mechanically-held impurities called 'motes' containing seed-coat fragments, adhered seeds, stem parts, and leaves that cling to the fibres are present. Apart from these, the loom-state fabric is also contaminated with processing lubricants, such as machine oils, tars, and greases from harvesting, ginning, spinning and weaving (or knitting) [1].

Excessive levels of seed coat fragments and trashy non-fibrous materials found in ginned bales are usually removed by opening, cleaning and carding. Therefore, their influences on the finished yarn's quality are minimised. However, other impurities are essentially unaltered during processing. Unless the fabric is uniform in whiteness, absorbency and chemical composition, and also has low levels of impurities, it is unlikely that it will take up dye or finish consistently to the maximum possible extent [1].

With the exception of natural colouring matters, which can be removed by bleaching using certain oxidants, many other impurities are removed by alkali treatment at the scouring stage. In common practice the latter involves boiling the cotton in sodium hydroxide (2-5%) for 1 hour [1, 2, 9]. The action of alkaline scouring saponifies any residual oils, neutralises carboxylic acids in the pectic substance leading to its dissolution, and dissolves any sizing material, as well as causes the dispersion of naturally occurring impurities in the natural fibre. In addition to this, sodium hydroxide reacts with motes and immature or dead cotton (low-crystallinity cellulose). Motes swell in alkali to form sodium cellulosates which tend to become softened, and are thus susceptible to easier bleaching or rinsing-off [6, 9].

Cotton bleaching with hydrogen peroxide is a well-established process in the textile industry [6]. However, the level of metals can vary considerably as a function of type and origin by a factor of eleven [3, 7, 8]. After peroxide bleaching, such differences give rise to completely different results. For this reason, the heavy metals must to a large extent be removed before peroxide bleaching in order to reduce the differences between the different grades of cotton. Optimisation of bleaching conditions, typically through the use of high temperature and pH values or an extended reaction time for cotton fabric constructed from different types of cotton fabric leads to unacceptable results. This is because the conditions required to produce good results for one fibre may be damaging to another.

A previous report described the coverage of immature cotton neps in dyed fabric using chitosan after-treatment [10]. However, to the author's knowledge there is no work in the literature describing the coverage of difference in the whiteness index or the colour shade arising from different grades of cotton fibres.

The current study is aimed essentially at covering the differences in fabric whiteness index and dyeing shade arising from different cotton fibre types. To achieve this goal, cotton fabric constructed from different types of cotton fibre is subjected to different pre-treatment processes and/or formulations with a view to determining the best pre-treatment formulations that can be applied to cotton fabrics and covering the differences in whiteness index and colour shade arising from different fibre quality, without fibre deterioration. In this regard, current modified recipes as well as a new approach to pretreatment and bleaching were undertaken. The modified pre-treatment process includes reductive scouring, oxidative scouring, enzymatic scouring, cationisation prior to dyeing, and grey mercerisation, whereas the new approach includes acid demineralisation prior to bleaching. The bleached fabric was monitored for the degree of polymerisation (*DP*), Eisenhute's tendering factor, whiteness and yellowness indices, residual wax content, tensile strength and elongation at break. The reactive dyed fabrics were evaluated for *K*/*S* after soaping.

■ Experimental

Materials

Cotton fabric and chemicals
Five different samples from greige 100% woven cotton fabrics were supplied by the El-Naser Company for Spinning, Weaving and Dyeing, Mehala El-Kubra (Egypt). All the samples had the following identical weaving construction: plain weave, warp 36 yarn/cm, weft 30 yarn/cm, fabric weight, 150 g/m². The samples had different physical properties, as indicated in Table 1. Chemical analysis carried out on the greige fabric showed that the fabric warps were sized with a starch-based sizing agent.

Sodium hydroxide, sodium carbonate, sodium chloride, sodium sulphate, ammonium persulphate, potassium peroxydiphosphate, acetic acid, gluconic acid, and D-glucose were of laboratory grade chemicals. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) (69%) of technical-grade chemicals was kindly supplied under the commercial name CR-2000 by Dow

Chemical Company, USA. Viscozyme L 120 apsu/g (acidic pectinase) and Bioprep L 3000 apsu/g (alkaline pectinase) from the Novo Nordisk BioChem Inc. [1 (apsu/g) unit is the amount of enzymes which catalysed the decrement in viscosity of 1% (w/v) pectin solution by 20% in 5 min at pH 3.4 and 25 °C] [11]. A nonionic wetting agent based on an ethylene oxide condensate (Egyptol®) and an anionic wetting agent (Espycon®) from Starch and Yeast Co., Alexandria (Egypt) were used. Hydrogen peroxide (50 wt.-%), a sodium silicate solution 48° Be', organic stabiliser, amylase enzyme and Sunzol Brilliant Red BB (C.I. Reactive Red 21) were chemicals of technical grade.

Methods

Desizing
Greige 100% cotton fabrics (100 g) were desized by padding the fabric in a solution containing diastase enzyme (2 g/l), sodium chloride (1 g/l), acetic acid (1 g/l), Egyptol® (4 g/l) and Espycon® (2 g/l). The samples were then squeezed to a wet pick up of 100% and stored at room temperature for 8 hrs. The samples were washed several times with hot water, then with cold water, and next dried in ambient conditions.

Scouring
Two techniques currently used by the industry were investigated for scouring the desized cotton fabric, exhaustion and pad-steam. In the exhaustion technique, 100 g of desized cotton fabric was treated with an aqueous solution containing NaOH (6 g/l), Egyptol® (2 g/l) and Espycon® (1 g/l) using a material to liquor ratio (LR) of 1 : 50 at 95 °C for 30 min. In the pad-steam technique, the samples were padded in an aqueous solution containing NaOH (40 g/l), Egyptol® (2 g/l) and Espycon® (1 g/l), then squeezed to a wet pick- up of 100%. The samples were then steamed for 30 min in a sealed stainless steel cup at 100 °C to avoid dryness. After scouring by either of the two techniques, the samples were washed several times with boiling water and cold water, and finally dried in ambient conditions.

One-step desizing and scouring (oxidative scouring)
In combined desizing and scouring, two techniques were used, pad-steam and cold pad-batch. The experimental technique adopted was as follows: 100 g of greige cotton fabric was padded in an aqueous solution containing NaOH (40 g/l), Egyptol® (4 g/l) and Espycon® (2 g/l) potassium peroxydiphosphate ($K_2P_2O_8$) (0.5 g/l). The samples was then squeezed to a wet pick-up of 100% and stored in s sealed stainless steel cup at 100 °C for 45 min. For those samples treated with the cold pad-batch, ammonium persulphate (2 g/l) was used instead of potassium peroxydiphosphate and the samples were aged in closed polyethylene bags at room temperature for 24 hrs. After the completion of the required time, in both cases the samples were washed several times with hot water, then with cold water and finally dried in ambient conditions.

Reductive scouring
Reductive scouring was carried out in the same way as the formulation and procedures employed in conventional scouring. The difference was the addition of 20 g/l or 5 g/l D-glucose (as a mild reducing agent) to the scouring formulation of the pad-steam or the exhaustion technique respectively.

Enzymatic scouring
Two kinds of enzyme were used independently to effect bio-scouring: Viscozyme L 120 apsu/g (acidic pectinase) and Bioprep L 3000 apsu/g (alkaline pectinase). The bio-scouring conditions as recommended by the supplier were as follows: amylase desized cotton swatches (20 × 20 cm) were first sewn around the edges to prevent unravelling during the treatments. The samples were then treated with enzymes in an agitation system (a laboratory-scale washing machine with 3 l capacity, circulating the liquor solution horizontally at 30 ± 2 rpm) at pH 4.5 (adjusted using a 0.1 M acetate buffer) for Viscozyme L 120,

Table 1. Major properties of cotton fabric under investigation and their statistical deviation; (a) R = Range, M.D = Mean deviation; V.C = Variance coefficient, (b) Wax content was determined after enzymatic desizing, (c) Tensile strength and elongation at break was measured on loom state fabrics.

Fabric Property	Substrate number					Statistical analysis (a)		
	I	II	III	IV	V	R	M.D	V.C
DP	3200	3090	3120	3070	3010	190.0	177.6	2.25
Wax (%)b	0.35	0.37	0.39	0.41	0.43	0.08	0.02	8.1
W.I	12.74	10.40	-5.30	-7.66	-11.61	24.35	47.1	3862
Y.I	1.46	2.33	2.58	5.62	21.17	19.71	6.98	124.85
T.S (kg.F)c	43	44	43	42	42	2.0	0.64	1.96
Elon. (%)c	15	16	16	17	16	2.0	0.40	4.42

or at pH 8 (adjusted using a 0.1 M phosphate buffer) for Bioprep L 3000. The liquor ratio adjusted at 1 : 50. The enzyme concentration was 2 g/L and the treatment time was 1 hour. Incubation temperature varied according to the enzyme used; for Viscozyme the temperature was adjusted to 40 °C, whereas for Bioprep L the temperature was adjusted to 55 °C. After the enzymatic treatment, the fabrics were washed twice in boiled water for 5 min each in order to deactivate the enzyme. Finally the fabric was washed with cold water and dried in ambient conditions.

Acid demineralisation

Acidic demineralisation treatments of tested cotton fabric were conducted either in combination with enzymatic desizing or separately in washing liquor before the H_2O_2 bleaching process. The combined enzymatic desizing and acidic demineralisation was performed by adding 15 g/l D-gluconic acid to the amylase desizing formulation (indicated above). A separate step for acidic demineralisation of cotton sample was performed by washing the desized and scoured cotton samples in an aqueous solution containing 5 g/l D-gluconic acid at 60 °C for 20 min using a liquor ration of 1:50. The sample was then washed with water, and submitted to the H_2O_2 bleaching process.

Bleaching

Similar to scouring, two techniques were used to affect bleaching, namely exhaustion and pad steam. In the exhaustion method, scoured cotton fabrics were treated with an aqueous solution containing H_2O_2, (6 g/l of pure H_2O_2 or 12 g/l of 50% H_2O_2 solution), sodium silicate (2 g/l), organic stabiliser (1 g/l). The pH was adjusted to 10.5 using an aqueous NaOH solution. A material to liquor ratio of 1 : 50 was used, and the bleaching process was carried out at 95 °C for 45 min. The fabric was then washed several times with boiling water, then with cold water and finally dried in ambient conditions. In the pad-steam method, the fabric samples was padded in a solution containing H_2O_2 (15 g/l of pure H_2O_2) and sodium silicate (5 g/l) at pH 10.5 (adjusted by NaOH). The fabric was then squeezed to a wet pick-up of 100% and stored in a sealed stainless steel cup at 100 °C for 45 min. After bleaching, the sample was washed several times with hot water, then with cold water, and finally dried in ambient conditions.

Mercerisation

To carry out mercerisation on grey and bleached fabric, all the samples under investigation were sewn together and mercerised on an industrial-scale chainless mercerising machine built at the El-Naser Company for Spinning, Weaving and Dyeing, Mehala El-Kubra (Egypt). The NaOH concentration was kept constant at 28%. The samples were washed several times with hot water, then with cold water and dried in ambient conditions.

Cationisation of scoured and bleached cotton fabric

Scoured, or scoured & bleached cotton fabrics were cationised using the cold pad-batch method. The experimental procedure adopted was as follows: 100 g/l from 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) (69%) (CR-2000) was mixed in a solution with 40 g/l sodium hydroxide. 50 g of bleached cotton fabric was padded through this mix and squeezed to a wet pick-up of 100%, then batched at room temperature overnight in a sealed plastic bag. At the end, the fabric samples were washed with cold water and 1% acetic acid, then washed several times with cold water and finally dried in ambient conditions.

Dyeing

The bleached samples under investigation were dyed using Sunzol Brilliant Red BB (C.I: Reactive Red 21). The procedures adopted was as follows: 0.25 g of the dye was dissolved in 1000 ml of water along with 20 g Na_2SO_4 (half the amount of salt) at room temperature. The fabric sample was then introduced into this dye solution, keeping the liquor ratio (LR) at 1 : 100 (in this case, the dye shade is 2.5% based on the weight of fabric). After 10 minutes, the second half of the salt (20 g/l) was added. The temperature was gradually raised to 60 °C over 10 min. Then, during the next 30 min, the required amount of sodium carbonate (20 g/l) was added in three stages. The dyeing process was continued for another 45 min, and then the sample was washed in an aqueous solution containing 5 g/l soap at 100 °C for 15 min. Finally the sample was washed with cold water. Cationised cotton fabrics were subjected to salt-free dyeing using the same dye, and using similar procedures, except neither the alkali nor the salt was added.

Testing and analysis

The degree of polymerisation (DP) of 100% cotton fabric was measured according to the method reported in [12]. Eisenhute's tendering factor (T.F) of the bleached fabric was calculated as follows:

$$T.F = \frac{1}{\log 2} \cdot \log\left[\frac{2000}{DP_X} - \frac{2000}{DP_{tx}} + 1\right] \quad (1)$$

where: DP_x = DP value after bleaching, DP_{tx} = DP value of grey fabric (untreated)

The residual wax content of the sample was determined according to the method reported in [13]. The known weight of the fabric sample was Soxhlet-extracted using tetrachloroethylene solvent for 6 hours. The percentage loss in fabric weight after extraction represents the residual wax content of the fabric.

Wettability was assessed in terms of drop disappearance, measured by allowing a drop of water to fall on the sample, and recording the time required for the drop to disappear [14].

Residual starch on fabric was determined according to the method reported in [15].

Tensile strength and elongation at break were determined according to the ASTM standard test method [16].

The degree of the fabric sample's whiteness, expressed as a whiteness index, was measured according to the reported method [17].

The colour strength (expressed as K/S value) of the dyed fabric samples before and after DMF extraction was measured using a I.C.S Texicon spectrophotometer (England). The K/S value was determined by the Kubelka-Munk equation [18].

The nitrogen content of the cationised samples was determined by the Kjeldhal method [19]. The fixation percentage ($F\%$) was calculated according to the Equation 2.

Statistical measure of dispersion

The values of each property obtained before and after treatment were statistically analysed in order to validate each pre-

$$F\% = \frac{Amount\ of\ nitrogen\ fixed\ (detected)}{Total\ amount\ of\ nitrogen\ of\ CHTAC\ applied} \times 100 \quad (2)$$

Equation 2.

treatment process in covering the difference in fabric characteristics among all the substrates under investigation; especially, the degree of whiteness (*W.I*) and the colour strength (*K/S*). In our study, the dispersion measures include range (*R*), mean deviation (*M.D*) and variance coefficient (*V.C*). These parameters are defined by Equations 3 - 5. The, range (*R*):

$$R = X_H - X_L \qquad (3)$$

where X_H is the higher value, and X_L is the lower value.

Mean deviation

$$M.D = \frac{\sum_{i=1}^{n} \left| X_i - \overline{X} \right|}{n} \qquad (4)$$

Variance coefficient

$$V.C = \frac{S}{\overline{X}} \times 100 \qquad (5)$$

where:

S = Standard deviation

$\overline{X}$ = Arithmetic mean value

■ Results and discussion

Preliminary investigation

At the outset, preliminary investigations were undertaken to elucidate the effect of different pre-treatment processes on the difference in the whiteness index (*W.I*) and colour strength (*K/S*) between bleached and dyed cotton substrates. Thus five cotton substrates with different characteristic properties (Table 1) were individually subjected to various pre-treatment processes followed by H_2O_2 bleaching. These pre-treatments included conventional scouring, reductive scouring, oxidative scouring, acidic pectinase scouring, alkaline pectinase scouring, acidic demineralisation after scouring combined desizing and demineralisation and grey mercerisation. For the other set of samples, mercerisation and cationisation were carried out after bleaching. The latter were conducted using the pad-steam technique, and the formulation was kept constant for all substrates. The fabrics were monitored for *W.I* after

bleaching and for *K/S* after being dyed with Sunzol Brilliant Red BB (C.I: Reactive Red 21). The suitability of each pre-treatment process in covering the difference in degree of whiteness (W.I) and colour strength (K/S) between all the substrates under investigation (five cotton substrates in our case) was determined by calculating the range (R), mean deviation (M.D) and variance coefficient (V.C) of the W.I and K/S values after each treatment. These parameters were defined previously by Equations 3-5, and the results obtained are set out in Tables 2 and 3. The results obtained with conventionally-treated samples, along with that of greige (untreated) fabric, are also set out in the same Tables for comparison.

The results of Tables 2 and 3 depict the following:

1. The loom state cotton substrates under investigation show a wide range of *W.I* values. as indicated by the higher magnitude of deviation parameters. Both the range (*R*), mean deviation (*M.D*) and

Table 2. *Effect of pretreatment conditions on W.I. and K/S of cotton substrate bleached as per pad-steam method;* [a] *All cationized cotton samples under investigation shows approximately identical nitrogen content amounted 0.24 % and the fixation percent equal 50%. These samples were subjected to no-salt, no alkali dyeing. Scouring and bleaching were carried as per pad-steam technique.*

Treatments	No	Substrate No.									
		I		II		III		IV		V	
		W.I	K/S	W.I	K/S	W.I	K/S	W.I	K/S	W.I	K/S
Blank (loom-state)	G	12.74	-	10.40	-	-5.30	-	-7.66	-	-11.61	-
Conventional desizing, scouring and bleaching	1	78	6.84	71	7.37	69	7.53	65	7.55	63	7.59
Reductive scouring	2	85	6.50	85	6.51	84	6.52	83	6.50	83	6.53
Oxidative scouring	3	86	6.13	80	6.45	77	6.49	73	6.52	68	6.52
Acidic pectinase scouring	4	85	6.50	84	6.51	81	6.52	82	6.53	82	6.53
Alkaline pectinase scouring	5	83	6.63	75	6.67	73	6.68	70	6.71	67	6.73
Acid demineralization after scouring	6	86	6.61	85	6.62	85	6.63	84	6.65	84	6.64
Combined desizing and demineralization	7	85	6.61	85	6.61	84	6.63	84	6.65	83	6.64
Mercerization after bleaching	8	78	9.55	72	9.55	69	9.59	65	9.61	65	9.61
Grey mercerization	9	75	9.29	71	9.29	69	9.30	69	9.35	61	9.35
Cationization after bleaching [a]	10	70	17.31	69	17.33	65	17.35	65	17.33	61	17.35

Table 3. *Effect of pretreatment conditions on statistical deviation in W.I and K/S of bleached and dyed cotton substrate;* [a] *R = Range, M.D = Mean deviation; V.C = Variance coefficient.*

Treatments	No	Statistical analysis [a].					
		W.I			K/S		
		R	M.D	V.C	R	M.D	V.C
Blank (loom-state)	G	24.35	47.1	3862	-----	------	------
Conventional desizing, scouring and bleaching	1	15	4.24	5.6	0.75	0.22	4.2
Reductive scouring	2	2	0.8	1.19	0.03	0.01	0.2
Oxidative scouring	3	18	5.04	3.6	0.39	0.12	2.5
Acidic pectinase scouring	4	4	1.36	1.98	0.03	0.029	0.11
Alkaline pectinase scouring	5	16	4.32	8.23	0.1	0.029	0.58
Acid demineralization after scouring	6	2	0.64	0.987	0.04	0.014	0.27
Combined desizing and demineralization	7	2	0.64	0.987	0.04	0.014	0.27
Mercerization after bleaching	8	13	4.16	7.8	0.06	0.026	0.32
Grey mercerization	9	14	3.2	7.3	0.06	0.028	0.34
Cationization after bleaching	10	9	2.8	5.46	0.04	0.012	0.10

variance coefficients amounted to 24.35, 47.1 and 3862 respectively.

2. Conventional scouring and bleaching of the cotton substrates under investigation affect the differences in W.I values among all five substrates only weakly. This was evidenced by the lower decreases in the magnitude of range (R), mean deviation (M.D) and variance coefficient (V.C) from 24.35, 47.1 and 3862 to 15, 4.24 and 5.6 respectively. The same holds true for the colour strength of the reactive dyed samples, where the magnitude of R, M.D and V.C calculated from K/S values amounted to 0.75, 0.22 and 4.2 respectively. These outstanding higher statistical dispersion measures of W.I and K/S among all the substrates indicate that conventional scouring and bleaching failed to cover the differences in W.I and K/S among all the bleached and dyed substrates arising from the diff-erent fibre qualities.

3. Similar results were obtained when cotton substrates were subjected to oxidative desizing before bleaching. Although oxidative desizing enhances the W.I of all the substrates under investigation compared with the conventional pre-treatment process (Table 2), it failed to decrease the difference in W.I after bleaching or K/S after reactive dyeing.

4. Alkaline pectinase scouring before bleaching decreases only the differences in K/S values among the dyed samples, compared with those substrates which were conventionally pre-treated and then similarly dyed. It is further observed that the magnitude of R, M.D and V.C values calculated from K/S values decreases from 0.75, 0.22 and 4.2 in conventional pre-treatment samples to 0.1, 0.029 and 0.58 respectively, on using alkaline pectinase scouring before bleaching. However, alkaline pectinase scouring also failed to cover the differences in W.I between all substrates, where the calculated values of R, M.D and V.C for W.I remained as high as 16, 4.32 and 8.23 respectively.

5. Reductive scouring using glucose and NaOH followed by H_2O_2 bleaching decreases the difference in W.I among the bleached cotton substrates. The calculated values of R, M.D and V.C decrease to 2, 0.8 and 1.19 respectively. The same holds true for colour strength of dyed samples, where the magnitudes of R, M.D and V.C values were much lower and amounted to 0.03, 0.01 and 0.2 respectively. This indicated a higher uniformity in colour strength among all the dyed substrates. Similar results were also

obtained when the cotton substrates under investigations were subjected to one of the following pre-treatments before bleaching and/or dyeing: acidic pectinase scouring, acidic demineralisation after scouring, combined desizing and demineralisation.

6. Both mercerisation after bleaching and grey mercerisation before bleaching enhance the K/S of the dyed samples, and decrease the difference in colour strength among all the dyed substrates. The results in Table 3 show that the magnitude of R, M.D and V.C values decreases to 0.06, 0.026 and 0.32 respectively. Although the improvement in the colour yield of cotton fabric after mercerisation is a well-known phenomenon, the decrements in the variance coefficient (V.C) of all five dyed substrates to 0.32, compared with 4.2 obtained with conventional pre-treatment, is quite promising. The results in Table 3 also show that both mercerisation and grey mercerisation have little influence on covering the differences in W.I between all the five substrates under investigation, and that the magnitude of V.C values remains as high as 7.8 and 7.3 respectively. Greige cotton fabric contains a substantial amount of immature (dead) fibres depending on its type and origin [1, 6, 9]. The dead fibres are underdeveloped, and appear as flat or slightly twisted tapes. They are non-crystalline, convolutions are sometimes absent, the cell walls are extremely thin and the lumen is collapsed [1], and so they do not acquire dye to the same extent as matured fibres. Mercerisation or grey mercerisation dissolves and removes immature (dead) fibres, leading to a level dyeing effect on the cotton fabrics. Different cotton substrates would have different amounts from dead cotton, which on removing by mercerisation improves not only the colour yield but also decreases the percentage difference in K/S between the dyed substrates. On the other hand, immature cotton did not contribute to the yellowish or creamy colour of the greige cotton fabric, either before or after bleaching. This would account for the small effect of mercerisation or grey mercerisation on the difference in W.I among all the samples after bleaching.

7. Cationisation of bleached cotton fabric is another tool that has recently been employed to enhance the dyeing properties (especially in no-salt dyeing) of cotton fabric [20 - 23]. In our study, the cotton fabric was cationised with 3-chloro-2-hydroxy-propyl trimethyl ammonium chloride (CHTAC) in a strong alkaline

medium. The quaternary ammonium group $-^{\oplus}N(CH_3)_4$ has a very high positive charge, and can thus lead to the formation of ionic bonds (salt linkages) with negatively-charged anionic groups, such as those found in a wide array of anionic dye classes. The results in Tables 2 and 3 make it clear that the cationisation of conventionally bleached cotton fabrics is a powerful tool which can cover the difference in colour shades arising from different cotton types. The results also show that the magnitude of V.C calculated from the K/S values of all the dyed substrates does not exceed 0.1 when these samples were cationised and then dyed in the reactive salt-free, alkali-free method. However, cationisation did not completely cover the difference in W.I between all the substrates under investigation, and the magnitude of V.C remains as high as 5.6.

The increasing cost of chemicals, water, machinery, labour, effluent control and the recovery of caustic soda make the process of mercerisation and cationisation less attractive ways of solving the problem. Moreover, the two treatments failed to cover the differences in W.I. Therefore, it could be assumed from Tables 2 and 3 that the most appropriate methods to cover the differences in W.I after bleaching or in K/S after reactive dyeing all the cotton substrates under investigation were the following: reductive scouring, acidic pectinase scouring, and acidic demineralisation (conducted either after scouring or in combination with the desizing formulation). Fabrics pre-treated with this method are characterised in detail below. It should be mentioned here that both acidic demineralisation after scouring and in combination with desizing formulation gives identical results. Therefore, in subsequent investigations we shall deal with acidic demineralisation after scouring.

Reductive scouring vis-à-vis conventional scouring

During the kier boiling of cotton-based fabrics, a sodium hydroxide solution can form oxycellulose in the presence of oxygen. Traditionally, oxygen is removed from the kier before scouring starts, but even a small quantity of air entrapped in the fabric layers may cause fabric tendering. A recently developed technique involves adding a small amount of reducing agent such as sodium bisulphite, sodium hydrosulphite, and thioureadioxide to the kier formulation to prevent the oxidation of cellulose during the scouring operation. In our study, we

have chosen D-glucose as a mild reducing agent in an alkaline medium in the scouring formulation. This is because D-glucose is much safer for the environment and commercially available on the local market.

Under the scouring conditions, D-glucose is converted by the occluded (entrapped) oxygen into D-gluconic acid. The latter indeed adduces several benefits to the scouring and bleaching process. It removes heavy metal contaminants from cotton fabric by forming soluble and stable complexes with metal cations over a wide range of pH [3, 7]. Another benefit is that D-glucose converts metal cations to a lower oxidation state (valances); this in turn facilitates complexing and increases the solubility of metal cations in liquor. Removing metal cations from cotton fabric prevents the catalytic degradation occurred by these cations during H_2O_2 bleaching. As mentioned previously, cotton fabric may have different amounts of heavy metals cations depending on its type, origin and quality. These metal impurities catalytically accelerate the decomposition of H_2O_2, leading to unaccepted whiteness; at the same time, the differences in W.I among different cotton substrates increase depending on the amount of metal cations in each substrate.

Table 4 summarises the major properties and statistical deviations of cotton substrates traditionally scoured and with bleaching, whereas Table 5 summarises the same properties when the samples were reductive-scoured with glucose/NaOH before peroxide bleaching. The properties include total loss in fabric weight, degree of polymerisation (DP), Eisenhute's tendering factor (T.F), residual starch (R.S), residual wax content, yellowness index (Y.I), retained tensile strength (R.T), and elongation at break. Statistical deviation measures included R, M.D and V.C.

The results of Table 4 are self-explanatory, and show that the percentage loss in fabric weight after bleaching change marginally according to the type of cotton substrate, ranging from 5.7% to 6.3%. The results also show that the residual starch encountered with all cotton substrates ranged from 0.19% to 0.17%, which lies within the acceptable range [1]. The most important features observed in the results in Table 4 is the degree of polymerisation (DP) of bleached fabric and Eisenhute's tendering factor (T.F) as calculated thereof. The magnitude of R, M.D and V.C calculated from the DP values of all cotton substrates amounted

to 95, 21.5 and 2.2 respectively, whereas those encountered with T.F were equal to 0.4, 0.014 and 5,03 respectively. Keeping in mind that the same bleaching recipes were employed to bleach all substrates, the observed higher variance in T.F after bleaching would explain the rule of heavy metal cations contaminated with each substrate in tendering cotton cellulose that was brought about by the catalytically accelerated decomposition of H_2O_2 in the bleaching process. The results also showed that the retained tensile strength (R.T) of all the cotton substrates after bleaching varies according to the kind of substrate, and correlates to T.F where the higher the T.F is, the lower the retained tensile strength, and vice versa. It is further observed (Table 4) that the Y.I values of the conventionally bleached fabrics give rise to higher V.C values, and amounts to 20.8. Also, the residual wax percentage after bleaching is approximately similar, and amounts to 0.06%.

It could be shown from the results in Table 4 that although the conventional scouring and bleaching reduces the wax percentage and residual starch amount of all the cotton substrates promptly, the process needs further adaptation to reduce the excessive tendering of cotton cellulose and to cover the differences in W.I and Y.I after bleaching, and K/S after

reactive dyeing, among all the substrates under investigation.

Table 5 summarises the major properties of the bleached cotton substrates which underwent reductive scouring prior to peroxide bleaching. Table 5 features four main points:

i) the T.F values after bleaching were very comparable with all the cotton substrates and, at the same time, lower than that obtained with conventional scoured and bleached samples. The magnitude of V.C calculated from the T.F values decreases from 5.03 in the case of conventional scoured and bleached samples to only 0.9 when the reductive scouring using glucose/NaOH was conducted prior to H_2O_2 bleaching, which elucidates the effect of removing heavy metal cations from the cotton fabric before H_2O_2 on using D-glucose in the scouring bath to induce reductive scouring.

ii) The retained tensile strength (R.T%) of all cotton substrates after reductive scouring and bleaching were higher than those obtained with conventionally scouring and bleaching. At the same time, the magnitude of the V.C decreases from 3.9 for conventional pre-treated to 0.5 on using reductive scouring.

iii) The percentage loss in fabric weight and the residual wax of all the bleached

Table 4. *Deviation of major properties of conventionally desized, scoured and bleached cotton fabrics under investigation;* (a) *R = Range, M.D = Mean deviation; V.C = Variance coefficient, R.S = residual starch content, D.P = Degree of polymerization after bleaching, T.F = Eisenhute's Tendering Factor, Y.I= Yellowness Index, R.T = Retained tensile Strength, Elon. = Elongation at Break. Scouring and bleaching were effected as per pad-steam method.*

Fabric Properties	Substrate number					Statistical analysis (a)		
	I	II	III	IV	V	R	M.D	V.C
Weight loss, %	5.7	5.9	6.2	6.3	6.3	0.60	0.244	4.44
R.S, %	0.17	0.18	0.17	0.17	0.19	0.02	0.006	5.11
D.P	1725	1680	1710	1670	1630	95	21.5	2.20
T.F	0.61	0.63	0.62	0.63	0.65	0.04	0.014	5.03
Y.I	1.80	2.15	2.63	2.95	3.01	1.21	0.426	20.8
Wax, %	0.05	0.06	0.07	0.06	0.07	0.02	0.006	13.5
R.T, %	83.5	80.6	81.3	80.5	77.6	5.9	1.35	3.49
Elon., %	18	18	20	20	19	3.0	1.18	7.4

Table 5. *Deviation of major properties of bleached cotton fabrics under investigation after reductive scouring with glucose/NaOH;* **Remark:** *see Table IV.*

Fabric Properties	Substrate number					Statistical analysis (a)		
	I	II	III	IV	V	R	M.D	V.C
Weight loss, %	5.7	5.8	6.1	6.3	6.3	0.60	0.23	4.64
R.S, %	0.12	0.13	0.15	0.14	0.15	0.03	0.01	9.4
DP	1805	1750	1775	1740	1710	95	12.2	1.15
T.F	0.57	0.57	0.57	0.58	0.58	0.01	0.005	0.9
Y.I	1.10	1.55	1.35	1.50	1.55	0.45	0.17	13.48
Wax, %	0.05	0.05	0.07	0.07	0.07	0.02	0.26	112.5
R.T, %	93.7	94.5	93.7	93.21	93.5	1.29	0.32	0.51
Elon., %	17	16	18	18	19	3.0	0.88	6.48

cotton substrates are comparable with those conventionally scoured and bleached samples, which indicates that the additions of D-glucose to scouring formulation did not enhance or decline the removal of these impurities from cotton fabrics.

iv) The yellowness index, and the magnitude of the *V.C* calculated thereof, of all cotton substrates were lower in case of reductive scouring than that obtained with conventional scouring.

Based on the above, it may be concluded that adding 20 g/l D-glucose to the scouring formulation to induce reductive scouring prior to H_2O_2 bleaching improves the fabric performances and covers the differences in *W.I* arising from different kinds of cotton fibre in the fabric.

Acidic demineralisation before H_2O_2 bleaching

Table 6 summarises the major properties of cotton substrates demineralised with D-gluconic acid after scouring and before H_2O_2 bleaching. The results obtained were similar to that obtained previously with reductive scouring, and could be explained on a similar basis.

A comparison between the results obtained with reductive scouring (Table 5) and those obtained with acidic demineralisation before H_2O_2 bleaching would reveal that *T.F* is lower when the fabrics were reductively scoured than when these substrates were demineralised with acid before H_2O_2 bleaching. This was observed with all the cotton substrates under investigation. This may be attributed to the protective action of D-glucose to cotton cellulose during the scouring process.

Acidic pectinase scouring

The bio-preparation of cotton fabric is a valuable and environmentally-friendly alternative for preparing cotton to the harsh alkaline chemicals. Table 7 summarises the major properties of bleached cotton substrates pre-scoured with acidic pectinase using the exhaustion technique followed by H_2O_2 peroxide bleached using the pad-steam technique. The results in Table 7 signify that both the *DP* and retained tensile strength of the bleached cotton substrates were much higher than those obtained previously with reductive scouring or acidic demineralisation followed by bleaching. This was observed with all the cotton substrates under investigation. The same holds true for tendering factors (*T.F*), where their values are lower on using acidic pectinase scouring, compared with those obtained with reductive scouring or acidic demineralisation before bleaching.

A close examination of the results in Tables 3 – 7 reveals that both the tendering factors and the retained tensile strength of the cotton substrates after bleaching depend on pre-treatment conditions prior to bleaching, and have the following order:

Acidic pectinase scouring < reductive scouring < acidic demineralisation < traditionally scoured

Effect of pre-treatment technique

In order to demonstrate the effect of pre-treatment techniques on the difference in whiteness indexes after bleaching and *K/S* after dyeing, the exhaustion technique was used to effect reductive scouring, acidic demineralisation using gluconic acid as well as acidic pectinase scouring for all the cotton substrates under investigation. The samples were then subjected to H_2O_2 bleaching using the exhaustion technique as detailed in the experimental part. The magnitudes of deviation in *W.I*

after bleaching and *K/S* after dyeing were assessed by statistical calculation of the mean deviation (*M.D*) and the variance coefficient (*V.C*). The results obtained are set out in Table 8. It should be noted here that the results obtained previously with acidic pectinase scouring (Table 7) represent those values obtained when the scouring was carried out according to the exhaustion technique, then bleached using the pad-stem technique.

The results of Table 8 show that carrying out reductive scouring and bleaching according to the exhaustion technique increases the magnitude of *M.D* and *V.C* for both *W.I* and *K/S* among the bleached and dyed samples. The *M.D* and *V.C* as calculated from the W.I values of all the substrates were 1.83 and 2 respectively. This compares to 0.8 and 1.9 respectively on using the pad-steam technique to conduct the reductive scouring and bleaching. The same holds true for *M.D* and

Table 6. *Deviation of major properties of bleached cotton fabrics under investigation after gluconic acid demineralization;* **Remark:** *see Table IV.*

Fabric Properties	Substrate number					Statistical analysis [a]		
	I	II	III	IV	V	R	M.D	V.C
Weight loss, %	5.9	5.7	5.9	6.1	6.1	0.40	0.128	2.86
R.S, %	0.12	0.12	0.13	0.14	0.15	0.03	0.01	10.60
DP	1790	1735	1755	1725	1695	95.0	12.0	1.13
T.F	0.58	0.59	0.59	0.59	0.60	0.02	0.04	1.7
Y.I	1.12	1.25	1.15	1.10	1.35	0.25	0.084	11.30
Wax, %	0.05	0.05	0.07	0.07	0.07	0.02	0.264	113
R.T, %	91.60	90.50	90.70	91.21	91.5	1.10	0.40	0.53
Elon., %	18	18	20	20	19	2.0	0.80	5.3

Table 7. *Deviation of major properties of bleached cotton fabrics under investigation after acidic pectinase scouring;* **Remark:** *see Table IV.*

Fabric Properties	Substrate number					Statistical analysis [a]		
	I	II	III	IV	V	R	M.D	V.C
Weight loss, %	3.7	3.8	4.2	4.5	4.5	0.8	0.31	9.18
R.S, %	0.20	0.21	0.19	0.19	0.20	0.02	0.006	4.04
DP	1850	1815	1825	1805	1775	75	12.2	1.14
T.F	0.54	0.54	0.54	0.54	0.55	0.01	0.01	1.85
Y.I	1.16	1.75	1.85	1.96	2.01	0.85	0.24	20.1
Wax, %	0.06	0.07	0.08	0.09	0.09	0.03	0.01	17.95
R.T, %	95.6	95.5	94.7	94.21	94.5	1.39	0.52	1.05
Elon., %	21	20	20	22	21	2.0	0.64	4.04

Table 8. *Effect of pretreatment technique on covering the difference in whiteness index after bleaching and K/S after reactive dyeing of cotton substrate; M.D = Mean deviation; V.C = Variance coefficient,* [a] *The pretreatment and H_2O_2 bleaching were carried out as per exhaustion technique,* [b] *Acidic pectinase scouring and acidic demineralization were carried out using exhaustion technique, whereas reductive scouring and H_2O_2 bleaching were carried out using pad-steam technique.*

Pre-treatment method	Exhaustion technique [a]				Pad-steam technique [b]			
	W.I		K/S		W.I		K/S	
	M.D	V.C	M.D	V.C	M.D	V.C	M.D	V.C
Reductive scouring	1.83	2.3	0.31	0.40	0.80	1.9	0.01	0.20
Acid demineralization	0.57	0.87	0.011	0.19	0.64	0.98	0.014	0.27
Acidic pectinase scouring	1.39	1.98	0.030	0.12	1.36	1.98	0.029	0.11

V.C calculated from the K/S values. This results indicates that reductive scouring using glucose/NaOH is much more effective when the pad-steam technique was used to effect reductive scouring rather than exhaustion. It is likely that in the pad-steam technique, the glucose is converted to gluconic acid in considerable amounts compared to the exhaustion technique. The results of Table 8 also show that acidic demineralisation with gluconic acid using the exhaustion technique is more effective than pad-steam in reducing the deviation in W.I and K/S among all the bleached and dyed cotton substrates. This was evidenced by the lower M.D and V.C of both the WI and K/S values obtained when the exhaustion technique was used. In the case of acidic pectinase scouring prior to peroxide bleaching, both the pad-steam and exhaustion techniques give comparable M.D and V.C results.

■ Conclusion

The most effective pre-treatment method that reduces the differences in W.I and the depth of colour among the bleached and reactive dyed cotton fabrics of different fibre quality are:
a- Reductive scouring of cotton fabric using D-glucose along with sodium hydroxide,
b- Acidic demineralisation with D-gluconic acid,
c- Acidic pectinase scouring.

Pre-treatment cotton fabric with reductive scouring prevents the oxidation of cellulose to oxycellulose during the alkali boil-off, and therefore prevents fabric tendering. In acidic pectinase scouring, in addition to its effectiveness at covering the difference in W.I the and colour strength of bleached and reactive dyed cotton fabrics, it decreases tendering to a great extent in comparison to those obtained with reductive scouring or demineralised with acid before peroxide bleaching. Mercerisation and grey mercerisation improve the colour yield and greatly decrease the differences in K/S values among the dyed samples, but both failed to cover the differences in W.I. It was also found that the cationisation of conventionally bleached cotton fabrics is a powerful tool that can cover the differences in the colour shade arising from different cotton types, if these cationised cotton samples were reactively dyed in the absence of salt and alkali. However, cationisation did not completely cover the differences in W.I. The results further show that the pad-steam technique is more effective than the exhaustion technique at achieving reductive scouring with glucose/NaOH, whereas the exhaustion technique is more effective than the pad-steam technique in demineralisation with gluconic acid.

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