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ORIGINAL PAPER

Effect of chemical modification with 4-vinylpyridine on dyeing of cotton fabric with reactive dyestuff

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Abstract Cotton fabrics were pre-treated with 4-vinylpyridine before dyeing to increase dye uptake. Various treatments for the application of monomers to fabrics were tried in different combinations and after dyeing the best result was obtained with alkali impregnation and monomer exhaustion. After decisions had been made on the processes to be applied before dyeing, different amounts of monomer, dyestuff and salt were used in reactive dyeing baths at different pHs. The results were evaluated in terms of color coordinates, color strength, FT-IR and fastness to washing, rubbing and perspiration. The best results were obtained with 3 ml of 4-vinylpyridine dissolved in 10 ml of alcohol, in the presence of 25 g L^{-1} of salt and in neutral medium at 5% dyestuff concentration. Color strength from this dyeing process was higher than from the conventional dyeing at the same dyestuff concentration. FT-IR analysis demonstrated the presence of monomer on the surface of the fabric. Fastness values showed that this method could be used as an alternative to the conventional method.

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Keywords Cotton · Surface modification · 4-vinylpyridine · Alkali-free · Salt-free · Reactive dyeing

Introduction

In the textile industry, cotton is used extensively because of its excellent properties such as non-conductive electric properties, hygroscopicity, air permeability, and biodegradability (Wang and Lewis 2002; Wang et al. 2009; Teng et al. 2011). Reactive dyes are widely used for dyeing of cellulosic goods due to their wide range of hue, high wet fastness, brilliancy, application versatility, etc. (Chattopadhyay et al. 2006; Fang et al. 2013; Arivithamani and Giri Dev 2016). One of the most important disadvantages of commercial reactive dyes is the requirement of salt which varies between 60 and 80 g L^{-1} according to the structure of dye, color depth and the dyeing method used (Farha et al. 2010; Khatri et al. 2015). In the reactive dyeing bath, an electrolyte is needed for the transfer of water-soluble anionic charged reactive dyes from solution to the fiber surface since the negatively charged fiber surface repels the anionic dyes. Glauber's ($Na_2SO_4.10\ H_2O$) or common salt (NaCl), which is the most preferred electrolyte, effectively eliminates the zeta potential and removes the barrier initially formed between the dye/fiber

interface (Chattopadhyay et al. 2006; King 2007; Tarbuk et al. 2014). If the dyeing bath does not contain sufficient salt, 100% dyestuff exhaustion could not be provided and the remaining dyestuff in the alkaline dyeing bath will be hydrolysed. Some of the hydrolysed dyes are also exhausted but remain unfixed at the same time. The hydrolysed and unfixed dye must be removed in order not to reduce wet fastness values, and this causes high amounts of water, time and energy consumptions. Therefore, highly salty and colored waste water remains after reactive dyeing (Forgacs et al. 2004; Chattopadhyay et al. 2006; Chinta and Vijaykumar 2013). Moreover, high oxygen demand of this waste water (Ali et al. 2014) containing highly dissolved solids (Khatri et al. 2013) and adsorbable organic halides (AOXs) (Bashar and Khan 2013) is a major problem due to sustainable apparel demands of "ethical" consumers (Parisi et al. 2015). Because of aforementioned reasons, sanctions for environmental laws in the sustainable production by regulatory authorities have forced the dyers to work on reducing salt load in waste water after reactive dyeing.

Methods used to reduce or eliminate the amount of salt used in reactive dyeing can be grouped under five main headings:

- cotton modification prior to dyeing by various ways such as applications of chemicals, enzymes, and nanoparticles, plasma and ozone treatments etc. (Burkinshaw et al. 2000; Zhang et al. 2007b; Kamel et al. 2011; Patiño et al. 2011; Zheng et al. 2012; Gashti et al. 2013; Hao et al. 2016),
- improvements in structures of reactive dyes (Taylor 2000; Paluszkiewicz et al. 2002; Singha et al. 2012),
- using organic compounds in dyeing baths (Guan et al. 2007; Liu and Yao 2009; Khatri 2011),
- decreasing the liquor ratio via developments in machinery and processes (Kalliala and Talvenmaa 2000; Khatri et al. 2015),
- wastewater treatments (Allègre et al. 2006; Shukla 2007; Vishnu and Joseph 2008; Yonar 2011).

Among these methods, the most promising one is the chemical modification of the cotton with various agents to form cationic groups on the surface. In the literature, materials used for surface modification of cotton fibers can be summarised as follows: chitosan (Kitkulnumchai et al. 2008; Bhuiyan et al. 2014), starch & their derivatives (Pal et al. 2005; Kitkulnumchai et al. 2008; Arivithamani et al. 2014), choline chloride (Kim and Choi 2014), amino-terminated hyperbranched polymers (Wu and Chen 1993; Zhang et al. 2007a), reactive polymeric quaternary ammonium compounds, amines or amides (Gopalakrishnan et al. 2018) like tertiary amine cationic polyacrylamide (Teng et al. 2011), 2-hydroxypropyltrimethylammonium chloride hemicellulose (Ren et al. 2006), 2-hydroxypropyltrimethylammonium chloride starches (Heinze et al. 2004), quaternized polyglykol ether of fatty amine (Ristić and Ristić 2012), polyepichlorohydrin-amine polymers (Evans et al. 1984), poly(vinylamine chloride) (Ma et al. 2005), 3-chloro-2-hydroxypropyl trimethylammonium chloride (Wang et al. 2009; Fu et al. 2013; Tarbuk et al. 2014; Arivithamani and Giri Dev 2017; Gopalakrishnan et al. 2018), dendrimers (Burkinshaw et al. 2000; Froehling 2001; Sadeghi-Kiakhani and Safapour 2015; Salimpour Abkenar et al. 2015), poly (4-vinylpyridine) quaternary ammonium (Tutak and Ozdemir 2011). In addition to various synthetic and natural polymers, monomers have also used in the cationization of cotton (Bashar and Khan 2013). Some of them are N-methyl-N-(2,3-epoxypropyl)-morpholinium chloride (Gipp et al. 1977), Glyac-A (Lewis and Xiaoping 1989), N-methylol co reactant to attach chloline chloride (Harper and Stone 1986), bis-reactive and bis-quaternary compound (Evans et al. 1984), 2, 3-epoxypropyltrimethylammonium chloride (Hauser and Tabba 2001).

The poly (4-vinylpyridine) quaternary ammonium compounds are highly substantive to the cellulosic fibers due to the combination of hydrogen bonding, ion–ion interactions and van der Waals forces. Cationic groups in the chemical agents and the anionic carboxylic acid groups in cotton constitute ion–ion interactions and lead to the adsorption of cationized agents onto cotton (Peters 1975; Nevell 1986). The attraction between the agent and the fiber is also provided by H-bonds between the OH groups of fiber and the delocalized π electron cloud called *Yoshida forces* (Yoshida et al. 1964). Moreover, the formation of ion–dipole forces between the nitrogen atoms of the pyridinium rings and the oxygen atom of the cellulosic hydroxyl groups may also be expected. An ionic association forms between the anionic groups of the dyestuff and the cationic groups present on cotton so that dyeing can be done without the addition of electrolyte to the dye bath (Blackburn and Burkinshaw

2003). The mechanisms of the action of 4-vinyl pyridine and dyeing of cationized cellulose are shown in Figs. 1 and 2, respectively (Blackburn and Burkinshaw 2002).

In this paper, cotton cationization with 4-vinylpyridine (4-VP) was reported to reduce and eliminate the amount of salt and alkali used in reactive dyeing. In this context, different pre-treatment processes were applied to cotton fabrics with various combinations and then dyeings were conducted. The effects of various independent variables on dyeing behaviour of the fabric were studied with color measurements (color coordinates and K/S values), and wash fastness, rubbing and perspiration tests. The conventionally dyed cotton fabrics were used as control samples. In addition, in order to see monomer presence on the fabric surface FT-IR analyses were performed.

Materials and methods

Materials

The desized, scoured, bleached plain-woven cotton fabric of 130 g m^{-2} was provided by *Yürek Textile* (Bursa, Turkey). The methanol ($\geq$ 99.8% purity), sodium chloride, and sodium hydroxide were of technical grade and supplied from *TEKKİM Kimya Sanayi Tic. Ltd. Şti* (Bursa, Turkey).The 4-vinylpyridine (4-VP) (contains 100 mg L^{-1} hydroquinone as an inhibitor, 95%) was supplied from *Sigma–Aldrich*. The reactive dye *Drimaren Orange HF2GL* was purchased from *Archroma*. Pre-treatments were operated by *Werner Mathis AG (VFM 32,592)*, and *XIAMEN RAPID (IR-24SM).* The *XIAMEN RAPID (H-TS-3)* was used for drying and fixation. Fabrics were dyed in *XIAMEN RAPID (IR-24SM).*

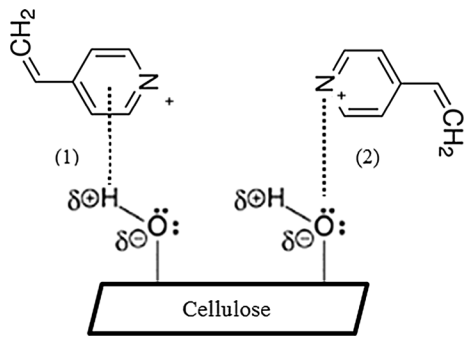


Fig. 1 Monomer binding onto cellulose (1) Yoshida H-bonding and (2) ion–dipole interactions between cellulose hydroxy groups and monomer

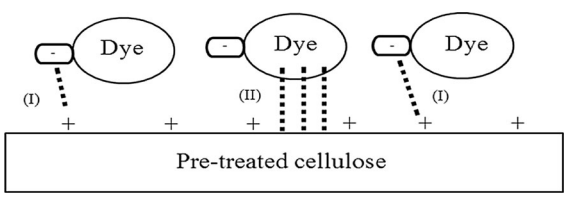


Fig. 2 Mechanism of pre-treated cotton with monomer and reactive dye (I) Ionic association (II) van der Waals and H-bonding

Methods

The application of the 4-VP to cotton fabric was optimized and then the effects of dyeing variables (pH, salt, amount of alcohol, monomer and dyestuff) on dyeing behaviour of fabric were investigated.

Process optimization

The 4-VP application to cotton fabric were optimized and the optimization were made as follows.

First, transfer of the monomer to the fabric at maximum efficiency was determined by the color strength of the dyeing process after the various pre-treatments were applied in different combinations. These pre-treatments were alkali impregnation, monomer impregnation, and monomer exhaustion. The alkali applied to fabrics by impregnation process with 0.01 mol L^{-1} NaOH to a wet pick-up of 100%. Drying process after alkali impregnation was carried out at 100 °C for 10 min. Monomer solutions used for monomer impregnation and exhaustion solutions were prepared by dissolving 3 and 10 ml of 4-VP in 50 and 150 ml of methanol, respectively, and completing the volume of these solutions with water to 1000 ml. These solutions were applied to cotton fabrics at 45 °C for 30 min at 30:1 liquor ratio for the exhaustion method and at 10:1 liquor ratio to a wet pick-up of 100% with two-dip-two-nip for impregnation method. The fixation process was done at 150 °C for 3 min. Secondly, reactive dyeings were carried out at 65 °C in 30:1 liquor at 65 min by changing in dyestuff concentrations (3% and 5%) and monomer presence of dyeing baths. Dyed samples were washed as follows: cold, warm, boiling with soap, warm, and cold rinsings, respectively. Details of processes are given in Table 1.

Table 1 Sample codes and details of process optimization

Sample code	Alkali impregnation	Drying	Monomer exhaustion	Alcohol monomer (ml/ml)	Monomer impregnation	Fixation	Dye cone. (%)
A^x	−	−	−	50/3	−	−	5
B^x	−	−	+	50/3	−	+	5
C^y	−	−	+	50/3	−	+	5
D^y	+	+	−	150/10	−	−	5
E^z	−	−	+	50/3	−	+	5
F^x	+	+	+	50/3	−	+	5
G^x	+	+	+	50/3	−	+	5
H^x	+	+	−	50/3	+	+	5
I^x	+	+	−	50/3	+	+	5
J^y	+	+	+	50/3	−	+	5
K^z	+	+	+	50/3	−	+	5
L^y	−	−	−	150/10	−	−	5
M^y	−	−	+	150/10	−	+	5
N^y	+	+	+	150/10	−	+	5
O^z	+	+	+	150/10	−	+	5

Dyeing bath contents x: water, y: same monomer exhaustion bath, z: fresh monomer solution

Effects of variables on color strength

After process optimization step, the effects varying applications of alcohol, salt, pH of the bath, monomer, dyestuff concentrations on the color depth have been investigated in order to obtain the highest color strength with reactive dyes. The conventional dyeing was carried out at increasing concentrations of dyestuffs (2, 3, 4, and 5%) in the presence of Na_2CO_3 (20 g L^{-1}) and salt (60 g L^{-1}) conventionally dyed samples were used as control samples. The details of the processes are summarized in Table 2.

The results of dyeings were analysed using the following methods.

FT-IR ATR The infrared spectra of the pre-treated and dyed cotton fabrics were recorded in a *NICOLET iS50 FT-IR* spectrophotometer and measurements were performed at 20 °C and at a relative humidity of 65%.

Measurement of color strength The L*, a*, b*, C*, and h° values were calculated by reflectance measurements (under D65 illuminant and 10° standard observer) the *Konica Minolta CM-3600D* spectrophotometer by *ColorMission* software (v.3.4.1 by Argetek). The K/S values were calculated using the *Kubelka–Munk* equation. The color strength (K/S) formula is presented in Eq. 1.

$$K/S = \frac{(1-R)^2}{2R} \quad (1)$$

In the Eq. 1, R is the decimal fraction of the reflectance of fabric, K is the absorption coefficient, and S is the scattering coefficient (Pisuntornsug et al. 2002).

The color difference (ΔE*) values were calculated according to *CIELAB 1976* equation is given in Eq. 2.

$$\Delta E^*_{CIELAB} = \sqrt[2]{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

In the Eq. 2, ΔL* is the lightness coordinate difference between treated (dyed fabric after pre-treatment) and control (conventionally dyed fabric) samples; Δa* is red/green difference between treated and control samples; Δb* is yellow/blue difference between treated and control samples. ΔE* is described as the distance between two color points by the length of a straight line and this distance is described with Euclidean geometry because CIELAB 1976 color space is isometric to the Euclidean geometry.

Table 2 Dyeing variables and sample codes

Sample code	Alcohol	pH	Dye conc. (%)	Mo nomer (ml)	Salt (g/l)	Alkali (g/l)
X1	10	7	2	0.5	20	–
X2	10	7	2	1	20	–
X3	10	7	2	3	20	–
X4	10	9	5	3	–	–
X5	10	10	5	3	–	–
X6	10	11	5	3	–	–
X7	10	9	5	3	15	–
X8	10	10	5	3	15	–
X9	10	11	5	3	15	–
X10	10	9	5	3	20	–
X11	10	10	5	3	20	–
X12	10	11	5	3	20	–
X13	10	7	2	0.5	25	–
X14	10	7	2	1	25	–
X15	10	7	2	3	25	–
X16	10	7	3	0.5	20	–
X17	10	7	3	1	20	–
X18	10	7	3	3	20	–
X19	10	7	3	0.5	25	–
X20	10	7	3	1	25	–
X21	10	7	3	3	25	–
X22	10	7	4	0.5	20	–
X23	10	7	4	1	20	–
X24	10	7	4	3	20	–
X25	10	7	4	0.5	25	–
X26	10	7	4	1	25	–
X27	10	7	4	3	25	–
X28	10	7	5	3	–	–
X29	10	7	5	3	15	–
X30	10	7	5	0.5	20	–
X31	10	7	5	1	20	–
X32	10	7	5	3	20	–
X33	10	7	5	0.5	25	–
X34	10	7	5	1	25	–
X35	10	7	5	3	25	–
X36	50	9	5	3	–	–
X37	50	10	5	3	–	–
X38	50	11	5	3	–	–
X39	50	9	5	3	15	–
X40	50	10	5	3	15	–
X41	50	11	5	3	15	–
X42	50	9	5	3	20	–
X43	50	10	5	3	20	–
X44	50	11	5	3	20	–
Conventional 2	–	12	2	–	60	20

Table 2 continued

Sample code	Alcohol	pH	Dye conc. (%)	Mo nomer (ml)	Salt (g/l)	Alkali (g/l)
Conventional 3	–	12	3	–	60	20
Conventional 4	–	12	4	–	60	20
Conventional 5	–	12	5	–	60	20

Fastness testing Fastness properties of the pre-treated and dyed samples were determined according to standard methods of TS EN ISO 105-C06/A1M (color fastness to domestic and commercial laundering), EN ISO 105-X12:2002-12 (color fastness to rubbing), and TS EN ISO 105-E04 (color fastness to perspiration).

Results and discussion

FT-IR analysis

Figure 3 illustrates the FT-IR of the bleached cotton fabric, monomer, dyestuff and dyed fabric after alkaline and monomer pre-treatments.

The characteristic vibrations of pyridine ring were present at 1594, 1546, 1494, 1407 cm^{-1} (Xue and Xiao 2015). These absorption bands corresponding to C–C and C–N stretching in pyridine ring (Khalig 2012). The 3067–3025–2984 cm^{-1} absorption bands were characteristics of aromatic CH stretching vibrations due to monomer structure. The peak at 1218 cm^{-1} was assigned to in-plane CH bends of pyridine. The bands at 828 (CH wag), and 787 cm^{-1} (5 adjacent H wag) were attributed to out-of-plane CH bends of monomer.

Dyestuff in the form of trifluoropyrimidine structure gave the characteristic FT-IR spectrum of pyrimidine (Lord et al. 1957). Although it was thought that the strong peaks between 1600–1500 cm^{-1} and 1400–1000 cm^{-1} came from the ring-stretching bands of pyrimidine and CF bonds, respectively (Brian 1999), a detailed analysis could not be done because the exact chemical structure of the dye was not known.

In the spectrum of bleached cotton fabric the absorption bands at 3331 (OH stretching), 1637 (H_2O), 1427 (CH_2 deformation), 1359 (CH deformation), 1314 cm^{-1} (OH deformation) appeared. In addition, the CO stretching in the COC and COH groups were observed in the absorption bands 1159, 1107, 1052, 1030 cm^{-1}. The peak at 895,96 cm^{-1} was assigned to ring semi-circle stretching for cotton fabric.

3069–3028 cm^{-1} (CH stretching) wide absorption bands could be shown as a proof of monomer existence on fabric surface because these bands did not appear in the dyestuff and bleached fabric. The presence of 1597 and 1557 cm^{-1} strong IR bands appeared as a result of quadrant ring stretching vibrations in the fabric because of pyridine. It was thought that the cause of the peak seen at 1415 cm^{-1} (ring semi-circle stretching) in the dyed fabric was the strong band of the pyridine at 1407 cm^{-1}. The dyed fabric peak at 1217 cm^{-1} was attributed to in-plane CH bends of pyridine. Moreover, IR spectra of dyed fabric at 819 cm^{-1} was also dominated by pyridine at 828 cm^{-1} (Brian 1999; Li et al. 2007; Meléndez-Ortiz et al. 2009; Larkin 2011).

Color strengths

Process optimization

In this work, to find out suitable conditions for introducing positive site of 4-VP onto cotton fabrics, pre-treatment with alkali and/or monomer (padded or exhausted) by various combinations were applied and K/S values of each process are given in Fig. 4.

The positive effect of alkali impregnation on K/S values was observed via D and L. The alkali impregnation caused approximately 20% increase in color strength. To see the effect of monomer exhaustion pre-treatment A–B samples were compared to each other. The monomer exhaustion process accomplished to increase K/S by 11%. Using monomer exhaustion bath (C) instead of water (B) in the dyeing increased K/S (70%). When fresh monomer solution was used for dyeing, K/S increased 11% compared to monomer exhaustion pre-treatment bath re-used (C–E). Moreover, applications of monomer via exhaustion and impregnation (F–G–H–I) were compared, it was found

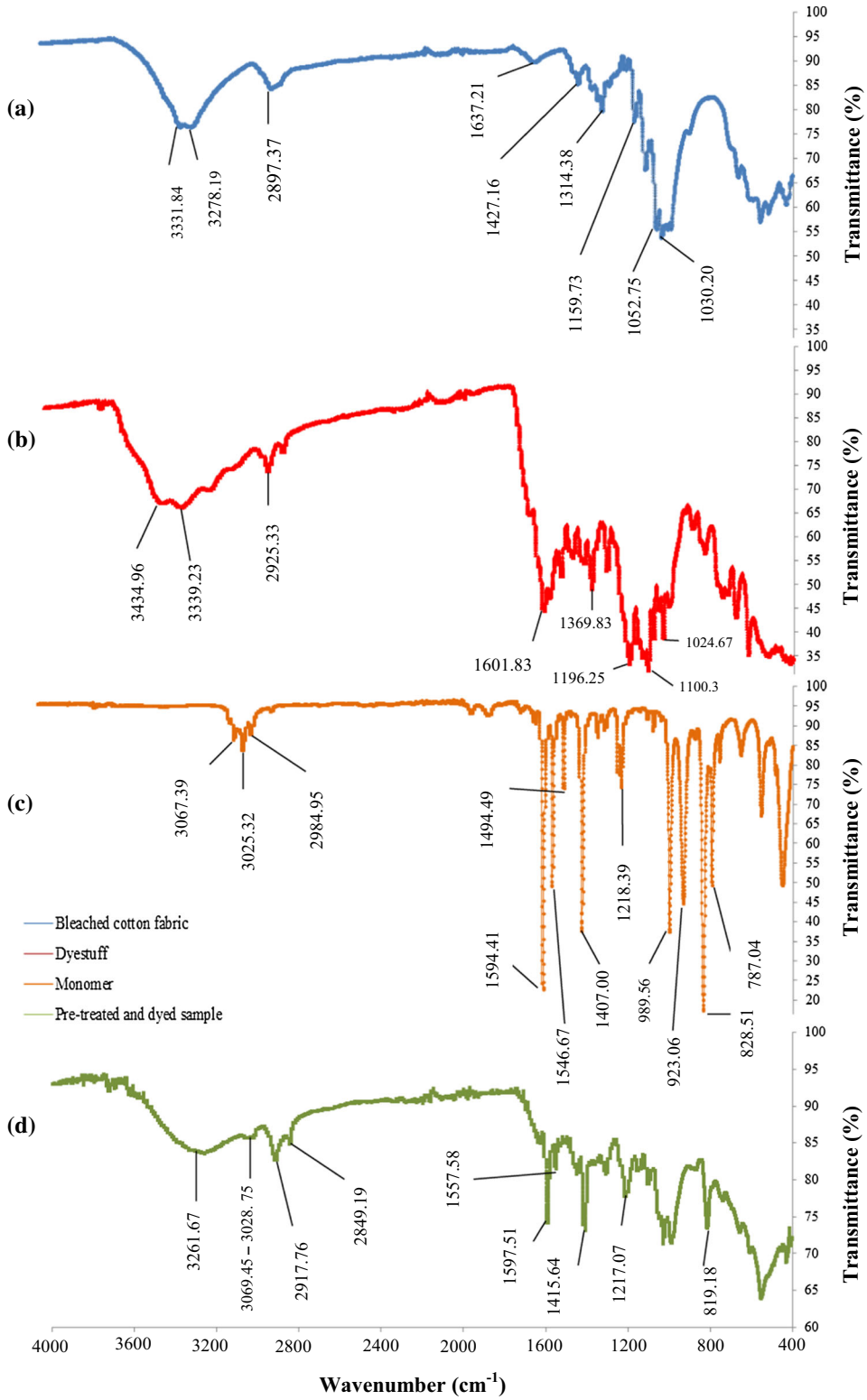


Fig. 3 FT-IR spectrum of (**a**) bleached cotton fabric, (**b**) dyestuff, (**c**) monomer and (**d**) dyeing after the pre-treated fabric

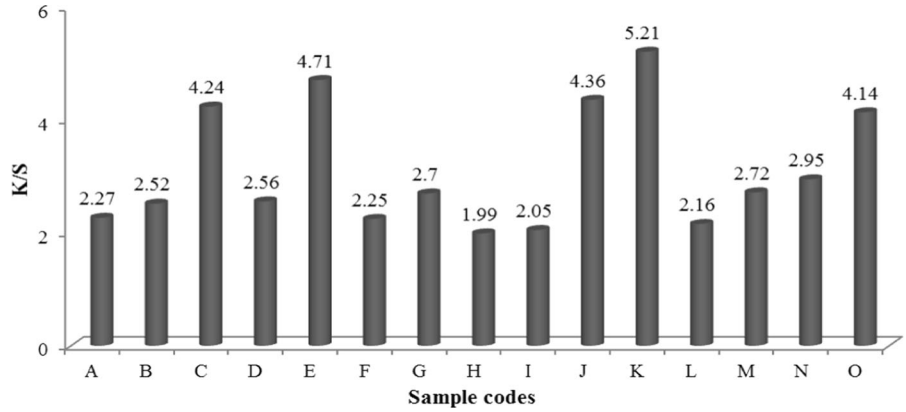


Fig. 4 K/S values of different processes

that the exhaustion was more effective on the K/S than the impregnation. Alkali impregnation and the monomer exhaustion pre-treatments were applied respectively (N), the color yield was found to be higher than only one of these two treatments (D–M) were applied. The highest K/S value was observed when alkali impregnation and monomer exhaustion pre-treatments were performed before dyeing which includes fresh monomer solution and dyestuff (K). Therefore, this situation revealed that all pre-treatments had to be done before dyeing. The effects of fresh monomer solutions using in the dyeing which was done after all pre-treatments were obvious when compared to N–O and J–K and increasing at the K/S by 40% and 20%, respectively. When the effect of alcohol was investigated on dissolution of monomer, it was found that smaller amounts of alcohol provide higher color efficiency.

Effects of variables on color strength

The color coordinates and K/S values of all samples are shown in Table 3. The color differences (ΔE*) of the samples were calculated by comparing them to the samples dyeing according to the conventional method. Significant differences were observed in color values when 4-VP was used. The L* values showed differences according to the processes. As the salt concentration of dyeing bath increased, the L* values decreased because more dyestuff was migrated to the fabric. The L* decreased with increasing amount of monomer, while increased by raising pH. The a* and b* coordinates generally showed a decrease with respect to the conventionally dyed sample, i.e. the monomer pre-treatment caused the yellow color to fade by a shift to the grey point. This was expected because 4-VP had its own color.

Salt and pH effects on dyeing The effects of pH and salt content of the dyeing bath on color depths are shown in Figs. 5 and 6. In both figures, as the pH increased, K/S values decreased. It was expected since vinylpyridine is a base, so the ratio between dissolved and emulsified monomer depends on pH (Fitzgerald and Fuoss 1950). This could be explained by the deprotonated amine moieties in the monomer by increasing pH (Meléndez-Ortiz et al. 2009). It was thought that desorption characteristic of monomer (Dautzenberg et al. 1994) caused a decrease in the amount of dye attached to the fabric. Moreover, these figures showed that the addition of salt to the dyeing bath caused very high increase in color strength because salt increases dye uptake of fibers by simplifying dye migration from bath to fiber (Zhang et al. 2007a).

Alcohol, monomer and dyestuff concentrations effects on dyeing The effects of monomer (dissolved in different amounts of alcohol) and dye concentrations on K/S values are shown in Figs. 7 and 8. The increase in monomer concentration (0.5–1–3 ml) caused significant increase in K/S because more dyestuff could be bound to fabric. As expected, the color depth increased as the concentration of dyestuff increased, as well.

Figure 9 shows the effect of alcohol which was used to dissolve monomer on the color strength. In this figure, pH and salt effects could also be examined. Higher K/S values were obtained in the dyeing process after dissolving the monomers in 10 ml of alcohol than

Table 3 Color coordinates and K/S values for all samples

Sample code	L*	a*	b*	C*	h°	ΔE*	K/S
Conventional 2%	63.33	31.15	62.75	70.06	63.60		10.55
XI	69.73	21.44	46.64	51.33	65.31	19.87	3.32
X2	64.74	23.74	47.61	53.20	63.50	16.92	4.83
X3	60.80	23.88	46.26	52.06	62.70	18.20	5.97
X13	68.06	22.38	47.93	52.90	64.97	17.86	3.92
X14	64.22	24.21	49.18	54.81	63.79	15.28	5.35
X15	60.33	25.16	47.49	53.74	62.09	16.67	6.47
Conventional 3%	63.75	36.58	68.55	77.70	61.92		13.05
X16	67.80	22.65	47.88	52.97	64.69	25.25	3.99
X17	61.96	25.39	49.65	55.77	62.92	22.03	6.37
X18	57.79	26.63	50.07	56.71	61.99	21.82	8.83
X19	63.40	24.69	48.69	54.59	63.12	23.15	5.57
X20	59.67	28.15	54.17	61.05	62.54	17.16	9.38
X21	59.34	25.67	48.16	54.58	61.94	23.53	11.27
Conventional 4%	61.12	38.22	68.40	78.35	60.81		15.98
X22	63.11	26.52	51.88	58.26	62.92	20.34	6.54
X23	59.22	28.12	53.24	60.21	62.16	18.31	9.23
X24	53.76	30.01	50.72	58.93	59.39	20.84	12.33
X25	63.26	25.97	51.61	57.78	63.29	20.89	7.61
X26	59.10	27.52	52.41	59.19	62.30	19.34	9.70
X27	57.47	25.77	50.08	56.32	62.76	22.44	12.46
Conventional 5%	59.27	39.09	66.81	77.40	59.67		17.11
X4	67.79	20.48	47.14	51.40	66.51	28.38	4.23
X5	68.92	19.48	48.35	52.13	68.05	28.61	3.85
X6	70.68	17.77	46.61	49.88	69.13	31.51	3.16
X7	54.61	28.71	52.04	59.43	61.12	18.64	14.53
X8	58.33	26.82	56.79	62.81	64.72	15.86	11.78
X9	58.82	27.07	57.12	63.21	64.64	15.44	11.28
X10	51.04	29.57	50.38	58.42	59.59	20.69	15.63
XI1	55.99	28.31	56.36	63.07	63.33	15.36	13.86
X12	56.92	27.44	57.16	63.40	64.36	15.31	13.2
X28	66.63	22.31	48.32	53.22	65.22	26.03	7.68
X29	52.86	30.66	51.72	60.13	59.34	18.43	14.56
X30	62.62	28.51	52.67	59.89	61.57	17.97	7.68
X31	61.01	27.62	53.46	60.17	62.67	17.68	10.35
X32	51.04	32.31	52.48	61.62	58.38	17.86	17.4
X33	63.21	27.29	52.46	59.13	62.51	18.99	9.02
X34	58.64	30.33	55.08	62.88	61.16	14.64	12.27
X35	49.54	32.98	52.27	61.80	57.75	18.53	19.95
X36	67.52	20.58	47.59	51.85	66.62	27.93	4.1
X37	69.91	17.45	44.72	48.01	68.69	32.70	3.1
X38	72.62	16.35	43.26	46.24	69.30	35.35	2.42
X39	51.55	31.64	54.20	62.76	59.72	16.55	12.7
X40	58.58	26.23	56.54	62.32	65.12	16.47	11.34

Table 3 continued

Sample code	L*	a*	b*	C*	h°	ΔE*	K/S
X41	59.29	25.63	55.99	61.58	65.40	17.26	10.37
X42	53.50	30.76	54.85	62.89	60.72	15.67	14.4
X43	58.26	26.81	56.36	62.41	64.56	16.15	11.46
X44	57.68	26.06	55.96	61.73	65.03	17.02	10.42

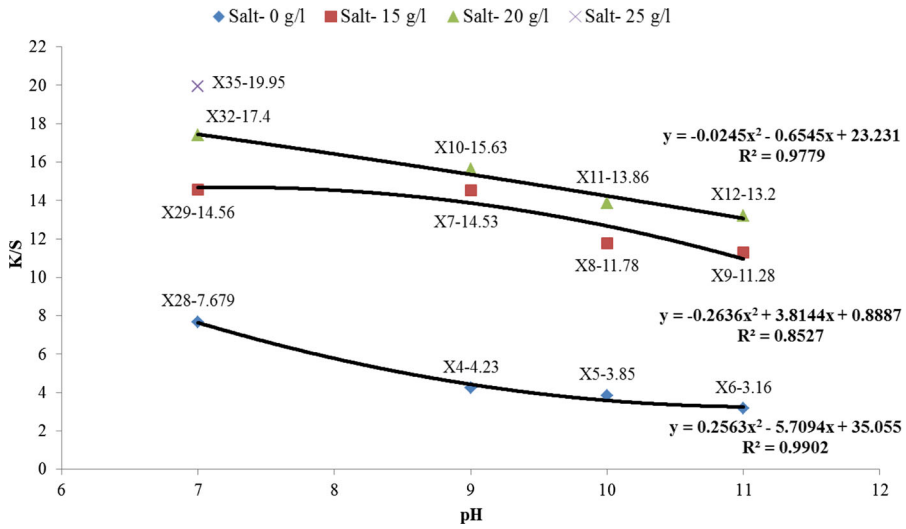


Fig. 5 K/S values of the dyeings in different pH and salt concentrations (3 ml 4-VP–10 ml alcohol)

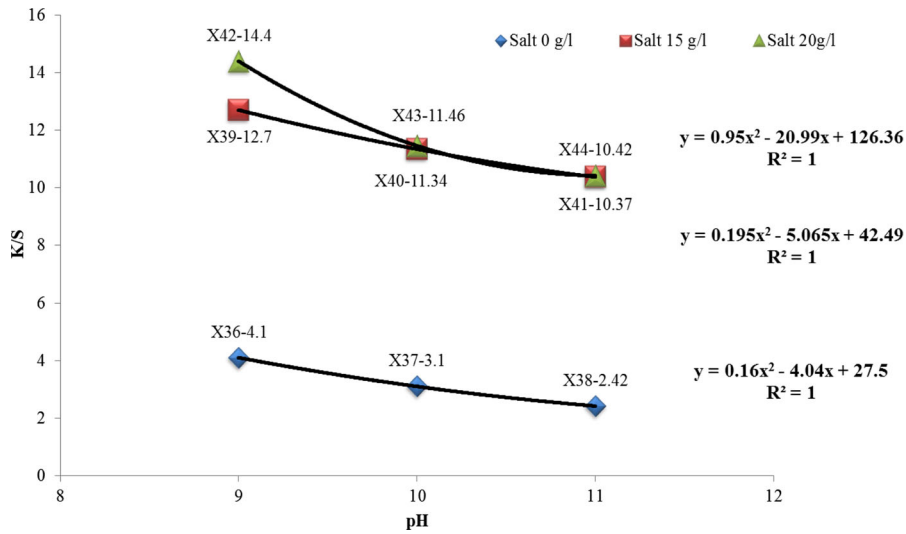
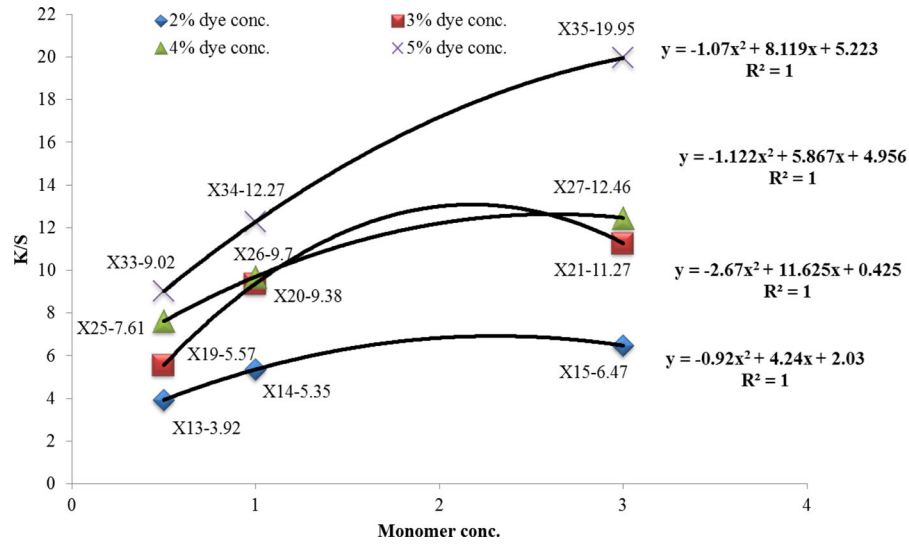


Fig. 6 K/S values of the dyeings in different pH and salt concentrations (3 ml 4-VP–50 ml alcohol)



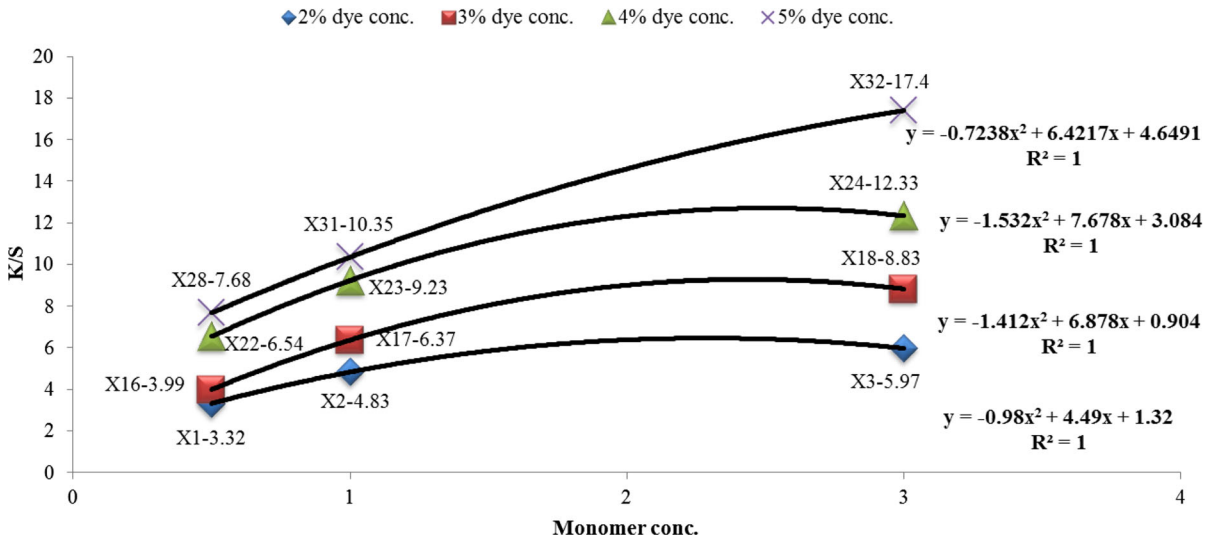


Fig. 7 K/S values of the dyeings in different monomer and dye concentrations (3 ml 4-VP–10 ml alcohol)

Fig. 8 K/S values of the dyeings in different monomer and dye concentrations (3 ml 4-VP–50 ml alcohol)

in dissolving in 50 ml of alcohol. The cause of this situation was thought to be decreasing polarity by addition of alcohol (Ouyang et al. 2007).

Figure 10 compares color strength of conventional and pre-treated fabrics which were obtained the highest results after dyeings. As the concentration of the dyestuff increased, the K/S values of the conventional dyeings for that concentration were reached more and for 5% dyestuff concentration, the K/S value of conventional dyeing was reached and this value was exceeded.

Fastness testing

The washing, rubbing and perspiration fastness properties of the pre-treated and dyed cotton fabric at various pH, dye, monomer and salt concentrations were measured and results are given in Table 4.

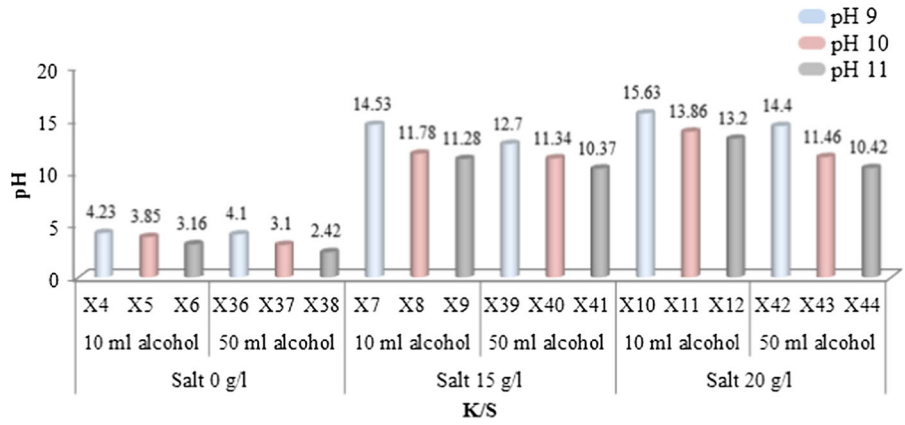


Fig. 9 The effect of alcohol used for monomer dissolution on K/S values

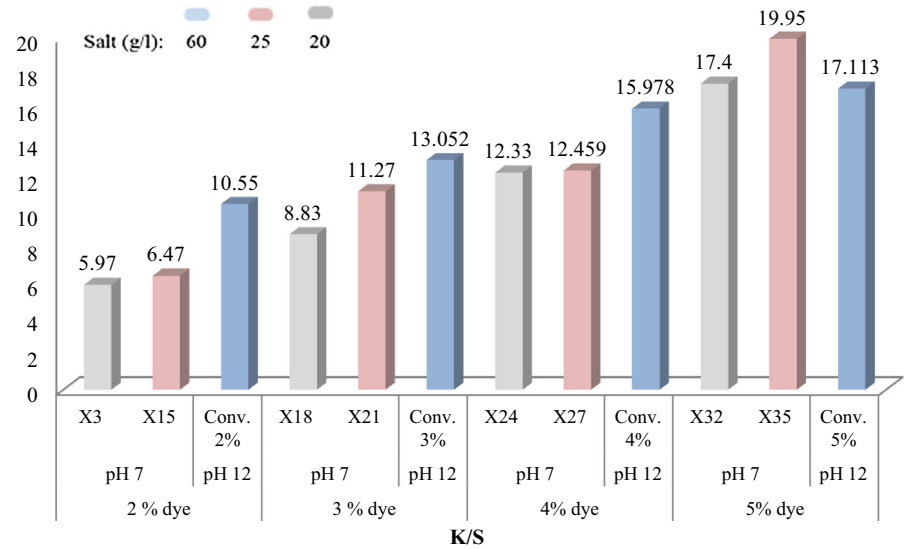


Fig. 10 Comparison of the highest K/S values obtained at different dyeing concentrations

The results for washing, rubbing and perspiration fastness showed that fastness results were good to excellent (4, 4/5, 5). These values were similar to those of conventionally dyed fabrics. The explanation for this could be that once exhausted with the monomer, the anionic reactive dye undergoes strong bonds with the pre-treated cellulose.

Conclusions

The alternative dyeing process which was desired to be developed by eliminating or reducing use of salt and alkali in the reactive dyeing was obtained by alkali impregnation, drying, and exhaustion of 4-VP before the dyeing as a result of process optimization processes. This proved that surface cationization of the cotton was achieved using 4-VP and presence of the monomer was proved by FT-IR analysis. After investigation of variables effects, it was found that the K/S value obtained using 20 g L^{-1} salt, which was one-third of the amount used in conventional dyeing, and 3 ml of 4-VP which was dissolved in 10 ml methanol was equal to the conventionally dyed sample's. Moreover, fastness results had shown that this method could be used as an alternative to conventional reactive dyeing.

Table 4 Color fastness results

Sample	Washing						Rubbing		Perspiration											
							Wet	Dry	Alkaline						Acidic					
	Wo	PAN	PET	PA	CO	CA			WO	PAN	PET	PA	CO	CA	WO	PAN	PET	PA	CO	CA
XI	5	5	5	4/5	4/5	5	4/5	5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X2	5	5	5	4/5	4/5	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4	4/5	5
X3	5	5	5	4/5	4/5	5	4	4	5	5	5	4/5	4/5	5	5	5	5	4/5	5	5
X4	5	5	5	4/5	4	5	4/5	5	5	5	5	5	5	5	5	5	5	5	4/5	5
X5	5	5	5	4/5	4/5	5	4/5	5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X6	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5
X7	5	5	5	4/5	4/5	5	4	4	5	5	5	5	5	5	5	5	5	4/5	4/5	5
X8	5	5	5	4/5	4	5	4	4/5	5	5	5	5	5	5	5	5	5	4/5	4/5	5
X9	5	5	5	4/5	4	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5
X10	5	5	5	4/5	4	5	4	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5
XI1	5	5	5	5	4/5	5	4	4/5	5	5	5	4/5	5	5	5	5	5	4/5	4/5	5
X12	5	5	5	4/5	4	5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5
X13	5	5	5	4/5	4/5	5	4/5	5	5	5	5	5	4/5	5	5	5	5	5	4/5	5
X14	5	5	5	4/5	4/5	5	4	5	5	5	5	5	4/5	5	5	5	5	5	4/5	5
X15	5	5	5	4/5	4/5	5	4	5	5	5	5	5	5	5	5	5	5	4/5	5	5
X16	5	5	5	4/5	4/5	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X17	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X18	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X19	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X20	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X21	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X22	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X23	5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X24	5	5	5	4/5	4/5	5	4	4	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X25	5	5	5	4	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X26	5	5	5	4/5	4/5	5	4	4/5	5	5	5	5	4/5	5	5	5	5	4/5	4/5	5
X27	5	5	5	4	4	5	4	4/5	5	5	5	5	4/5	5	5	5	5	5	5	5
X28	5	5	5	4/5	4/5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5
X29	5	5	5	5	4/5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5
X30	5	5	5	4	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5

Table 4 continued

Sample	Washing						Rubbing		Perspiration											
							Wet	Dry	Alkaline						Acidic					
	Wo	PAN	PET	PA	CO	CA			WO	PAN	PET	PA	CO	CA	WO	PAN	PET	PA	CO	CA
X31	5	5	5	4/5	4/5	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X32	5	5	5	4/5	4/5	5	4	4	5	5	5	5	5	5	5	5	5	5	5	5
X33	5	5	5	4/5	4/5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5
X34	5	5	5	4	4	5	4	4/5	5	5	5	4/5	4	4/5	5	5	5	4/5	4/5	5
X35	5	5	5	4	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	4/5	4/5	5
X36	5	5	5	4/5	4/5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5
X37	5	5	5	4/5	4/5	5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5
X38	5	5	5	4/5	4/5	5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5
X39	4/5	5	5	4/5	4	5	4	4/5	5	5	5	4/5	4/5	5	5	5	5	5	5	5
X40	5	5	5	4/5	4	5	4	5	5	5	5	5	5	5	5	5	5	5	4/5	5
X41	5	5	5	4/5	4	5	4	4/5	5	5	5	5	5	5	5	5	5	4/5	5	5
X42	5	5	5	4/5	4	5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5
X43	5	5	5	4/5	4	5	4	5	5	5	5	4/5	4	5	5	5	5	4/5	4/5	5
X44	5	5	5	5	4/5	5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5
Conv. 2%	5	5	5	4/5	4	5	4/5	4/5	5	5	5	5	4/5	5	5	5	5	5	5	5
Conv. 3%	5	5	5	4/5	4	5	4/5	4/5	5	5	5	4/5	4	5	5	5	5	4/5	4/5	5
Conv. 4%	4/5	4/5	4/5	4/5	4	5	3/4	4/5	4/5	4/5	4/5	4/5	4	5	4/5	4/5	4/5	4	4	5
Conv. 5%	4/5	4/5	4/5	4/5	4	5	3	4/5	4/5	4/5	4/5	4/5	4/5	5	4/5	4/5	4/5	4/5	4/5	5

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