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Dyes and Pigments 66 (2005) 27–32

DYES and PIGMENTS

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Synthesis of a novel bridge compound having hetero-bi-functional reactive groups. Part 2: the characteristics of disperse dyeings

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Received 12 April 2004; received in revised form 21 June 2004; accepted 23 August 2004

Abstract

A novel hetero-bi-functional reactive compound was synthesized. It was designed to provide different reaction behaviors resulting from α,β-dibromopropionylamido and dichloro-*s*-triazinyl reactive group. To determine whether the reactive compound (DBDCBS) as a bridging part could combine disperse dyes and cellulosic fibers, three different disperse dyes were used to dye the cotton fibers pretreated with the novel reactive agent. The disperse dyes used were 1,4-dihydroxyanthraquinone (DHAQ), 1-amino-4-hydroxyanthraquinone (AHAQ) and 1,4-diaminoanthraquinone (DAAQ). These dyes contain none-, mono- and di-amino groups in their structures, respectively. Especially, the satisfactory dyeing results were achieved by the disperse dyeings of 1,4-diaminoanthraquinone (DAAQ) due to having two amino groups within the structure. The fastness properties of DAAQ dyeings showed very higher grades in terms of grey scale assessments due to their covalent bonding characteristics.

Keywords: Hetero-bi-functional; Bridge compound; Reactive group; Disperse dyes; Amino group

1. Introduction

Over the years, various researches for modification of cellulosics, especially towards cotton fibers, have been conducted to enhance the substantivity or the adsorption property of the dyes. In general, the modification methods comprise of the cationization and the anionization of the cotton fibers, which impart ionic attraction sites to the substrates [1–9].

In the previous study [10], a novel hetero-bi-functional reactive compound, sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate (DBDCBS), was synthesized and characterized. A wide range of fundamental experiments was carried out to examine its adsorption properties. To play an important role as a bridging function, this novel reactive compound was designed to possess two different reactive groups, namely α,β-dibromopropionylamido group and dichloro-*s*-triazinyl group. The α,β-dibromopropionylamido group used for *Lanasol* dyes for wool shows reactivity towards amines or amino groups at acidic condition and high temperatures (90–100 °C) [11,12]. In contrast, the dichloro-*s*-triazinyl group used for *Procion MX* dyes for cellulosics has reactivity towards hydroxyl groups at alkaline condition and room temperatures (20–30 °C) [13–15]. The previous results showed that as expected, the dicholoro-*s*-triazinyl group of the bridging compound (DBDCBS) successfully reacted with hydroxyl groups of the cotton fibers at low temperature and alkaline condition. The salt addition promoted substantivity of the reactive agent towards the surface of cotton fibers due to reducing the ionic repulsion forces between

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0143-7208/$ - see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2004.08.010

the fiber substrates and the negative DBDCBS. In the case of treatment time, proper fixation efficiency was sufficiently achieved in 1 h. Also considering the practical application aspect of the DBDCBS, the optimum amount was appropriate to be 10% owf of the DBDCBS.

In this part of study, the effect of the dye structures on the color strength was investigated under various experimental conditions. The disperse dyes having amino groups in molecular structures could covalently react with α,β-dibromopropionylamido group of the DBDCBS within the pretreated cotton fibers. Three different disperse dyes were used. These dyes were 1,4-dihydroxyanthraquinone (DHAQ), 1-amino-4-hydroxyanthraquinone (AHAQ) and 1,4-diaminoanthraquinone (DAAQ). The dyes have none-, mono- and di-amino groups in the structures, respectively. In addition, one-bath two-stage dyeing process was examined where the reactive compound as a bridging operation may combine disperse dyes with cotton fibers using the single bath [16]. Finally, the fastnesses tests of the dyeings to washing, dry cleaning, dry heating, chlorinated water, rubbing and light were also investigated.

2. Experimental

2.1. Preparation of hetero-bi-functional reactive compound (sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate, DBDCBS)

The novel reactive compound shown in Fig. 1 was prepared to apply to cotton fibers. The synthesized methods of the DBDCBS and its corresponding analysis data were described in the previous part of this paper [10].

2.2. Treatment of DBDCBS to cotton fibers

Cotton fabrics (1.0 g, warp 20 tex/yarn 28 yarns/cm, weft 16 tex/yarn 27 yarns/cm, 100 ± 5 g/m^2) were treated with DBDCBS (10% owf) at 30 °C for 60 min. The liquor ratio was 1:20. Sodium carbonate (5 g/l) and sodium sulfate (100 g/l) were used as an alkali and a neutral salt. At the end of treatment, the fabrics were removed and rinsed thoroughly in boiling water. To eliminate the unfixed DBDCBS of the substrates, extraction was carried out using 25% aqueous pyridine solution and then washed with a plenty amount of water.

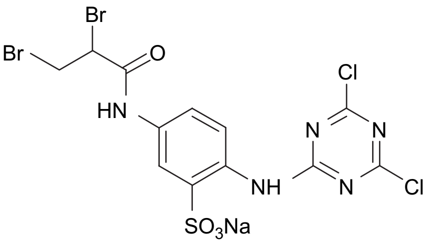


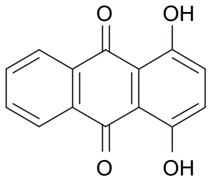
Fig. 1. The structure of DBDCBS (sodium-2-(2,3-dibromopropionylamino)-5-(4,6-dichloro-1,3,5-triazinylamino)-benzenesulfonate).

2.3. Dyeing properties of three disperse dyes

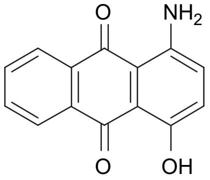
The cotton fabrics pretreated with DBDCBS were dyed with three disperse dyes shown in Fig. 2. The disperse dyes used were DHAQ, AHAQ and DAAQ; these three types of dyes show non-, mono- and di-amino groups in molecular structures, respectively. The dyeings were carried out at various temperatures (70–130 °C) for 1 h and the dye concentrations were varied with the ranges of 0.5–10% owf. The pH values (3–11) and the liquor ratio of 1:20 were used. At the end of dyeing, the dyed samples were washed with acetone in order to eliminate unfixed dyes from the fiber surfaces. Thereafter, the samples were washed with a plenty amount of water and dried.

2.4. One-bath dyeing process

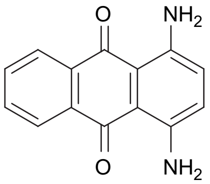
The feasibility of one-bath two-stage dyeing process containing both DBDCBS and disperse dyes in the same bath was examined. The DBDCBS (10% owf), sodium carbonate (5 g/l) and sodium sulfate (100 g/l) were



1,4-Dihydroxyanthraquinone (DHAQ)



1-Amino-4-hydroxyanthraquinone (AHAQ)



1,4-Diaminoanthraquinone (DAAQ)

Fig. 2. Disperse dyes used in experiments.

added into the initial bath. The cotton fibers (1.0 g) were used and the liquor ratio was 1:20. The bath was slowly heated up to 30 °C and the temperature was maintained for 60 min. Thereafter, without a change of the treatment liquor for new one, the disperse dyes were added into the bath. The pH of the bath was readjusted to the acidic pH of 3 using appropriate amounts of acetic acid. The bath was heated up to 100 °C and at the temperature dyeings were continued for 60 min. At the end of dyeing, the dyed samples were washed with acetone. Thereafter, the samples were washed with a plenty amount of water and dried in the open air.

2.5. Measurement of color strength

All colorimetric measurements were determined using the equipment and procedure described previously [10].

2.6. Color fastness

The fastnesses properties of the dyeings to washing, dry cleaning, dry heating, chlorinated water, rubbing and light were tested using the methods of ISO 105-C06 A1S, ISO 105-D01, ISO 105-P01 (180 °C, 30 s), ISO 105-E03, ISO 105-X12 and ISO 105-B02 (20 h), respectively. For the fastness tests, the sample dyed with DAAQ having two amino groups was only used.

3. Results and discussion

3.1. Absorbance measurement of the DBDCBS

As described in previous paper [10], the synthesis and the analysis of the DBDCBS were carried out and determined. In order to apply the DBDCBS to cotton fibers, the important requirement of this agent could be its absorption ranges, which may impart unintended color staining to the cotton substrates. In this context, Fig. 3 shows the UV/VIS spectrum of the DBDCBS. It was found that the λ_{max} in water was observed at 298 nm.

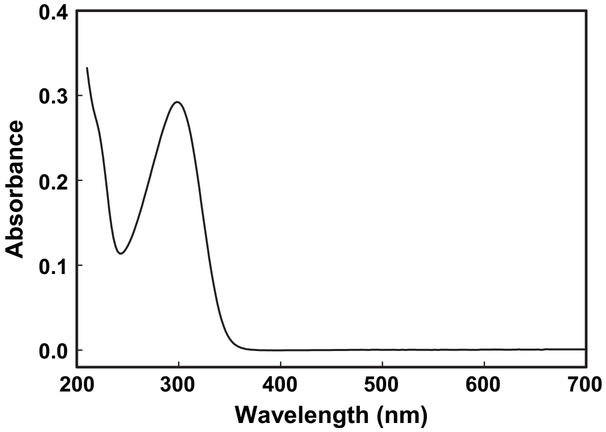


Fig. 3. UV/VIS spectrum of the DBDCBS in water.

This result explains that the prepared DBDCBS is a colorless material and that it does not cause any unintended shade changes to the treated fabric samples. Table 1 clearly represents the colorimetric data and the color difference between untreated and treated samples. The results from Table 1 support the findings displayed in Fig. 3 that when compared to the colorimetric data of both samples, virtually similar values were obtained by the DBDCBS treated sample. Thus, it is assumed that the prepared novel reactive compound imparted little color changes to the treated cotton substrates.

3.2. Disperse dyeing properties to the DBDCBS treated cotton

After the dichloro-*s*-triazinyl group of the DBDCBS reacted with the hydroxy group of the cotton fibers, the remained α,β-dibromopropionylamido group of the DBDCBS was supposed to react with other materials containing amino groups, namely disperse dyes in this study. It was obvious that in the previous part of this study [10], the disperse dye having amino group in the structure was dyed on to the DBDCBS treated cotton where covalent bonds between disperse dye and α,β-dibromopropionylamido group in the treated substrates were formed.

In order to verify the reaction properties of the α,β-dibromopropionylamido group with the amino groups of disperse dyes, the disperse dyeings were carried out in various conditions. Herein, three different disperse dyes were selected to determine the reactivity of the α,β-dibromopropionylamido groups. Fig. 4 shows the effect of pH on the color strength of the DBDCBS treated cotton fibers. As shown in Fig. 4, the color strength of disperse dyeings increased with decreasing pH.

This finding can be explained that because disperse dyes are generally weak in alkaline conditions, they could be decomposed during dyeing process [17]. Thus, in practical uses the dyeing bath should be adjusted to the acidic conditions. Besides, the cotton fibers treated with DBDCBS have a lot of anionic sites ($-SO_3^-$) induced from sodium sulfonate ($-SO_3Na$) of the DBDCBS and in acidic condition the amino groups of the disperse dyes could be temporarily cationized by the

Table 1
The colorimetric data of untreated and DBDCBS treated samples[a]

Samples	L^*	a^*	b^*	C	h^0	ΔE
Untreated	97.34	−0.57	1.07	1.21	118.14	–
Treated	97.10	−0.48	1.15	1.24	115.86	0.27

[a] Colorimetric data represented as L^* (lightness), and a^* and b^* (chroma coordinates in CIELAB color space).

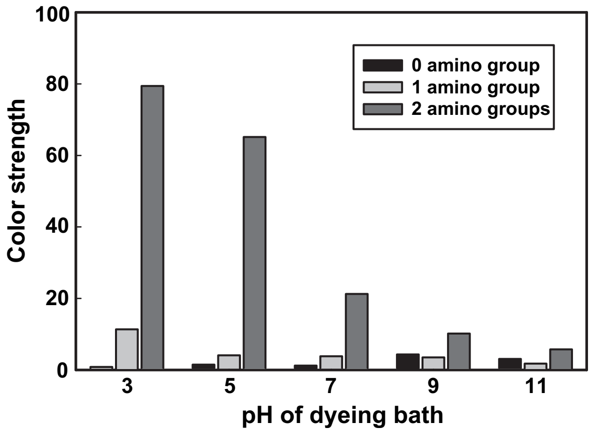


Fig. 4. Effect of pH on the color strength of the DBDCBS treated cotton fibers dyed with three disperse dyes having different number of amino groups.

protonation of the groups ($-NH_3^+$). In this condition, the attraction ionic forces could be operated between the protonated disperse dyes and the anionized cotton fibers and it could increase the adsorption of the disperse dyes towards DBDCBS treated cotton fibers so that more disperse dyes could react with the α,β-dibromopropionylamido group within the modified cotton substrates. In this context, the increase of the color strength under acidic conditions may be explained by not only the stability of disperse dyes but also the increase of adsorption of the dyes on to the DBDCBS treated fibers.

Generally, the dichloro-*s*-triazinyl group shows reactivity at lower temperature, even at room temperature. In contrary, the α,β-dibromopropionylamido group reacts at higher temperature. Thus, in order to determine optimum reaction temperature, the cotton fibers treated with DBDCBS were dyed in the temperature ranges of 70–130 °C at pH 3. In Fig. 5, as the temperature increased up to 100–110 °C, the color strength increased to the maximum value. However, above the temperature of 110 °C, the extent of color strength significantly decreased. Therefore, the temperature of 100 °C was considered as optimum reaction temperature and this temperature was used in subsequent experiments.

Fig. 6 shows the dyeing rate or reaction rate of the disperse dyes containing amino groups towards the α,β-dibromopropionylamido groups in the DBDCBS treated cotton fibers. As shown in Fig. 6, it is ascertained that the maximum color strength was successfully reached with dyeing reaction time for 60 min. In the case of DAAQ dye having two amino groups, the color strengths showed very higher values compared to the others. This satisfactory dyeing results with DAAQ were attributable to the strong affinity between di-amino groups of the dye and α,β-dibromopropionylamido groups of the treated cotton substrates. These findings also support the results from Figs. 4 and 5 that this α,β-dibromopropionylamido group showed greater reactivity towards amines or amino groups at acidic condition and high temperature (90–100 °C). Because of DAAQ dye possessing two amino groups in the structure, the color strength of dyeing was much higher than that of DHAQ dye having one amino group.

Another important consideration for practical dyeing applications is the build-up property. To carry out this experiment, the 10% owf of DBDCBS was treated to cotton fibers. According to the previous study [10], it was revealed that 44 mg (0.077 mmol) of DBDCBS was fixed to 1.0 g of cotton fibers. The amount of disperse dyes used in this build-up experiment was in the ranges of 0.5–10% owf. As shown in Fig. 7, the color strength of DAAQ dyeings rapidly increased up to 1% owf of the dye concentration and then the extent of adsorption increase gradually decreased. Above 5% owf of the

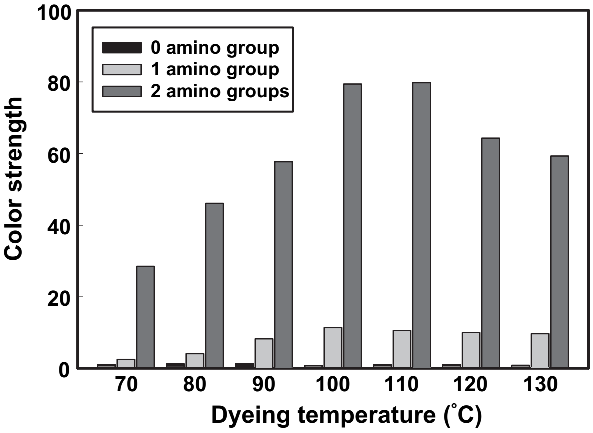


Fig. 5. Effect of dyeing temperatures on the color strength of DBDCBS treated cotton fibers.

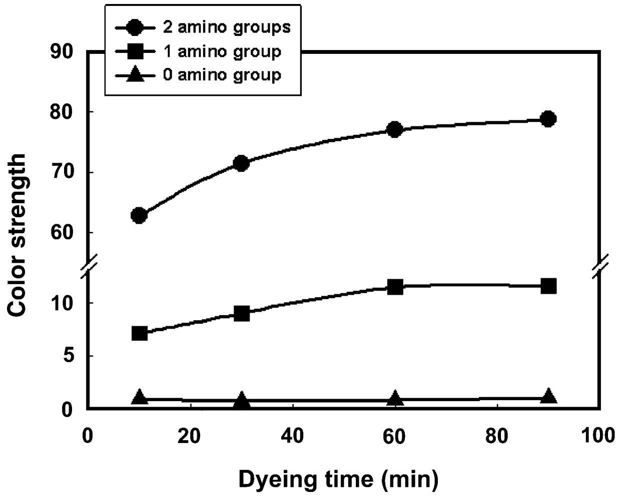


Fig. 6. Effect of dyeing time on the color strength of DBDCBS treated cotton fibers.

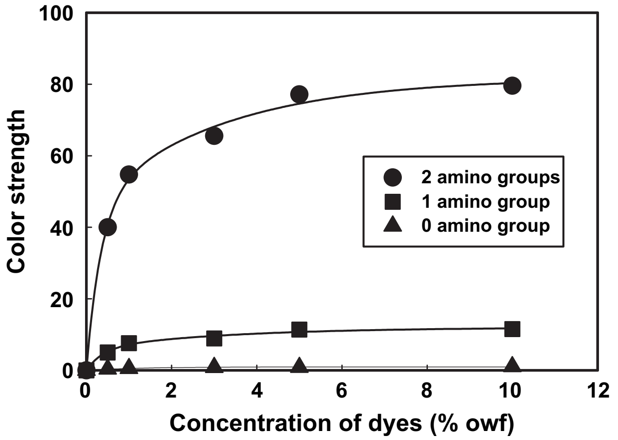


Fig. 7. Build-up properties of disperse dyes having different number of amino groups.

dyes, the color strength was reached to the maximum value.

In all experiments, the DHAQ dye having non-amino group was not dyed on to DBDCBS treated cotton fibers and its resulting color strength was very low. Virtually it seemed to be original white fabrics. These findings represent that because the DHAQ have two hydroxyl groups in the structure, this dye does not react with α,β-dibromopropionylamido group of the DBDCBS. However, AHAQ containing mono-amino group was a little exhausted to the modified cotton substrates. In the case of DAAQ having di-amino groups, the color strength greatly increased.

In a series of these experiments, the reaction mechanism of this hereto-bi-functional reactive compound may be proposed that the DBDCBS is firstly bonded to cotton fibers and that the disperse dyes having amino groups are then linked to the DBDCBS treated substrates. This reaction model is represented in Fig. 8. The hetero-bi-functional reactive compound as a bridge function is bonded to both disperse dyes and cotton fibers. Theoretically, one α,β-dibromopropionylamido group could react with two amino groups [11,12]. However, its reactivity also depends on not only the steric effects of the disperse dyes but also the linked positions of the DBDCBS within the molecular chains of cellulosic fibers.

As mentioned earlier, this novel hetero-bi-functional reactive compound has different types of two reactive groups that react with different groups at opposite pH conditions. In this context, another attempt for the one-bath two-stage process could be considered. Temperature of the treatment bath initially containing DBDCBS, sodium carbonate and sodium sulfate was slowly raised up to 30 °C and at this temperature the treatment was continued for 60 min. Thereafter, without changing the bath liquor for new one, the disperse dyes were added into the same bath and the pH was then readjusted to

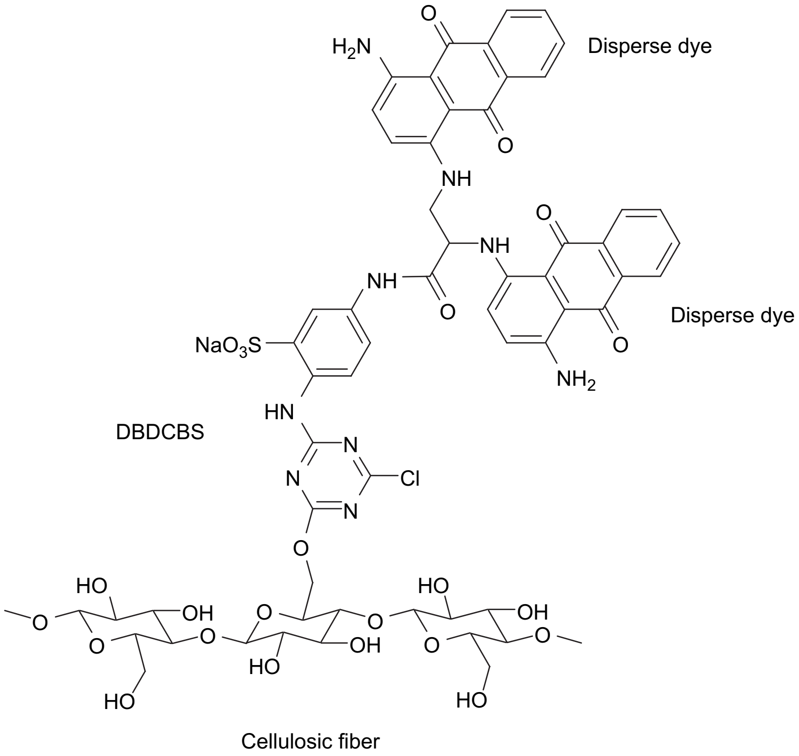


Fig. 8. A schematic model representing disperse dyes covalently bonded to cotton fibers by the bridge effect of the DBDCBS.

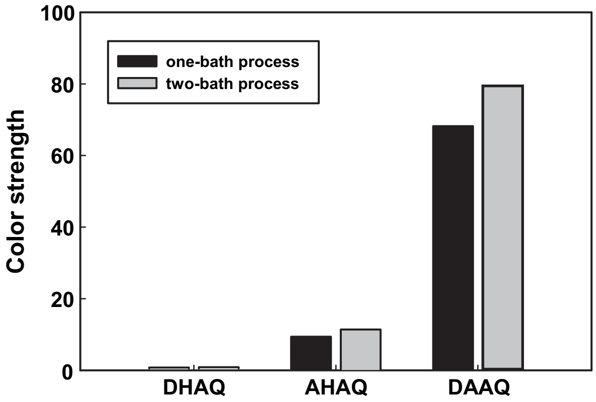


Fig. 9. Comparison of the color strengths between one-bath process and conventional two-bath process.

the range of pH 3 using acetic acid. The bath was heated up to 100 °C and the dyeings were conducted at the temperature for 60 min.

The result was shown in Fig. 9. Even though the color strengths of one-bath dyeing process were a little lower than those of conventional two-bath dyeing process, its values were quite acceptable levels considering this attempt provided the advantages in terms of time consuming and cost effectiveness.

Because the DBDCBS combined disperse dyes with cotton fibers by covalent bonds, its dyeing results were expected to provide higher fastnesses properties. The fastness tests to washing, dry cleaning, dry heating, chlorinated water, rubbing and light were conducted and the corresponding results were summarized in Table 2.

As expected, all types of fastness showed higher grades in terms of grey scale assessments. In general, disperse dyes show low dry heating fastness, because disperse dyes basically display non-polar characteristics and have lower molecular weights than other classes of dyes [18]. Therefore, disperse dyes are easily sublimed when the dyed samples are subjected to the heat treatments. In the case of this study, however, because the disperse dyes were fixed onto cotton fibers by covalent bonding mechanism, the fastness property to dry heating or sublimation was shown to be excellent.

Table 2
Color fastnesses properties of the DBDCBS treated cotton fibers dyed with 1,4-diaminoanthraquinone (DAAQ) dye

<table>
<tr><th rowspan="2">Fastnesses to</th><th rowspan="2">Change in color</th><th colspan="6">Staining</th></tr>
<tr><th>Acetate</th><th>Cotton</th><th>Nylon</th><th>PET</th><th>Acrylic</th><th>Wool</th></tr>
<tr><td>Washing</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td></tr>
<tr><td>Dry cleaning</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td></tr>
<tr><td>Dry heating</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td><td>4–5</td></tr>
<tr><td colspan="2" rowspan="2">Chlorinated water</td><td colspan="6">Concentration of active chlorine</td></tr>
<tr><td colspan="2">20 mg</td><td colspan="2">50 mg</td><td colspan="2">100 mg</td></tr>
<tr><td colspan="2"></td><td colspan="2">4–5</td><td colspan="2">4–5</td><td colspan="2">4</td></tr>
<tr><td colspan="2">Rubbing</td><td colspan="3">Dry</td><td colspan="3">Wet</td></tr>
<tr><td colspan="2"></td><td colspan="3">4</td><td colspan="3">4</td></tr>
<tr><td colspan="2">Light</td><td colspan="6">4</td></tr>
</table>

4. Conclusions

The disperse dyes having different number of amino groups were used to dye the cotton fibers. The disperse dyeings were successfully achieved by using the novel hetero-bi-functional reactive compound. The DBDCBS treated cotton fibers were optimally dyed at pH 3 and at the temperature ranges of 100–110 °C. In terms of build-up properties, the highest color strength was obtained by using the dye concentration of 5% owf. Even though the color strengths of one-bath dyeing process were a little lower than those of conventional two-bath dyeing process, its values were quite acceptable levels. In addition, the color fastnesses were very higher grades due to their covalent bonding characteristics.

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