Method of Chemical Modification of Cellulosic Fibers to Improve Their Dyeability with Reactive Dyes

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The reactive nucleophilic dye site was successfully incorporated into cellulose structure by chemical modification using a dichlorotriazine derivative as a modifying agent. The modifying agent was prepared and characterizations were done by FTIR and HPLC analysis. An elemental analyzer was used to measure the total nitrogen content of the modified cotton fabrics. The dyeing of modified cotton fabrics with commercial reactive dye in the absence of alkali metals was then investigated. The results showed that dyeability properties of modified cotton fabrics were markedly improved and the concentration of the modifying agent suitable for modifying cotton fabrics was in the range between 5 g/l and 15 g/l.

Key words: Dichlorotriazine derivative, cellulose, modification, dyeability.

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การดัดแปรเส้นใยเซลลูโลสโดยวิธีทางเคมีเพื่อปรับปรุงสมบัติการติดสีรีแอคทีฟ

กาวี ศรีกูลกิจ และปภาพิดา พรสุริยะศักดิ์ (2541)
วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย, **23 (2)**

ได้ทำการดัดแปรเส้นใยเซลลูโลสด้วยวิธีทางเคมีโดยใช้อนุพันธ์ไดคลอโรไตรอะซีน (dichlorotriazine derivative) เป็นสารดัดแปรเพื่อให้ได้เส้นใยเซลลูโลสที่มีหมู่นิวคลีโอไฟล์ที่มีความว่องไวในการทำปฏิกิริยากับสีรีแอคทีฟ ได้ทำการสังเคราะห์สารดัดแปรขึ้นและการวิเคราะห์สารดัดแปรได้อาศัยเทคนิค FTIR และ HPLC ส่วนการวิเคราะห์หาปริมาณไนโตรเจนทั้งหมดบนเส้นใยเซลลูโลสที่ผ่านการดัดแปรได้อาศัยเครื่องวิเคราะห์ธาตุ (elemental analyzer) การศึกษาการย้อมทำได้โดยนำผ้าฝ้ายดัดแปรมาย้อมด้วยสีรีแอคทีฟในสภาวะไร้ด่าง ผลการย้อมแสดงให้เห็นว่าความสามารถในการทำปฏิกิริยากับสีของผ้าฝ้ายดัดแปรเพิ่มขึ้นอย่างเห็นได้ชัดเจน โดยความเข้มข้นของสารดัดแปรที่ให้ผลการย้อมที่ดีพบว่าอยู่ระหว่างช่วง 5 กรัมต่อลิตร ถึง 15 กรัมต่อลิตร

คำสำคัญ อนุพันธ์ไดคลอโรไตรอะซีน เซลลูโลส การดัดแปร และคุณสมบัติการย้อมติดสี

INTRODUCTION

Cellulose fibers can be dyed with various classes of dyes. Most importantly, reactive dyes are widely employed for dyeing cellulose fibers because of their brilliance, wide shade gamut and excellent fastness properties. However, dyeing of cellulose fibers with reactive dyes still suffers from two major disadvantages; one is poor dye uptake and the other is unsatisfactory dye fixation. Poor dye uptake is related to the existence of the charge barrier effect between the negatively charged fiber surface and anionic reactive dyes. This problem can be solved by adding a large amount of electrolytes to the dye bath in order to suppress the negative charge on the fiber surface and then allowing reactive dye molecules to diffuse inside the fiber. In the case of poor dye fixation, the contributing factor is the presence of inactive hydrolyzed dye. Since fixation of reactive dyes onto cellulose fibers requires alkaline dyeing conditions in order to activate the hydroxyl group of cellulose to be able to react with the dye, some of the reactive dye can inevitably undergo the competing hydrolysis reaction with hydroxide nucleophiles, resulting in a reduction in the efficiency of the reaction with the cellulose substrate.

Increasing concern on environmental impacts has prompted regulators to enact tougher environmental legislation to mandate dye users to minimize color in dyehouse effluent. To meet such requirements, the dyeing industry has to adopt a more efficient dyeing process as well as selecting dyes which have a high dye fixation value. Growing demand for reactive dyes, which have higher substantivity as well as higher fixation values, has forced dye manufacturers in the western hemisphere to shift their research focus to the development of new dye ranges such as bifunctional reactive dyes, neutral fixation reactive dyes and polyfunctional dyes;(1-3) the first two types have been commercially available. In other targeted research, the chemical modification of cellulose substrate to improve the reactive dye uptake, to reduce the high concentration of electrolytes used in the dye bath, and to increase dyeability properties has attracted much attention. A number of patents and publications have considered the modification of cellulosic fibers with different classes of amides. Lewis and coworkers(4-7) have proposed the treatment of cellulosic fibers with polycationic agents in order to introduce quaternary, tertiary or secondary amino residues into cellulose. An example of this type of modifying agents is polyamide-epichlorohydrin, commercialized as Hercosette by Hercules, Inc. Good dyeing results could be achieved when Hercosette-treated fabric was dyed without salt at pH 5. Unfortunately, ring dyeing of the fibers and yarns was clearly evident and as a result light fastness was reduced by 1-2 levels. Low molecular weight compounds have been proposed as alternative modifying agents to solve the problem of ring dyeing and low light fastness. N-(2-epoxypropyl)-trimethyl ammonium chloride, commercialized by Protex as Glytac A, was tested.(8) Bayer(9) also marketed another quaternized cationic amine, which is glycidyl-N-methylmorpholinium chloride. These two quaternized amino products can react with cellulose under alkaline conditions. Both of these modified cellulose products could be dyed with reactive dyes in the absence of electrolytes under neutral conditions and have excellent dye uptake and dye fixation. However, the limitation of application to only a pad-thermosol procedure (high temperature treatment process) restricts the widespread use of these types of compounds.

The aim of this work is to explore the use of chlorotriazine derivatives as modifying agents for cellulose fibers. A chlorotriazine derivative which was employed in this experiment is 2,4-dichloro-6-pyridino-s-triazinyl chloride. The 2,4-dichloro-6-pyridino-s-triazinyl chloride possesses two highly reactive chloride atoms and one pyridinium cationic pendent groups. The highly reactive chloride atoms have been well known to be able to covalently react with hydroxyl groups in cellulose under alkaline conditions and the pyridinium cationic pendent group plays an essential role in not only assisting this compound to be water soluble but also promoting the absorption of the compound into the fiber. These two properties are of great importance for this compound to be commercially practicable.

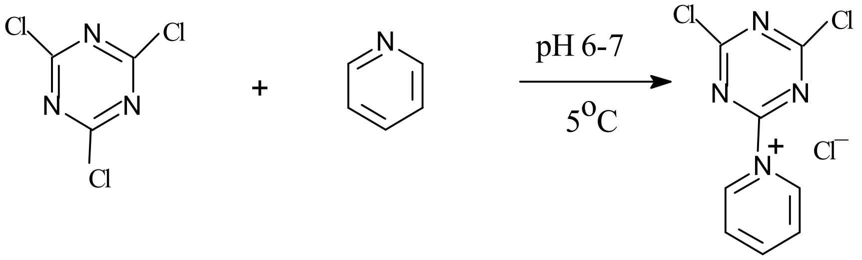
EXPERIMENTAL

Materials

Bleached, plain woven cotton fabric was used as a source of cellulose throughout this work. Chemicals used in this work were as follows: cyanuric chloride, pyridine and ethylenediamine were of laboratory reagent grade. A reactive dye, Cibacron F-B (kindly supplied by Ciba-Geigy) was of commercial grade and used as received. Non-ionic detergent was kindly supplied by U.N.T Chemical Co., Ltd.

Synthesis of the modifying agent, 2, 4-dichlro-6-pyridino-s-triazinyl chloride (DCPT)

A 13.8 g (0.075 mole) amount of cyanuric chloride and 70 ml of water were added into a beaker which was placed on a magnetic stirrer. The mixture was then stirred in an ice bath at the temperature of 5°C. A solution of pyridine (5.9 g, 0.075 mole) and water (30 ml) from a dropping funnel was added dropwise into the suspension for over 30 min. The pH of the reaction mixture was maintained between 6 and 7 by the addition of $NaHCO_3$ and the temperature was kept below 5°C and stirred throughout. When the reaction mixture became evidently clear, the reaction product was precipitated in acetone, filtered out and dried in a desiccator. This reaction may be written as shown in Scheme 1.



Scheme 1. The preparation of 2,4-dichloro-6-pyridino-s-triazinyl chloride.

Identification of 2,4-dichloro-6-pyridino-s-triazinyl chlorine (DCPT)

HPLC analysis

The purity and chemical stability of 2,4-dichloro-6-pyridino-s-triazinyl chloride were checked by HPLC on a Shimadzu LC-3A liquid chromatograph using a C_{18} column. The mobile phase was a mixture of acetonitrile and water.

FT-IR analysis

FT-IR analysis of DCPT was performed on a Nicolet Impact 400D FT-IR spectrometer using a diffuse reflectance attachment to obtain transmission IR spectra. The method of sample preparation used in this experiment is the pressed-disc technique by mixing the sample in potassium bromide (KBr) at a ratio of 1:50. The IR spectrum of the sample was collected using parameters as follows: scanning number: 32, resolution: 4 cm^{-1}, scan range: 4000-450 cm^{-1}.

Method of modification of cotton fabric with DCPT

Cotton fabric was treated in solutions of different concentrations of DCPT, ranging from 0 to 30 g/l (note: the concentration of DCPT was empirically estimated, based on an assumption that cyanuric chloride was totally converted to 2,4-dichloro-6-pyridino-s-triazinyl chloride); the treatment was carried out in a sealed stainless-steel dyepot housed on the Ahiba Polymat laboratory dyeing machine at a liquor to goods ratio of 10:1. Treatment was commenced at 55°C for 15 min. and then sodium bicarbonate (20 g/l) was added to the dyepot, and the temperature was kept at 55°C for an additional 45 min. The DCPT dyepot was taken out and 10 g/l of ethylenediamine was added. The dyepot was then placed in the Ahiba Polymat laboratory dyeing machine again. The temperature was then raised to 85°C and maintained there for 45 min. Finally, the modified cotton was taken out and rinsed thoroughly in tap water and then soaped in boiling water to remove unreacted chemicals before being dried in the open air.

Total nitrogen content determination

The total nitrogen content of the treated cotton fabric was measured according to the rapid combustion method by an elemental analyzer (Perkin Elmer PE 2400 Series II).

Dyeing of modified cotton fabrics

Modified cotton fabric was dyed in solutions of various concentrations of commercial monofluorotriazinyl dye (Cibacron F-B, Ciba-Geigy) and 20 g/l NaCl (for a higher NaCl concentration there was a similar percentage of dye uptake(10)). All dyeings were carried out in sealed stainless steel dyepots housed on an Ahiba Polymat laboratory dyeing machine at a liquor to goods ratio of 10:1. No alkali additives were required. Dyeing of modified cotton fabric was commenced at 85°C for an hour. The dyed cotton fabric was taken out and rinsed thoroughly in tap water and cut into equal portions. One of these portions was soaped in a solution containing non-ionic detergent (5 g/l) and boiled 15 min. The color yield expressed as the measured K/S value of soaped and unsoaped dyed samples.

Measurement of dye exhaustion and dye fixation(11)

Exhaustion was the total amount of dye taken up by modified cotton fabrics, which was measured by sampling the dye bath at the beginning and the end of the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of maximum absorption (λ_{max} = 540 nm) using a UV/Vis spectrophotometer. Percentage of dye exhaustion (%E) was calculated using the following equation:

$$\%E = 100(1-A_1/A_0)$$

where A_0 and A_1 were the absorbances of the dye solution at the beginning and at the end of the dyeing process, respectively.

Determination of dye fixation

To find out how much dye covalently fixed onto the fiber, the extraction of any unfixed dye from the dyed material was carried out by washing dyed fabric in the solution of non-ionic detergent while boil for 15 min. By using a I.C.S. Micromatch color measurement system (Macbeth 7000), the reflectance values at λmax (540 nm) of dyed fabric before and after washing were obtained. The color yield of the colored fabric was expressed as K/S values which could be calculated by using the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R,$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the colored fabric at λ_{max}.

The K/S value was proportional to the dye concentration on the fiber and then the extent of dye-fiber fixation could be calculated using the following equation:

$$\text{Total dye fixation } (\%T) = \frac{K/S \text{ after soaping x } (\%E)}{K/S \text{ before soaping}}$$

RESULTS AND DISCUSSION

FT-IR Study of the modifying agent (DCPT)

The FT-IR spectrum of the DCPT collected between 4000 cm^{-1} and 450 cm^{-1} is illustrated in Figure 1. The chemical structure of 2,4-dichloro-6-pyridino-s-triazinyl chloride is characterized by the absorption peaks at 795 cm^{-1}, 1620 cm^{-1} and in the region of 3,500-3,300 cm^{-1}.(12) These peaks can be assigned to the C-Cl stretching vibration, -C=N stretching vibration in the triazinyl ring, and C-H stretching vibration in the pyridinium residue respectively.

Figure 1. FT-IR spectrum of 2,4-dichloro-6-pyridino-s-triazinyl chloride.

HPLC analysis of the DCPT

The HPLC technique was used to follow the reaction between cyanuric chloride and pyridine as well as to check the chemical stability of the product.

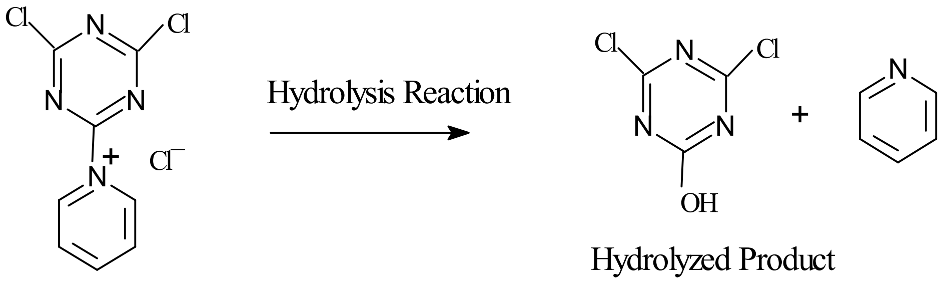
Figures 2 and 3 show HPLC chromatograms of cyanuric chloride and pyridine alone, respectively. Figure 4 demonstrates the chromatogram of the reaction product.

Figure 2. HPLC chromatogram of cyanuric chloride.

Figure 3. HPLC chromatogram of pyridine.

Figure 4. HPLC chromatogram of 2,4-dichloro-6-pyridino-s-triazinyl chloride.

From the chromatogram of cyanuric chloride, a single peak representing the presence of cyanuric chloride can be observed at the retention time of 2 min. From Figure 3, the chromatogram shows that pyridine reaches the detector in 2.51 min., slower than cyanuric chloride. In Figure 4, the chromatogram indicates that the reaction mixture taken at the end of reaction has two components. The peak at a retention time of 1.81 min. is believed to represent the peak of DCPT. Another peak at a retention time of 1.36 min. is thought to be the peak of the hydrolysis product of DCPT, the 2,4-dichloro-6-hydroxyl-s-triazine derivative. This conclusion is based on the fact that the ionic compound migrates slower than non-ionic compounds in the acetonitrile/water (65:35) mobile phase. The hydrolysis reaction may be written as follows:



Scheme 2. Hydrolysis reaction of 2,4-dichloro-6-pyridino-s-triazinyl chloride.

The presence of 2,4-dichloro-6-hydroxyl-s-triazine derivatives suggests that the DCPT is unstable and susceptible to undergo further hydrolysis reactions. The instability of the DCPT in a water medium was also investigated. The DCPT solution was kept at room temperature for 1 hour and then subjected to HPLC analysis. The result from Figure 5 illustrates that the intensity ratio between the peak at a retention time of 1.55 min. (2,4-dichloro-6-hydroxyl-s-triazine derivative) and 2.09 min. (DCPT) increases significantly, confirming that DCPT can be easily hydrolyzed. The result of the hydrolysis reaction gives a 2,4-dichloro-6-hydroxyl-s-triazine derivative and a pyridine. The presence of all three components, DCPT, the hydrolyzed product, and pyridine, was confirmed by ^{13}C MNR.(10) Hence, in this project the application of the DCPT product to cotton fabric was carried out immediately without isolation from the reaction mixture to prevent the hydrolysis of the DCPT.

Figure 5. HPLC chromatogram of DCPT solution after being kept at room temperature for 1 hour.

Total nitrogen determination of modified cotton fabric

The total nitrogen content of treated fabric, before and after adding ethylenediamine, was measured in order to determine the actual amount of DCPT covalently bonded to cotton fiber. The results are shown in Table 1.

Table 1. Total nitrogen content of modified cotton fabrics at different DCPT concentrations.

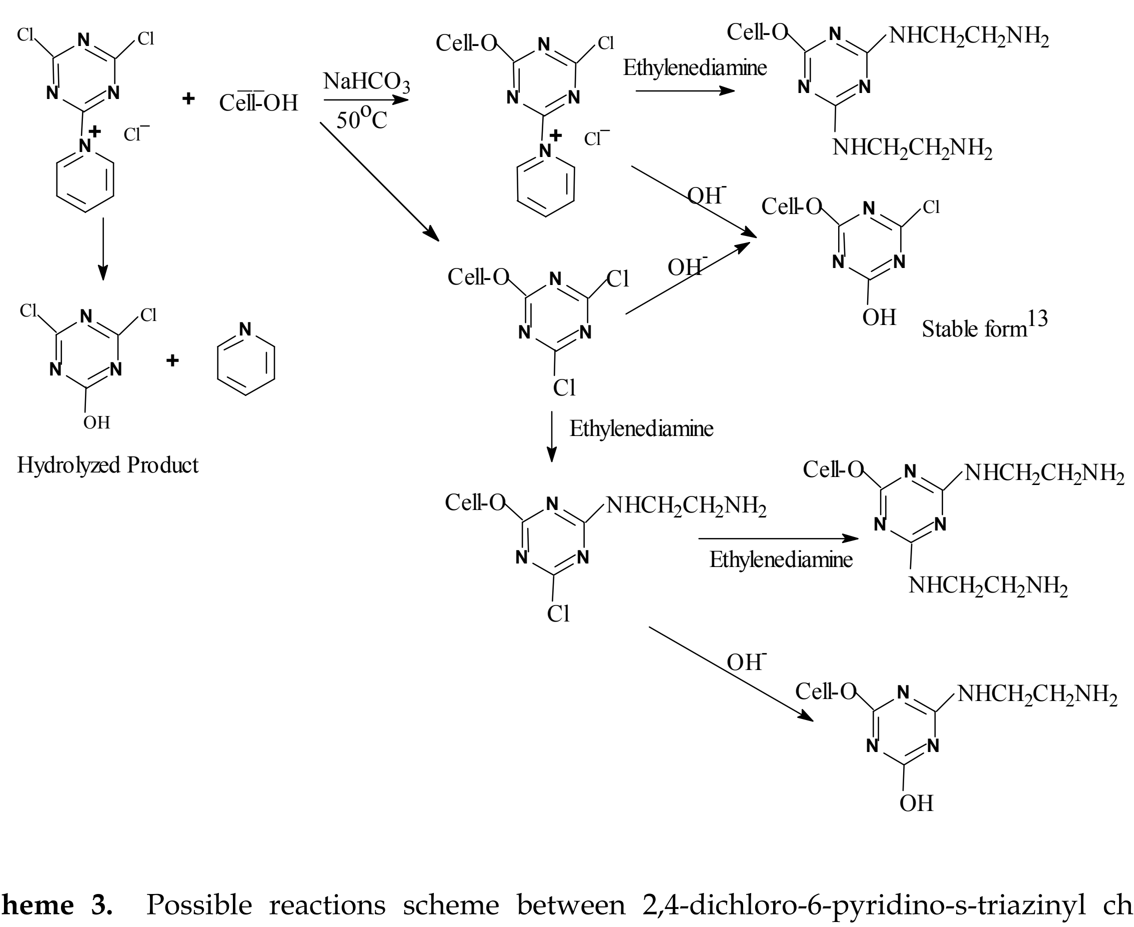
Estimated Conc. of DCPT (g/l)	Total Nitrogen Content (%)		Total Nitrogen Content Ratio
	Before Adding Ethylenediamine	After Adding Ethylenediamine	
5	0.257	0.261	1.016
10	0.369	0.393	1.065
15	0.464	0.624	1.345
20	0.559	0.697	1.247
25	0.758	0.828	1.092
30	0.841	0.891	1.059

The total nitrogen content of DCPT cotton is shown in column 2 while the total nitrogen content of DCPT cotton further treated with ethylenediamine is given in column 3. It can be seen that the total nitrogen content value of treated cotton before adding ethylenediamine increases with an increase in the concentration of DCPT. However, it may not be correct to conclude that the higher total nitrogen content value implies a higher amount of dye sites. In fact, the additional increase in total nitrogen content value after DCPT cotton fabric is further treated with ethylenediamine as shown in column 3 indicates that the free amino dye site was incorporated. Furthermore, the nitrogen content ratio given in column 4 provides information about the actual conversion of DCPT cotton fabric to ethylenediamine treated DCPT cotton fabric. The highest conversion ratio found at 15 g/l DCPT concentration is 1.345; however, this is still far below the calculated conversion ratio of 1.75. This is probably because some of the reactive sites on DCPT cotton fabric undergo a hydrolysis reaction, hence reducing the amount of reaction sites for ethylenediamine. The possible reactions involved may be written as shown in Scheme 2.

Application of commercial reactive dye to the modified cotton fabric

A. Effect of increasing DCPT concentration on dye color yield (dye uptake) and dye fixation

The dyeing of modified cotton fabric in the absence of alkali additives was investigated. Cotton fabrics modified with various concentrations of the DCPT were dyed with 2% on weight of fiber (o.w.f.) commercial reactive dye, Cibacron F-B at 85°C for 1 hour in the presence of 20 g/1 NaCl. The color yields, dye exhaustion, and fixation values of resulting dyed fabrics are shown in Table 2. The result obtained from the control cotton fabric (first row) demonstrates that the color yield and degree of dye fixation were quite low, indicating that it is essential to modify cotton fiber by incorporating reactive dye sites in order to be dyed in the absence of alkali additives. After being modified, the significant increase in dye exhaustion and the degree of dye fixation could be achieved at the concentration of DCPT of 5 g/l. An increase in DCPT concentration from 5 g/l to 15 g/l brings about an insignificant change. However, a further increase in DCPT concentration from 15 g/1 to 30 g/1 causes a gradual reduction in the degree of dye fixation. It is quite surprising that the higher amount of dye sites at higher DCPT concentrations does not bring about a



Scheme 3. Possible reactions scheme between 2,4-dichloro-6-pyridino-s-triazinyl chloride, cellulose, and ethylenediamine.

higher dye fixation value. Partly, this may be due to the dominant steric hindrance effect caused by the presence of the triazinyl ring of DCPT that prevents dye molecules from reaching the dye sites. As demonstrated in Table 2, the DCPT concentrations suitable for modifying cotton fabrics should be in the range between 5 g/1 and 15 g/1. From further study of this table, it can be observed that the dye exhaustion value is limited to about 75% exhaustion. This may be caused by a gradual increase in the negative charge barrier as more negatively charged dyes diffuse inside the fiber, hence reducing the efficiency of dye exhaustion as well as the dye fixation value.

Table 2. Color Yields, dye exhaustion and fixation values of modified cotton fabric at various DCPT concentrations.

Conc. of DCPT (g/l)	K/S (color yield)		% Dye Exhaustion	% Dye Fixation
	Before Soaping	After Soaping		
0	6.44	2.17	15.63	5.27
5	22.38	20.89	74.05	69.12
10	23.67	22.07	75.52	70.42
15	22.36	20.88	76.90	71.81
20	23.06	20.11	75.34	65.70
25	20.96	18.36	74.54	65.29
30	19.49	16.63	74.84	63.86

Table 3. Build-up of commercial Cibacron F-B on modified cotton fabrics at 15 DCPT concentration.

Dye Conc. (% o.w.f)	**Color Yield**		**% Dye Exhaustion and Dye Fixation**	
	K/S Before soaping	K/S After soaping	% Exhaustion	% Total (Apparent) dye fixation
1	15.37	14.72	74.14	71.00(95.77)
2	23.32	21.59	72.67	67.28(92.58)
3	26.94	24.68	68.90	63.12(91.61)
4	28.25	26.13	63.17	58.43(92.50)

B. Effect of increasing dye concentration on the color yield and the degree of dye fixation

Dyeing of modified cotton fabrics at four depths of shade, 1%, 2%, 3% and 4% o.w.f, respectively, were carried out using the method described above. Modified cotton fabric treated with the 15 g/l DCPT concentration was chosen. The results obtained are summarized in Table 3.

The results demonstrate that an increase in dye concentration brings about a gradual decrease in the dye exhaustion value as well as the degree of total dye fixation. The gradual leveling-off of the dye exhaustion value as the dye concentration increases is found to be in agreement with results obtained from dyeing of typical reactive dyes. This is a common phenomenon found in dyeing of negatively charged reactive dyes where the build-up of sulphonated dyes acts as a negative charge barrier to prevent dyes in solution from diffusing inside. Further studying this table, it is interesting to point out that in all cases, as many as 90% of dyes which can get inside the fiber undergo reactions with free amino reactive groups, indicating that hydrolysis of dyes is minimal. However, with the current dye the total dye fixation value is not satisfactory due to the medium substantivity of this dye. An improvement in the total dye fixation value may be achieved upon replacement with higher substantive dyes. The high apparent fixation rate would suggest that it should be possible to obtain heavy shade dyeings with good dye build-up.

CONCLUSIONS

This study confirmed that cotton fabric could be dyed with commercial reactive dyes in the absence of alkali additives. The technique used in this study involved the introduction of a reactive nucleophilic dye site into the cellulose structure. By doing so, cellulose was treated with 2,4-dichloro-6-pyridino-s-triazinyl chloride (DCPT), followed by the further reaction of DCPT cellulose with ethylenediamine. Dyeing of modified cotton fabric using commercial reactive dye in the absence of alkali additives showed that the high degree of dye fixation was dependent on the availability of accessible free amino reactive dye sites. The results demonstrated that the DCPT concentrations suitable for modifying the cotton fabrics should be in the range between 5 g/l and 15 g/l. It was also noticed in this study that deep depths of shade could be obtained at relatively lower concentrations of dye, e.g., between 3-4% o.w.f. This is the advantage of alkali-free dyeing in terms of minimizing hydrolyzed dyes, reducing color in dye house effluent, and saving the production costs.

However, a drawback was found during the preparation of the modifying agent in that the compound was so chemically unstable that isolation was quite difficult to achieve. It is necessary that any compound to be used as a modifying agent should be easy to handle. Therefore, searching for more stable dichlorotriazine derivatives is a worthwhile target for continuing research.

ACKNOWLEDGMENT

The authors would like to express their gradtitude to the National Metal and Materials Technology Center (MTEC) for financial support of this work.

REFERENCES

1. Lutringer J.P., American Association of Textile Chemist and Colorist Book of Papers (1992) 318.
2. Parham R.J., American Association of Textile Chemist and Colorist Book of Papers (1994) 398.
3. Srikulkit K., Ph.D Thesis, University of Leeds, 1997.
4. Lewis D.M. and Lei X.P., Textile Chemist and Colorists, **21** (1989) 23.
5. Burkinshaw S.M., Lei X.P and Lewis D.M., Proc. Conf. on Reactive Dyes (Leeds University), 1989.
6. Burkinshaw S.M., Lei X.P and Lewis D.M., Journal of Society of Dyers and Colourists, **105** (1989) 391.
7. Leweis D.M. and Lei X.P., Journal of Society of Dyers and Colourists, **107** (1992) 102.
8. Rupin Met al., Textile Chemist and Colorists, **8** (1976) 139.
9. Gipp et al., German Offen, 2407, 147.
10. Pornsyriyasak P., M.Sc Thesis, Chulalongkorn University, 1998.
11. Lewis D.M. and Shao J.Z., Journal of Society of Dyers and Colourists, **111** (1995) 146.
12. Silverstein R.M., Bassler Clayton G, and Morrill T.C., Spectrometric Identification of Organic Compounds, 5th Edition, John Wiley & Sons, Inc., 1991.
13. Shore J., Cellulosics Dyeing, Society of Dyers and Colourists, England, 1995.

Received: May 18, 1998
Accepted: August 17, 1998