# Dyeing of Glass Fiber Fabrics Having Amino Groups with Acid Dyestuff and After-Chroming

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*Received 12 December 1996; accepted 15 March 1997*

**ABSTRACT:** The glass fiber fabrics treated with a coupling agent that contains aminoethyl groups are used as a dye with a procedure similar to that for nylon with acid dyestuff and after-chroming. Furthermore, we investigated the dyeing parameters and physical properties. Results revealed that the glass fiber fabrics treated with the coupling agent were dyeable. The best conditions for acid dyestuff are at pH = 6 and at 5% owf (on the weight of fiber) concentration of dyestuff; for after-chroming, they are at 1.4% owf concentration of potassium dichromate and at 70°C for 50 min. In addition, the fabrics dyed have much better colorfastness (4–5 grade), and the average dyeing evenness is lower than 1.5. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 1039–1048, 1997

**Key words:** glass fiber fabrics; acid dyestuff; surface-treated; coupling agent; dyeing fastness; after-chroming

## INTRODUCTION

Glass fiber was developed about a half a century ago. Because the glass fibers have many good properties, they are applied extensively in many facilities and in materials such as fiber-reinforced plastics.[1] However, glass fibers cannot be dyed easily and satisfy optical sensitivity, due to the compositions of the glass fibers containing far less hydroxyl groups on the surface.[2–4] Since hydroxyl groups cannot be bonded strongly with the dyestuff, even with a small amount of bonding in them, the colorfastness of the glass fibers dyed is poor. Therefore, those glass fiber artifacts, such as vessels, cabin cruisers, crash helmets, etc., cannot be dyed with dyestuff but can be dyed with a pigment that can be peeled easily.

Hence, the object of this work uses the silane coupling agent that contains the aminoethyl groups to treat the glass fibers[2,5] to increase the bonding of the glass fibers with acid dyestuff and after-chroming by chemical bonding. Furthermore, we investigate the best dyeing conditions and the physical properties of after-chroming.

Journal of Applied Polymer Science, Vol. 66, 1039–1048 (1997)
 CCC 0021-8995/97/061039-10

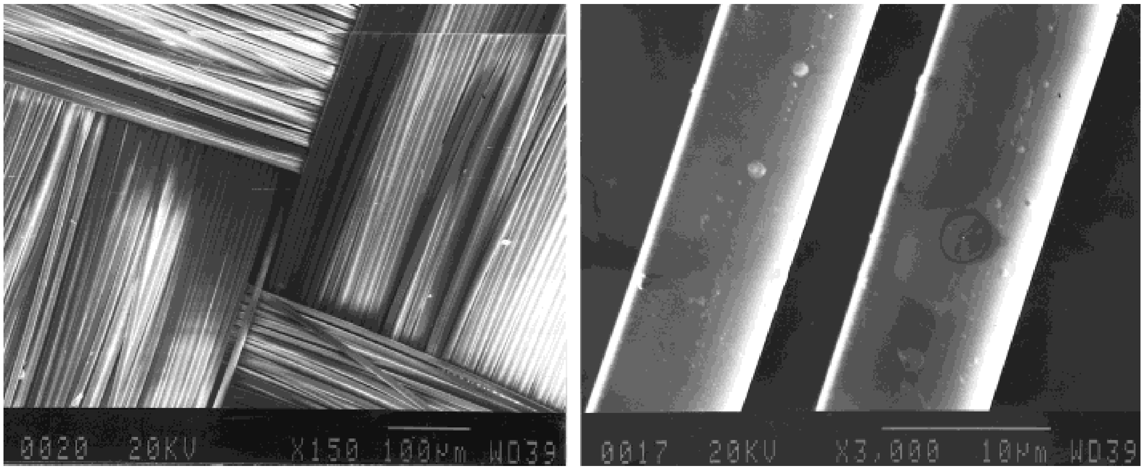
## EXPERIMENTAL

### Materials

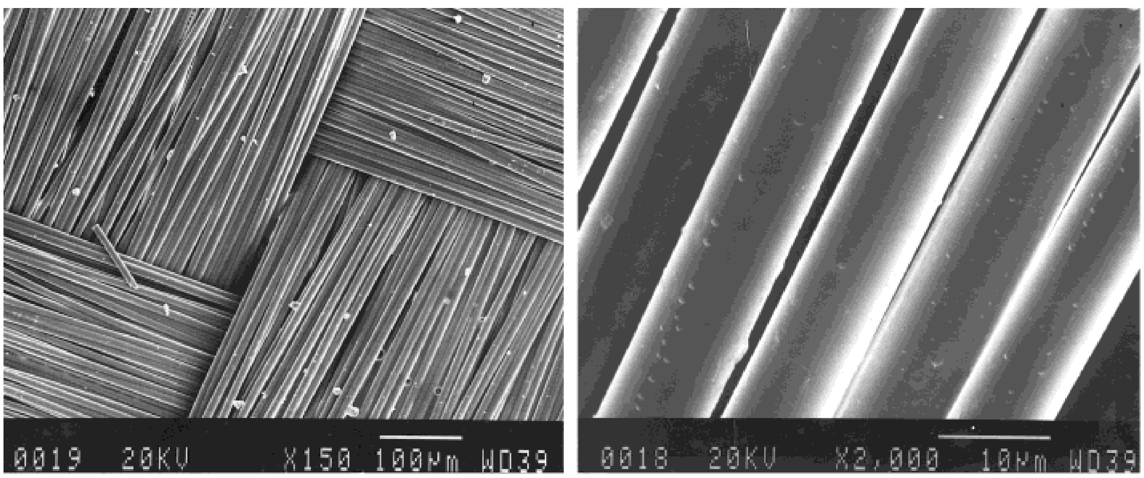
E-glass fiber cloth of 44 × 34 roving/in. (Taiwan Plastic Co.) was used, with roving fineness 66Tex (91 D). The diameter of a single filament was 9 $\times 10^{-6}$ m (9 $\mu$m). The silane coupling agent was *N*-($\beta$-aminoethyl)-$\gamma$-aminopropyl trimethyoxy silane from Dow Corning Co. and the acid dyestuff was C.I. Acid Blue 158 (I.C.I., England).

### Instruments

The dyeing machine was model H-24D-A000 from Rapid® Labortex, Taiwan. Multifunction scanning electron microscopy was performed on a (M-SEM; JXA-840 from Jeol, Japan). Infrared mea-




(a)




(b)

**Figure 1** Scanning electron micrograph of the surface of glass fiber and glass fabric: (a) after desizing; (b) treated with coupling agent.

surements were made on Model IR-408 from Shimadzu, Japan). We also used a standard lauder tester (LM-8DS, Suga, Japan), a dyeing rubber tester (BSHV, JIS-L0801,0823 method), and a color meter (ND-300A, Japan; according to the JIS-Z-8729 method).

## Procedures

### *Desizing of Glass Fiber Cloth*

The glass fiber cloths were immersed in 1% potassium nitrate for 70 min, then dried in an oven at 120°C, followed by heat cleaning in a furnace at 400°C for 70 min for the complete desizing.[1]

### *Surface Treatment of Glass Fiber Cloth*

The preparation of silane coupling agent[5–7] was done as follows. The silane coupling agent was hydrolyzed for 24 h in distilled water, using glacial acetic acid to adjust the pH. The cloth was immersed in the solution and then cured at 140°C for 20 min in a dyeing machine. Afterward, the cloth was taken out and dried at room temperature for one day, then dried in an oven at 100°C.

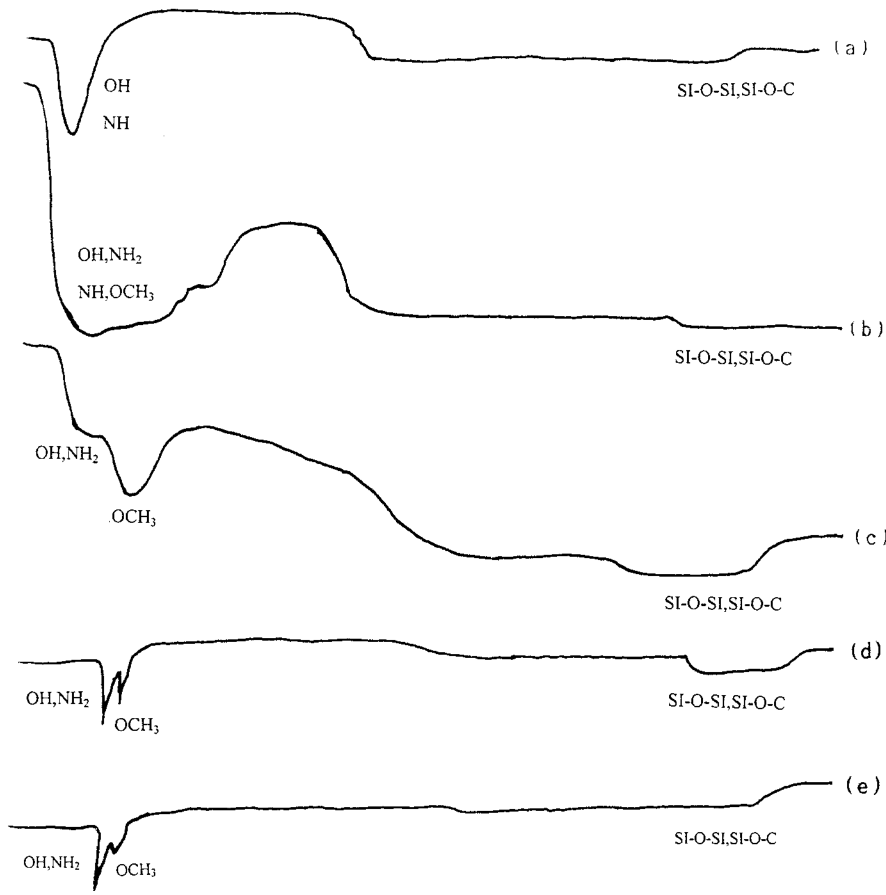



**Figure 2** Fourier transform absorption infrared absorption spectrum: (a) glass fabrics; (b) coupling agent; (c) glass fabric treated with coupling agent; (d) specimen; (c) dyed with acid dye; (e) specimen; (d) after chroming.

### *Dyeing*

The steps for dyeing[8] are to fill with water to the required level (liquid ratio = 1 : 30) and then to heat to 50°C. Chemicals such as sodium sulfate 5 g L and acetic acid (1–2%) are then added, and the solution is adjusted to pH of 5–7. Afterward, dissolved dyestuff is added and heated to 100°C at 1°C per min, then dyed at 100°C for 30 min, and then cooled to 50°C. Potassium dichromate (0.2–2.2% owf) was added for after-chroming. The final procedures are to heat to 100°C, then to add the sodium thiosulfate and to dye at 70–120°C for 10–60 min. Finally, those samples were cooled, rinsed, and dried.

### *Test*[9–11]

With the multifunction scanning electron microscopy (M-SEM) were observed the surface of glass fiber fabrics and glass fibers after desizing or surface treatment, as shown in Figure 1. Analyzing the chemical bonding by infrared (IR) spectroscopy, the functional groups on the surface of glass fibers treated with the coupling agent were examined. With use of the methods of JIS-L0821,0844 and JIS-L0801,0823, we tested the colorfastness to laudering and the colorfastness to crocking, respectively. The bending length test was according to ASTM method D1388-64.

## RESULTS AND DISCUSSION

### Infrared Analysis of Glass Fibers Before and After Coupling Agent Treatment and Dyeing

The IR spectrum are shown in Figure 2. The absorption of the functional groups such as the hydroxy group (3600–3700 $cm^{-1}$), the amino group (3400–3530 $cm^{-1}$), and the methoxy group

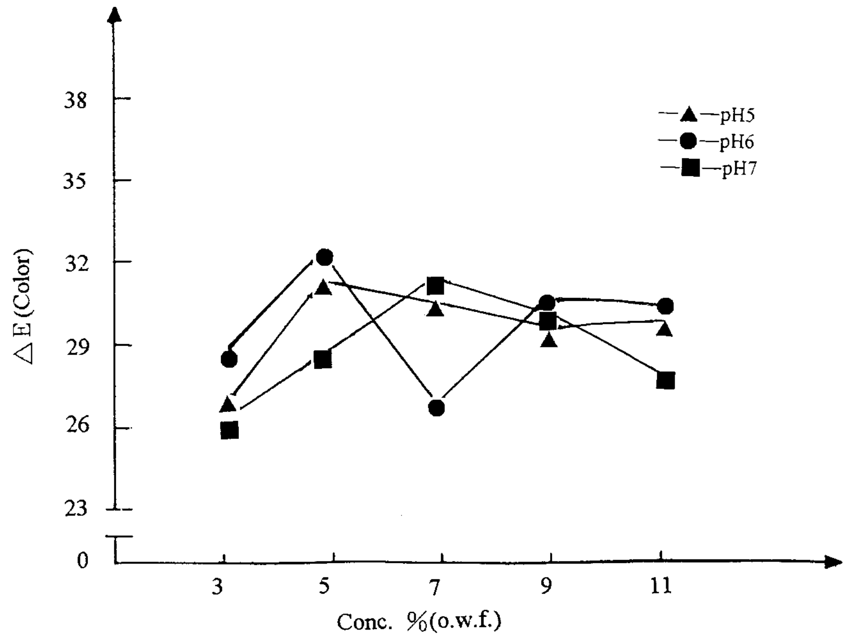



**Figure 3** Effect of pHs and concentrations of acid dye on dyeing of glass fabrics (dyeing condition: 100°C at 30 min).

(2815–2835 $cm^{-1}$), and —Si—O—Si—, —Si—O—C— at 1015–1095 $cm^{-1}$, had been changed for glass fibers before and after the coupling agent treatment and dyeing. Hence, the coupling agent would be confirmed to bond with the glass fiber and dyestuff. It is also identified in Figure 1(b).

## Dyeing Conditions of the Glass Fiber Fabrics with Acid Dyestuff

### *Relationship of ΔE Color (Color Difference) and pH Value and Concentration of Dyestuff*

Figure 3 shows that the best conditions are at pH 6 value and at 5% owf concentration of dyestuff.

**Table I Fastness Evaluation of Glass Fabrics Treated with Coupling Agent, Followed by Dying, in Various pH Values and Concentrations of Acid Dye**

| Item | pH Value | Concentration of Dye (%) owf | Grade | | | | |
|---|---|---|---|---|---|---|---|
| | | | 3 | 5 | 7 | 9 | 11 |
| Colorfastness to laundering | 5 | Staining | 4 | 4–5 | 4 | 4–5 | 4–5 |
| | 5 | Change in color | 4–5 | 4–5 | 4–5 | 4–5 | 5 |
| | 6 | Staining | 4 | 5 | 5 | 4–5 | 4–5 |
| | 6 | Change in color | 4–5 | 4–5 | 4–5 | 4 | 4–5 |
| | 7 | Staining | 4 | 4–5 | 4–5 | 4 | 4–5 |
| | 7 | Change in color | 4–5 | 4–5 | 5 | 4–5 | 5 |
| Colorfastness to crocking | 5 | Staining | 4 | 4–5 | 4 | 4 | 3–4 |
| | 5 | Change in color | 4 | 4 | 4 | 4 | 4 |
| | 6 | Staining | 4–5 | 4–5 | 4 | 3–4 | 3–4 |
| | 6 | Change in color | 4–5 | 4–5 | 4 | 4 | 4 |
| | 7 | Staining | 4 | 4–5 | 3–4 | 4 | 4 |
| | 7 | Change in color | 4 | 4–5 | 4 | 4–5 | 4 |

**Table II Bending Length of Glass Fabrics Dyed with Acid Dye**

| pH Value | Concentration of Dye [(%) owf] | | | | |
|---|---|---|---|---|---|
| | Bending Length (mm) | | | | |
| | 3 | 5 | 7 | 9 | 11 |
| 5 | 83 | 84 | 81 | 82 | 84 |
| 6 | 80 | 83 | 82 | 83 | 82 |
| 7 | 81 | 80 | 83 | 82 | 83 |

Bending length of glass fabrics after desizing is 67 mm; bending length of glass fabrics treated with coupling agent is 72 mm.

This is due to the dyestuff belonging to the milling type, and to bath-controlled dyeing under a weak acid state. The dyestuff bonds easily with the aminoethyl groups of the coupling agent on the glass fibers. On the other hand, the concentration of dyestuff cannot be used more than this (5% owf). Otherwise, it will cause more water pollution. The glass fiber itself does not have almost the absorptive property and lacks the dyeing bond with acid dyestuff.

### *Colorfastness of the Glass Fiber Fabrics*

As shown in Table I, all the colorfastness to laundering is very good, especially at the pH 6 value. In addition, due to the glass fiber fabric belonging to brittle material, the evaluated grade of the colorfastness to crocking is worse.

### *Bending Length*

The bending lengths of glass fiber fabrics dyed with acid dyestuff are indicated in Table II. The bending lengths are between 75 and 90 mm, while the bending length of glass fiber fabrics desized or treated with coupling agent are 67 or 72 mm, respectively. The data show that the glass fiber fabrics are rigid fabrics. In addition, the coupling agent was bonded to the glass fibers so that the bending length increased.

## Effect of After-Chroming on the Dyeing Properties of the Glass Fiber Fabrics

### *Effect of Temperatures, Concentrations, and Times*

Figures 4 to 9 reveal that the $\Delta E$ (color) obviously differs in accordance with the temperature for after-chroming. When the temperature for after-

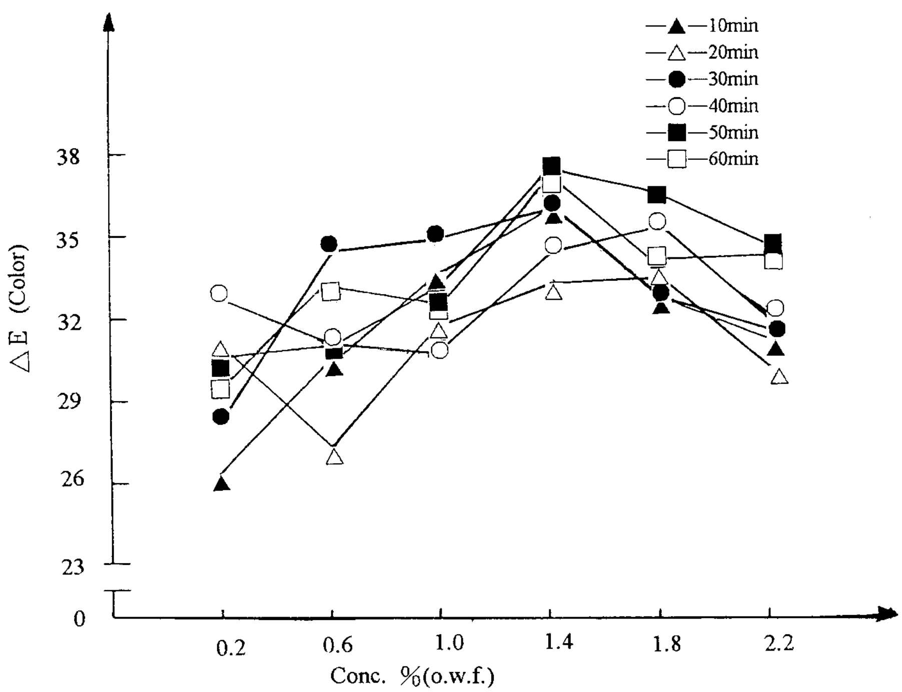



**Figure 4** Effect of concentrations of chromate and treated times at 70°C on dyeing (fabrics dyed with acid dye as shown, in Figure 3, with a concentration of acid dye of 5% owf and a pH of 6).

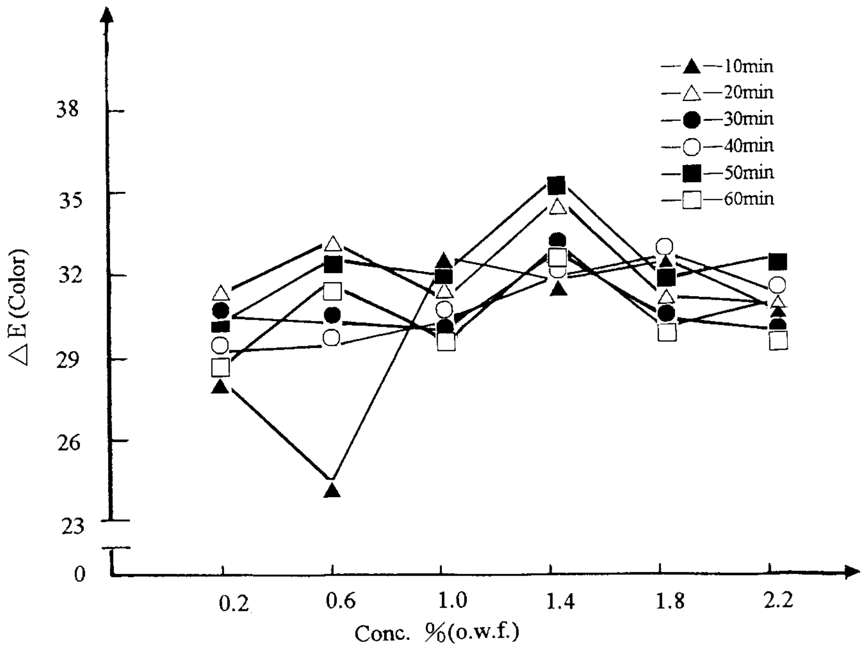



**Figure 5** Effect of concentrations of chromate and treated times at 80°C on dyeing (fabrics dyed with acid dye, as shown in Figure 3, with a concentration of acid dye of 5% owf and a pH of 6).

chroming is much higher, the $\Delta E$ (color) is much lower. This is because higher temperature will cause the dyed acid dyestuff to migrate and to decline the $\Delta E$ (color) value. In addition, the concentration at 1.4% owf has the highest dyeing exhaustion. This is because the dyeing site has their

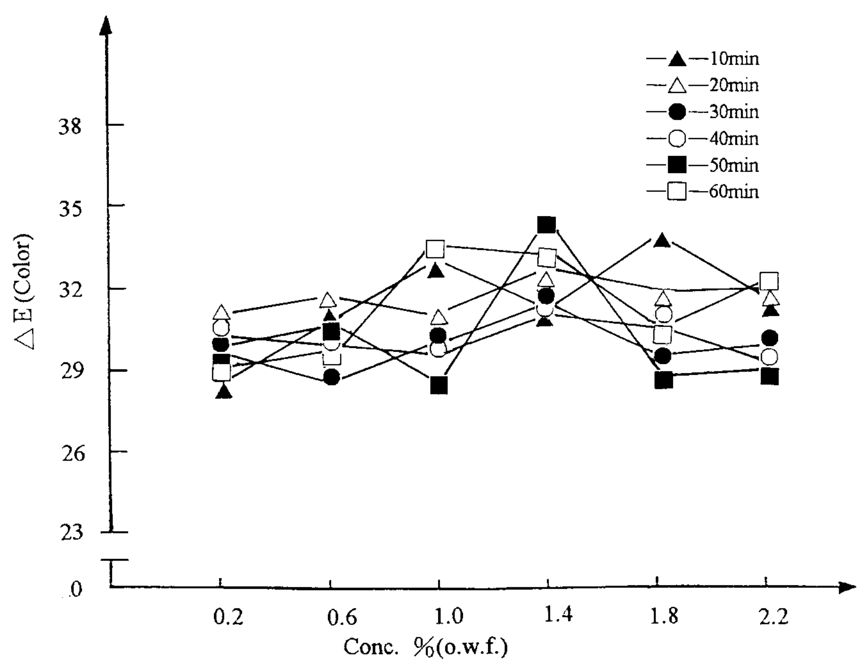



**Figure 6** Effect of concentrations of chromate and treated times at 90°C on dyeing (fabrics dyed with acid dye, as shown in Figure 3, with concentration of acid dye of 5% owf and a pH of 6).

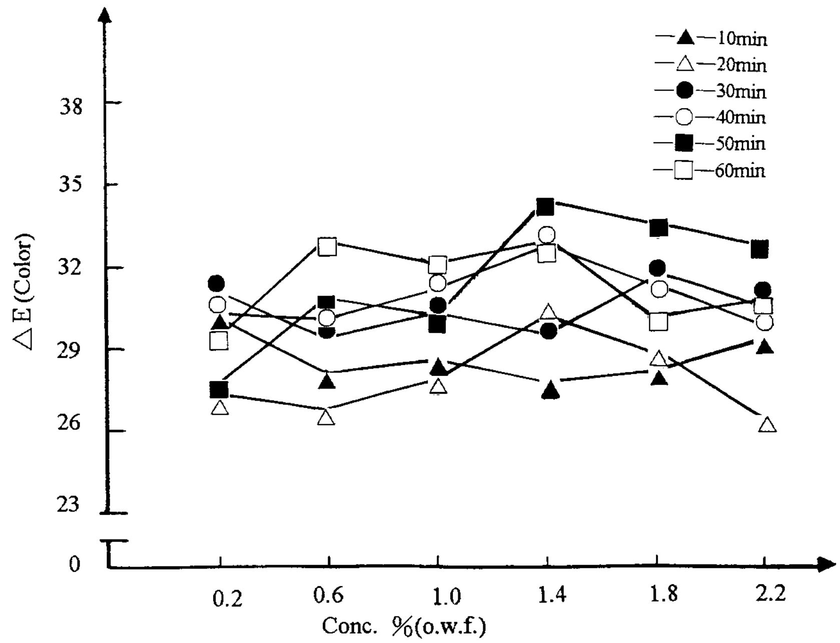



**Figure 7** Effect of concentrations of chromate and treated times at 100°C on dyeing (fabrics dyed with acid dye, as shown in Figure 3, with a concentration of acid dye of 5% owf and a pH of 6).

amount at that concentration, and the precipitation of chromic ions are exactly saturated. If it is more than this, the dyestuff will be wasted and, hence, will cause the $\Delta E$ (color) to decrease. On the other hand, the treated time of 50 min is the best; 10–40 min will be too short to fix all the

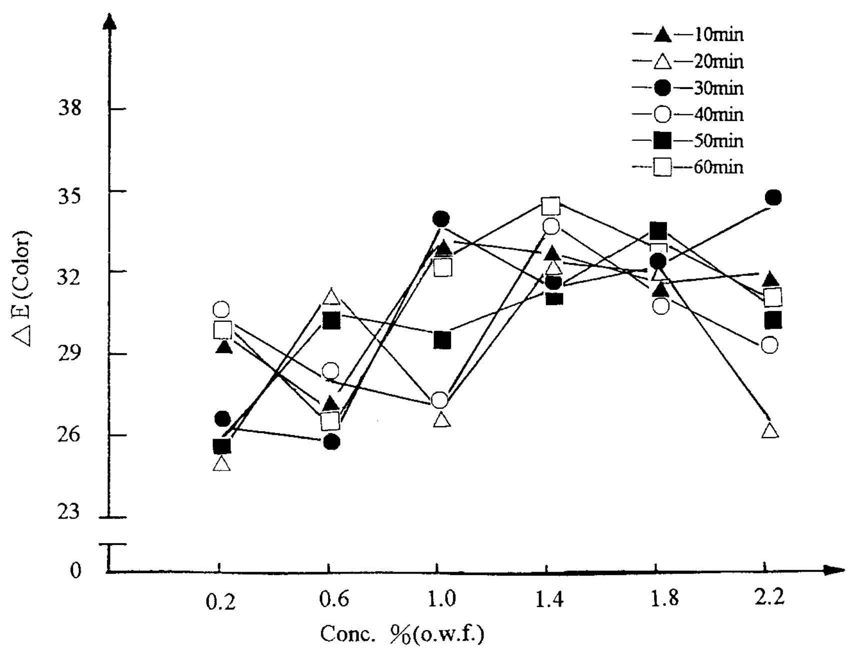



**Figure 8** Effect of concentrations of chromate and treated times at 110°C on dyeing (fabrics dyed with acid dye, as shown in Figure 3, with a concentration of acid dye of 5% owf and a pH of 6).

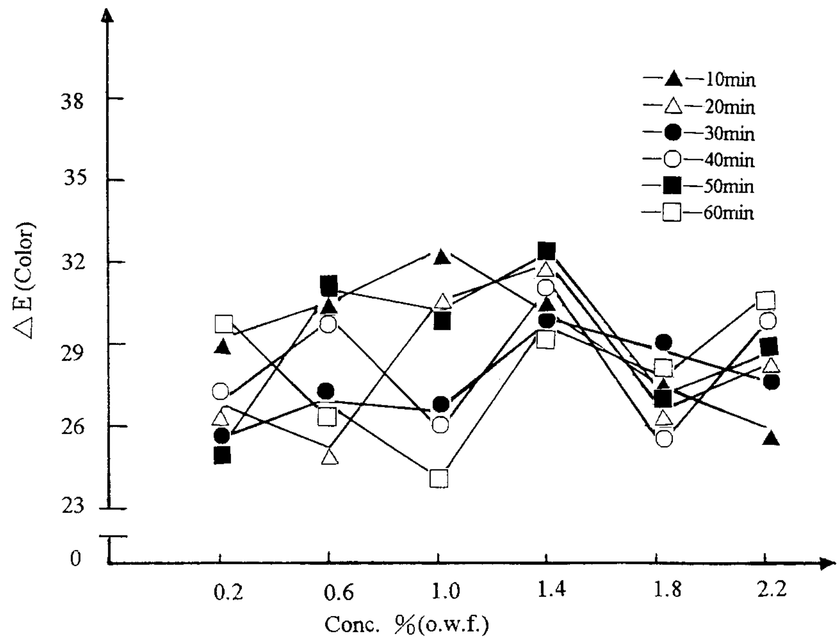



**Figure 9** Effect of concentrations of chromate and treated times at 120°C on dyeing (fabrics dyed with acid dye, as shown in Figure 3, with a concentration of acid dye of 5% owf and a pH of 6).

chromic ions, while 60 min will be so much longer that the dyestuff will escape. Hence, the $\Delta E$ (color) value becomes lower. The dyeing $\Delta E$ (evenness) values at best condition of after-chroming are all lower than 1.5; this indicates that the average dyeing evenness is excellent.

### *Effect of Physical Properties on After-Chroming*

All the colorfastness in the laundering of those glass fiber fabrics after chroming can reach the 4–5 grade level, as shown in Table III. The reason is that the bonding of glass fibers with dyestuff

**Table III Colorfastness to Laundering for Glass Fabrics Dyed with Acid Dye, Followed by After-Chroming (Concentration of Chromate of 1.4% owf)**

| Treated Temperature (°C) | Grade | Time of After-Chroming (min) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 |
| 70 | Staining | 4–5 | 4–5 | 4–5 | 4–5 | 4–5 | 4–5 |
| 70 | Change in color | 5 | 5 | 5 | 5 | 5 | 5 |
| 80 | Staining | 4–5 | 4–5 | 4–5 | 4–5 | 4–5 | 4–5 |
| 80 | Change in color | 5 | 5 | 5 | 5 | 5 | 5 |
| 90 | Staining | 4–5 | 4–5 | 4–5 | 4 | 4–5 | 4–5 |
| 90 | Change in color | 5 | 5 | 5 | 4–5 | 5 | 5 |
| 100 | Staining | 4–5 | 4–5 | 4–5 | 3–4 | 4–5 | 4–5 |
| 100 | Change in color | 5 | 5 | 5 | 4 | 5 | 5 |
| 110 | Staining | 4–5 | 4–5 | 4–5 | 4 | 4–5 | 4–5 |
| 110 | Change in color | 5 | 4 | 5 | 4–5 | 5 | 5 |
| 120 | Staining | 4–5 | 4–5 | 4 | 4–5 | 4–5 | 4–5 |
| 120 | Change in color | 5 | 5 | 4–5 | 5 | 4 | 5 |

**Table IV Colorfastness to Crocking for Glass Fabrics Dyed with Acid Dye Followed by After-Chroming (Concentration of Chromate of 1.4% owf)**

| Treated Temperature (°C) | Grade | Time of After-Chroming (min) 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|
| 70 | Staining | 3–4 | 4–5 | 4 | 4–5 | 4–5 | 4–5 |
| 70 | Change in color | 4–5 | 4 | 4 | 4–5 | 4–5 | 4–5 |
| 80 | Staining | 4 | 3–4 | 4 | 4–5 | 3–4 | 3–4 |
| 80 | Change in color | 4–5 | 4 | 4–5 | 5 | 4 | 4 |
| 90 | Staining | 3–4 | 3–4 | 3–4 | 3 | 3 | 4–5 |
| 90 | Change in color | 4 | 4 | 4 | 4 | 4 | 4–5 |
| 100 | Staining | 4–5 | 3–4 | 3–4 | 4–5 | 3 | 4–5 |
| 100 | Change in color | 5 | 4 | 4 | 4–5 | 4 | 4–5 |
| 110 | Staining | 4–5 | 3–4 | 3–4 | 4–5 | 4 | 3 |
| 110 | Change in color | 5 | 4 | 4 | 5 | 4–5 | 4 |
| 120 | Staining | 4–5 | 3 | 3 | 3–4 | 3–4 | 3–4 |
| 120 | Change in color | 4–5 | 4 | 4 | 4 | 4 | 4 |

molecules coordinate covalent bonds. The colorfastness to crocking partially reached the 4–5 grade level. While at an after-chroming temperature of 120°C, the stainness and change in color are only 3–4 grade. This is because the glass fiber fabrics are brittle material, as shown in Table IV. In addition, the bending length of the glass fiber fabrics after chroming is indicated in Table V. The bending length is between 70 and 80 mm because the glass fiber fabrics dyed before and after both belong to a rigid fabric.

## CONCLUSION

1. From the IR analysis and the scanning electron microscopy graphs of glass fiber fabrics treated with coupling agent, the bonding functional groups with dyestuff exist in the fibers.
2. The results reveal that the best dyeing conditions are at the pH 6 value, and at the temperature and time of 100°C for 30 min under 5% owf concentration of dyestuff.
3. The best after-chroming conditions are at 70°C for 50 min and 1.4% owf concentration of potassium dichromate. The dyeing properties and physical properties are both better.
4. The evaluated grade of dyeing properties for glass fiber fabrics dyed with acid dyestuff and after-chroming is wholly excellent (4–5 grade), and the average dyeing evenness is lower than 1.5. Hence, we suggest the dyeing process is worth investigating.

**Table V Bending Length of Glass Fabrics Dyed with Acid Dye, Followed by After-Chroming (Concentration of Chromate of 1.4% owf)**

| Treated Temperature (°C) | Time of After-Chroming (min) / Bending Length (mm) 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|
| 70 | 80 | 75 | 72 | 77 | 76 | 77 |
| 80 | 75 | 76 | 72 | 74 | 80 | 79 |
| 90 | 80 | 80 | 75 | 73 | 78 | 78 |
| 100 | 70 | 72 | 74 | 77 | 75 | 70 |
| 110 | 76 | 73 | 78 | 76 | 73 | 77 |
| 120 | 77 | 80 | 77 | 74 | 79 | 72 |

Bending length of glass fabrics after desizing is 67 mm; bending length of glass fabrics treated with coupling agent is 72 mm.

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