Dyeing Mechanism and Model of Nylon 6 Fiber Dyeing in Low-Temperature Hydrogen Peroxide–Glyoxal Redox System

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ABSTRACT: This article reports the results of a study of nylon 6 fiber dyed in a low-temperature hydrogen peroxide–glyoxal redox system. It was expected that the dyed fiber would have better dye fastness and higher economic value than would conventional fiber. In addition, this article presents the proposed mechanism for and model of a free-radical dyeing system as well as a derived theoretical equation. From the experimental results, it was found that formation of covalent bonds by the coupling of the dye and the fiber radical in free-radical dyeing was only 25%–40%, whereas with the conventional type of ionic dyeing, it was almost 60%–75%. Because the initiation efficiency of free-radical formation is affected by many factors, such as the pH of the dye bath and the concentrations of the oxidant and reductant, the aims of this study were to investigate the formation of free radicals and the effects on dye uptake of the concentrations of dye, oxidant, and reductant and of the fiber amine end group. In addition, the dyeing properties of dyed fiber were investigated, and the dyeing order and rate constant of the rate equation were evaluated from the experimental data. From the experimental results, the following conclusions were drawn. (1) The hydrogen peroxide–glyoxal redox system produced many free radicals in the dye bath as temperature reached 70°C. (2) The amine end group in the nylon fiber was the main site of ionic and covalent bonding between nylon 6 fiber and dye. (3) The proposed model of free-radical dyeing showed, from the fit of the experimental data into the equation and the evaluation of the equation parameters, that the order fit the theoretical value well, with the rate constant dependent on the dyeing conditions; at pH = 3, it could match the equation's best (rate equation of the proposed model: $d[D]_R/dt = k_A[GO]^1[H_2O]^m[D]^{1/2}[F]^{1/2}$). (4) The optimum dyeing conditions in the hydrogen peroxide–glyoxal redox system were: $[H_2O_2] = 0.15$–$0.20M$, $[glyoxal] = 0.07$–$0.10M$, pH = 3, dyeing temperature = 70°C, and dyeing time = 45–50 min. (5) The redox dyeing system had better dye fastness than did the conventional system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4197–4207, 2006

Key words: nylon; dyes; initiators; redox

INTRODUCTION

Nylon was successfully made by W. H. Carothers (DuPont Co.) in 1930. He used hexamethylene diamine and adipic acid monomers by condensation polymerization to obtain nylon 6,6 of polyamide. After spinning, the first synthetic fiber of nylon 6,6, which had extreme intensity, elasticity, and dyeability, was invented. In 1938 Schlack of Germany made a nylon 6 fiber. He used ε-amino caproic acid chloride salt as the catalyst and reacted it with ε-caprolactam to produce nylon 6. With that development, the fiber industries had entered the age of synthetic fibers.

Commonly used dyes in the dyeing of nylon fiber are acid, metal–complex, mordant, disperse, and reactive dyes. Of these, acid dye is the most useful and most popular because of its good solubility and variety of colors. Acid dye produces color that is shiny and easy to color-match.[1–2] However, because of its dense structure, when acid dye is employed to dye nylon, it requires a high dyeing temperature (90°C–100°C). Thus, it wastes energy and time. In addition, the fabrics are apt to have moire and staining.[1–2] Especially for the dyeing of nylon carpet, acid dye requires a low dyeing temperature to avoid shape change, structure distortion, and the Barré effect. Although many methods had been developed to improve these shortcomings,[1,3–4] there has not been much improvement in dyeing time and energy saving. Acid dye requires special chemicals and has some restrictions on its use. Thus, in this article, a new dyeing method, the hydrogen peroxide–glyoxal oxidation–reduction (redox) method, is suggested. This method can use conventional acid dyes and dyes at low temperature, enabling the attainment of a low dyeing temperature, savings in energy use, a shortened dyeing time, and good dyeing properties.

There are many kinds of oxidation–reduction (redox) systems.[5–28] Rao used the hydrogen peroxide–glyoxal redox system[25] to dye wool at low temperature. But the actual dyeing mechanism was not well described. In this article, a free-radical initiation mechanism is proposed, the dyeing mechanism and dyeing conditions are discussed, and the evaluation of the dyeing parameters of the rate equation using the experimental data is reported.

Theory

Conventional acid dyeing of nylon 6 fiber

Conventional dyeing of nylon fiber with acid dyes, no matter the level or milling type, needs to occur in an acidic bath (level type, pH 4–6; milling type, pH 6–7). The dyeing mechanism uses the ionic bonding of an sulfonic acid dye anion to nylon amino positive-charge group in an acidic bath.[1,6,28] Because nylon fiber has a dense, fine structure, conventional dyeing still requires a long time (45–60 min) under high temperature (95°C–100°C).[6] In addition, as with protein fiber, during dyeing in the acidic bath, the benzoic amino end group of nylon fiber will absorb a proton that is then replaced by the acid dye because of its high affinity. The ionic model of dye bonding is depicted as
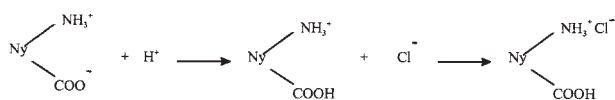
and then

As can be seen in the above, nylon first absorbs a proton combining with a chlorine ion on the fiber. Finally the chlorine ion is replaced by a sulfuric anion of acid dye because of the high affinity of the dye anion. In all, in the conventional dyeing method, an acid dye forms an ionic bond of a D—SO_3Na structure in the dye bath.

Hydrogen peroxide–glyoxal redox dyeing system at low temperature

The hydrogen peroxide–glyoxal oxidation–reduction (redox) dyeing system is a low-temperature dyeing method that uses chemicals to initiate free radicals. As in redox grafting copolymerization,[12,13,15,17–18] nylon 6 fiber is considered a grafted material, and the acid dye is considered a monomer. The oxidant and reductant agents generate free radicals and transfer these radi-

cals to the fiber and the dye, respectively. The free radicals of fiber and dye can be coupled to covalently bond. As indicated by the following, this redox dyeing method enables fiber to be dyed at low temperature with improved dyeing properties.

1. In an oxidation–reduction system, the formation of free radicals does not require high temperature (only about 50°C).
2. Because the bonding of free radicals is covalent, which is stronger than ionic bonding, dye fastness improves.
3. Because free radicals can activate the amino end group on the undyed site of the fiber by chain transfer, it increases the rate of dyeing.
4. The rate of mutual coupling of radicals is faster than that of the ionic bonding. Thus, in the free-radical dyeing of the redox system, it is easy for the fiber to reach dyeing equilibrium.
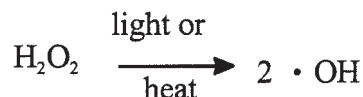
Because generating free radicals is the initial step in the free-radical dyeing of the redox system, free radicals may be produced through the following mechanisms:

1. *By the oxidizing decomposition of a formic acid:* Glyoxal and hydrogen peroxide can form a glyoxalic acid or oxalic acid by an oxidizing reaction.[14] Oxalic acid can further react with hydrogen peroxide to form formic acid. This can be proved by reducing formic acid with mercuric chloride to produce a large amount of white mercurous chloride precipitate.[26,27] Formic acid is a strong reducing agent that can form a free radical by its oxidation. The whole reaction scheme is:
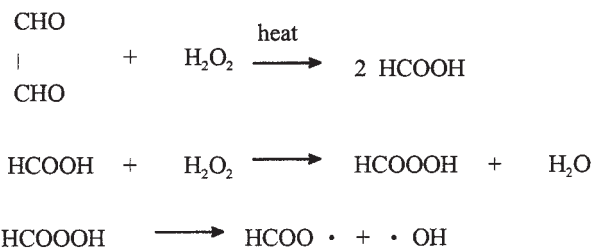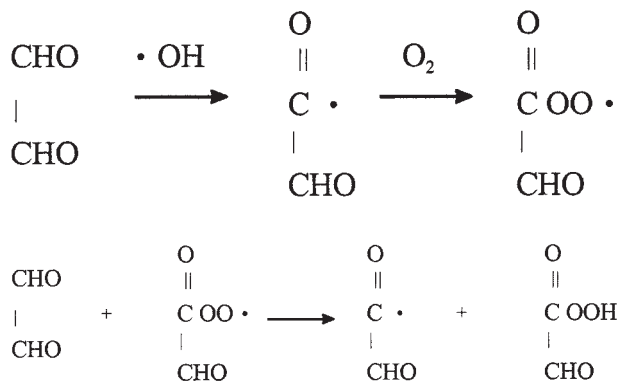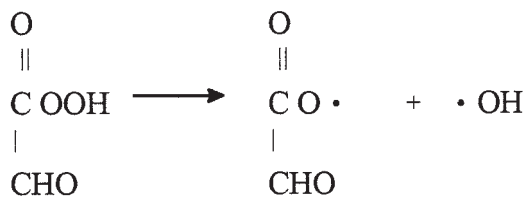

(unstable)

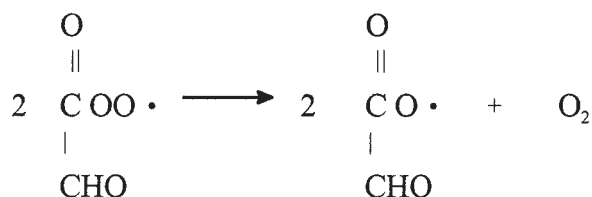2. *By self-decomposition of hydrogen peroxide*[80]:

3. *By autoxidation:*

$$CHO \quad \cdot OH \qquad \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\cdot}} \qquad \overset{O_2}{\longrightarrow} \qquad \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,OO\cdot}}$$

$$\underset{\overset{|}{CHO}}{CHO} \;+\; \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,OO\cdot}} \longrightarrow \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\cdot}} \;+\; \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,OOH}}$$

Because peracid is an unstable chemical compound, it can further form free radicals by self-decomposition:

$$\overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,OOH}} \longrightarrow \overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,O\cdot}} \;+\; \cdot OH$$

or

$$2\;\overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,OO\cdot}} \longrightarrow 2\;\overset{O}{\underset{\overset{|}{CHO}}{\overset{||}{C}\,O\cdot}} \;+\; O_2$$

As described above, although various kinds of free radicals are produced in the whole system, only the formation of free radicals by oxidation decomposition of formic acid is considered the key step.

Dyeing mechanism of fiber with dye

As a large amount of free radicals are generated in the system, the free radicals will transfer to the dye and the nylon fiber by chain transfer, putting the dye and fiber in a free-radical state and making them couple by a covalent bond. A description of this process follows:

1. The mechanisms of free-radical chain transfer: D + R$^\bullet$ → D$^\bullet$ + R and Ny + R$^\bullet$ → Ny$^\bullet$ + R
2. The mechanism of fiber and dye radical coupling: Ny$^\bullet$ + D$^\bullet$ → Ny − D

As shown above, the free radicals of the dye (D$^\bullet$) and the fiber (Ny$^\bullet$) can be coupled by a covalent bond. Because there are no bifiber or bidye molecules, it is believed that fiber radicals combining with fiber radicals or dye radicals combining with dye radicals does not occur.
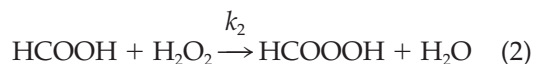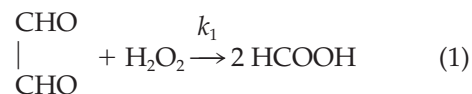
Dynamic model of free-radical dyeing method in redox system

Before deriving the rate equation of the free-radical dyeing method, the system can be simplified by making the following assumptions:

1. The rate of coupling of a dye radical to a fiber radical is much faster than that of a dye radical to a dye radical or a fiber radical to a fiber radical, that is, coupling of the latter two is ignored.
2. As the dyeing sites of fiber become saturated, free-radical coupling would be unable to proceed. Only conventional ionic dyeing could occur.
3. The production of free radicals occurs mainly via the oxidation of formic acid in the system.
4. The fiber and dye can form a free radical only at a specific site (e.g., NH$_2$ group), and each nylon molecule possesses only one such site.

With the above assumptions, the rate equation can be derived through the initiation, transfer, and coupling of free radicals in free-radical dyeing.

1. *Formation of free radicals:* As hydrogen peroxide reacts with glyoxal, it forms free radicals according to the following step.

$$\underset{CHO}{\overset{CHO}{|}} + H_2O_2 \overset{k_1}{\longrightarrow} 2\,HCOOH \tag{1}$$

$$HCOOH + H_2O_2 \overset{k_2}{\longrightarrow} HCOOOH + H_2O \tag{2}$$

As the effect of acid in the system is neglected because the dyeing reaction being under a buffer condition, the peracid decomposes into two free radicals:

$$HCOOOH \overset{k_i}{\longrightarrow} HCOO^\bullet$$

$$+ {}^\bullet OH \text{ (represented by R}^\bullet \text{and R}^{\bullet\prime}) \tag{3}$$

where k_i is the initiation rate constant of the free radicals, [GO] is the concentration of glyoxal, [H$_2$0$_2$] is the concentration of hydrogen peroxide, and [PFA] is HCOOOH. The formation of free radicals in the system is mainly a result of the decomposition of peracid, that is,

$$\frac{d[PFA]}{dt} = k'[GO]^l[H_2O_2]^m \tag{4}$$

where l and m are the reaction orders and k' is the rate constant. From eqs. (3) and (4), it can be rewritten as

$$R_i = \frac{d_{[R^\bullet]}}{dt} = 2k'_i[GO]^l[H_2O_2]^m$$

$$= k''_i[GO]^l[H_2O_2]^m \qquad (5)$$

2. *Chain transfer reaction of free radicals:*

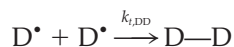$$Ny + R^\bullet \xrightarrow{k_{tr,F}} Ny^\bullet + R \qquad (6)$$

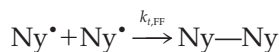$$D + R^\bullet \xrightarrow{k_{tr,D}} D^\bullet + R \qquad (7)$$
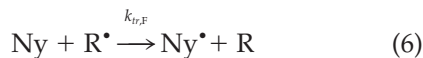
where $k_{tr,F}$ and $k_{tr,D}$ are the chain transfer rate constants of fiber and dye, respectively. The rate of formation of the fiber and dye radicals is written as

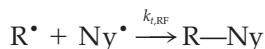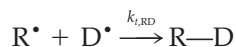$$R_{tr,F} = \frac{d_{[F^\bullet]}}{dt} = k_{tr,F}[Ny][R^\bullet] \qquad (8)$$

$$R_{tr,D} = \frac{d_{[D^\bullet]}}{dt} = k_{tr,D}[D][R^\bullet] \qquad (9)$$

where $[Ny^\bullet]$ is expressed as $[F^\bullet]$.

3. *Termination of free-radical dyeing:*

$$Ny^\bullet + D^\bullet \xrightarrow{k_{t,FD}} Ny—D \qquad (10)$$

$$Ny^\bullet + Ny^\bullet \xrightarrow{k_{t,FF}} Ny—Ny$$

$$D^\bullet + D^\bullet \xrightarrow{k_{t,DD}} D—D$$

From experimental observations, $k_{t,FF} = k_{t,DD} = 0$, that is, the termination reaction only occurs in accordance with eq. (10). Moreover, it may also have the following reactions,

$$R^\bullet + R^\bullet \xrightarrow{k_{t,RR}} R—R \qquad (11)$$

$$R^\bullet + D^\bullet \xrightarrow{k_{t,RD}} R—D$$

$$R^\bullet + Ny^\bullet \xrightarrow{k_{t,RF}} R—Ny$$

Because $[R^\bullet] \gg [D^\bullet]$ or $[F^\bullet]$ in the dyeing bath and the reactivity of the free radical, $R^\bullet$, is far greater than that of $D^\bullet$ or $F^\bullet$, $k_{t,RD}$ and $k_{t,RF}$ can be neglected,

$$R_{t,RR} = k_{t,RR}[R^\bullet]^2 \qquad (12)$$

where $k_{t,RR}$ is the self-termination rate constant of the free radicals during termination.

Assuming the system is in a steady state, the free-radical concentration of each species does not vary, that is, the production rate of a specific free radical is equal to its termination rate, that is,

1. The concentration of fiber free radicals is a constant,

$$R_{tr,F} = R_{t,FD} \qquad (13)$$

with $k_{tr,RF}[R^\bullet][F] = k_{t,DF}[F^\bullet][D^\bullet]$

2. The concentration of dye free radicals is a constant,

$$R_{tr,D} = R_{t,FD} \qquad (14)$$

i.e., $k_{tr,RD}[R^\bullet][D] = k_{t,DF}[F^\bullet][D^\bullet]$
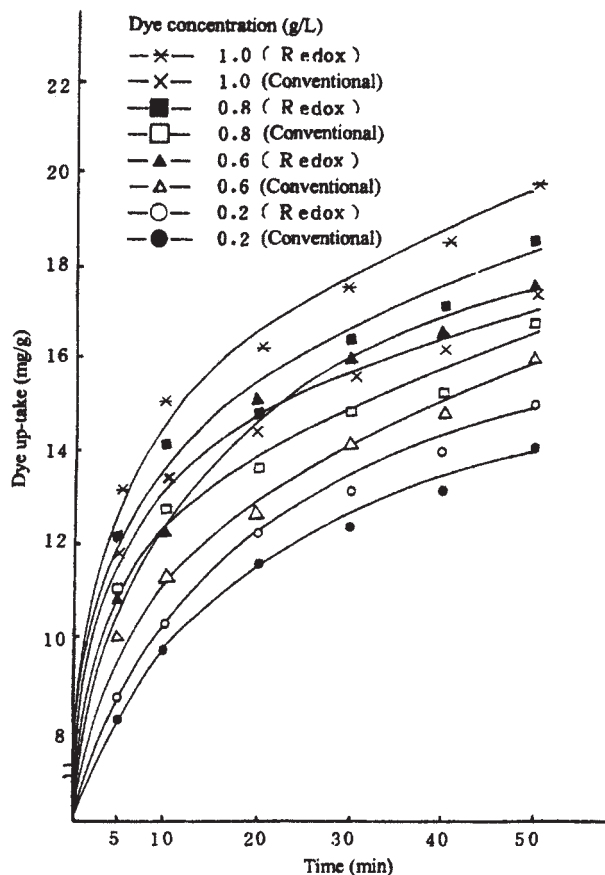

Figure 1 Relationship of dye uptake and reaction time at various concentrations of dye and pH = 3.
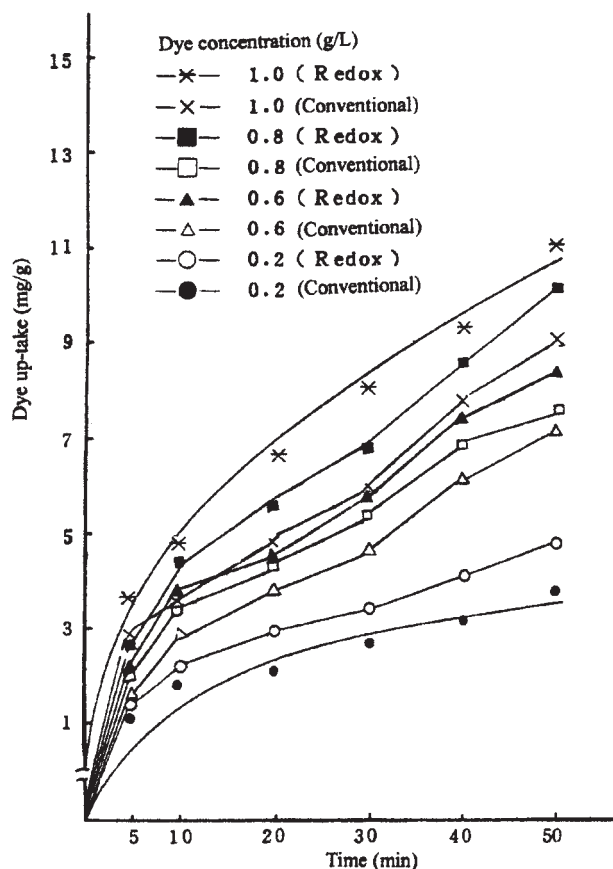
Figure 2 Relationship of dye uptake and reaction time at various concentrations of dye and pH = 9.

3. The concentration of total free radicals is a constant, $R_i = k_{t, RR}[R^\bullet]^2$, or

$$R^\bullet = \frac{R_i}{(k_{t,RR})^{1/2}} = k_{t,RR}^t R_i \tag{15}$$

Therefore, the rate of dye consumption in the free-radical dyeing mechanism from eqs. (13) and (14) is

$$\frac{d[D]_R}{dt} = R_{t,FD} = k_{t,DF}[F^\bullet][D^\bullet]$$

$$= k_{tr,RD}[R^\bullet][D]$$

$$= k_{tr,RF}[R^\bullet[F] \tag{16}$$

or

$$\left(\frac{d[D]_R}{dt}\right)^2 = (k_{tr,RD} \cdot k_{tr,RF})[R^\bullet]^2[D][F] \tag{17}$$

Substituting eqs. (5) and (15) into eq. (17), the dyeing rate equation of the redox dyeing system in the free-radical mechanism is

$$\frac{d[D]_R}{dt} = k_A[GO]^l[H_2O_2]^m[D]^{1/2}[F]^{1/2} \tag{18}$$

where

$$k_A = (k_{tr,RD} \cdot k_{tr,RF})^{1/2}k_i'' \cdot k_{t,RR}' \tag{19}$$

Using the dyeing rate equation, the reaction orders l and m and the reaction rate constant, k_A, could be evaluated by experimental data; thus, more of the free-radical dyeing behavior can be understood.

EXPERIMENTAL

Materials

Nylon 6 fiber was supplied from Taiwan Chemical Co. To remove the oil and impurities from the nylon 6 fiber, a general pretreatment was carried out.[19–20] Its amine end group was found to be 54 mmol/kg. Acetylated nylon 6 with different amine groups was obtained by swelling with a phenol (0.08M) solution at 95°C and treated with acetic anhydride at 138°C, then washed and cleaned with benzene, acetone, and water until the fiber was in a neutral condition. Finally, at room temperature the fiber was dried.
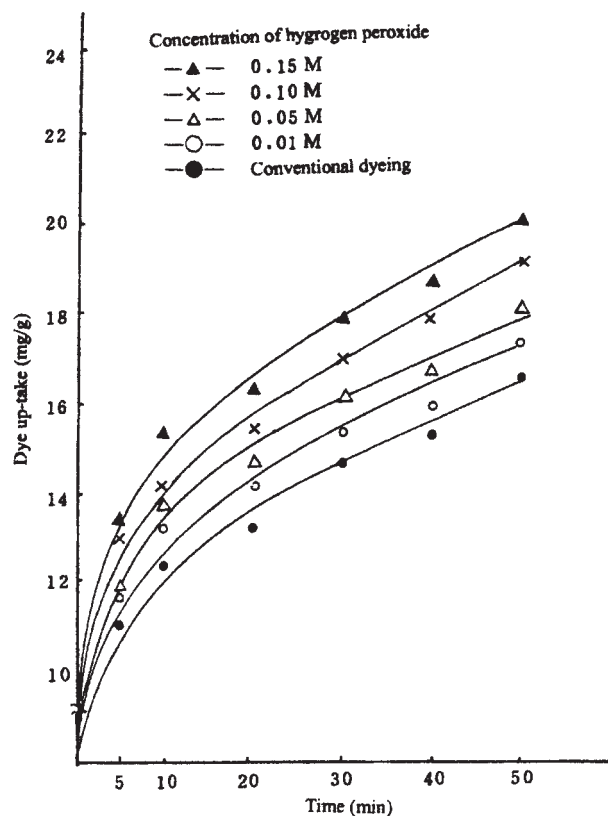

Figure 3 Relationship of dye uptake and reaction time at various concentrations of hydrogen peroxide and pH = 3.
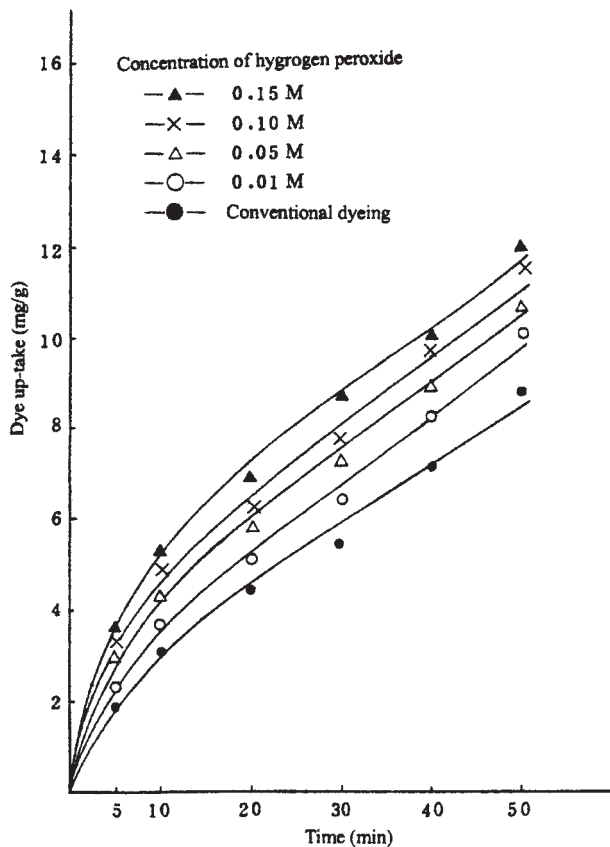
Figure 4 Relationship of dye uptake and reaction time at various concentrations of hydrogen peroxide and pH = 9.
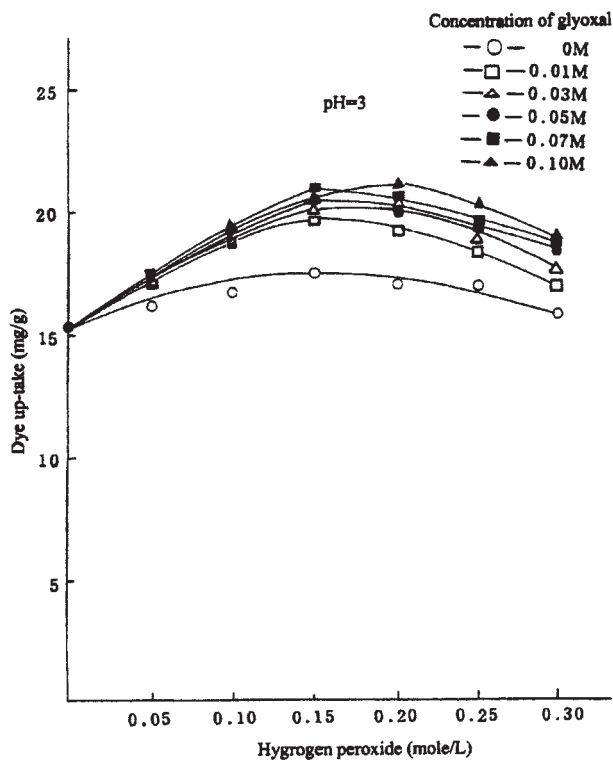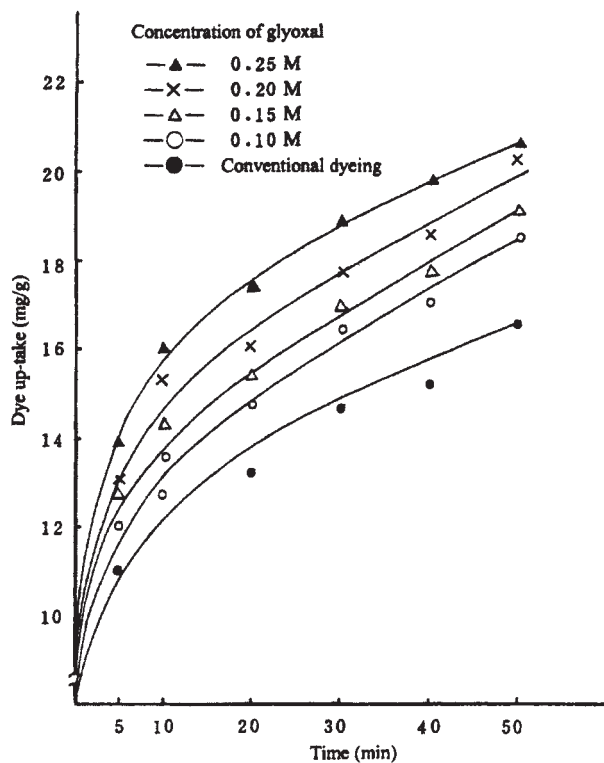

Figure 6 Relationship of dye uptake and reaction time at various concentrations of glyoxal and pH = 3.

Figure 5 Relationship of dye uptake and hydrogen peroxide at various concentrations of glyoxal and pH = 3.

Figure 7 Relationship of dye uptake and reaction time at various concentrations of glyoxal and pH = 9.
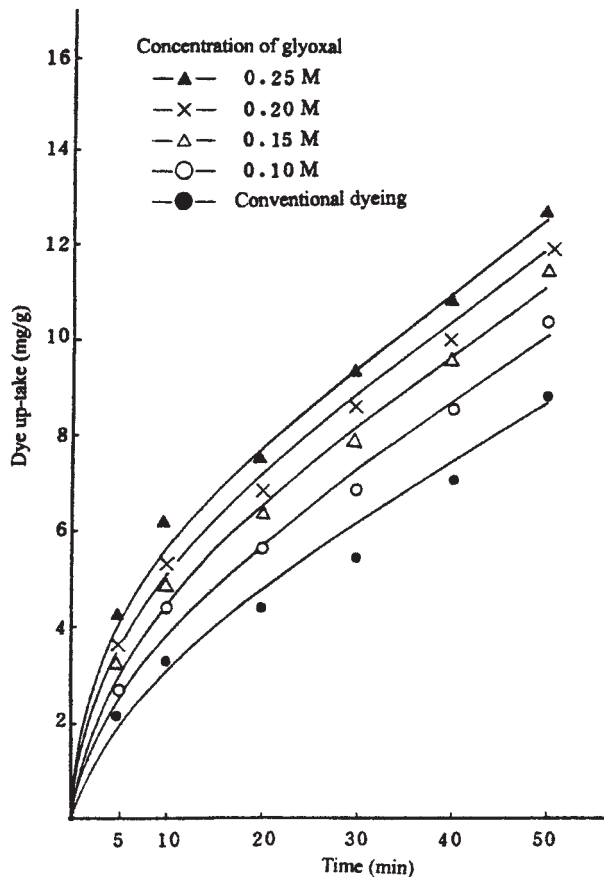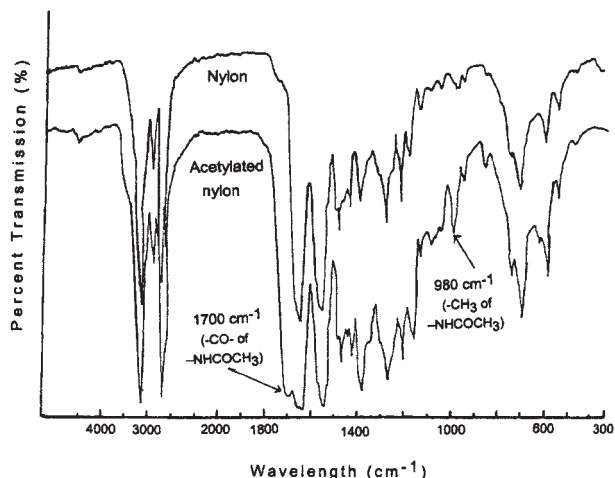
Figure 8 FTIR spectra of nylon 6 and acetylated nylon.

Hydrogen peroxide (35%), the oxidant, and glyoxal (40%), the reductant, were used without further purification. The dye, Supracen Red B (C. I. Acid Red 42; Bayer Company, Leverkusen, Germany), was purified until it possesses the same absorption coefficient (extinction coefficient) as the largest wavelength of the absorption peak.

Experimental method and conditions

First, 1.25 g of nylon 6 fiber was placed in a four-necked bottle to which were added 2 L of pure water
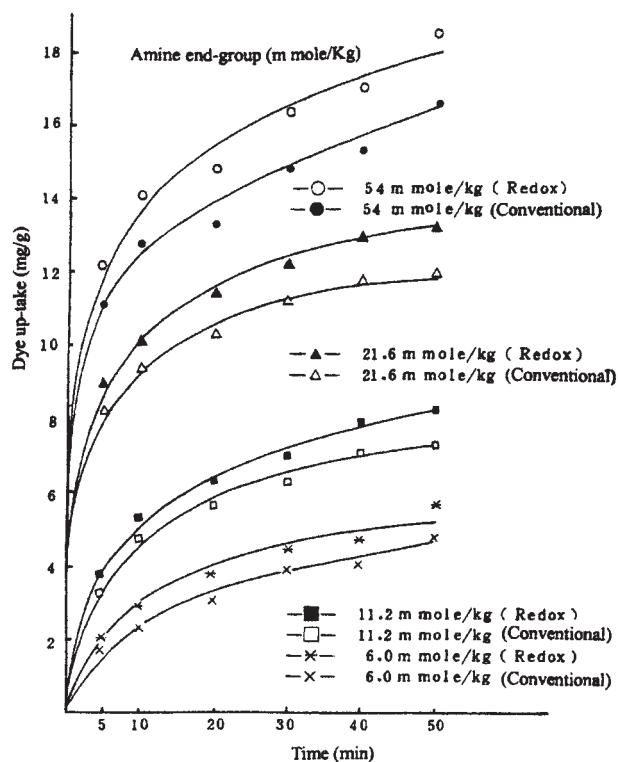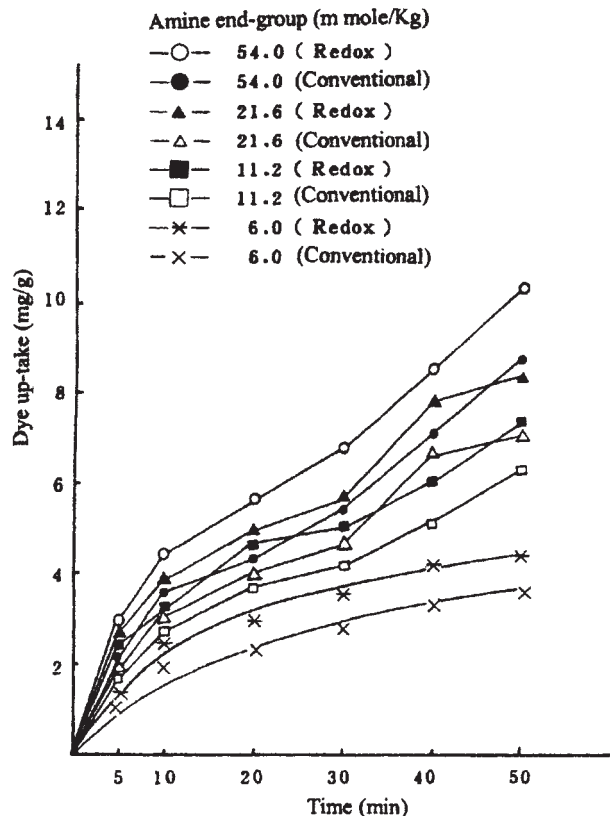

Figure 10 Relationship of dye uptake and reaction time with various amino end groups and pH = 9.

and 1.2 g of dye (dye bath concentration 0.06 g/L; liquid ratio 1:1600). The pH in the dye bath was adjusted to 3, 7, or 9, and the dye bath was heated to a temperature of 50°C, 70°C, or 90°C. Then oxidant concentrations of 0, 0.05, 0.10, 0.15, 0.20, 0.25, or 0.30 mol/L and reductant concentrations of 0, 0.01, 0.03, 0.05, 0.07, or 0.10 mol/L were added to the dye bath. The dyeing procedure follows:
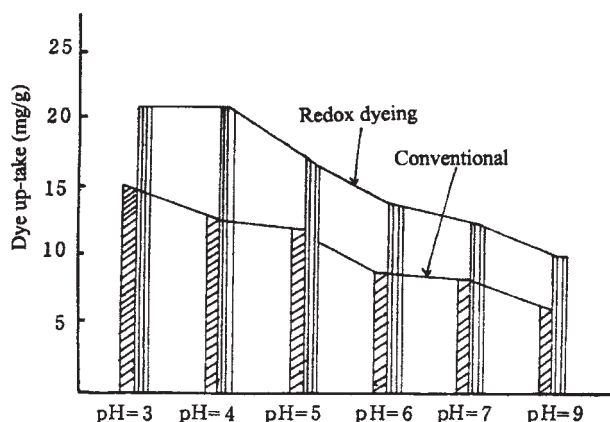

Figure 9 Relationship of dye uptake and reaction time with various amino end groups and pH = 3.

Figure 11 Relationship of dye uptake and pH with redox and conventional dyeing systems.

TABLE I
Effect of pH on Dyeability of Different Dyeing Systems

Dye uptake (mg/g) \ PH Dyeing System	3	4	5	6	7	9
Redox	21.2	20.84	16.67	12.5	12.32	9.84
Traditional	15.32	12.68	12	8.70	8.10	6.16
Difference in dye uptake	5.88	8.16	4.67	3.8	4.22	3.68
Dyeing conditions of redox System	$H_2O_2 =$ 0.20M Glyoxal = 0.10M	$H_2O_2 =$ 0.20M Glyoxal = 0.10M	$H_2O_2 =$ 0.20M Glyoxal = 0.10M	$H_2O_2 =$ 0.20M Glyoxal = 0.10M	$H_2O_2 =$ 0.20M Glyoxal = 0.10M	$H_2O_2 =$ 0.20M Glyoxal = 0.10M
	Dye = 0.6 g/L; time = 2 h; liquid ratio = 1:1600; temperature = 70°C					
Dyeing conditions of conventional system	Dye = 0.6 g/L; time = 2 h; liquid ratio = 1:1600; temperature = 70°C; Na_2SO_4 = 2 g/L					
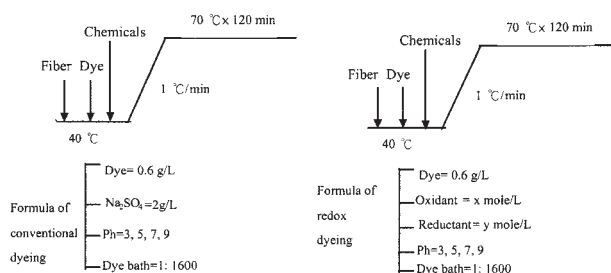
After being dyeing, the fiber was dissolved in formic acid, and its absorption intensity was measured using a UV spectrometer (Shimadzu Seisakasho, Ltd., Kyoto, Japan) and compared with that of the standard to determine the dye uptake of the fiber.

To determine the amount of amine end groups in modified nylon 6, 1 g of nylon 6 fiber was dissolved in 50 mL of phenol/methanol (70:30) solvent, which was then stirred for 2 h until the fiber was dissolved evenly at room temperature. To titrate and calculate the amine end groups, a 0.02N hydrochloric acid solution was used, with thymol blue as the indicator (color change range was pH = 1.2–2.8).

Moreover, the water-washing fastness and light fastness of each dyed fiber were tested in accordance with AATCC Test Method 61-1985 and AATCC Test Method 16E-1978, respectively.

RESULTS AND DISCUSSION

Effect of dye concentration on dye uptake

As depicted in the previous diagram, the acid Supracen Red B (C.I. Acid Red 42) was used to dye the fiber with the conventional and redox dyeing systems at pH = 3 or 9. Dye uptake is shown in Figures 1 and 2, which indicate that the redox dyeing system had more dye uptake than did the conventional one. Moreover, in the same dyeing conditions, dye uptake increased with increasing dye concentration. This indicated that

except for the ionic dyeing, dye uptake in the redox dyeing system still involved a free-radical dyeing mechanism; thus, its dye uptake was relatively greater.

### Effect of oxidant and reductant concentrations on dye uptake

As can be seen in Figures 3–5, it was found that the effect of the oxidant concentration at pH = 3 or 9 to dye uptake initially increased with an increasing oxidant concentration. However, when the oxidant concentration became excessive, dye uptake had a tendency to decrease. This could be explained by the ability of the excess hydrogen peroxide to form a large quantity of active-state oxygen and destroy the ionic bond between fiber and dye. Moreover, the excess hydrogen peroxide also could decompose and form an oxygen molecule that might react with the free radical and make it stable like the free-radical inhibitor.[12] This decreased the efficiency of free-radical dyeing. The optimum hydrogen peroxide concentration for acidic dyeing was found to be in the range of 0.15–0.20M.

As also can be seen in Figures 6 and 7, whether the solution was acidic or basic, dye uptake always increased with an increasing concentration of reductant. This could be explained by the large concentration of reductant generating more radicals. Thus, dye uptake increased with increased reductant concentration.

Effect of amine end-group concentration on dye uptake

Acetylation of the amine end group of nylon 6 using acetic anhydride yielded a different equivalent of that amine end group. Its FTIR spectra are shown in Figure 8. As nylon 6 fiber was acetylated, a —CO^- stretching vibration of the acetylated amine groups (—NH-$COCH_2$) appeared at 1700 cm^{-1}. In addition, a rocking
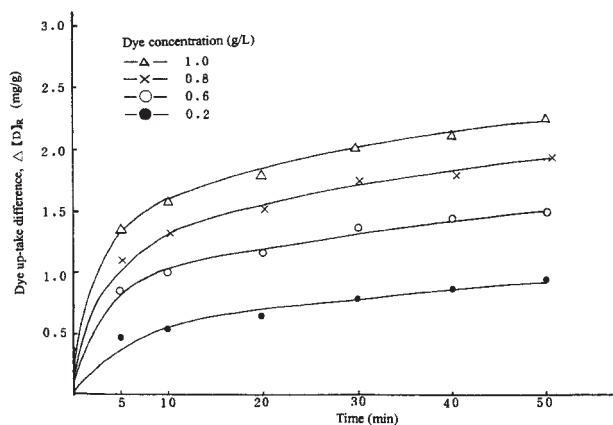
Figure 12 Relationship of dye uptake difference and reaction time at various concentrations of dye and pH = 3.
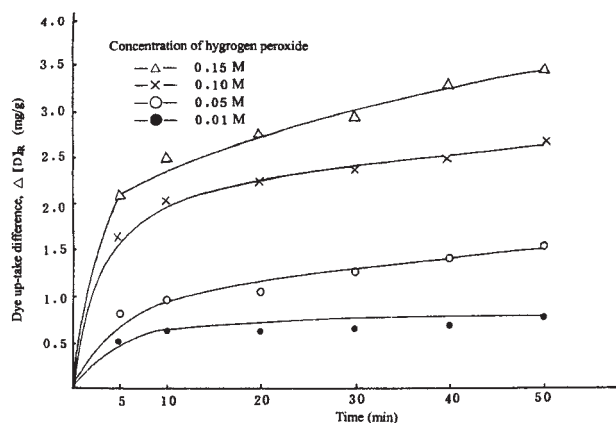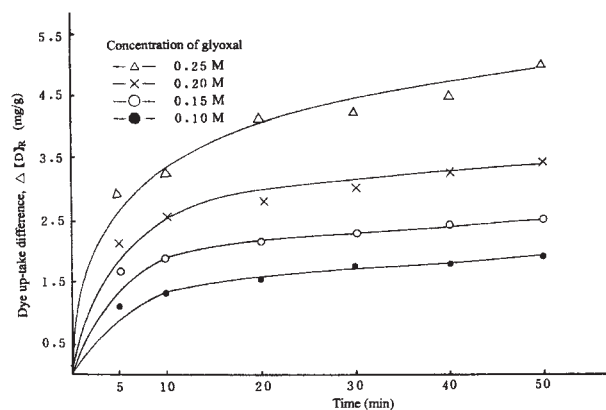

Figure 14 Relationship of dye uptake difference and reaction time at various concentrations of glyoxal and pH = 3.

vibration of CH_3 in the —$NHCOCH_3$ group of acetylated nylon also appeared as a stronger absorption peak at 980 cm^{-1} than that of pure nylon 6 fiber. In addition, as can be seen in Figures 9 and 10, in both conventional and redox dyeing dye uptake increased with an increasing amount of amine end groups at pH = 3 or 9. From that, it could be concluded that the amine end group of nylon 6 plays an important role in dyeing in the conventional and the redox systems.

Effect of ph value on dye uptake

In this study, acid dye was preferred to dye at pH = 3–4. As can be seen in Figure 11, as the pH increased and exceeded pH = 5, dye uptake apparently would drop. This was because of a large amount of ionic bonding of dye molecules reduced. In addition, the hydrogen peroxide was easy to decompose and release the oxygen molecules into the basic bath. This was unfavorable to the formation of free radicals, and desorption appeared in the basic bath. It was con-
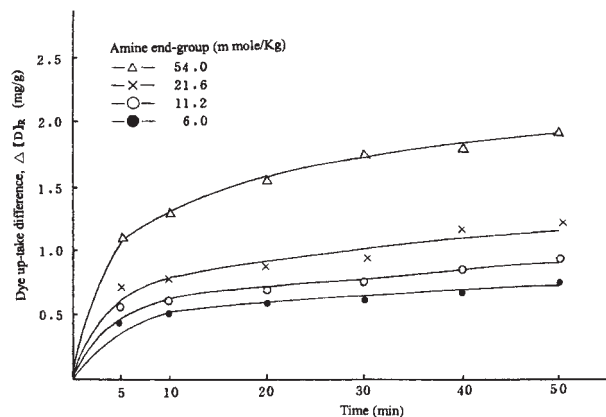
cluded that redox dyeing was favorable to dye in an acidic rather than in a basic bath.

In all, the factors that affected the dyeability of the redox dyeing system were numerous. Only a proper choice of dyeing conditions could yield better dye uptake in redox dyeing.

Comparisons of redox and conventional dyeing systems

As can be seen in Table I, dye uptake in the redox dyeing system was larger than that in the conventional one. In addition, dye equilibrium was easy to reach in a short time in the redox system. Therefore, the redox dyeing system not only shortened dyeing time but also enabled dyeing under low temperature. It was economical, as well. Table I shows the difference in dye uptake between the redox and conventional dyeing systems, which indicates that dye uptake increased by the free-radical dyeing mechanism.

As can be seen in Figures 12–15, the difference in dye uptake between redox and conventional dyeing

Figure 13 Relationship of dye uptake difference and reaction time at various concentrations of hydrogen peroxide and pH = 3.

Figure 15 Relationship of dye uptake difference and reaction time with various amino end groups and pH = 3.
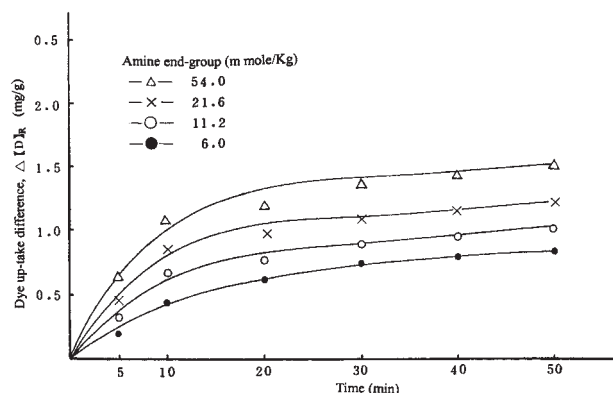
Figure 16 Relationship of dye uptake difference and reaction time with various amino end groups and pH = 9.

increased with increased concentrations of the dye, the oxidant, the glyoxal, and the amine end groups. This indicated that the increases in concentration would increase the rate of redox dyeing. Therefore, the difference between conventional and redox dyeing in how much dye was taken up was significant. In addition, because an increase in the amine end-group concentration could increase dye uptake in redox dyeing, it could be concluded that the amine end group of nylon fiber was a possible site for the chain transfer of free radicals.

Application of rate equation at different pHs

Because the dye was suitable for dyeing at a pH of 3–4, Figures 12–16 show the difference in dye uptake between the redox and conventional dyeing systems at pH = 3 (the difference in dye uptake was considered part of the free-radical dyeing of the redox dyeing system). From these data, reaction orders m and l of the theoretical equation [eq. (18)] as well as the reaction rate constant, k, could be calculated. The rate equation at pH = 3 was

$$\frac{d[D]_R}{dt} = 6.30 \times 10^2 [H_2O_2]^{0.51}[GO]^{0.80}[D]^{0.58}[F]^{0.45}$$

$$(20)$$

As indicated in the above equation, the order of experimental values of $[D^\bullet]$ and $[F^\bullet]$ was very close to the theoretical values (0.5) at pH = 3. Therefore, the theoretical equation was considered rather reasonable. In other words, formation of free radicals and the reaction process might be in accord with the model proposed for the acidic bath.

The difference in dye uptake between the redox and conventional dyeing systems at pH = 9 is shown in Figure 16. Its reaction orders m and l and reaction rate constant, k, could also be calculated from the data, resulting in:

$$\frac{d[D]_R}{dt} = 1.16 \times 10^3 [H_2O_2]^{0.44}[GO]^{1.37}[D]^{0.61}[F]^{0.38}$$

$$(21)$$

From the above equation, the order of experimental values of $[D^\bullet]$ and $[F^\bullet]$ also was rather close to the theoretical values (0.5) at pH = 9. Therefore, the theoretical equation derived from our assumptions showed reasonable accuracy. In other words, whether the bath was acidic or basic, the formation of free radicals and the reaction process would be in accord with the proposed model. The range of the reaction rate constant, k, of pH 9 > pH 3 indicated that a more violent reaction between the hydrogen peroxide and the glyoxal occurred in the basic bath. Therefore, the k in the basic bath was relatively larger.

Comparison of dye fastness of redox and conventional dyeing systems

As can be seen in Table II, because of the formation of covalent bonds in the free-radical dyeing, the redox dyeing system exhibited better fastness, including water-washing fastness, sunlight fastness, and wear-resistance fastness, than did the conventional one. From those, it was concluded that the redox dyeing system was more favorable to dye than was the conventional one.

TABLE II
Dye Fastness of Redox and Conventional Dyeing Systems

Testing Items			Conventional	Redox	
Wash fastness	Fading of color		3–4	4–5	AATCC61
		Wool	4	5	Test III A
		Acrylic	4	5	45 min × 71°C
	Staining	Polyester	4	4–5	
		Nylon	3–4	4–5	
		Cotton	4	5	
		Acetate	4	5	
Abrasion fastness		Dry	4	5	AATCC8
		Wet	4	5	
	Light fastness		4	5	AATCC 16E

CONCLUSIONS

In summarizing the theoretical and experimental results of this study, we concluded the following:

1. The hydrogen peroxide–glyoxal redox system generates a large amount of free radicals and forms covalent bonds between dye and fiber.
2. When nylon 6 fiber is dyed with C.I. Acid Red 42 at pH = 3–4, this system has better dyeing results.
3. Dye uptake is increased with a dyeing temperature in the range of 50°C–70°C at pH = 3–4. Nevertheless, if the temperature is too high, the oxidant (hydrogen peroxide) can decompose too fast and does not favor the formation of free radicals.
4. The amine end group of nylon 6 fiber is the site of formation of the free radicals. For better dyeability, a proper combination of oxidant, reductant, and pH in the dye bath is required in redox dyeing. The better dyeing conditions in this redox dyeing system were: concentration of hydrogen peroxide = 0.15–0.20M, concentration of glyoxal = 0.07–0.10M, dye bath pH = 3, and dye temperature = 70°C.
5. Because the orders of the experimental and theoretical (0.5) values of [D$^\bullet$] and [F$^\bullet$] were rather close at pH = 3 and pH = 9, it is believed that the theoretical equation derived from our assumptions is reliable and consistent. In other words, the formation of free radicals and the reaction process may follow the same route in both acidic and basic baths.
6. The redox dyeing system can shorten dyeing time by about 15–20 min compared with the conventional one. It also lowers the dye temperature about 25°C–30°C. Both dye fastness and dye properties are improved. Therefore, the redox dyeing system is an energy-saving process that shortens dyeing time and improves the quality of the dyeing of dyed fiber.

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