

Reduction of colorants in nylon flock dyeing effluent

Qinguo Fan*, Sunil Hoskote, Yuejun Hou

Department of Textile Sciences, University of Massachusetts Dartmouth, 285 Old Westport Road, North Dartmouth, MA 02747, USA

Received 30 December 2002; received in revised form 8 April 2004; accepted 9 April 2004

Available online 4 June 2004

Abstract

The batch dyeing of fiber materials such as staple fibers and flock is usually carried out by exhaustion methods. However, the dyeing of flock fibers, either nylon, PET or acetate, with acid or disperse dyes is not 100% efficient in terms of dye utilization. Therefore, the remaining dyes in the spent dye bath are generally not reused, and are usually discharged with minimum treatment, together with the dyeing chemicals into the sewage wastewater system causing environmental pollution. We found that the colorants and chemical auxiliaries in the fiber dyeing effluents can be reduced by: (1) optimizing the acid dyeing conditions such as salt addition and pH control; (2) reuse of the spent dye bath that remain after the original dyeing process. In the lab scale trials, we have successfully raised the acid dye exhaustion to over 90% by optimizing the dyeing conditions. The reuse of the spent acid dye bath also showed promising results with dye exhaustion ranging from 91 to 93% after four times of reuse.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Acid dye; Dyeing; Effluents; Nylon; Reused dyebath

1. Introduction

Dyeing is usually a textile wet process to impart color to textile materials. Today, textiles can be dyed with almost any color to achieve a variety of aesthetic and functional purposes. But by using currently available techniques, the dyeing process often has detrimental environmental impacts. Unfixed dyestuffs and auxiliary chemicals in wastewater are some of the potential problems. Moreover, dyes like pre-metallized dyes used in nylon dyeing include chrome (Cr), copper (Cu), zinc (Zn) or nickel (Ni) as one component in the dye chromophore. These metals ions, after entering the environment when the dye house discharges its wastewater, can cause serious health problems and environmental pollution.

Other types of issues concerned with textile dyeing are the use of salt, water, and energy. Some dyes require as much as 250–300 g/l of salt to have high dye exhaustion from the dye bath to the target textile materials. The salts used are generally sodium sulfate and sodium chloride. These salts when

discharged in high concentrations are toxic to aquatic life and are harmful to the sewer system as well. The major use of energy in the dye process involves heating of water for the dye bath in order to facilitate a quick dyeing process and better dye penetration into textile materials. The less water used, the lower the heat energy required. The main objective of this research is to explore the possibilities to reduce the colorants and chemical auxiliaries in the fiber dyeing effluents by: (1) the improvement of the dye exhaustion onto the target fibers with optimized dyeing conditions; (2) reuse of the dye bath and the chemicals that remain after the original dyeing process.

1.1. Nylon fibers

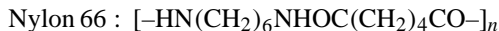
Nylons are a group of aliphatic polyamides, one of the most common polymers used as textile fibers. As flock fibers, they are mainly used in furnishing, upholstery and decorative products. Nylon has a linear polymer structure and is thermoplastic. The most important chemical group in nylon polymer is the polar amide group, $-\text{CO}-\text{NH}-$. It owes its polarity to the slightly negative charge on the oxygen atom, and slightly positive charge on its hydrogen atom. The other important group is amino group, $-\text{NH}_2$ found at the end of

* Corresponding author. Tel.: +1-508-999-9147; fax: +1-508-999-9139.

E-mail address: qfan@umassd.edu (Q. Fan).

the nylon molecular structure. These chemical groups are the ones that can form hydrogen bonds in the nylon polymer system. The terminal group, $-\text{NH}_2$ on nylon provides the dye sites for dye molecules.

The nylon 66 polymer has a linear but zig-zag arrangement of carbon atoms.

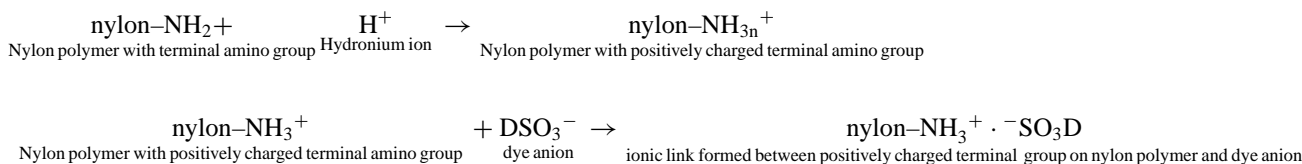


Another commonly used nylon is nylon 6. It is different from nylon 66 in the polymer structure since it only has one kind of carbon chain which is six atoms long in its repeating unit.



1.2. Dyeing of nylon using acid dyes

Most acid dyes are sodium salts of organic sulfonic acids and the anion is the active colored component. There are a few of acid dyes containing carboxyl groups. The acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath. The most significant assistant in the application of these acid dyes onto nylon is the acid added to the dye bath. Many acid dyes will not exhaust at all unless the dye bath has been acidified. Not only is the amount of dye adsorbed by the fiber influenced by the amount of acid, but also the rate of exhaustion is dependent upon acidity of the dye bath. Acid dyeing of nylon results in ionic bonds or salt links between the dye molecules and the polymer. The dye site where the ionic link is formed is the terminal amino group of nylon. The dyeing of nylon with acid dyes can be represented as follows:



In addition to the dominant ionic bonds, hydrogen bonds and Van der Waals forces play a role in the bonding between dye molecules and the nylon fibers. Those additional bondings take place between the other part of the colored anion and the fiber. Usually, large dye molecular structure will have a higher affinity to the fiber and better washfastness. However, uneven dyeing would happen more easily with large molecule dyes. From time to time, salt is also used to control the evenness of dyeing.

Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is usually used as a leveling agent. It acts as a retarding agent. When dissolved in water, sodium sulfate will dissociate and generate SO_4^{2-} anion. These smaller anions in the dye liquor are attracted more quickly than the larger dye anions, DSO_3^- , to the positively charged nylon fibers, nylon-NH_3^+ . The dye anions moving at a much slower rate will gradually replace

the sulfate anion on the dye sites due to the high affinity of their molecular structure, resulting in a much more even dyeing.

Acid is used to promote dyeing exhaustion. Depending on acid dye molecular size, acid strength and concentration used should be carefully selected. The smaller the dye structure, the more acid or stronger acid is required to have a lower pH. However, exhaustion of high affinity dyes at higher rate or at low pH would cause uneven dyeing because of the difficulty of dye migration which is necessary to have an even dyeing results.

The acid dyes are relatively easy to dissolve in water because of the presence of water solubilizing group, $-\text{SO}_3^+$. However, care must be taken to avoid the possibility of undissolved particles becoming deposited on the goods. The required amount of dyestuff is dissolved in water better through a pasting step, preferably with a small amount of anionic wetting agent. The nylon fiber should be well scoured before dyeing to remove any impurities that would cause dyeing problems, otherwise. Then the exhaust dyeing with acid dyes can be carried out as shown graphically in Fig. 1.

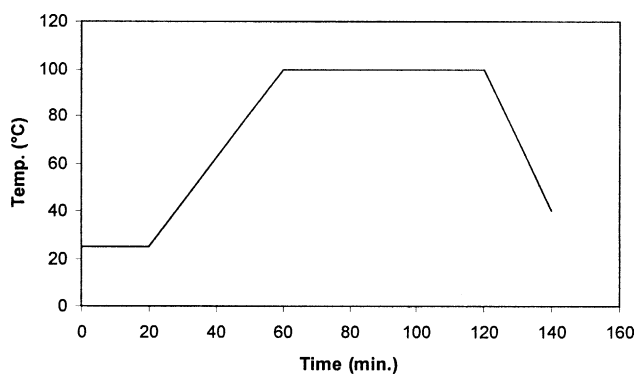
1.3. Previous work

Most of the previous research in this area has been concentrated on nylon fabric or yarn dyeing. Little work has been done on the dyeing of nylon flock fibers. Kumazawa et al. [1] indicated that the driving force of dye diffusion into a polymer is the dye concentration difference between the dyebath and the substrate, and affected by the presence

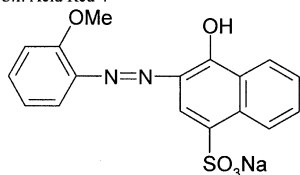
of salts. Sada et al. [2] concluded that the application of an acid dye to nylon can reasonably be explained as a diffusion process with instantaneous Langmuir-Nerst type dual adsorption, so as to make it clear that the dyeing process is heterogeneous in character.

An ion sorption model for polyamides dyeing was proposed by Yang et al. [3]. This model considered both ionic interaction and physical interactions and treated both interactions as functions of other ions in the system. Some electrolytes, such as sulfates and phosphates, can increase the sorption of negatively charged dye ions on positively charged polyamide because of their ability to increase the physical attraction between the dye and the polymer.

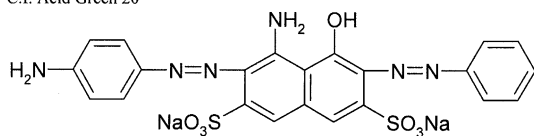
A novel method [4] for dyeing nylon articles and the like at room temperature was to apply an aqueous dye so-



C.I. Acid Red 4



C.I. Acid Green 20



C.I. Acid Black 164

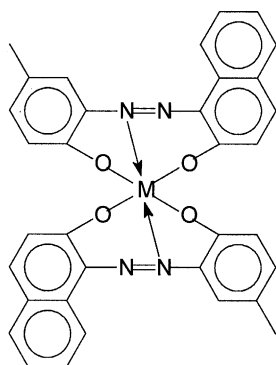


Fig. 1. Dyeing profile. C.I. Acid Red 4; C.I. Acid Green 20; C.I. Acid Black 164.

lution consisting essentially of an acid dye and 30–60% formic acid by volume to the area of the nylon article to be dyed. An acceptable color depth can be achieved in 1–3 min.

In practical dyeing, sufficient considerations are required for the selection of surfactants, a very important type of dyeing auxiliary. Nemoto et al. [5] studied the interaction between dyes and nonionic surfactants. They found that when a hydrophobic surfactant is adopted for a hydrophobic dye so that strong interaction may take place accompanying the formation of stable complexes in the dye bath, the dye is not completely exhausted to the fiber even at high temperature. This phenomenon is also observed with hydrophilic surfactants when the concentrations are higher. These complexes

are less soluble in water and readily adhere to a fiber, thus the apparent rate of dyeing rapidly increases in the initial stages. This is due to the adherence of complex onto fiber and such a dyeing cannot be regarded as real dyeing. However, the complex on the fiber would dissociate into each component, surfactant and dye, when temperature increases gradually. The dye dissociated is partially dissolved into the dye bath and adsorbed again onto the fiber. Thus the final amount of dye adsorbed onto the fiber is less than the initial exhaustion.

2. Experimental

2.1. Materials and equipment

- Flock fiber: nylon 66, 1.5 denier, 0.05 in. long.
- Acid dyes: three dyes are selected for the investigation because of their different molecular structures, namely:
 - C.I. Acid Red 4
 - C.I. Acid Green 20
 - C.I. Acid Black 164. Its detailed chemical constitution is not disclosed. But has been believed that it has a general structure as indicated.
- Flocking adhesive: BFG FL1059B, BF Goodrich
- Dyeing machine: Ahiba Polymat, pressure dyeing machine
- Spectrophotometers: (a) Ocean-optic 2000 fiber optic spectrophotometer used for the measurement of dye concentration in solution; (b) Macbeth Color-Eye 2020 spectrophotometer used for the measurement of color depth (K/S) of dyed materials
- Tensile tester: Instron Materials Testing Instrument 5569 with Instron Merlin Software
- APG1000 Maag Flockmaschinen abrasion tester: Number B-5 chisel was used at 15 cycles/min. A total of 20 cycles was carried out to compare the samples in question.

2.2. Dyeing conditions

The dyeing conditions are listed here:

- Flock (2.0 g);
- glauber's salt (4.0% owf);
- nonionic surfactant (1.0% owf);
- temperature (100 °C);
- duration (60 min);
- formic acid, acetic acid, or sulfuric acid used for adjusting the dyeing pH.

2.3. pH change in dyeing

The dye concentrations used were 0.1, 0.2, 0.5, 1, 1.5, and 2% owf. The pH of dyeing solution was monitored before and after dyeing with a pH meter to find out how pH changes

Table 1
Factors and levels of the dyeing parameters

| Dyeing parameters | Level 1 | Level 2 | Level 3 |
|----------------------------------|---------|---------|---------|
| Factor A: salt concentration (%) | 5 | 4 | 3 |
| Factor B: time (min) | 60 | 45 | 30 |
| Factor C: temperature (°C) | 95 | 90 | 85 |
| Factor D: liquor ratio | 1:50 | 1:40 | 1:30 |

in dyeing. At the same time, dyeing auxiliaries such as salt and surfactants were used at set conditions.

2.4. Determination of dye concentrations by using standard absorption curves of the dyes

By using a dyeing method that has no pH control, the standard absorption curves for each dye was first obtained at different concentration levels. These curves were used to determine the dye concentration in the dye bath. The dye bath concentration can be obtained by using related regression equations. If dilution was made to facilitate the measurement of absorbance, the actual dye concentration should be adjusted accordingly.

2.5. Reuse of dye bath and dye exhaustion

This experiment was carried out to determine the effect of reuse of dye bath on the dyeing results at the dye concentration of 1% owf and dyeing pH 4.5. After the fresh bath dyeing was finished, a certain amount (fixed percentage from 25% through 75% in an increment of 10%) of the spent dye bath was reused. Addition of dye and chemicals was conducted to compensate for any consumption and loss in the previous dyeing cycle. pH adjustment was also necessary. The dye bath was reused in this way for a total of four times.

The dye exhaustion was determined by measuring the absorbances of the diluted dyebath before and after each dyeing at the wavelength of maximum absorbance of the dye used. The calculation was based on the following Eq. (1):

$$\text{Dye exhaustion (\%)} = \left(\frac{1 - A_1}{A_0} \right) 100 \quad (1)$$

where A_0 and A_1 are the absorbances of the diluted dyebath, before and after the dyeing respectively.

2.6. Effects of some dyeing parameters on dye exhaustion

A series of experiments based on the following conditions (Tables 1 and 2) was carried out to better understand their effects on dyeing for the purpose of establishing a group of optimized dyeing parameters for maximum exhaustion of acid dyes on the nylon flock fibers. Apart from the conditions

Table 2
Combination of dyeing parameters used in the experiments

| Experiment | Factor A (%) | Factor B (min) | Factor C (°C) | Factor D |
|------------|--------------|----------------|---------------|----------|
| 1 | 5 | 60 | 95 | 1:50 |
| 2 | 5 | 45 | 90 | 1:40 |
| 3 | 5 | 30 | 85 | 1:30 |
| 4 | 4 | 60 | 90 | 1:30 |
| 5 | 4 | 45 | 85 | 1:50 |
| 6 | 4 | 30 | 95 | 1:40 |
| 7 | 3 | 60 | 85 | 1:40 |
| 8 | 3 | 45 | 95 | 1:30 |
| 9 | 3 | 30 | 90 | 1:50 |

listed, dyeing pH and dye concentration was pre-selected according to the previous dyeing results.

2.7. Dye uptake (K/S)

Dye uptake on fibers/fabrics can be obtained by measuring the reflectance of the fiber/fabrics. The calculation for the dye uptake can be done using the following Eq. (2):

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

where R is the reflectance reading from spectrophotometer, K the coefficient of absorption, and S the coefficient of scatter. According to the Kubelka–Munk theory, K/S is directly proportional to the color strength of a solid surface.

2.8. Effect of sulfuric acid on exhaustion of Acid Red 4

Sulfuric acid was used to maintain a pH of 2.5 and its corresponding effect on dye exhaustion was noted. Finally, the abrasion resistance of the dyed flock fibers at a pH of 2.5

Table 3
pH before and after dyeing for the three dyes used alone

| | | | | | | | |
|---------------------------|------|-----|-----|-----|-----|-----|--|
| Acid Red 4 | | | | | | | |
| Dye concentration (% owf) | 0.2 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | |
| pH before dyeing | 7.5 | 7.6 | 7.6 | 7.6 | 7.8 | 7.9 | |
| pH after dyeing | 7.4 | 7.4 | 7.5 | 7.6 | 7.6 | 7.7 | |
| pH difference | 0.2 | 0.2 | 0.1 | 0.0 | 0.2 | 0.2 | |
| Average pH difference | 0.15 | | | | | | |
| Acid Green 20 | | | | | | | |
| Dye concentration (% owf) | 0.2 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | |
| pH before dyeing | 7.2 | 7.1 | 7.3 | 7.2 | 7.3 | 7.3 | |
| pH after dyeing | 6.9 | 7.2 | 7.4 | 7.4 | 7.4 | 7.4 | |
| pH difference | 0.3 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | |
| Average pH difference | 0.15 | | | | | | |
| Acid Black 164 | | | | | | | |
| Dye concentration (% owf) | 0.2 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | |
| pH before dyeing | 7.8 | 7.8 | 8.1 | 8.3 | 8.3 | 8.4 | |
| pH after dyeing | 7.2 | 7.5 | 7.6 | 7.9 | 8.2 | 8.3 | |
| pH difference | 0.6 | 0.3 | 0.5 | 0.4 | 0.1 | 0.1 | |
| Average pH difference | 0.33 | | | | | | |

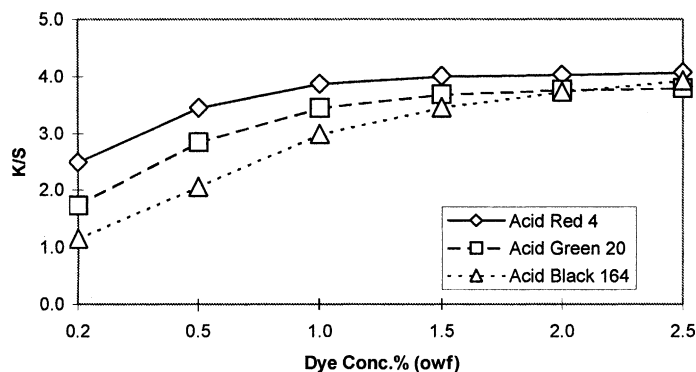


Fig. 2. *K/S* vs. dye concentration (% owf).

was compared with standard undyed nylon flock. The flock fibers were first flocked onto a nylon fabric substrate. Water based acrylic adhesive supplied from BF Goodrich company was used as flocking adhesive. A dc electrostatic flocking instrument was used for flocking. The abrasion resistance of dyed and control samples was determined using APG1000 Maag Flockmaschinen abrasion tester.

3. Results and discussion

3.1. pH change in dyeing

Table 3 shows how the pH of the dyeing solution varies before and after dyeing when each of the three dyes were used alone. Since the dyeing pH was not controlled in this group experiment, the dye exhaustion was poor and not measured. This suggested that pH control is necessary for acid dyes to have a good exhaustion onto nylon flock.

From Table 3, it can be seen clearly that as the dye molecular structure increases (Acid Black 164 has the largest molecular structure), the average pH change increases with the pH after dyeing being lower than that before dyeing. It is also worth noting that the pH difference at the lower dye concentration is generally larger than that at higher dye concentration with the exception of Acid Red 4 which has a near constant pH difference across the concentration range used. From this group of data, we can derive an acid dyeing guild line. With large acid dye molecules, pH control is important in order to achieve a constant pH during dyeing, which can lead to an optimum dye exhaustion, and the use of pH buffer is recommended. For small dye molecules, pH adjustment can be done easily using acidic chemicals without use of pH buffer.

3.2. Effect of dye concentration on dye uptake of nylon flock fiber

From Fig. 2 it can be seen that the dye uptake (*K/S*) increases with increasing dye concentration in the dye bath.

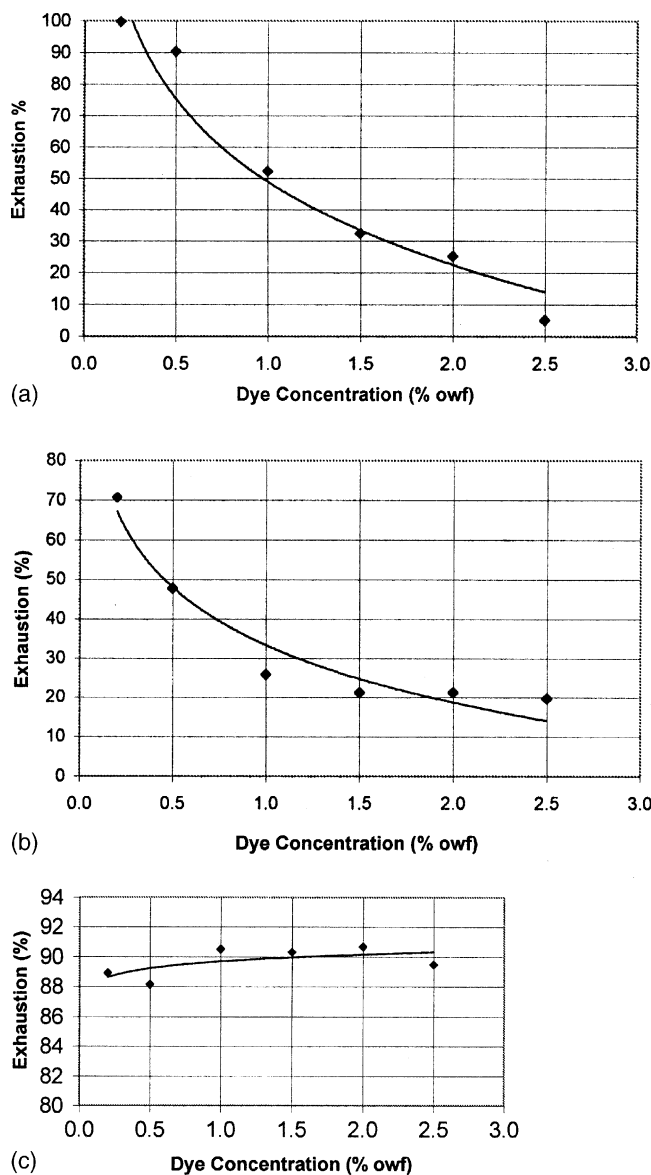


Fig. 3. (a) Dye exhaustion of Acid Red 4. (b) Dye exhaustion of Acid Green 20. (c) Dye exhaustion of Acid Black 164.

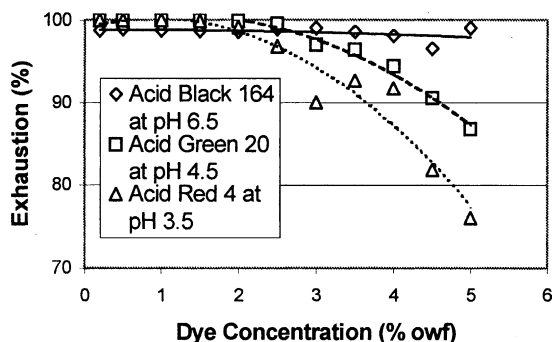


Fig. 4. Dye exhaustion of acid dyes with controlled pH.

However, the dye uptake reached an equilibrium at a concentration of about 2.5% under the used dyeing conditions. It is understood that the dye sites on nylon fiber are those ending $-NH_2$ groups and their amount is limited under fixed dyeing conditions. This contributed to the limited dye uptake on the fibers. Based on this observation, we believe that optimization of dyeing conditions like the pH and salt addition may lead to a high dye uptake, meaning a better dye utilization and less discharged dye to the environment.

3.3. Dye exhaustions at different dye concentrations

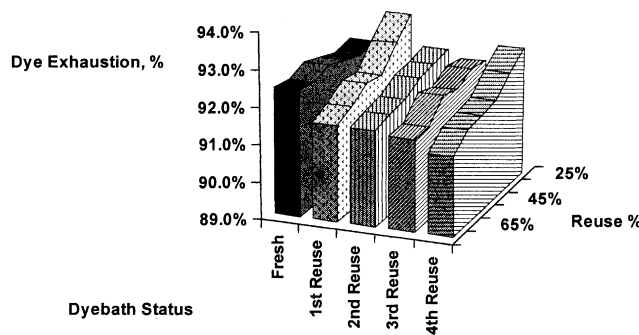
Fig. 3 (a–c) shows the exhaustion obtained for the three types of dyes on nylon flock fiber at different dye concentrations. In this experiment, the dyeing pH was not controlled. The exhaustion of Acid Red 4 decreased quickly with increasing depth of shade on fiber (dye concentration, % owf). The exhaustion of Acid Green 20 had a similar trend as Acid Red but at a slower rate. Acid Black 164 showed a very stable and high exhaustion. It is obvious that the dye

exhaustion is directly related to the dye molecule structure. Larger molecules usually means more intermolecular interaction due to van der Waals force. The van der Waals force between acid dyes and nylon fiber contributed a great part in the dye exhaustion.

Fig. 4 shows the results involving dye exhaustion percentage versus dye concentrations for the three types of dyes with controlled dyeing pH. The pH was chosen based on the dye molecular structure. Smaller structure needs to have lower pH because ionic attraction at low pH between the acid dye and nylon fiber can increase the needed substantivity, thus higher exhaustion can be achieved. From Fig. 4 it can also be seen clearly that the dye exhaustions of Acid Red 4 and Acid Green 20 were increased significantly at the selected dyeing pH. However at concentrations over 3% owf the dye exhaustions decreased gradually to about 76 and 82 % respectively, with increasing of dye concentration. Acid Black 164 can still have about 98% exhaustion at high dye concentration. It also shows that pH control is very important in the nylon dyeing and proper pH for individual dye can improve the dye exhaustion.

3.4. Reuse of acid green 20 dye bath

The results for the reuse of dye bath from 25 to 75% reuse percentage at an increment of 10% is shown in Fig. 5. It can be seen clearly that the dye exhaustion decreases slightly with increasing the reuse percentage as well as with increasing reuse cycles. This decreased dye exhaustion can be contributed to the accumulation of impurities in the dye bath. However, this kind of change is so small that it would not cause any significant color deviation in bulk dyeing operation. That means, reuse of dye bath is feasible under the experimental conditions.



| | 25% | 35% | 45% | 55% | 65% | 75% |
|-------------|-------|-------|-------|-------|-------|-------|
| ■ Fresh | 92.2% | 92.1% | 92.3% | 92.5% | 92.3% | 92.4% |
| ▨ 1st Reuse | 93.0% | 92.6% | 92.0% | 92.1% | 91.8% | 91.6% |
| ▩ 2nd Reuse | 92.2% | 92.1% | 92.0% | 91.8% | 91.7% | 91.6% |
| ▧ 3rd Reuse | 92.0% | 92.1% | 91.8% | 92.0% | 91.5% | 91.5% |
| ▦ 4th Reuse | 92.5% | 92.1% | 91.7% | 91.6% | 91.5% | 91.1% |

Fig. 5. Exhaustion of Acid Green 20 on nylon flock under different reuse percentage and times of reuse.

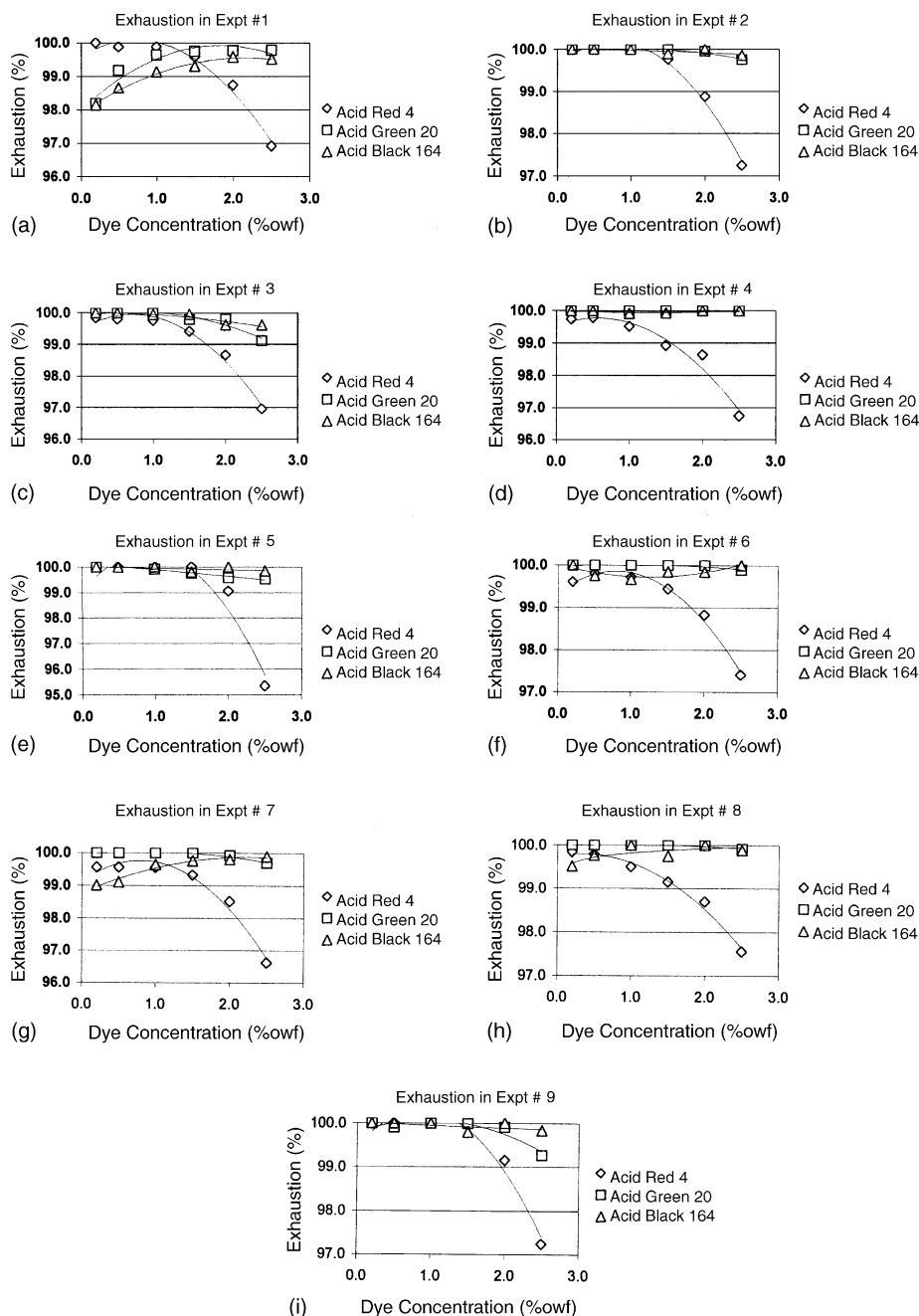


Fig. 6. (a) Exhaustion in experiment #1; (b) exhaustion in experiment #2; (c) exhaustion in experiment #3; (d) exhaustion in experiment #4; (e) exhaustion in experiment #5; (f) exhaustion in experiment #6; (g) exhaustion in experiment #7; (h) exhaustion in experiment #8; (i) exhaustion in experiment #9.

3.5. Effects of some dyeing parameters on dye exhaustion

The results of the experiments listed in Tables 1 and 2 are shown in Fig. 6(a) through (i). From the results of the experiments, it can be seen that Acid Green 20 and Acid Black 164 have almost perfect (over 98%) exhaustion no matter what combination of the dyeing conditions are used in the experiments.

However, the exhaustion of Acid Red 4 is sensitive to its concentration. When dye concentration is over 2% owf, the exhaustion starts decreasing. It suggests that this dye has a

tendency to stay in aqueous solution more than onto nylon fiber. In other words, Acid Red 4 has a lower affinity to nylon fiber than Acid Green 20 and Acid Black 164. Compared to the results shown in Fig. 4, it is apparent that use of salt increased dye exhaustion.

3.6. Effect of sulfuric acid on Acid Red 4 dye exhaustion

Fig. 7 shows The effect of a low pH of 2.5, using sulfuric acid on dye exhaustion of Acid Red 4, without salt. From

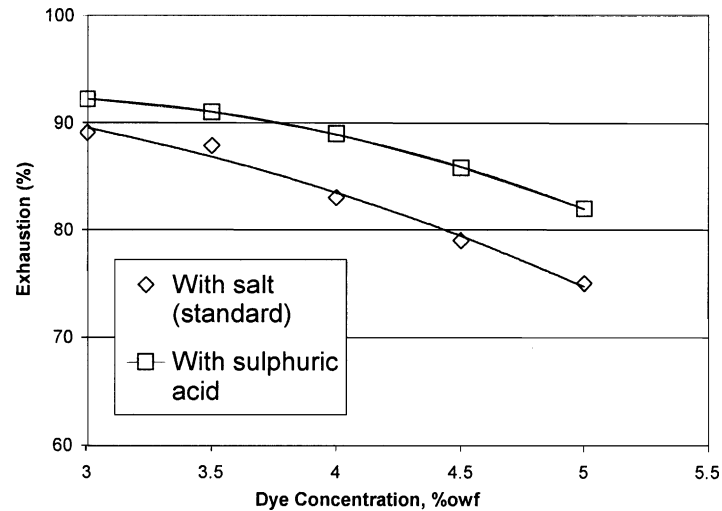


Fig. 7. Effect of Dyeing pH 2.5 on Acid Red 4 exhaustion.

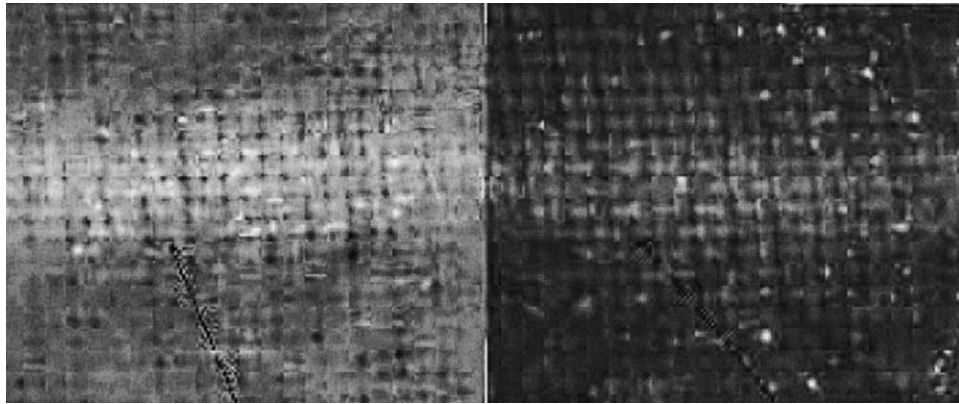


Fig. 8. Abraded nylon flock samples (left: undyed nylon flock, right: pH 2.5 dyed nylon flock).

Fig. 7, it can be seen that the exhaustion of Acid Red 4 on nylon flock can be promoted by lower dyeing pH. At the highest dye concentration (5% owf), pH 2.5 can increase dye exhaustion by 7% (from 75 to 82%) compared to the dyeing results achieved using salt and at pH 3.5. This dyeing has an extra benefit to the environment because no salt is needed.

Fig. 8 compares of the abraded surfaces of flocked nylon dyed at pH 2.5 with undyed nylon flock. From visual observation it can be noted that there is no appreciable difference in abrasion resistance of the two samples.

The effects of dyeing pH 2.5 on the tensile and tear resistance of nylon fabrics were determined. Tables 4 and 5 show the tensile and tear strength of Acid Red 4 dyed nylon fabric at dyeing pH 2.5 and the control undyed nylon fabric. It can be seen that the nylon fabrics dyed at pH 2.5 shows no decrease in tensile strength and tensile extension, but a minute decrease in tear strength. In flocked samples, these tear strength changes will not cause any significant practical problems since the flock fibers are implanted into the adhesives and will not actually be subject to any tear forces in use.

Table 4
Tensile strength of dyed and undyed nylon fabric

| Sample | Tensile strength (lb) | | Tensile extension (in. strain %) | |
|---------------------------------|-----------------------|-------|----------------------------------|------------|
| | WARP | WEFT | WARP | WEFT |
| Control | 32.21 | 30.27 | 1.20(20) | 1.60(26.7) |
| Dyed with Acid Red 4, at pH 2.5 | 34.50 | 32.27 | 1.32(22) | 1.60(26.7) |

Table 5
Tear strength of dyed and undyed nylon fabric

| Sample | Average tear strength (lb) | |
|---------------------------------|----------------------------|------|
| | WARP | WEFT |
| Control | 3.88 | 4.47 |
| Dyed with Acid Red 4, at pH 2.5 | 3.62 | 4.10 |

4. Conclusion

Among the three dyes, Acid Red 4, Acid Green 20 and Acid Black 164, Acid Red 4 has the smallest structure. Its exhaustion decreases with increasing depth of shade on nylon flock fiber. Based on the results obtained, at 4.5% owf dye concentration, an exhaustion of above 90% for Acid Green 20 and above 96% for Acid Black 164 can be obtained at pH of 3.5 and 6.5 respectively, whereas Acid Red 4 requires a lower pH of 2.5 with the use of sulfuric acid to achieve 87% exhaustion at the dye concentration of 4.5% owf. It was also found that large acid dye molecules tends to cause a big pH change before and after dyeing, which implies that the use of pH buffer is necessary for large dye molecules to be exhausted optimally. When the use of sulfuric acid in dyeing nylon flock fiber has shown no difference in abrasion resistance as compared with an undyed sample. Tear and tensile strength tests on nylon fabric dyed with Acid Red 4 at pH 2.5 showed no appreciable loss in these mechanical proper-

ties. The reuse of dyebath showed that the dye exhaustion decreases slightly with increasing reuse percentage as well as with increasing reuse cycles. This decreased dye exhaustion can be contributed to the accumulation of impurities in the dye bath. However, this kind of change is so small that it would not cause any significant color deviation in bulk dyeing operations. That means, reuse of dye bath is feasible under experimental conditions.

Acknowledgements

This research was supported by the STEP funding of the Commonwealth of Massachusetts. Undergraduate student Cathryn Adams performed the dye reuse experiment of this project.

References

- [1] H. Kumazawa, E. Sada, T. Ando, *J. Polym. Sci., Polym. Chem. Ed.* 22 (1984) 61.
- [2] E. Sada, H. Kumazawa, T. Ando, *J. Soci. of Dyers Colorist* 98 (1982) 121.
- [3] Y. Yang, S. Li, T. Lan, *J. Appl. Polym. Sci.* 51 (1994) 81.
- [4] J. Kane, R. La Conte, United States Patent 4,309,177. (5 January 1982).
- [5] Y. Nemoto, H. Funahashi, *Ind. Eng. Chem. Prod. Res. Develop.* 19 (1980) 136.