

pH Control for Dyebath Reuse in Dyeing of Polyamide with Binary Mixtures of Acid Dyes

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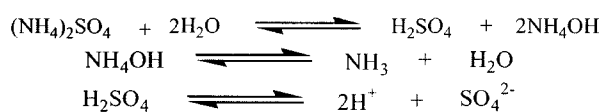
Abstract: Hydrolyzable organic esters were compared with ammonium sulphate as an acid donor for the pH control in dyebath-reuse system of acid dyes mixtures. The ability of pH control, levelness, dyeing properties and reproducibility in dyebath-reuse system were investigated comparatively. Hydrolyzable organic esters showed higher exhaustion and color yield than ammonium sulphate. In addition, hydrolyzable organic ester exhibited very low conductivity less than 0.5 mS, while ammonium sulphate give high conductivity. However, we could not observe any difference in levelness of dyed samples between two kinds of acid donors in laboratory scale dyeing. Over 10 cycles of reuse, hydrolyzable organic esters showed higher reproducibility than ammonium sulphate. No deterioration of the color fastness and levelness occurs over 10 cycles of reuse.

Keywords: Hydrolyzable organic ester, Acid donor, pH control, Dyebath-reuse

Introduction

In the process of dyeing polyamide with acid dyes, batch-to-batch reproducibility and the quality of dyeing are influenced by many factors, including the temperature and pH control. The main objective for controlling the pH throughout the dyeing cycle is to permit the dyer to produce level, reproducible results. Generally, in the dyeing of polyamide with acid dyes, color reproducibility and the levelness of dyed materials can be ensured by pH control systems such as the use of a buffer system or a pH sliding system [1].

A pH sliding system is particularly useful for non-migrating acid dyes on nylon. The controlled lowering of the pH can be achieved by using products that release more acidic compounds as they undergo decomposition as the dyeing temperature increases. Typically, these include ammonium salts (e.g. sulphate, acetate, tartrate), with the most widely used being ammonium sulphate, since it consists of the salt of a strong acid and a weak base. At boiling temperature, ammonium sulphate decomposes gradually liberating ammonia and sulphuric acid, a strong acid that subsequently lowers the pH as the ammonia escapes [2,3]; ammonium salt hydrolyses into ammonium hydroxide in water and it decomposes with the liberation of ammonia which is evolved with the steam leaving the acid. However, in enclosed or partially enclosed machines, this system is not very efficient, because ammonia



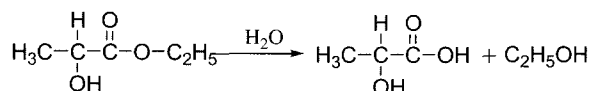
Scheme 1. Hydrolysis of ammonium sulphate.

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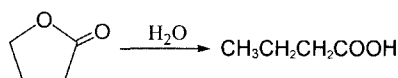
is prevented from escaping (Scheme 1) [1,4].

An alternative method for obtaining a pH that slides in the direction of acidity is to use organic esters that hydrolyse to alcohol and acid under the conditions of processing. The use of hydrolyzable esters dates back to 1953 when Brotherton Co. Ltd. introduced their Estrocon process, which is based on the addition of diethyl tartrate or ethyl lactate, for dyeing wool with acid milling dyes and chrome dyes by the single-bath method (Scheme 2) [5]. The technique, which involved the decomposition of one compound *in situ* to produce acid, was first utilized by Sandoz with the 'Sandacid V' process over 20 years ago, in which γ -butyrolactone undergoes hydrolysis to produce butyric acid (Scheme 3) [6]. Although this procedure is technically sound, it is not used widely, probably because of the increase in processing costs. However, recently there has been renewed interest in the use of hydrolyzable esters, particularly in the application of high-fastness dyeings and dyebath-reuse systems [7-12].

There are many advantages of dyebath-reuse, including less water to heat, less effluent to treat, and a reduced consumption of energy, dyes, and chemical auxiliaries. Because of the potential economic and environmental advantages involved in this process, clearly it is deserving of further



Scheme 2. Hydrolysis of ethyl lactate.



Scheme 3. Hydrolysis of γ -butyrolactone.

investigation [13]. Dyebath-reuse using pH-sliding system has been investigated in the dyeing of polyamide with a single acid dye in a previous study [8].

The present study was undertaken to investigate dyebath-reuse using pH-sliding system in the dyeing of polyamide with binary mixtures of acid dyes. The dyeing properties, fastness and color reproducibility were compared between the pH-sliding agents.

Experimental

Materials

Scoured nylon fabric (Taslan, 205T) was used for dyeing. Albigal SET (amphoteric; Ciba Specialty Chemicals) and Nylofixan PM (anionic; Clariant) were used as the leveling and fixing agent, respectively. The dyes used in this study were Rifa Acid Orange G (C.I. Acid Orange 56, milling type; Rifa), Rifa Acid Cyanine 5R (C.I. Acid Blue 113, milling type; Rifa), and Rifa Acid Red S2B (C.I. Acid Red 128, milling type; Rifa) (Figure 1). Reagent grade sodium carbonate, ammonium sulphate (AS), γ -butyrolactone (GBL), ethyl lactate (EL), and diethyl tartrate (DET) were used.

Dyeing

A 100 ml dyebath, containing two acid dyes (1.0 %owf each), leveling agent (0.5 g/l) and acid donors for pH control was prepared. A nylon fabric sample (3.0 g) was then immersed in the dyebath and the dyeing was performed for 60 min at 98 °C in an Ahiba Nuance laboratory dyeing machine (Ahiba, Switzerland). After dyeing, all the samples were hot rinsed and treated with a fixing agent (Nylofixan PM, 1.5 g/l, 70 °C, 20 min) followed by washing and air-

drying. The application details for dyeing and aftertreatment which were used in this study have been described in a previous paper [7].

Dyeing was performed with three binary mixtures of acid dyes; Mixture 1 (C.I. Acid Orange 56 + C.I. Acid Blue 113), Mixture 2 (C.I. Acid Orange 56 + C.I. Acid Red 128), and Mixture 3 (C.I. Acid Red 128 + C.I. Acid Blue 113).

Dyebath pH Control System

Dyebath pH was controlled by four pH sliding systems. The optimum concentrations of each acid donor were determined by comparing the pH control ability at various concentrations of each acid donor in previous work (AS: 2.0 g/l, GBL, EL and DET: 0.1 %v/v) [7].

Dyebath-reuse Procedure

After dyeing, the fabrics were removed, the dyebaths were analysed colorimetrically to determine the quantities of two dyes necessary to reconstitute the bath, and the residual dyebath was left to cool to room temperature. At the end of each cycle, the dyebath was replenished with 20 ml of water containing the necessary amount of dyes, leveling agent and acid donors to compensate for evaporation and fibre drag-out losses. The addition of auxiliaries at the level commensurate with the fresh water necessary to keep a stable liquor ratio in the original volume has been found sufficient to allow several cycles of reuse, as Carr and Cook reported [14]. Thus the leveling agent was added to the spent dyebath at a constant fraction (0.5 g/l) of their mass in the initial run without detailed analysis of exhaustion. Assuming that acid donors would be hydrolyzed completely during the dyeing time, a constant amount of acid donors were replenished at the end of each cycle without considering residual amounts of acid donors in the spent dyebath. This dyebath-reuse sequence was repeated nine times (ten dyeings in total). The initial pH of the dyebath containing AS or hydrolyzable organic esters (GBL, EL and DET) were adjusted to 8.0 with a dilute solution of sodium carbonate after each dyeing.

Dyeing Properties

After dyeing, dyebath exhaustion (%E) was calculated from the absorbance values, which were measured using a UVVis spectrophotometer (HP8452A, Hewlett Packard) and each residual dyebath pH, as well as the conductivity, was also measured. The color of the dyed samples was measured using a spectrophotometer (Color-Eye 3000, Macbeth, standard light D65, 10° standard observer, specular component included) interfaced with a personal computer. The levelness of the dyed fabric was assessed using an instrumental method which is described in previous work [7].

Color Fastness Test

The color fastness was determined according to international standards. The specific tests used were: ISO 105-C06/A1S

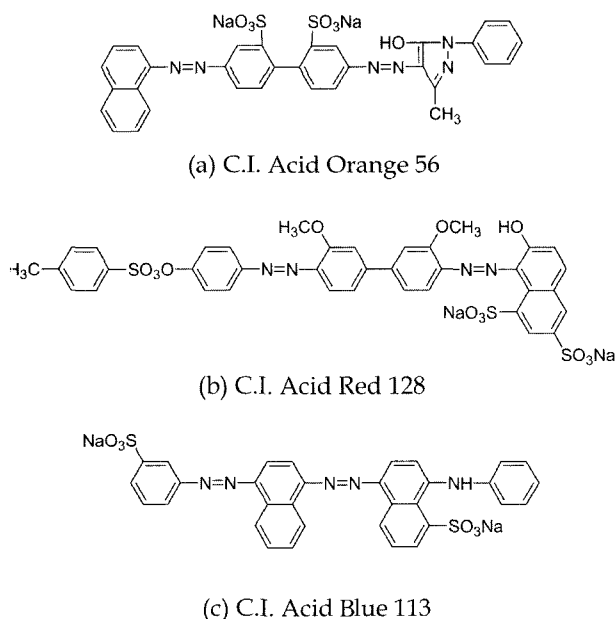


Figure 1. Chemical structures of dyes used in this study.

(color fastness to washing), ISO 105-E04 (color fastness to perspiration) and ISO 105-X12 (color fastness to rubbing). Staining and change in color were assessed instrumentally, in order to determine gray scale ratings according to ISO 105-A05.

Results and Discussion

Dyeing Properties

In the dyeing of polyamide, ion-ion electrostatic interactions, operating between the dye anion and the protonated amino groups in the substrate, can be expected to contribute to the dyesubstrate substantivity. Therefore, the presence of acid in the dyebath has the effect of severing the salt linkages between the molecular chains and thereby increasing the available number of positively charged sites [2]. Thus the relative contribution of ionic forces is governed by the pH of the dyebath, and is a major factor by which a dyer will control the rate and extent of dye uptake. Previous work showed that the use of hydrolyzable organic esters as acid donors for pH control offered distinct advantages in the dyeing of polyamide with acid dyes. Hydrolyzable organic esters give an effective pH shift with small quantities required, as compared with ammonium sulphate and sodium dihydrogen phosphate [7].

Figure 2 shows the residual dyebath pH with the number of dyebath-reuse cycles. As the number of reuse cycles increased, the residual pH of the dyebath containing AS decreased slowly, but not below 8.00, while that of the dyebaths containing GBL, EL, and DET was controlled in the range of 5.70-5.92, 5.55-5.84, and 5.4-5.54, respectively.

Figure 3 shows the exhaustion (%) of dyes with the number of dyebath-reuse cycles. The hydrolyzable organic esters showed high and stable exhaustion (%), close to 100%, while AS showed relatively low and fluctuating values. The same trends were observed in the case of *K/S* values, which could be supported by the data on the residual dyebath pH (Figure 2).

The CIELab a^* and b^* values of the dyed fabrics with the number of dyebath-reuse cycles are shown in Figure 4. Mixture 1 (C.I. Acid Orange 56 + C.I. Acid Blue 113) showed excellent color repeatability, irrespective of the acid donors. This results can be attributed to the high exhaustion (%) value of the dyes applied [10]; probability of occurrence of an error due to extensive exhaustion of one dye component in the analysis of the residual dyebath solution can be decreased.

In the case of Mixtures 2 and 3, especially in terms of b^* value, AS gave somewhat scattered values over a relatively larger area (Standard deviation, Mixture 2, 8.82, Mixture 3, 6.73) while the hydrolyzable organic esters gave concentrated values over a limited range (Standard deviation, GBL, Mixture 2, 5.3, Mixture 3, 3.27; EL, Mixture 2, 5.65, Mixture 3, 4.58; DET, Mixture 2, 6.52, Mixture 3, 4.18) on the CIELab a^*b^*

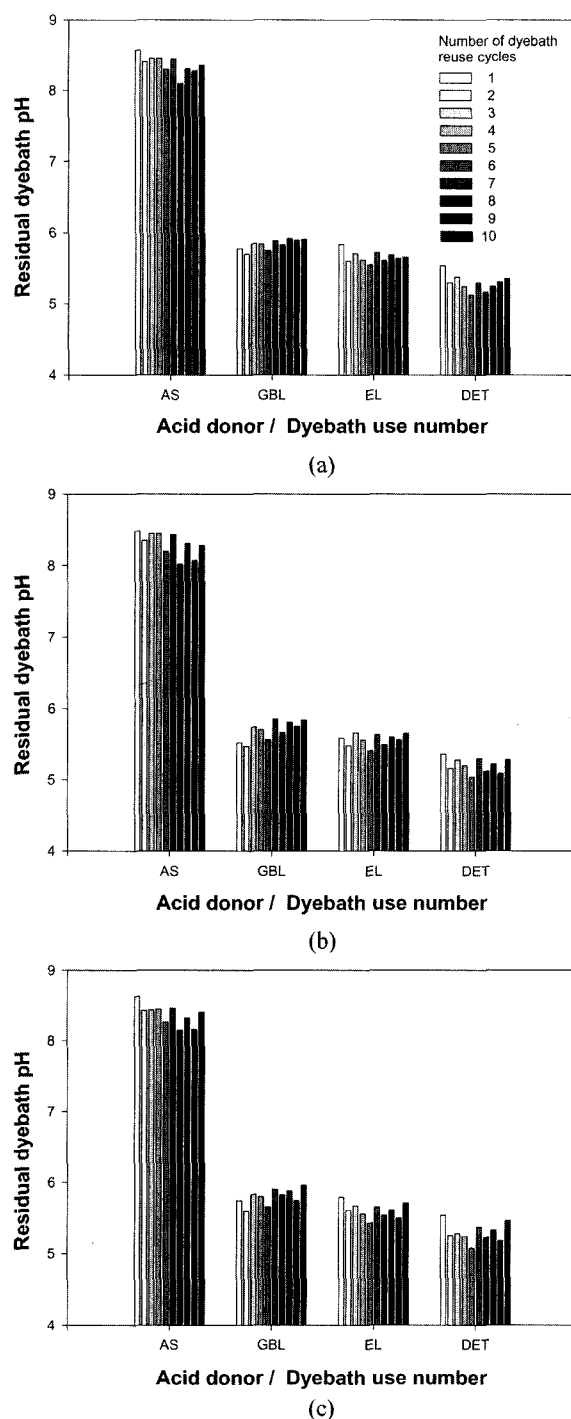
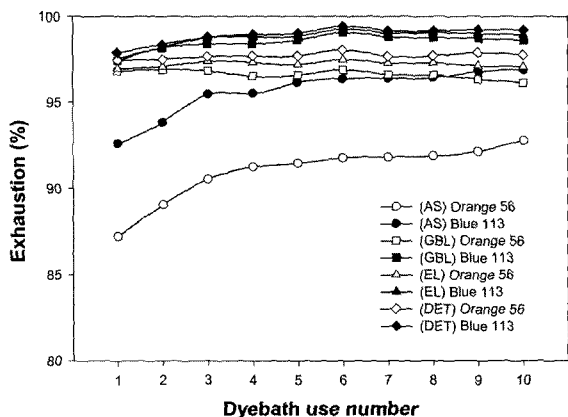


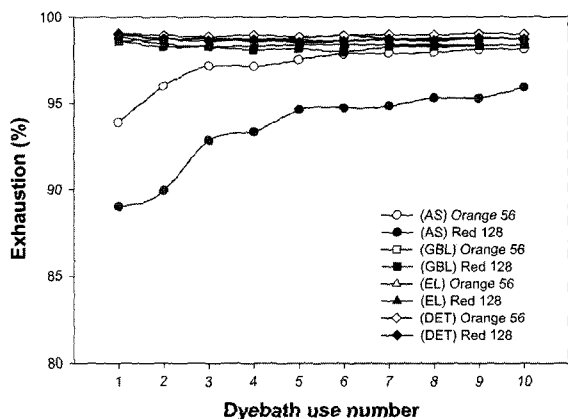
Figure 2. Residual dyebath pH with number of dyebath-reuse cycles (a) Mixture 1 (b) Mixture 2 (c) Mixture 3.

diagram in the dyebath-reuse system; use of hydrolyzable organic esters resulted in better color reproducibility than AS over 10 cycles of dyebath-reuse.

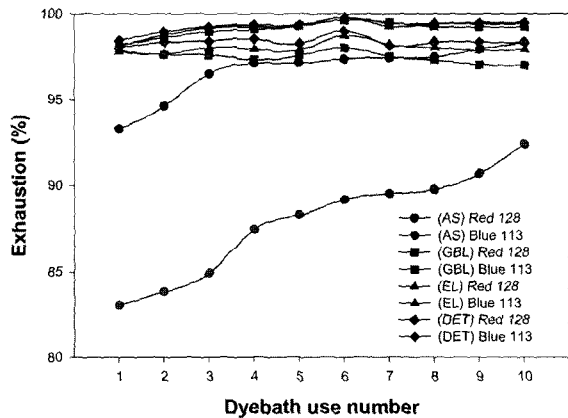
Figure 5 shows the residual dyebath conductivity with the number of dyebath-reuse cycles. AS gave high conductivity, which is an indication of the amount of salt present in the



(a)



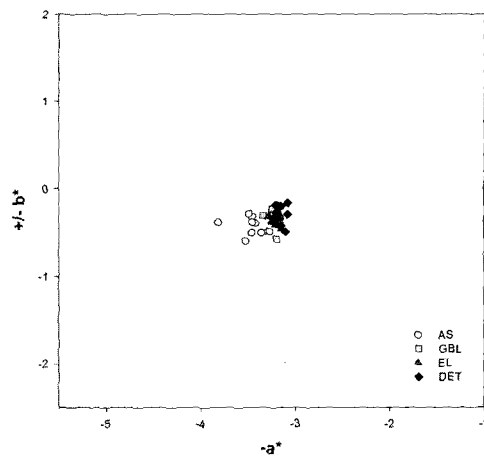
(b)



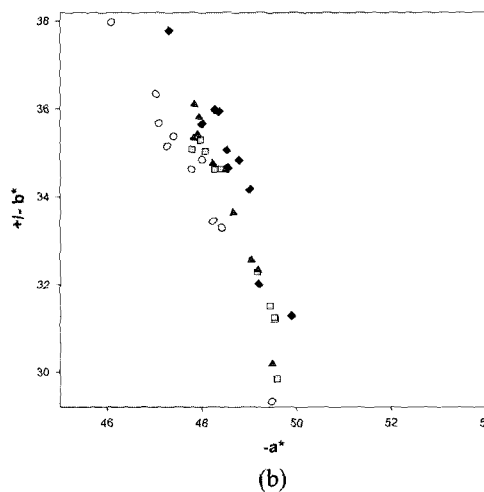
(c)

Figure 3. Exhaustion (%) of dyed fabrics with number of dyebath-reuse cycles (a) Mixture 1 (b) Mixture 2 (c) Mixture 3.

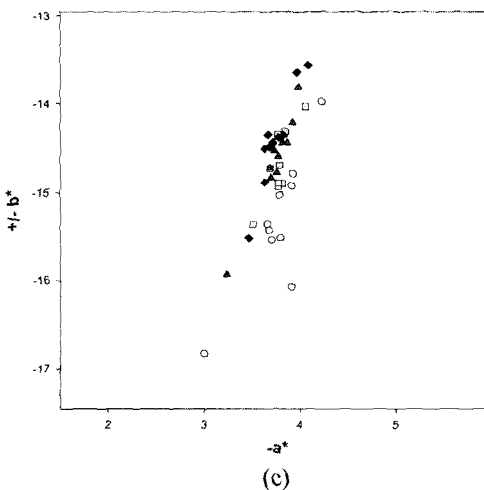
residual dyebath. The hydrolyzable organic esters showed very low conductivity, less than 5.0 mS. Therefore, it would be expected that, since AS has potentially higher electrolyte concentration than the other acid donors, the large amount of salt present in the dyebath might ultimately lead to dye aggregation and result in unlevel dyeing [15]. However, no differences were detected in the levelness of the samples



(a)



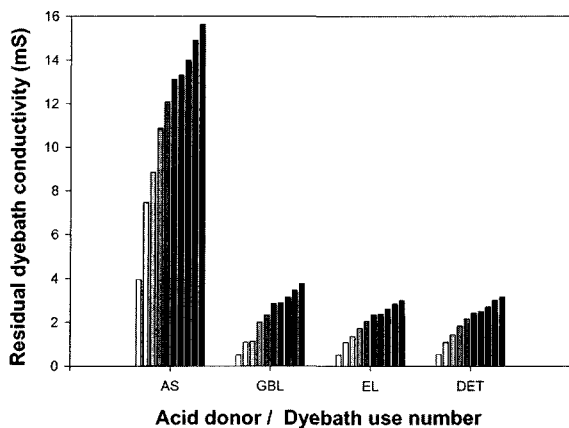
(b)



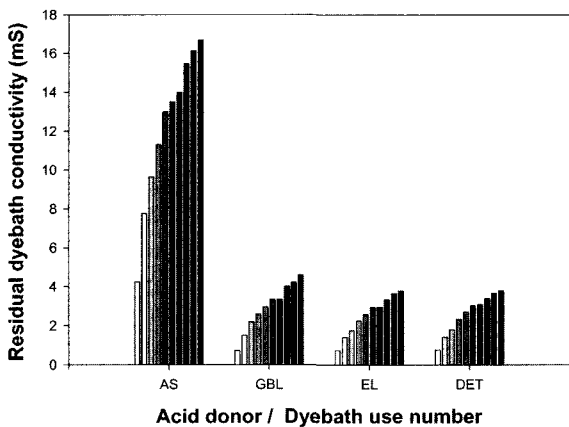
(c)

Figure 4. a^* and b^* values of dyed fabrics with number of dyebath-reuse cycles (a) Mixture 1 (b) Mixture 2 (c) Mixture 3.

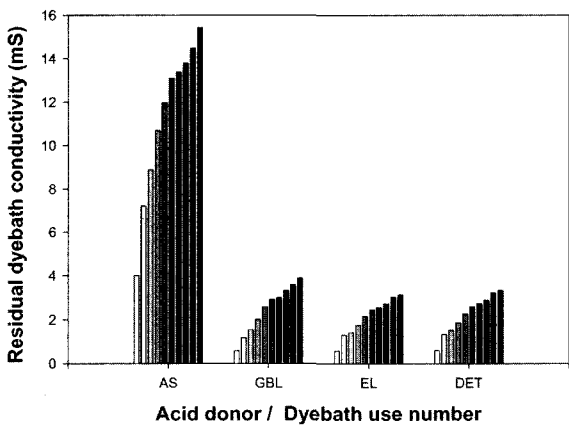
dyed with the four acid donors. The levelness achieved over successive reuses was excellent, irrespective of the type of acid donor used. These results can also be ascribed to the excellent leveling properties of Taslan fabrics or could also



(a)



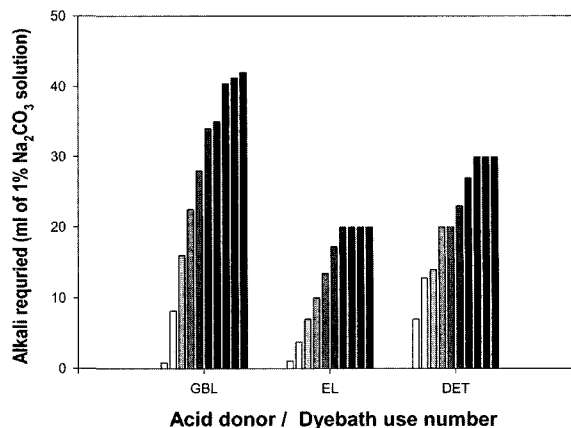
(b)



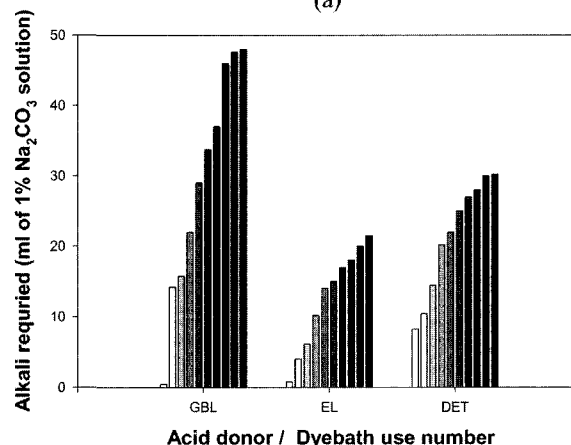
(c)

Figure 5. Residual dye bath conductivity with number of dye bath-reuse cycles; for key see Figure 2 (a) Mixture 1 (b) Mixture 2 (c) Mixture 3.

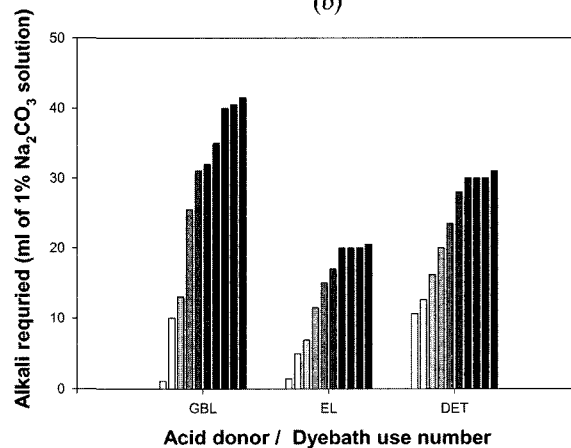
indicate that the amount of electrolyte present in the dye bath is not sufficient to cause problems with leveling, regardless of the substrate being dyed. However, the lower degree of aggregation seems a likely reason for the comparative success of the dye bath-reuse with the hydrolyzable organic esters,



(a)



(b)



(c)

Figure 6. Amount of Alkali required for the adjustment of dye bath pH to 8.0; for key see Figure 2 (a) Mixture 1 (b) Mixture 2 (c) Mixture 3.

and supports the suggestion that the difficulties experienced with fluctuating pH and exhaustion values in reused dye baths where ammonium sulphate was used as the pH controlling agent were due to the aggregating effect derived from a build-up of electrolyte.

Table 1. Color fastness to washing of dye Mixture 1 on polyamide

Reuse no.	1st Bath			10th Bath		
	Change	Staining		Change	Staining	
		Nylon	Cotton		Nylon	Cotton
AS	5	5	5	5	5	5
GBL	5	5	5	5	5	5
EL	5	5	5	4/5	5	5
DET	4/5	5	4/5	5	4/5	4/5

Table 2. Color fastness to perspiration of dye Mixture 1 on polyamide

Reuse no.	Acid donor	Test	1st Bath			10th Bath		
			Change	Staining		Change	Staining	
				Nylon	Cotton		Nylon	Cotton
AS	Acid	4/5	4/5	5	4/5	4	4/5	
	Alkali	5	5	5	5	5	5	
GBL	Acid	4/5	4	5	5	4	5	
	Alkali	5	5	5	5	5	5	
EL	Acid	4/5	4	5	4/5	4	4/5	
	Alkali	5	5	5	4/5	5	5	
DET	Acid	4/5	4/5	5	5	4/5	5	
	Alkali	4/5	5	5	5	5	5	

Figure 6 shows a comparison of the amounts of sodium carbonate solution (1 %) required to achieve the same initial dyebath pH of 8.0 over 10 reuses. Of the three hydrolyzable organic esters, GBL required larger amounts of alkali than EL and DET to adjust the pH of the dyebath to 8.0 for the next reuse. The cost of GBL, EL and DET relative to AS, which is commonly used in the dyeing of polyamide, is 1.02, 1.13, and 12.0, respectively [16]. Therefore, in the case of GBL and EL, the excellent pH control ability in the dyebath-reuse system could offset the higher cost, especially when used in a closed dyeing system.

Color Fastness

Color fastness figures were similar, irrespective of the pH control system and number of cycles of dyebath-reuse. The ratings of color fastness to washing were in the range of 4.5 to 5 (Table 1). The ratings of color fastness to perspiration were in the range of 4 to 5 (Table 2). All the samples gave a value of 5 for color fastness to rubbing. These results demonstrate that no deterioration in color fastness could be detected for the fabrics dyed during 10 cycles of dyebath-reuse.

Conclusions

This study has demonstrated that the use of hydrolyzable organic esters as acid donors for pH control offers distinct

advantages in the dyeing of polyamide with a reused dyebath. Compared with ammonium sulphate, the hydrolyzable organic esters gave stable and more effective pH control, and more stable and higher exhaustion values in the dyebath-reuse system. A comparison of CIELab values showed that dyeing reproducibility was better when the hydrolyzable organic esters were used in the reused dyebaths, than when ammonium sulphate was used.

In addition, hydrolyzable organic esters showed much lower levels of salt present in the residual dyebath than when ammonium sulphate was used. However, there were no observable differences in the levelness of dyed samples among the four acid donors in the laboratory-scale dyeing. In order to better evaluate the leveling properties, it would be necessary to determine the levelness of dyed fabrics obtained from pilot-scale dyeings.

The color fastness of all the samples were good and similar, irrespective of the pH control system and dyebath-reuse number. There was no deterioration in the color fastness of the dyed fabrics over 10 cycles of dyebath-reuse.

Of the three hydrolyzable organic esters, ethyl lactate showed less amount of alkali required to re-adjust the initial pH of the reused dyebath than γ -butyrolactone and ethyl tartrate. Considering the pH control ability and chemical cost together, it seems to be most feasible to use ethyl lactate as a pH control agent in the dyebath-reuse system.

Acknowledgement

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