Effect of Some Metal Salt Pretreatments on Acrylic Printing

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ABSTRACT: Acrylic fabrics were pretreated with metal salts (aluminum sulfate, copper sulfate, ferrous sulfate, and potassium dichromate) in different concentrations. The tensile strength, elongation, and moisture regain of pretreated and untreated samples were examined. The effects of various concentrations of the metal salts, the pH of the printing paste, and the thickening agent on the color strength and fastness properties of the printed fabrics were studied to determine the optimum printing conditions. The pretreatment improved the printability of acrylic modified with a cationic dye and the fastness properties. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 130–134, 2004

Key Words: acrylic fiber; metal salts; cationic dye; printing

INTRODUCTION

An important characteristic of polyacrylonitrile (PAN; i.e., acrylic fabrics) is that it contains strong acid groups that can act as dyeing sites. These anionic groups are sulfonic acid or carboxylic acid, and they are added as comonomers or end groups to polymers during polymerization.[1–3]

Usually, basic dyes have high shade brilliance but poor light fastness, and acrylic fibers containing acidic dye sites can be readily dyed with classical basic dyes, which have surprisingly high lightness and wash fastness in comparison with the same dyes on natural fibers.[4]

The pickup of an acid dye by as-spun acrylic fibers through the addition of Al^{3+}, Zn^{2+}, or Cr^{3+} ions to a bath was established by Abdurakhmanova et al.[5] They also examined the sorption of acid dyes by acrylic fibers, and the interaction mechanism between metallic cations and fibers was examined with IR,[6] which confirmed the orientation of fabric molecules such as CN side groups or CO side groups in PAN and PAN copolymers.

The rheological and printing properties of thickening agents based on crystal gum, starch derivatives, and low-concentration solutions of galactomanan ether based thickening agents have been studied through the rotary screen printing of tufted acrylic fabrics with basic dyes.[7,8] Genschow et al.[9] investigated the influential factors for the printing of acrylic fabrics with particular reference to the composition of the printing paste; they sought to make it easier to select the agents producing the best effect in printing.

The principal aim of this work was to study the effect of metal-ion pretreatments of acrylic fabrics before printing to improve the properties of printed fabrics.

EXPERIMENTAL

Materials

Acrylic fabrics supplied by Misr El Mehalla Co. (El Mehalla, Egypt) were used. The specification was 3.3 detx (3 denier), and they were purified through boiling in a 2 g/L nonionic detergent solution for 45 min at 60°C, followed by thorough water washing and drying.

Chemicals and dyes

The metal salts were aluminum sulfate, copper sulfate, ferrous sulfate, and potassium dichromate. The cationic dye was Maxilon Blue GRL 300% (Color Index: Basic Blue 41).

Thickening agents

Meypro gum was supplied by Misr El Mehalla.

Egyptian maize starch was kindly supplied by Misr Co. (Cairo, Egypt) for starch and glucose.

The synthetic thickener was poly(acrylic acid) (Alcoprint PTF Z328, Pigmafast, Milano, Italy).

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TABLE I
Printing Pastes Ingredients

	Thickener		
Ingredient	Meypro gum (g)	Starch (g)	Synthetic (g)
Water	940	870	940
Thickener	30	100	25
Glycerin	20	20	25
Dyes	10	10	10
Total	1000	1000	1000

Methods

Pretreatment procedure

The acrylic fabrics were treated with metal salts with a condenser system with a liquor ratio of 1:25. The treatment was carried out with different concentrations of the metal salts (1–8%) with respect to the weight of the fabrics (on weight of fiber) at 100°C for 25 min. The treated acrylic fabrics were washed with warm water, were thoroughly washed with cold water, and were air-dried at room temperature.

Printing

The pastes used for the printing of the acrylic fabrics with cationic dyes were prepared as shown in Table I. The starch powder was cooked via boiling for the preparation of each paste. The printing paste was prepared through the gradual addition of a thickener to water with stirring. Then, glycerin was added, and the whole stock was mixed well. The cationic dye (C.I. Basic Blue 41)was then added to the thickening stock and was followed by the addition of water to make the weight of the printing paste 1 kg.

The printing pastes were applied to the acrylic fabrics according to the screen printing method. After drying, the samples were fixed by 45 min of steaming at 125°C. The samples were then rinsed with cold water, soaped for 15 min at 60°C, washed with hot water, rinsed with cold water, and air-dried.

Measurements

Moisture regain

The measurements of the moisture regain of the acrylic samples were performed according to ASTM Standard 2654-76.[10]

The moisture regain of the acrylic samples were calculated as follows:

$$\text{Moisture regain (\%)} = \frac{W_1 - W_2}{W_2} \times 100$$

where W_1 is the weight of a sample (g) after saturation in a standard humidity atmosphere and W_2 is the constant weight of a dry sample.

Color strength

Spectral reflectance measurements of the printed fabrics were carried out with a recording filter spectrophotometer. The color strength, expressed as the ratio of the absorption coefficient (K) to the scattering coefficient (S), of the printed fabrics was determined with the Kubelka–Munk equation:[11]

$$K/S = \frac{(1 - R)^2}{R^2} - \frac{(1 - R_0)^2}{2R_0}$$

where R is the decimal fraction of the reflectance of the printed substrate and R_0 is the decimal fraction of the unprinted substrate.

Evaluation of the tensile strength and elongation

Four samples of treated acrylic fabrics (4% owf of metal salts) and one untreated sample (a control) were selected for the evaluation of the tensile properties before the printing. An Uster single-yarn strength tester was used for this purpose (Asano Machine Meg., Co., Ltd., Japan). Over five tests were performed for this work.

Color fastness

Color fastness to crocking

The color fastness to crocking was determined according to AATCC 8-1993.[10]

Washing fastness

Washing fastness tests were carried out according to BS1006:C02 Test 2 with a soap solution (5 g/L, liquor ratio = 50:1) for 45 min at 48–50°C.[12]

TABLE II
Moisture Regain of Treated and Untreated Acrylic Fabrics

Metal salt	Moisture regain
Untreated	1.1
Aluminum sulfate	1.3
Copper sulfate	1.5
Ferrous sulfate	1.8
Potassium dichromate	1.4

Treatment conditions: 4% metal salt (owf), liquor ratio = 1:25, and 25 min of boiling.

TABLE III
Tensile Strength and Elongation of Treated and Untreated Acrylic Fabrics

Metal salt	Tensile strength (g/detx)	Elongation (%)	Change in strength (%)	Change in elongation (%)
Untreated	84	35	—	—
Aluminum sulfate	70	44	−16.66	25.7
Copper sulfate	73	39.5	−13.1	12.9
Ferrous sulfate	78	38	−12	8.6
Potassium dichromate	71	42	−15.5	20

Treatment conditions: 4% metal salt (owf), liquor ratio = 1:25, and 25 min of boiling.

RESULTS AND DISCUSSION

Moisture regain

Table II summarize the data for the moisture regain of the untreated and pretreated acrylic fabrics. A relative increase in the moisture regain was generally observed for the treated acrylic samples with respect to the untreated sample.

Moreover, ferrous sulfate and copper sulfate increased the moisture regain in comparison with the other metal salts.

The increase in the moisture regain for the treated acrylic fabrics could be attributed to the opening of the fiber structure with the aid of the metal salts, which allowed more water vapor molecules to penetrate the fiber structure.

Change in the tensile strength and elongation

The results presented in Table III indicate that the control fabric possessed a tenacity of approximately 84 g/detx and an elongation value of 35%. The treatment with the metal salts adversely influenced the tensile properties of the fabrics. However, the loss of tenacity was around 12–17% for the acrylic fabrics pretreated with metal salts. This indicates that the strength could be retained by a treatment with ferrous sulfate. The elongation properties were interesting. The treated fabrics showed approximately 8–25% increases in their elongation.

Effect of various metal-ion concentrations in the pretreatment of the acrylic fabrics

The acrylic fabrics were pretreated with aluminum sulfate (1–8% owf), copper sulfate (1–5% owf), ferrous sulfate (1–8% owf), and potassium dichromate (1–5% owf) at 100°C for 25 min. The treated and untreated fabrics were then printed with a cationic dye and thickened with meypro gum. The initial pH of the printing paste was 3.5–4.The printed samples were steamed, washed, and dried. The color strength (K/S) of the printed samples at different concentrations of the metal salts was determined, as shown in Figure 1. The pretreatment with metal ions enhanced the color strength of the acrylic fabrics in comparison with the color strength of the untreated fabrics ($K/S = 3.5$) at 520 nm.

The K/S values of the printed samples increased as the metal concentration increased, without a change in the hue. On the other hand, the color strength of the printed fabrics depended on the kind of metal ion, as Figure 1 shows.

The increase in the color strength with metal ions could be attributed to the interaction mechanism between the metallic cations and the fiber,[6] which impaired the well-ordered structure of the fiber and thus loosened the fiber structure (increasing the amorphous parts). Subsequently, the color uptake also increased. This was confirmed by an increase in the elongation and a loss of tenacity in the aforementioned results.

Effect of pH of the printing pastes

For the determination of the optimum pH, the acrylic fabrics were pretreated with the metal salts (4% owf)

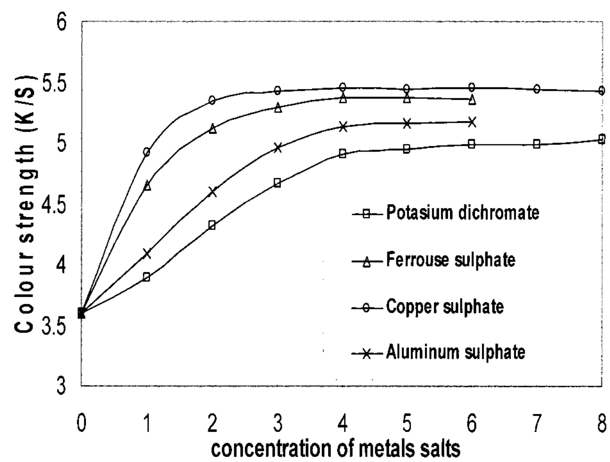

Figure 1 Effect of various concentrations of metal salts on the color strength of the printed acrylic fabrics. The treatment conditions were x % metal salt (owf), a liquor ratio of 1:25, and 25 min of boiling. The printing conditions were 1% C.I. Basic Blue 41 and pH 3.5–4. Steam fixation was carried out at 125°C for 45 min.

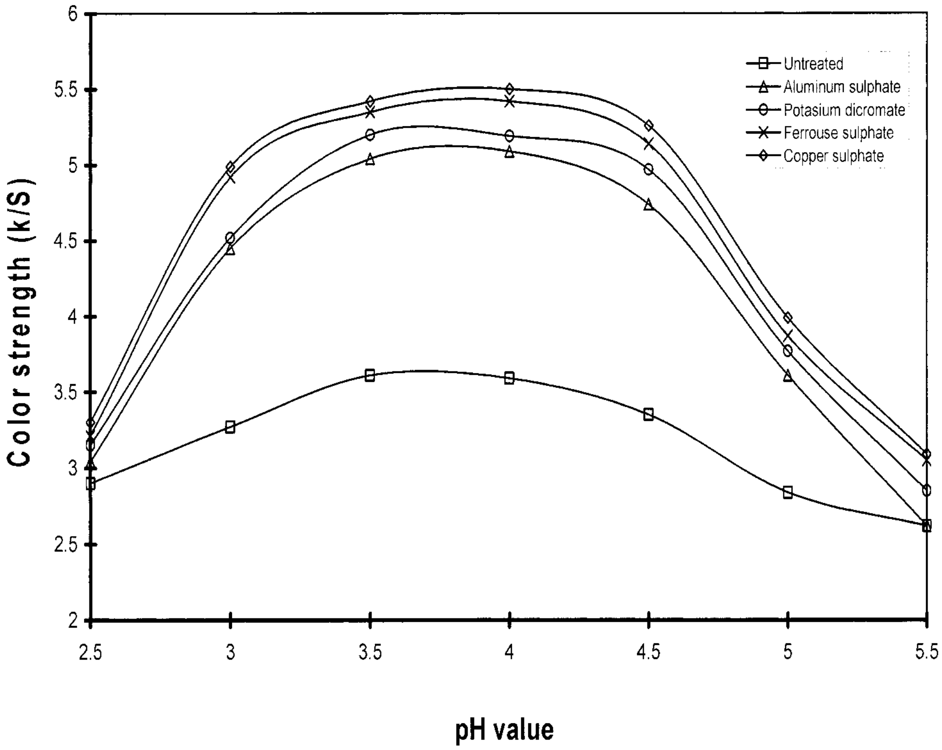

Figure 2 Effect of the pH value on the color strength of the printed acrylic fabrics. The treatment conditions were 4% metal salt (owf), a liquor ratio of 1:25, and 25 min of boiling. The printing conditions were 1% C.I. Basic Blue 41 and pH 3.5–4. Steam fixation was carried out at 125°C for 45 min.

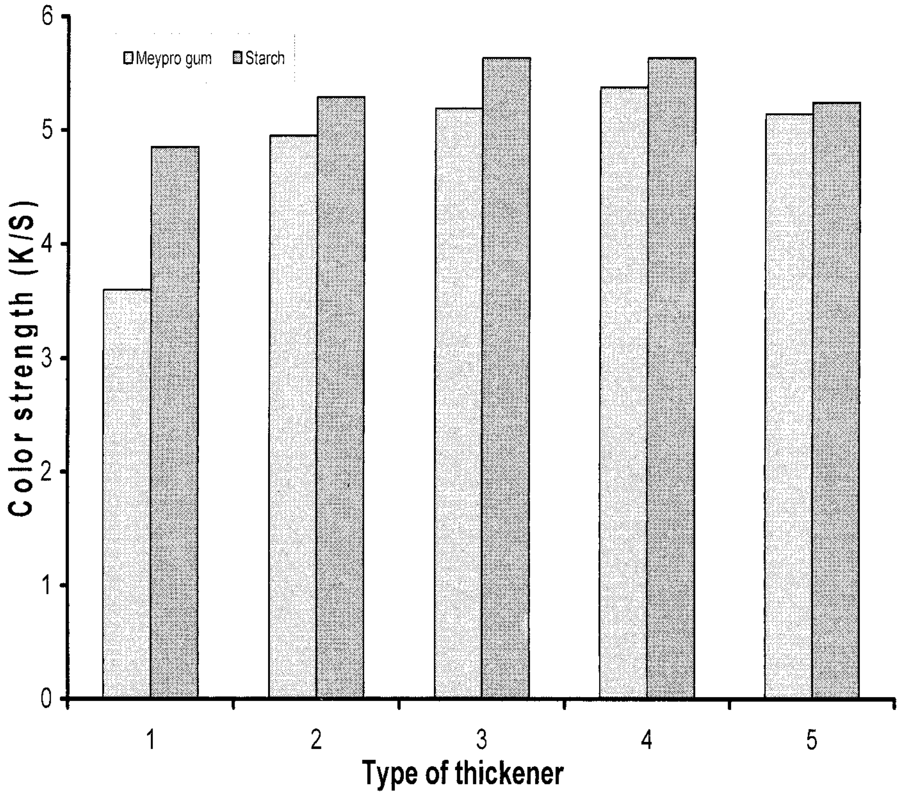

Figure 3 Effect of the thickening agent in the printing pastes on the color strength of the printed acrylic fabrics: (1) untreated, (2) aluminum sulfate, (3) copper sulfate, (4) ferrous sulfate, and (5) potassium dichromate. The treatment conditions were 4% metal salt (owf), a liquor ratio of 1:25, and 25 min of boiling. The printing conditions were 1% C.I. Basic Blue 41 and pH 3.5–4. Steam fixation was carried out at 125°C for 45 min.

TABLE IV
Crocking and Washing Fastness of Treated and Untreated Printed Acrylic Fabrics

Metal salt	Thickener	Crocking fastness		Washing fastness		
		Wet	Dry	St_a	St_c	Alt
Untreated	Meypro gum	3	3–4	4	3	3–4
Aluminum sulfate	Meypro gum	3–4	4–5	4–5	4	4–5
Copper sulfate	Meypro gum	4	4–5	4–5	4–5	4–5
Ferrous sulfate	Meypro gum	3–4	4	4–5	4–5	4–5
Potassium dichromate	Meypro gum	4	4	4–5	4	4–5

Alt = alteration; St_A = staining of acrylic fabrics; St_C = staining of cotton fabrics.
Treatment conditions: 4% metal salt (owf), liquor ratio = 1:25, and 25 min of boiling. Printing conditions: 1% C.I. Basic Blue 41 and pH 3.5–4.
Fixation: steam fixation was carried out at 125°C for 45 min.

at 100°C for 25 min. The treated and untreated fabrics were printed with printing pastes of different pH values (3–6). After printing, drying, and fixation, the washing fabrics were air-dried. Figure 2 shows the effect of pH on the color strength of the printed fabrics. The maximum color strength and level prints of the treated fabrics were observed in a moderately acidic medium (3.5–4), as Figure 2 shows.

The higher color strength in the moderately acidic printing paste could be attributed to the greater dissolution of the cationic dye in the acidic medium during the steaming. Subsequently, the opportunity for dye molecules to interact with anionic sites of the fiber increased.

The level prints observed with pretreated metal fabrics can be understood with respect to the suppression of the protonation onto the dye molecule in the presence of metal salts, which retarded the transfer of the dye onto the fiber and ensured even printing.

Effect of the thickening agent

In this work, meypro gum was used as a thickening agent. For comparison, three printing pastes were thickened with meypro gum, and starch and a synthetic thickener were prepared under the optimum conditions given previously (a 4% owf metal salt pretreatment and pH 3.5–4). The printed samples were steam-washed and then dried.

Regardless of the metal salt used, the best result (Fig. 3), on the basis of the shade depth, was obtained with a starch thickener with harsh handle, which was followed by meypro gum with soft handle.

The synthetic thickener based on poly(acrylic acid) had no affinity for printing acrylic fabrics, and this was confirmed by a reduction in K/S and unlevel prints.

The absence of an affinity of the synthetic thickener for printing acrylic fabrics was expected: the carboxylate ions of poly(acrylic acid) could enter into a chemical reaction with the cationic dye, and this reduced the migration of the color from the printed paste into the fiber.

Crocking and washing fastness

All the samples obtained with the meypro gum thickener for each mordant were subjected to tests for crocking and washing fastness. The rating of the washing fastness was made on the basis of the change in the color and the staining of the adjacent acrylic and cotton. The washing fastness of all the treated acrylic fabrics was very good to excellent (4–5), whereas the crocking fastness ranged between 3 and 4. The untreated sample (the control) showed good to very good (3–4) fastness with washing and crocking (Table IV).

CONCLUSIONS

The metal-salt pretreatments enhanced the color uptake, leveling, and fastness properties of cationic printing on acrylic fabrics. This was due to the metals opening up the fiber structure.

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