Research Article

An experimental study on production of intelligent textile by using ionocromic materials

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ABSTRACT

The production of an intelligent textile material that changes color under the influence of pH was researched in this research article. For this purpose, halochromic dyes were used. In halochromic dyes, bleeding and fastness problems are encountered after dyeing. In order to solve these problems; the dye is fixed with cationic fixators in the textile fiber. In this study, a woven nylon fabric was dyed with Alizarin Red S halochromic dyestuff by conventional dyeing method which was followed by post-treated by tannic acid/potassium antimony tartarate at different ratios (1%, 2%, 3%). After dyeing and post-treating, CIELab, K/S, ΔE* values were measured by spectrophotometer and compared. In order to investigate the effect of halochromics on the post-treated, dyed and post-treated fabrics were immersed in 5 different solutions prepared by using HCl and NaOH between pH 2 and 10, and the samples were removed after 1 hour and the color change in the samples was compared. After the process, the speed of fixation of the dye molecule onto the fiber was increased.

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1. Introduction

The textile material coloring is a well-known and broadly applicable process in which the focus is primarily on the textile material dyes development in fixed-color textile materials. [1,2]. Nowadays, interest in developing color-changing materials, such as pH sensitive textiles [8-15], has been increasing in the light of sensitive polymeric materials to stimulants [3-7].

These halochromic textiles may display a crop signal which can be effectively seen in a non-destructive manner.

Halochromatic materials alter colors once pH alterations are consisted. The ‘chromic’ locution can be described as a material can reversibly alter color in the existence of a factor. In this instance, the factor is pH, and the pH index have these properties. At the final color, A reversible change in pH is occurred. Chromaticity is procured by the formation of a new chromophore [16]. Halochromic materials are suitable for usage in mediums in which pH changes are frequently made or pH changes are excessive. Halochromic materials assign the changes in the material acidity, such as metal corrosion detection.

Halochromic material can be applied as an indicator to determine the pH level of solution with unknown level of pH. The gained color is compared with the color sighted once the index is confused with known pH solutions. Then, the unknown solution pH can be assumed. The clear deficits of this method contain the dependence of the human eye on the color sensitivity and that unknown solutions which have already colored cannot be applied.

Conventional dyeing methods have been used in the textile industry for the purpose of coloring products for many years due to their economic and easy application. Some of the studies in the literature on the development of textile surfaces that change color with pH, are generally the application of synthetic pH-indicator dyestuffs to conventional woven fabrics by conventional dyeing methods.

In these studies, the interaction of halochromic dyes and fiber structure and permanence of color change were investigated.
Schueren and Clerck [17] examined that color changes between pH 2-11 of cotton, polyamide 6 and polyamide 6,6 woven fabrics for dyeing with 10 different synthetic halochromic dyes. Polyamide based fabrics showed good dyeing performance with all dyestuffs and some dyestuffs in cotton fabric. pH-indicator dyes while changing color in liquids immediately; it was observed that the color change time was prolonged when they were transferred to textile fabrics. At the end of the study, it was concluded that bright yellow and alizarin halochromic dyes are more effective and fiber type affects halochromism.

Staneva and Betcheva [18] studied on the color change of viscose rayon fabric by using a new pH sensitive dyestuff which they synthesized. Fast and reversible color change was observed in pH 5.2-11.4 from yellow to orange–red. The effect of molecular structure of synthesized new halochromic dyestuff on the change of color and fluorescent properties in the alkaline pH range was emphasized.

In this study, polyamide 6,6 woven fabric was dyed by using Alizarin Red S dye at 98 °C for 1 hour. For enhancing wet fastness, four different commercial fixators and tannic acid were used after the treatment. As a result of this study, water fastness test was applied, it was found that 3% Setafix S imparted the greatest water fastness improvement. The samples which were post-treated by tannic acid also showed good water fastness results. The washing fastness of the samples were recorded to good values, but the same results were not obtained on the original colored samples.

2. Experimental Study
2.1 Chemical Materials
All the chemical materials used for dyeing of polyamide 6,6 were of commercial grade. All solvents used were either of analytical grade or redistilled commercial grade. The following anionic fixators were used: Setafix S, Erional FRN, Polyfix PA and Hydrocol APR.

2.2 Dyeing Methods
Dyeing of polyamide 6,6 fabric was carried out using a procedure reported in the literature (Figure 3).

2.3 Procedure
Alizarin dye was provided by Sigma-Aldrich and it applied with hydrochloric acid (1mol/L), acetic acid (1M) and sodium hydroxide (50m %) for pH adjustment. pH level measure was earned by a pH meter.

10 mg/L solution’s UV/vis spectra was measured on a spectrophotometer in the interval of 300-700 nm (together with a resolution of 1nm).

The measurement of the transmission in the solution and the reflection measurements of the fabrics were calculated according to absorptivity and values of Kubelka-Munk (K / S), respectively.

Each polyamide 6,6 fabric was immersed at a liquor ratio of 20:1 in a 0.7%, 1% and 1.5% on dye solution of mass fibre (omf%) that buffered at pH5.

The mix was then heated in the dyeing machine of the laboratory to 98 °C and dyeing was maintained at this temperature for 1 hour, accepting the dye molecules diffusion in the fabric [19].

The Alizarin Red S molecule chemical structure is presented in Figure 1.

The Alizarin Red S dye concentration was concluded at 520 nm. pH of the solutions was measured using a pH/ion meter and the absorption works were realized by UV - Visible spectrophotometer.

In solution, pH is an agent in the absorption treatment since it effects useful groups on surface of the absorbent and assigns the dye solubility in the aqueous solution. Figure 2 shows that the Alizarin Red S adsorption capacity was found to decrease with increasing pH in the 2-10 pH range. The adsorbent will be more positively charged sites through protonation of functional groups that increase with respect to higher pH levels, once the solution pH is about 2. According to the following reaction, under acidic conditions (pH<2), D-SO$_3$- sulfonate groups with H$^+$ reduce the Alizarin Red S adsorption capacity [20].

$$D-SO_3^- + H^+ \rightarrow D-SO_2H \quad (1)$$

Figure 1. Alizarin Red S Chemical Structure

Figure 2. The pH effect on 0.7% Alizarin Red S dye removal (adsorbent 2 dose =1g, temperature= 303K).
Conventional dyeing is an inexpensive and simple method in bringing the halochromic properties to textile materials. Dyeing was carried out as shown in Figure 3 at a liquor ratio of 1:20 in the laboratory-type sample dyeing machine. The dyed fabrics were rinsed under running water for 10 minutes. Dyeing processes was performed on the fabrics at different dye concentrations.

After the dyeing process, clean bath was taken, and two different processes were applied as shown in Figure 4 at 60 °C for 20 minutes at 1:20 liquor ratio.

After dyeing with Alizarin Red S dye was completed, four fixators and tannic acid were added to improve the wet fastnesses of the dyed samples.

3. Results and Discussion

The hypsochromic and bathochromic shifts occur in the halochromic dyes.

Acetic acid, sodium hydroxide and hydrochloric acid were used for the production of hypsochromic and bathochromic shifts of the Alizarin Red S dye used in this study.

3.1 UV-Visible Study

UV spectra of Alizarin Red S in aqueous solution (pH 7) exhibit one major absorption band in the region 300-700nm. One band is the result of n−π* transition owing to the presence of the first group, which is not bonded by the intramolecular hydrogen bond.

A spectacular change occurred showing a red shift in the wavelength from 380 to 580 nm in aqueous medium even at the smallest value of sodium hydroxide was added into dye solution as shown in Figure 5.

3.2 The effect of post-treatment with anionic fixator and tannic acid on the color values

The effects of post-treating with anionic fixators and tannic acid on color coordinates of L* and b* were shown in Figures 6, 7, 8 and 9.

It can be observed in Figures 6 and 7 that the color became darker for samples dyed with Alizarin Red S after the application of anionic fixators. The darker in color is above the specified limits. The use of anionic fixators darkens the color. The color brightness increased as the fixator concentration increased. The largest color changes were obtained at a concentration of 3% Setafix S fixator. Color was shifted to yellow.
It can be seen in Figures 8 and 9 that the color became darker and reddish after dyeing with Alizarin Red S and post-treated with tannic acid.

3.3 The effect of post-treatment with anionic fixator and tannic acid on the color yield

The effects of post-treating with anionic fixators and tannic acid on the color yield were shown in Figures 10 and 11.

As given in Figure 10, it was determined that amount of fixator (%) has an effect on color yield for samples dyed with Alizarin Red S and post-treated with anionic fixator. Since the amount of fixator (%) increased, the color yield decreased. As the color intensity increased, the amount of fixator affected the color more. Maximum color yield for applied anionic fixators was obtained at 1.0% dyeing concentration.

3.4 The effect of post-treating with fixator and tannic acid on rubbing, water and washing fastness

Wash fastness values of fabrics dyed with Alizarin Red S and treated with anionic fixators are given in Table 1. When wash fastness were examined, two replicates were made from each sample. The average of the results of these two repetitions were considered. Washing fastness values of fabrics dyed with Alizarin Red S and treated with tannic acid are given in Table 2.

The use of tannic acid in samples dyed with Alizarin Red S positively affected the color change values.

It can be seen in Table 3 that water fastness of fabrics dyed with Alizarin Red S and treated with anionic fixators increased.

3.5 Effects of post-treatment on color changes

Selected fabrics were immersed in nine different solutions prepared with HCl and NaOH between pH 2-13 and color change was observed after 1 hour (Figure 12).
### Table 1. Wash fastness of fabrics dyed with Alizarin Red S and treated with anionic fixators

| Dyestuff Ratio | Type of Fixator | Amount of Fixator | Microfiber Washing Fastness | Color Change |
|---------------|----------------|-------------------|-----------------------------|--------------|
| 0.7%          | Reference      | 5 5 5 5 5 5       | 1/2                         |              |
| 1%            | Setafix S      | 5 5 5 5 5 5       | 2                           |              |
| 2%            | Setafix S      | 5 5 5 5 5 5       | 2                           |              |
| 3%            | Setafix S      | 5 5 5 5 5 5       | 2/3                         |              |
| 1%            | Eronal FRN     | 5 5 5 5 5 5       | 1/2                         |              |
| 2%            | Eronal FRN     | 5 5 5 5 5 5       | 2/3                         |              |
| 3%            | Eronal FRN     | 5 5 5 5 5 5       | 2                           |              |
| 1%            | Polyfix PA     | 5 5 5 5 5 5       | 2                           |              |
| 2%            | Polyfix PA     | 5 5 5 5 5 5       | 2/3                         |              |
| 3%            | Polyfix PA     | 5 5 5 5 5 5       | 2                           |              |
| 1%            | Hydrocol APR   | 5 5 5 5 5 5       | 2/3                         |              |
| 2%            | Hydrocol APR   | 5 5 5 5 5 5       | 2                           |              |
| 3%            | Hydrocol APR   | 5 5 5 5 5 5       | 2/3                         |              |
| 1.5%          | Setafix S      | 5 5 5 5 5 5       | 2/3                         |              |
| 2%            | Setafix S      | 5 5 5 5 5 5       | 2                           |              |
| 3%            | Setafix S      | 5 5 5 5 5 5       | 2/3                         |              |
| 1%            | Eronal FRN     | 5 5 5 5 5 5       | 2/3                         |              |
| 2%            | Eronal FRN     | 5 5 5 5 5 5       | 2                           |              |
| 3%            | Eronal FRN     | 5 5 5 5 5 5       | 2/3                         |              |
| 1.5%          | Polyfix PA     | 5 5 5 5 5 5       | 2                           |              |
| 2%            | Polyfix PA     | 5 5 5 5 5 5       | 2/3                         |              |
| 3%            | Polyfix PA     | 5 5 5 5 5 5       | 2                           |              |
| 1.5%          | Hydrocol APR   | 5 5 5 5 5 5       | 2/3                         |              |
| 2%            | Hydrocol APR   | 5 5 5 5 5 5       | 2                           |              |
| 3%            | Hydrocol APR   | 5 5 5 5 5 5       | 2/3                         |              |

### Table 2. Water and rubbing fastness of fabrics dyed with Alizarin Red S and post-treated with fixators

| Dyestuff Ratio | Fixator Type | Fixator Content | Water Fastness | Rubbing Fastness |
|---------------|--------------|-----------------|----------------|------------------|
| 0.7%          | Reference    | 2/3             | 2              | 5 4/5            |
| Setafix S     | 1%           | 3/4             | 3/4            | 5 4/5            |
| 2%            | 4             | 4               | 4              | 5 4/5            |
| 3%            | 4/5           | 4/5             | 4/5            | 5 4/5            |
| Eronal FRN    | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| Polyfix PA    | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| Hydrocol APR  | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| 1%            | Reference    | 2/3             | 2              | 5 4             |
| Setafix S     | 1%           | 3/4             | 3/4            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| Eronal FRN    | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| Polyfix PA    | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |
| Hydrocol APR  | 1%           | 3/4             | 2/3            | 5 4/5            |
| 2%            | 4             | 3/4             | 5 4/5          |
| 3%            | 4             | 3/4             | 5 4/5          |

### Table 3. Water and rubbing fastness of fabrics dyed with Alizarin Red S and post-treated with fixators

### 3.6. Surface Treatment

The functionality of the color alteration of halochromic dyes in polyamide 6,6 is often realized by surface treatment, such as dyeing.

Polyamide 6,6 fabric dyed with the pH - sensitive dye Alizarin Red S altered color from yellow to red in the range of 3.7-5.2 pH. Thus, compared with the solution, only a slight broadening was found. However, the acidic wavelength displayed a bathochromic shift of maximum 15nm with showing the influence of the dye and fibre coactions [21]. Figure 13 shows the results.
tannic acid was well. Fabrics dyed a were obtained with Setafix S fixator. Water fastness of fastness of the post treatment with fixators. The best results were obtained fine results in the water while it was obtained fine results in the water fastness of polyester treated with fixators. The best results were obtained fine results in the water fastness of polyester treated with fixators. The best results were obtained fine results in the water fastness of polyester treated with fixators.

4. Conclusions

While it was obtained fine results in the water fastnesses, there was no significant effect on the rubbing fastness of the post-treatment with fixators. The best results were obtained with Setafix S fixator. Water fastness of fabrics dyed at low dye concentration and post-treated with tannic acid was well. It has been found that the use of tannic acid had no significant effect on improving of the rub fastness. It has been determined that wash fastness of fabrics dyed with Alizarin Red S and post-treated with tannic acid had not a significant effect. It has been determined that the use of tannic acid reduced color change. The use of a fixator is more appropriate because the color change must be fast and clear.

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References

1. Zollinger, H., Color chemistry: syntheses, properties, and applications of organic dyes and pigments. 2003, Switzerland: VHCA and Wiley-VCH, Inc.
2. Kim, S.H., editor. 2006, Functional dyes. Elsevier.
3. Bamfield, P. and Hutchings M.G., Chromic phenomena: technological applications of colour chemistry. 2010, UK: Royal Society of Chemistry.
4. Kirschning, A., Monenschein, H. and Wittenberg, R., Functionalized polymers—emerging versatile tools for solution-phase chemistry and automated parallel synthesis. Angewandte Chemie International Edition, 2001. 40(4): p. 650-679.
5. Vancoillie G., Pelz S., Holder E., Hoogenboom R., Direct nitrooxide mediated (co) polymerization of 4-vinylphenylboronic acid as route towards sugar sensors. Polymer Chemistry, 2012. 3(7): p. 1726-1729.
6. Pietsch, C., Schubert, U.S., and Hoogenboom, R., Aqueous polymeric sensors based on temperature-induced polymer phase transitions and solvatochromic dyes. Chemical Communications, 2011. 47(31): p. 8750-8765.
7. Fournier, D. and Du Prez, F., “Click” chemistry as a promising tool for side-chain functionalization of polyurethanes. Macromolecules, 2008. 41(13): p. 4622-4630.
8. Roy, D., Cambre, J.N. and Sumerlin, B.S., Future perspectives and recent advances in stimuli-responsive materials. Progress in Polymer Science, 2010. 35(1-2): p. 278-301.
9. De Meyer, T., Hemesoet, K., Van der Schueren, L., Pauwels, E., De Clerck, K., Van Speybroeck, V., Investigating the halochromic properties of azo dyes in an aqueous environment by using a combined experimental and theoretical approach. Chemistry—A European Journal, 2012. 18(26): p. 8120-8129.
10. Makedonski, P., Brandes, M., Grahn, W., Kowalsky, W., Wichern, J., Wiese, S., & Johannes, H.H., Synthesis of new kinds of reactive azo dyes and their application for fibre-optical pH-measurements. Dyes and Pigments, 2004. 61(2): p. 109-119.
11. Trupp, S., Alberti, M., Carofoglio, T., Lubian, E., Lehmann, H., Heuermann, R., Yacoub-George, E., Bock, K., and Mohr, G.J., Development of pH-sensitive indicator dyes for the preparation of micro-patterned optical sensor layers. Sensors and Actuators B: Chemical, 2010. 150(1), p. 206-210.
12. Kawai, T., Nakajima, H., Nanasawa, M. and Ueno, A., Color change indicators for molecules using methyl red-modified cyclodextrins. Analytical Chemistry, 1999.
13. Van der Schueren, L. and De Clerck, K., *The use of pH-indicator dyes for pH-sensitive textile materials*. Textile research journal, 2010. 80(7): p. 590-603.

14. De Meyer, T., Hemelsoet, K., Van der Schueren, L., Pauwels, E., De Clerck, K. and Van Speybroeck, V., *Investigating the halochromic properties of azo dyes in an aqueous environment by using a combined experimental and theoretical approach*. Chemistry–A European Journal, 2012. 18(26): p. 8120-8129.

15. De Meyer, T., Hemelsoet, K., Van Speybroeck, V. and De Clerck, K., *Substituent effects on absorption spectra of pH indicators: An experimental and computational study of sulfonphthaleine dyes*. Dyes and Pigments, 2014. 102: p. 241-250.

16. Bouas-Laurent, H. and Dürr, H., *Organic photochromism (IUPAC technical report)*. Pure and Applied Chemistry, 2001. 73(4): p. 639-665.

17. Schueren, L.V. and Clerck, K.D., *The Use of pH-indicator Dyes for pH-sensitive Textile Materials*. Textile Research Journal, 2010. 80(7): p. 590-603.

18. Staneva, D. and Betcheva, R., *Synthesis and Functional Properties of New Optical pH Sensor Based on Benzo [de]anthracen-7-one Immobilized on the Viscose*. Dyes and Pigments, 2007. 74(1): p. 148-153.

19. De Meyer, T., Steyaert, I., Hemelsoet, K., Hoogenboom, R., Van Speybroeck, V. and De Clerck, K., *Halochromic properties of sulfonphthaleine dyes in a textile environment: The influence of substituents*. Dyes and Pigments, 2016. 124: p. 249-257.

20. Gautam, R.K., Gautam, P.K., Chattopadhyaya, M.C. and Pandey, J.D., *Adsorption of Alizarin Red S onto biosorbent of Lantana camara: kinetic, equilibrium modeling and thermodynamic studies*. Proceedings of the National Academy of Sciences, India Section A: Physical Sciences, 2014. 84(4): p. 495-504.

21. Van der Schueren, L. and De Clerck, K., *Coloration and application of pH-sensitive dyes on textile materials*. Coloration Technology, 2012. 128(2): p. 82-90.