

Dyeing Performance of Dyes Derived from 2-Amino Heterocycles on Leather

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ABSTRACT

The dyeing properties of dyes synthesized from 2-amino-4-phenylthiazole (Dye 1) and 2-amino-4-methyl-5-carbathoxythiazole (Dye 2) on leather were studied. The effects of pH, temperature, dye concentration, dyeing time as well as rubbing and light fastness properties of the dyes were evaluated. Results obtained indicate that the dyes used were absorbed optimally at pH 3. It was found that increase in dyeing time increases percent exhaustion such that 60 % exhaustion in 20 min. was increased to 85-90 % in 40-60 min. The exhaustion of Dye 1 was 89.4 % at 50 °C while that of Dye 2 was 92 % at 65 °C. The dyeings showed very good fastness to rubbing and good fastness to light.

Keywords: 2-amino-4-phenylthiazole, 2-amino-4-methyl-5-carbathoxythiazole, monoazo, leather

INTRODUCTION

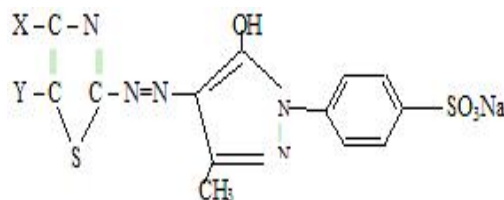
Acid dyes can be applied to nylon from acid dyebath in exactly the same manner in which they are applied to wool and silk fibres. The affinity of acid dyes for nylon is higher than their affinity for wool which accounts for the superior wet fastness and inferior migration properties on the former fibre [1]. Many innovations have been discovered in the past thirty-five years in the field of azo dye chemistry based on heterocyclic systems and studies in the synthesis of such derivatives have been reported. Azo dyes derived from heterocycles are not only important for their excellent properties as dyes for polymeric materials; they are also being used in areas such as reprographic technology, lasers, functional dye applications, photodynamic therapy and nonlinear optical systems. Although a variety of heterocyclic systems have been used for the synthesis of dyes, there remains much for the design and development of new chromophores [2-5].

Recent research has focused on structural variations of existing types for example variation in substituents on the side chains of the coupling components. In our previous work, we synthesized acid dyes derived from 2-amino-4-phenylthiazole and 2-amino-4-methyl-5-carbathoxythiazole and studied their dyeing performance on wool, silk and nylon [6]. To understand fully the dyeing characteristics of these dyes on another substrate, we investigated the dyeing performance of these dyes on leather.

MATERIALS AND METHODS

Materials

Chrome retanned leather was obtained from National Institute for Leather and Science Technology, Zaria. The leather was cut into straps measuring 3x12cm and soaked in water for a period of 12 hours after which the samples were weighed separately for dyeing trials. The structure of the dyes used are shown in Figure 1.



For Dye 1: X = C₆H₅, Y = H, for Dye2: X = CH₃,
Y = COC₂H₅

Figure 1: Structure of Dye 1 and Dye2

Methods

Dyeing trials

A stock solution containing 2% each of Dye 1 and Dye 2 respectively were prepared and used for dyeing trials. Dyeings on leather were carried out at various pH, temperature and time. Dye exhaustion was determined spectroscopically using Unicam spectrophotometer and percentage exhaustion was calculated by measuring the absorbance of the dye bath before and after dyeing using the relation:

$$E_{ha} \quad (\%) = \frac{A_0 - A_1}{A_0} \times 100 \dots \dots (1)$$

where A_0 = absorbance before dyeing and A_1 = absorbance after dyeing

Effect of pH on dyeing

This was carried out by measuring a calculated volume of the prepared 2% stock solution based on the weight of wetted leather samples, varying the pH values from 3 to 9 at an interval of 1 pH value. The pH of the dye baths were adjusted using dilute solutions of NaOH and HCl as required, after which the volumes were made up to 50mls. The dye baths with pH values from 3-9 were placed in a steam bath, the leather samples were immersed and then the dyeing carried out for one hour at 55°C.

Effect of temperature on dyeing

To determine the effect of temperature, dyeings were carried out within the temperature range of 50-70°C at an interval of 5°C. The pH of the dye baths were adjusted to pH3 being the best pH value obtained where the leather samples were introduced.

Effect of dye concentration

Solutions containing 1, 2, 3, 4, 5 and 6% dye were separately prepared. Six leather samples were separately weighed and treated with volumes of dye solution respectively depending on the weight of wetted leather sample. The pH of each solution was adjusted to 3 after which the volume of the dye bath was made up to 50ml. The leather samples were immersed into their respective dye baths placed into a thermostatic water bath at 50°C and dyeing continued for one hour.

Effect of time on dyeing

Twelve leather samples were soaked in distilled water for twelve hours, after which they were removed, blotted with tissue paper and separately weighed. A calculated volume of dye stock solution based on the wetted leather sample was taken and pH of the dye bath adjusted to 3. The volume of the dye bath was made up to 50ml, dyeing commenced immediately with continuous agitation for one hour. The dyeing time was varied for 10-120 min. at an interval of 10 min.

Dry and wet rub fastness

The dry and wet rub fastness properties of the dyed leather samples were carried out using the rub fastness tester (model THE INST) at 500 revolutions. The leather samples after rubbing were assessed using the grey scale.

Light fastness measurement

Eight blue wool standards and specimens (1 cm by 4.5 cm) each were placed side by side on a hinged opaque cover and the central one third of each covered with a black cover. The assembly was exposed to sunlight for 72 hours after which the samples are compared with the original unexposed samples. The change in colour was assessed using the blue wool standards [7-9].

RESULTS AND DISCUSSION

Effect of pH on dye exhaustion

Table 1 shows that the highest recorded percentage absorption of these dyes were 85% and 86% for Dye 1 and Dye 2 respectively at pH 3. At pH 4, 84 % absorption of Dye 2 was obtained. Conversely, at this pH, Dye 1 has the lowest percentage exhaustion (42.5%) The overall performance of the dyes within the pH range used indicate that both dyes are absorbed maximally at pH 3. As the pH value of the dyebath was raised from pH 3 to pH 6, the surface charge of leather varied from being positive to being negative and as a consequence, the electrostatic forces between the negatively charged leather and negatively charged acid dyes changed from attractive forces to repulsive forces. This change in the electrostatic forces reduced the uptake of acid dyes by leather with increasing pH value [10].

Table 1: Effect of pH on dye exhaustion

pH	Percentage exhaustion	
	Dye 1	Dye 2
3	85	86
4	42.5	84
5	67.5	64
6	52.9	56
7	66.0	51
8	64.0	58
9	45.7	54

Effect of temperature on dye exhaustion

The effect of temperature on dyeing performance of both dyes are shown in Table 2. The percentage dye exhaustion of Dye 1 was 89.4% at 50°C while that of Dye 2 was 92% at 65°C. The lowest percentage dye exhaustion for Dye 1 and Dye 2 are respectively 82.4% at 70°C 79% at 50°C. Increase in dyeing temperature from 50 to 65 °C increases dye exhaustion for Dye 2 and this may be due to the fact that increase in dyebath temperature increases the kinetic energy of the dye molecules in solution. The rate of dye diffusion into the fibre is thus increased hence the rate of dyeing. As the dyeing temperature is increased, the movement of the macromolecules

increases and the structure of leather opens up more thus the penetration of dye became easier leading to an increased dye sorption. For Dye 1, increase in temperature decreases percent exhaustion. It could be deduced that the saturated dye sorption of leather occurred at 50 °C. Dye molecules penetrated the interior of leather and occupied almost all of the dye sites at that temperature hence no additional interactions between leather and dye molecules even when temperature is increased [10].

Effect of time on dye exhaustion

From the results obtained, 94.5% of Dye 1 was the highest absorbed by the substrate after a period of 50 minutes while 100% of Dye 2 was absorbed after a period of 120 min. This means that for Dye 1 the extended dyeing time may probably lead to desorption of the dye into the dye bath which could explain the low percentage exhaustion with increase in time. For Dye 2, higher dyeing time generally favoured dye absorption by the substrate. This can be explained by the increase in percentage dye exhaustion with increase in dyeing time. The effect of time on dye exhaustion may be due to the fact that the dye is initially absorbed on the fibre surface and with time it slowly diffused into the innermost portion of the fibre to form ionic linkages with the amine end-groups. During dyeing, the concentration of dyes on the fibre surface increases with dyeing time while that in the dyebath decreases and equilibrium is reached at the fibre-dyebath interface when the concentration of dyes on the fibre does not change with time. Kert et al [11] confirmed the same phenomenon where percent exhaustion increased by prolonged dyeing time until equilibrium is reached and no change of sorption with time. Table 3 shows the effect of time on dye exhaustion.

Effect of dye concentration on percent exhaustion

Table 4 shows that the higher the concentration of each of the dyes, the lower the percentage dye exhaustion. This can be understood from the point that there is a maximum amount of dye that can be absorbed by the substrate; hence with higher concentration of the dyes there will naturally be more dyes left in solution. 100% of Dye 2 was absorbed at 1 and 2% dye concentration while 89.95 and 98.8% of Dye 1 was absorbed at dye concentrations of 1% and 6% respectively. Absorption of acid dyes is affected by dye structure, dyeing agents, liquor ratio, dyeing temperature, dyeing time as well as dye concentration [12-15].

Table 2: Effect of temperature on dye exhaustion

Temperature (°C)	Percentage exhaustion	
	Dye 1	Dye 2
50	89.4	79
55	86.4	88
60	84.0	85
65	82.4	92
70	82.4	88
75	-	81

Table 3: Effect of time on dye exhaustion

Time (min.)	Percentage exhaustion	
	Dye 1	Dye 2
10	68.75	72.5
20	84.09	72.0
30	85.42	89.0
40	72.24	91.1
50	94.58	92.2
60	83.91	92.2
70	86.66	90.8
80	85.37	90.0
90	88.63	93.0
100	90.48	96.25
110	80.95	100
120	81.13	100

Table 4: Effect of dye concentration on percent exhaustion

Dye concentration (%)	Percentage exhaustion	
	Dye 1	Dye 2
1	98.8	100
2	82.9	100
3	75	97.7
4	73.7	88.0
5	64.4	83.0
6	89.95	76

Light fastness test

Results in Table 5 showed that Dye 2 had better light fastness than Dye 1 at all pH values, temperature, concentration and dyeing time. There are many factors that affect colour fastness. Some of them are the depth of colour, the presence of foreign substances and the inherent photostability of the dye chromophore and the way in which this stability is affected by the chemical nature of the fabrics [7]. The introduction of the phenyl group to position 4 in the dye molecule lowers the photostability of the dye. This may be due to the fact that electron releasing groups lower light fastness because they release electrons to the azo group which is basically the site of photochemical interaction and cleavage.

Table 5: Light fastness ratings

Sample number	Light fastness rating	
	Dye 1	Dye 2
1	3/4	4/5
2	3	4/5
3	3	5
4	3	5
5	4/5	5
6	4/5	5

CONCLUSION

The dyes were applied on leather fabric at 2% shade as acid dyes. These dyes gave very good brightness, levelness and depth on leather. The dyed leather fabrics have moderate to good light fastness. A good levelness and brightness indicate good penetration and excellent affinity of these dyes for leather.

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