

Studies on dyeing wool with indigo

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Wool fabric was dyed with indigo through an exhaust technique at various pH values. The non-ionic form of indigo showed the highest substantivity, while the ionic ones exhibited relatively poor substantivity for wool. The wool fibres were best dyed in the appropriate acidic pH range. The chemistry of the indigo dyebath and wool fibres was taken into account to explain the effects of pH on colour strength. The results suggested that hydrogen bonding and ionic interactions were the main reasons for the exhaustion of indigo dye on wool fibres. The hydrogen bonding were established between the hydroxyl groups and amide groups of the dye and the fibres, respectively. The ionic interactions worked in the low pH range between the end-amino and ionized groups of the wool fibres and indigo dye, respectively.

Key words: wool, indigo, dyeing, dyebath analysis, colorimetric properties

1. Introduction

Although indigo is now exclusively applied on cotton, historical records show that about 4000 years ago it was wool that had first been dyed with indigo and it was about in 1500 A.D, when cotton was dyed with it [1, 2]. Stonewashed woollen fabrics have been reported in the literature [3]. Wool is a fibre that is obtained from animals in the Caprinae family, mainly sheep, although hair of other mammals e.g. goats, llamas and rabbits may also be considered as wool [4]. Wool has several qualities that distinguish it from hair or fur: it is crimped; it has a different texture or handle; it is elastic; and it grows in staples [5]. These properties impart greater bulk and heat insulation properties for which it is known. Out of 1.3 million tons per annum of wool, 60 % goes into apparel. Australia is the leading producer of wool and accounts for 25

% of the world wool production. The other producers are China and New Zealand with 18 and 11% share, respectively [6]. The main applications include the apparels, carpets, felt and insulation. Wool is dyed mainly with acid dyes; however other dyes such as basic, reactive and vat dyes are also used though their percentage share is very less [7-9]. The application of different classes of colorants clearly shows the versatile chemical nature of the fibre. Being Proteinous in nature, it contains acidic as well as basic sites in addition to sulphur-sulphur bonds and ionic salt linkages. It is very susceptible to hydrolysis; therefore, most of the dyeing of wool is carried out in appropriate acidic medium to avoid loss in mechanical properties.

The present work was undertaken to dye wool with Indigo. The goal was to examine the dyeability of wool

with vat dyes and studying the effect of different variables, mainly pH and temperature. Because of the popularity and use, indigo was selected for dyeing wool. One of our clients intended to produce denim look on woollen fabrics. Very little data was available about the effect of pH on the dyeability of wool with vat dyes. It was not known at what pH values, could we obtain ring or deep dyeing and what would be the optimum dyeing temperature conditions. Polyester-wool blends are important after Polyester-cotton ones. Previous work showed that good colour yield could be produced on polyester and nylon [10, 11]. It showed that PET-Wool blends could be dyed with the same dye thereby simplifying the process. In our case it worked very well because poor-light and sublimation fastness of indigo on polyester had helped in achieving very nice faded-

look effects which could be produced either by light or through chemical means.

Wool fabric dyed with indigo exhibited excellent shade depths as well as good fastness properties. It could be dyed in the acidic as well as basic pH regions. However, higher pH values almost destroyed the wool fabric. Wool, being a polypeptide, contains a large many amide groups in its structure. It also contains free amine groups at the end of its polymeric chains, although the number of free amine groups is less than the carboxylic groups so that the fibre posses a negative charge unless in the appropriate acidic pH range. These amide and amine groups provide excellent hydrogen bonding sites for the dye molecules and are considered to mainly contribute to the substantivity for the dye molecules.

Dyebath pH values at the very start as well as at the end of dyeing were monitored and the results presented. Effects of varying pH on the dyebath composition, colour strength and on the structure of the fibre were discussed. This work finds potential uses in the hosiery industry where polyester/wool blends are dyed with disperse/acid dye system. These polyester/wool blends can be dyed in a single bath with a single dye and excellent shade depth can be obtained.

2. Experimental

2.1. Material and machinery

Mathis Labomat IR dyeing machine was used to dye wool samples and the pH measured before and after dyeing using Henna Digital pH Meter PH-210. Reflectance and colour strength were measured on Datacolour 500 Spectrophotometer. Wool: 100% Wool yarn plain woven scoured fabric. Indigo dye (85 %), granular form, was obtained from BASF. All other chemicals were of laboratory grade.

2.2. Dyeing

Samples were dyed with Indigo to 0.1-2 % o.w.f shade depth. Sodium

dithionite 10 g/L, Temperature 60 °C, Time 30 min and LMR 40:1 was fixed while pH was varied from acidic to alkaline regions. All of the samples having been dyed were subjected to cold water rinsing. The dye was oxidized at ambient conditions with atmospheric oxygen. All of the samples were soaped with Sandopan DTC (soaping agent, Clariant) 5 g/L at 40 °C for 10 min; air-dried and then tested for colour values. Fig.1 showed the complete dyeing cycle and the scheme of the Reduction-Oxidation Cycle of Indigo.

2.3. pH Measurement

pH values of the fresh as well spent dyebaths were measured at room temperature. Δ pH (difference in pH between any two adjacent pH values) were measured and presented along with the pH values.

2.4. Colour measurement

Colour Strength (K/S) by SWL method [13] were measured at a specified wavelength (λ) using the following Kubelka-Munk equation:

$$K/S = [(1.0 - R_\lambda)^2] / 2.0 R_\lambda$$

Where, K - Coefficient of absorption of dye at λ_{max} , S - Coefficient of scattering at λ_{max} , R_λ - Reflectance of the specimen at λ_{max} .

Reflection of the samples was measured in the range of 400 – 700 nm at intervals of 20 nm.

2.5. SEM analysis

Surface morphology of the Wool fibers was investigated using Scanning Electron Microscope. Samples were sputter-coated with Au in Polaron coating unit, model E5100 followed by loading sampler holder in the Hitachi SEM, model S-3000N. Gun-to-sample distance was 8-9 mm and voltage of 5kV was applied to accelerate electron toward the samples under high vacuum. Electron beam focusing, image magnification and brightness/ contrast were adjusted to take the micrographs. SmatSEM software was used to acquire the micrographs.

3. Results and discussion

3.1. Analysis of dyebath pH

Fig.2 showed pH values of the chemical bath solution, in the absence of indigo, at the start of simulated dyeing in the presence of wool. A detailed description of dyebath behaviour is given elsewhere [10]. Fig.3 showed pH at the end of simulated dyeing. The behaviour of wool dyebath at the end of dyeing is quite different from other fibres [10, 11]. Here pH did not change that abruptly and this was attributed to hydrolysis of the peptide bonds in the fibre. Hydrolysis led to the appearance of new amine end groups which absorbed the acidic moieties. Alkaline pH had drastic effects on the strength of the fibre. Wool

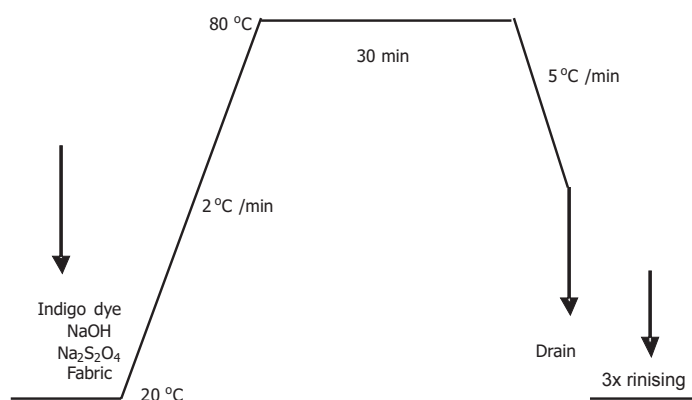
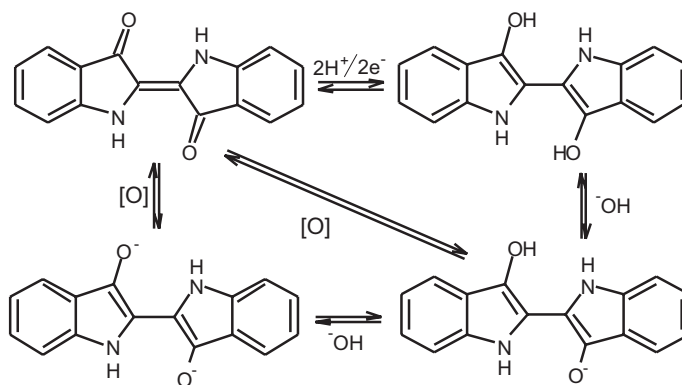


Fig.1 Dyeing process profile

fibres were almost destroyed and lost their integrity. The micrograph showed that surface of fibres was peeled off and the cuticles were completely dissolved away.

Fig.4 showed pH of the dyebath at the start of dyeing process in the absence of wool. The derivative of this curve showed two distinct peaks denoted as "a" and "b". Peak "a" appeared when alkali was increased from 0 to 0.2 g/L. Sodium dithionite produced acidic products during decomposition even at ambient conditions (25 °C). These acidic by-products lowered down the dyebath pH. When alkali was increased this started neutralizing the acidic products and so pH started increasing as could be seen from 0.4 upto 0.8 g/L. Peak "b" was appeared when alkali concentration was increased from 0.8 to 1.2 g/L. This peak showed that now alkali was in excess and that the acidic products generated by sodium dithionite were completely neutralized. The negative scale showed the equivalent amount of acid (hydrochloric acid in this case). When acid was increased, pH didn't change up to 0.2 g/L and thereafter there was a sudden drop in pH as shown by peak "a". Peak "a" showed that there were some species that were absorbing acid. This could be $-NH$ groups in indigo molecules.

Fig.5 showed the dyebath at the end of dyeing process. The same two peaks were there, however, the intensity of peaks was reduced. Since wool contained a lot of amino ($-NH_2$) groups in its polymeric structure, it was suggested that wool picked up acid generated by sodium dithionite. Peak "a" was shifted from 0 to 0.2 - 0.4 g/L alkali concentration. It is known from chemical kinetics that temperature increases the reaction rate. At the dyeing temperature (80 °C), sodium dithionite was completely dissociated into products. The highly acidic products consumed alkali which lowered down the rise in pH. In addition to byproducts generated by sodium dithionite, alkali was



Scheme I Reduction-oxidation cycle of indigo.

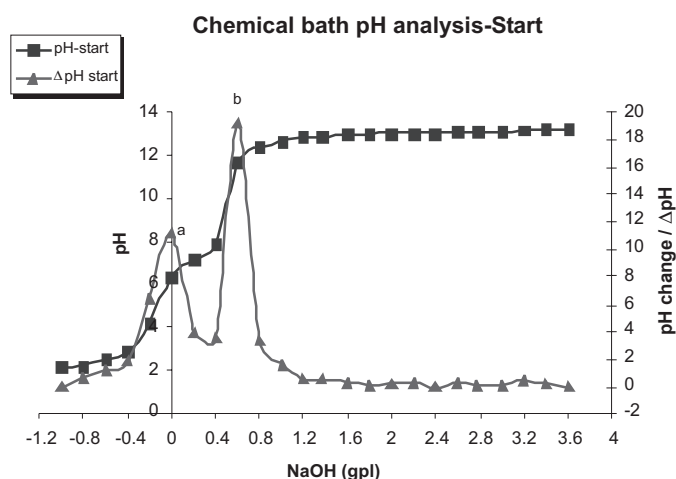


Fig.2 pH (start) of chemical bath at various alkali concentrations ($Na_2S_2O_4$ 10 g/L, 80 °C, 30 minutes, LMR 40:1)

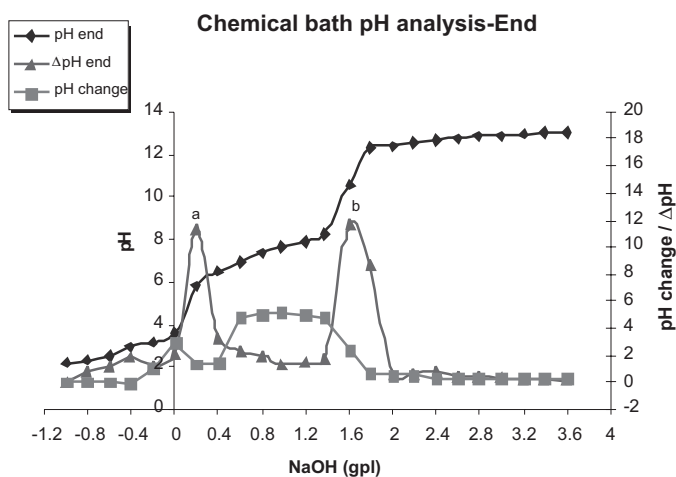


Fig.3 pH (end) of chemical bath at various alkali concentrations ($Na_2S_2O_4$ 10 g/L, 80 °C, 30 minutes, LMR 40:1)

consumed by wool and leuco vat acid molecules as well.

Fig.6 and 7 showed dyebath pH at the start and end of dyeing, respectively. It was evident that peaks "a" and "b"

move further away from each other at the end of dyeing. Peak "a" moved to the left which meant that pH was increased as could be read from the pH-difference curve. There was a negati-

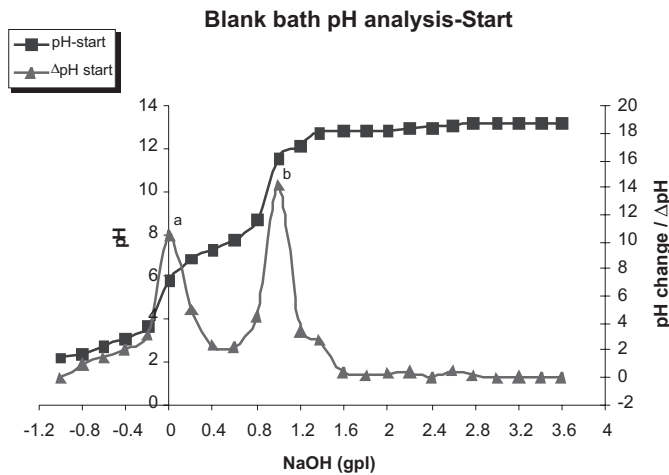


Fig.4 pH (start) of dyebath at various alkali concentrations in the absence of wool (shade: 1 % owf, $\text{Na}_2\text{S}_2\text{O}_4$ 10 g/L, 80 °C, 30 min. LMR 40:1)

ve dip in the pH-difference curve at 0.2 g/L alkali concentration which meant that at the start pH was low and at end of dyeing it was increased. This increase in pH was due to protonation of wool polymer in this region. On the negative alkali concentrations (as acid concentration increases) pH at the end was always higher than at the start.

It was possible to calculate different fractions of the leuco vat acid, shown in figure 4 which could be present at a particular pH by using the equations (1), (2) and (3) [12]. It was evident from Fig.8 that vat acid remained as the major moiety upto pH \approx 5.5 after which its concentration started drop-

ping steeply. As the pH increased, disodium form also started appearing. At pH \approx 9 both the curves of the leuco vat acid and mono-phenolate form crossed each other. Beyond this leuco vat acid diminished steeply and was converted in to the mono-sodium phenolate form. At a pH of 9-10, disodium form started appearing, although it was in minute amount.

$$\text{Fraction II} = 1 / (1 + 10^a + 10^b) \quad (1)$$

$$\text{Where } a = (\text{pH} - \text{pK}_1) \text{ and } b = (2\text{pH} - \text{pK}_1 - \text{pK}_2)$$

$$\text{Fraction III} = 1 / (1 + 10^c + 10^d) \quad (2)$$

$$\text{Where } c = (\text{pK}_1 - \text{pH}) \text{ and } d = (\text{pH} - \text{pK}_2)$$

$$\text{Fraction IV} = 1 / (1 + 10^e + 10^f) \quad (3)$$

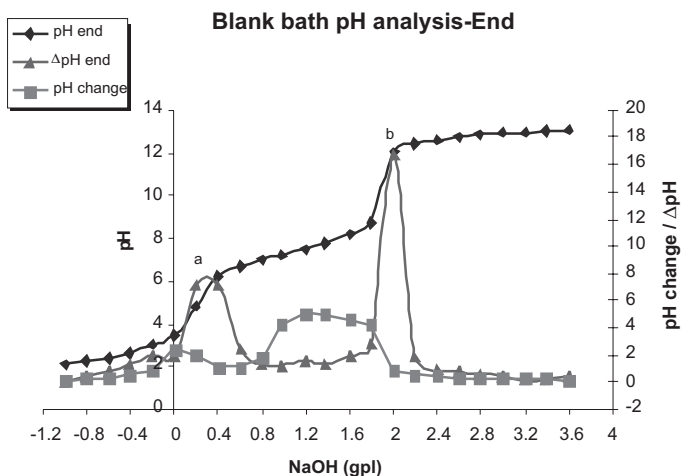


Fig.5 pH (end) of dyebath at various alkali concentrations in the absence of wool (shade: 1 % owf, $\text{Na}_2\text{S}_2\text{O}_4$ 10 g/L, 80 °C, 30 minutes, LMR 40:1)

Where $e = (\text{pK}_1 + \text{pK}_2 - 2\text{pH})$ and $f = (\text{pK}_2 - \text{pH})$

Fig.9 showed the reflection spectra of indigo dyed wool fibres in various pH regions. The results showed that light reflection was high when pH was less than 6 but more than 7. Since alkaline pH was deleterious for polypeptides, the pH should have been in the acidic side to get maximum colour strength with little damage. The reflection minima lie at 660 nm in all the cases.

3.2. pH vs. Colorimetric properties
Fig.10 showed the colour strength of indigo on wool at different pH values. The shade depth decreased steeply to the left of pH \sim 5 than on higher pH values. Reduction of sodium dithionite led to the formation of highly acidic products which were highly soluble in water. Vat acid itself is a very weak acid, pKa value 6, and so it is sparingly soluble in aqueous medium. Because of the presence of highly soluble acidic impurities, the solubility of the leuco vat acid was reduced to a large extent. If these acidic products are not consumed, then according to the Le Chatlier's principle the reaction should not proceed further i.e. proper colloidal dispersion of leuco vat acid.

It was suggested that below pH 4.0, the acidity was so high in the dyebath that most of the leuco vat acid precipitated out and this was supported by the observations that at end of dyeing in this region, a black dispersion was produced so very little dye exhausted to the wool samples. Although in the pH range of 3 – 5, leuco vat acid was the sole product of reduction reaction, due to its poor solubility most of the leuco vat acid precipitated from the solution. As pH increased above 5, there was a rapid change in pH. The pH jumped from 3.5 to 5.5 that derived the solubilisation of the leuco vat acid in the forward direction. At pH \approx 6 leuco vat acid still shared \approx 97% of the strength in the dyebath solution, Fig.8, so a maximum shade depth was produced. As the pH increased, the mono-sodium phenolate form also started appearing in the dyebath

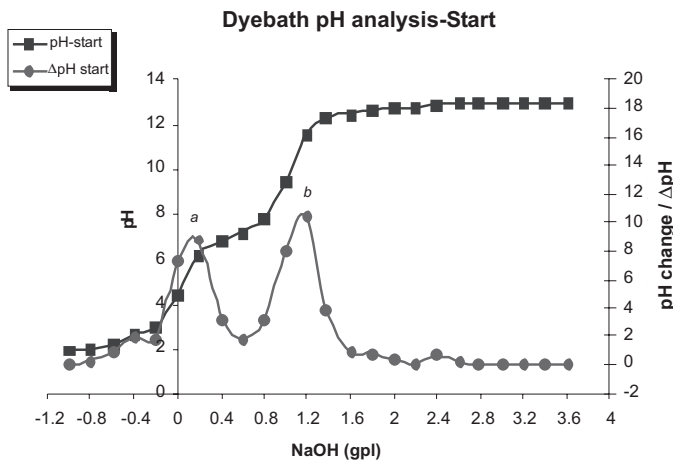


Fig.6 pH (start) of dyebath at various alkali concentrations in the presence of wool (shade: 1 % owf, Na₂S₂O₄ 10 g/L, 80 °C, 30 minutes, LMR 40:1)

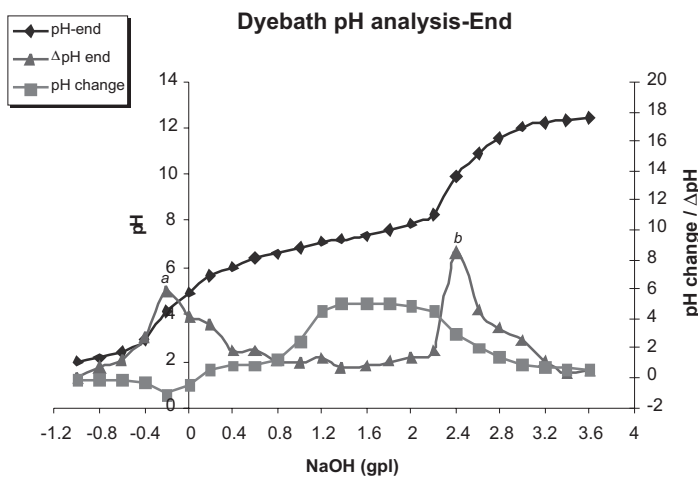


Fig.7 pH (end) of dyebath at various alkali concentrations in the presence of wool (shade: 1% owf, Na₂S₂O₄ 10 g/L, 80 °C, 30 minutes, LMR 40:1)

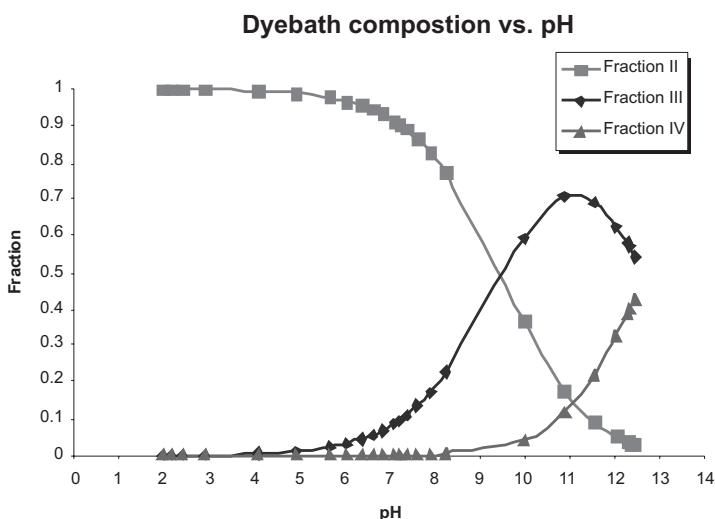


Fig.8 Fraction of leuco vat acid as a function of pH

but unlike polyester (PET), it was also absorbed by the wool fibres. A nearly flat plateau was formed in the pH range of 6 to 8.00. In the whole pH region, wool fibres continued to absorb the dye molecules. Above pH 8.00, wool fibres were de-protonated thereby leaving the mono-sodium phenolate form in the solution. However, the decreasing quantities of leuco vat acid continued to tint the fibre. The shade depth increased sharply above pH 5, Fig.6, therefore pH should be controlled carefully and never let be dropped below 5.5 otherwise there would be wastage of colorants. Another point from the graph was very clear that pH control was crucial because if pH were less than 6, there would be less shade depth being produced while pH higher than 6 upto 8 did not affect shade depth and there was severe damage to the fibres.

3.3. Effect of reducing agent

The following Fig.11 showed the effect of sodium dithionite on color yield of indigo on wool fibres. The sodium dithionite concentration was varied at a constant pH of 6. The results showed that upto a concentration of 6 g/L, the color strength was low; however, as the concentration was increased color strength increased as well. An increase in concentration of sodium dithionite decreased the color strength. The results showed that there should have been an optimum concentration of sodium dithionite. Too little a concentration was not sufficient to reduce all the dye molecules completely and therefore no dye buildup while increase in concentration of sodium dithionite above a certain concentration again reduced the shade buildup which was attributed to the dye over-reduction and side reactions.

3.4. Effect of temperature

The following Fig.12 showed the effect of dyeing temperature on color yield of indigo on wool fibres. It was observed that the graph was quadratic

and the maximum shade depth being produced at temperature of 80 °C. Heat is required to impart necessary kinetic energy to the polymer segments of the fibers and dye molecules. At lower temperatures the segmental mobility of polymer chains was low so the pore sizes were of very small dimensions. Higher tem-

peratures led to the formation of wider temporary voids in the fiber structure through which the dye molecules were diffused. Further increase in temperature increased the segmental mobility so high that dye molecules were easily moved in and out of the fiber structure. The net result was less dye being accumulated in

the fiber structure. During the experimentation it was observed that temperature above 100 °C severely damaged the wool fabrics and the dye was precipitated as well. Temperature in the range of 60 to 70 °C could safely be used to dye wool samples. The dyebath was subjected to HPLC analysis to study the effect of temperature. The following Fig.12 showed that higher temperature led to dye destruction and hence less color strength was achieved.

3.5. Effect of time

The following Fig.13 showed the effect of dyeing time on color yield of indigo on wool fibres. The results showed that color strength was high at the start and reached to equilibrium within 60 minutes but then started decreasing. It was concluded that indigo had a very high strike rate on wool, however, as the time passed the dye molecules started diffusing into the polymer matrix and so color strength reached to equilibrium. Higher dyeing times led to the reduction in color strength which was probably due to the over reduction of dye molecules leading to the formation of degradation products which did not have substantivity for wool fibers. High Performance Liquid Chromatography (HPLC) would be used to further investigate the hypothesis that longer dyeing time led to the formation of non-substantive products.

3.6. Build-up characteristics

The following Fig.14 showed the build-up curve of indigo on wool fibres at the mentioned process conditions. It could be seen that rate change of color strength was high and only 1 % o.w.f of indigo was sufficient to achieve the maximum color strength. Reflection spectra showed that maximum absorption i.e. λ_{max} of indigo on wool was 660nm which was the same when indigo was applied to cotton. The maximum absorption of indigo in dimethyl formamide (DMF) was at 610 nm. A higher absorption showed that indigo dye molecules existed in

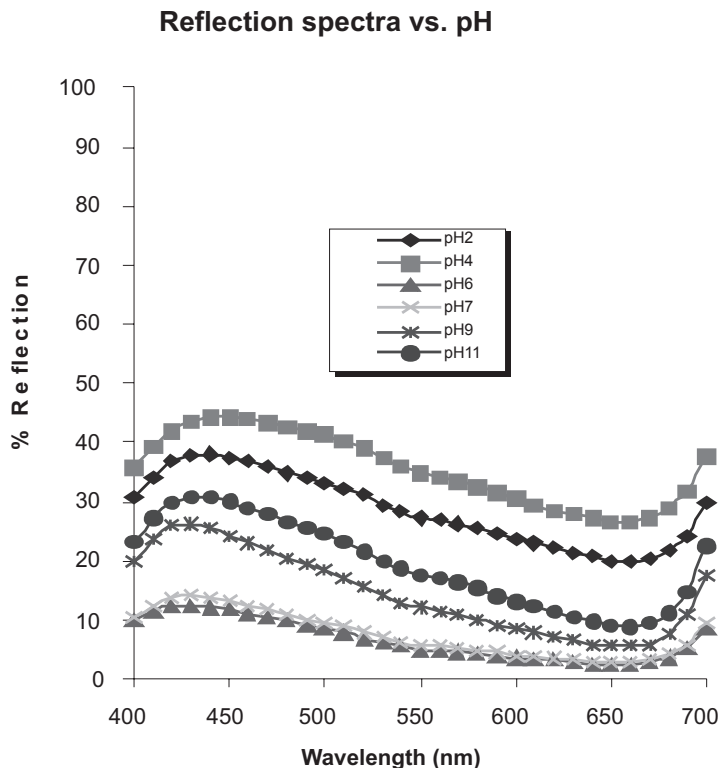


Fig.9 Colorimetric properties of indigo on wool as a function of pH

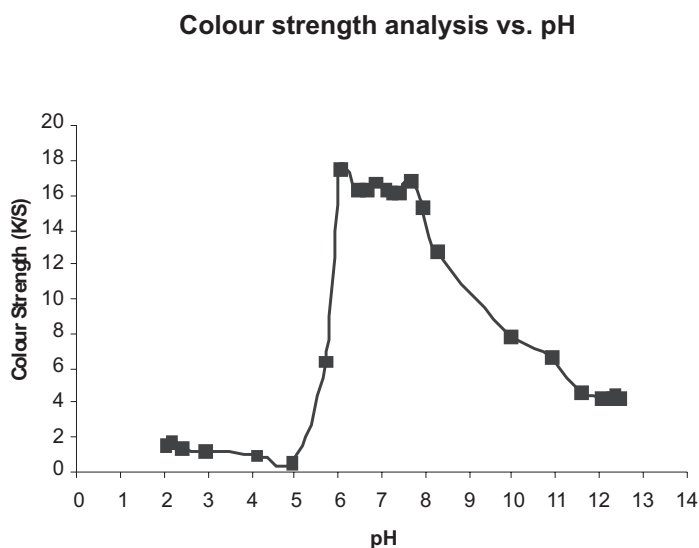


Fig.10 Colour strength as a function of pH

Colour strength analysis vs. Sodium dithionite

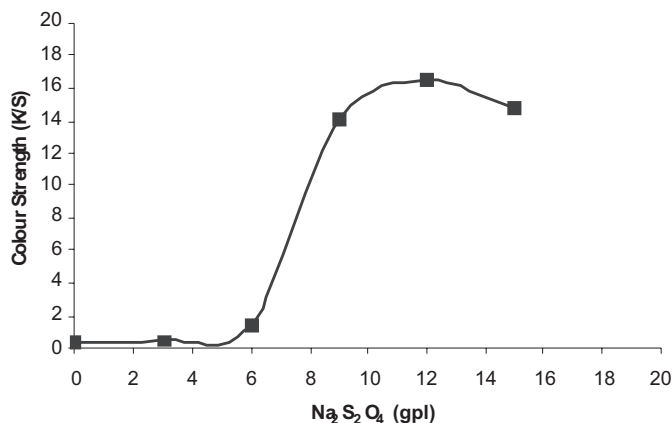


Fig.11 Colour strength versus sodium dithionite (shade 1 % owf, pH 6, 80 °C, LMR 40:1, 30 minutes)

Colour strength analysis vs. Temperature

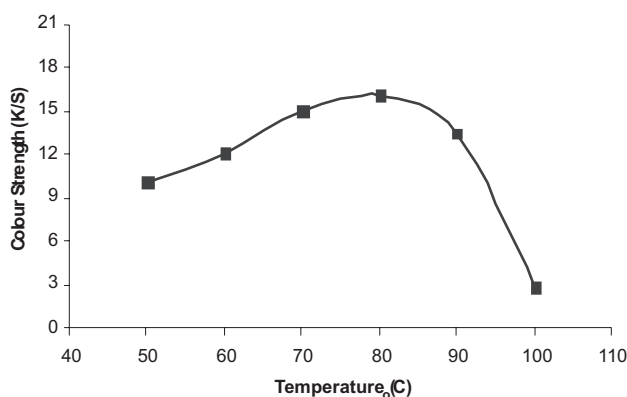


Fig.12 Colour strength versus temperature (shade 1 % owf, pH 6, LMR 40:1, 30 minutes)

Colour strength analysis vs. Time

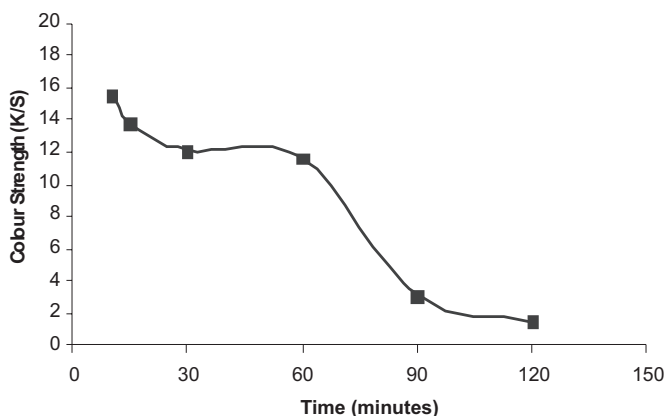


Fig.13 Colour strength versus time (shade 1 % owf, pH 6, 80 °C, LMR 40:1)

a different form in the wool matrix. It is known that indigo existed in the form of aggregates inside cotton polymer and the absorption maximum was 660 nm. It was concluded that indigo molecules were in the same state in wool polymer as well. Fig.15 showed the Reflection spectra and color coordinates of indigo on wool as a function of dye concentration. The color coordinates became redder and yellower as the shade depth was increased. Fig.16 showed the reflection spectra of indigo during the course of oxidation.

3.7. pH vs. Fibre chemistry

The following Fig.17 showed schematically the effects of acidic and alkaline pH on the chemistry of polypeptide polymer chains. In the acidic region amine and amide groups were protonated and therefore wool was safe while in the alkaline region amide groups were hydrolyzed. This hydrolysis led to depolymerisation and hence strength losses of the wool fibres. The SEM analysis showed that in the alkaline region wool fibres were severely damaged. Fig.17b showed the schematic interactions of leuco vat acid with wool. Wool has a lot of amine, amide, sulphide and carboxylic groups and all of these possess polar nature from the chemistry viewpoint. The suggested substantivity of leuco vat acid toward wool was attributed to the hydrogen bonding between the hydroxyl groups of leuco vat acid and the above mentioned wool functional groups. In the oxidized form, indigo did not exhaust while in the alkaline region these hydroxyl groups were ionized. It was the acidic region in which hydroxyl groups were preserved and imparted the required substantivity to the dye molecules.

3.8. SEM Analysis

The following Fig.18 from a) to f), showed the effects of pH on the morphology of wool fibres. The micrographs showed that there were negligible changes in surface morphology

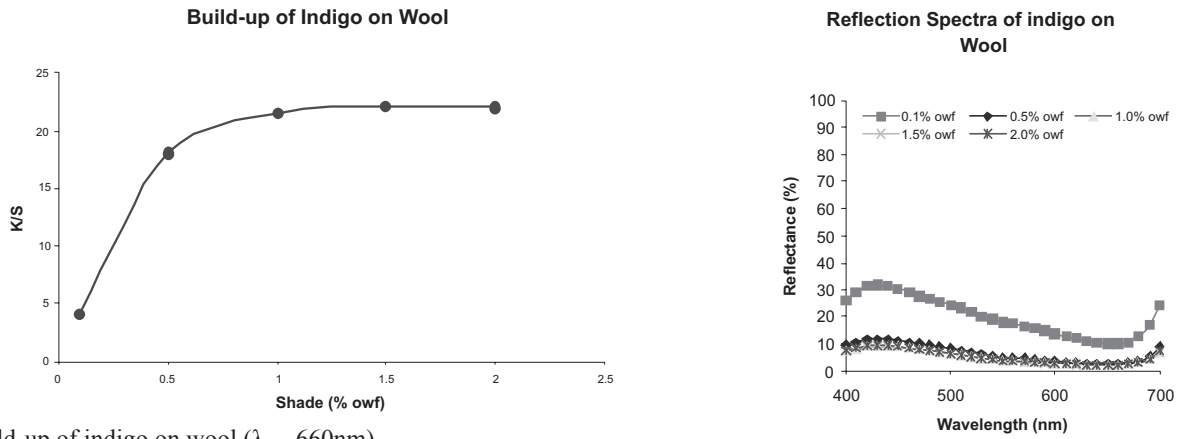


Fig.14 Build-up of indigo on wool (λ_{max} 660nm)

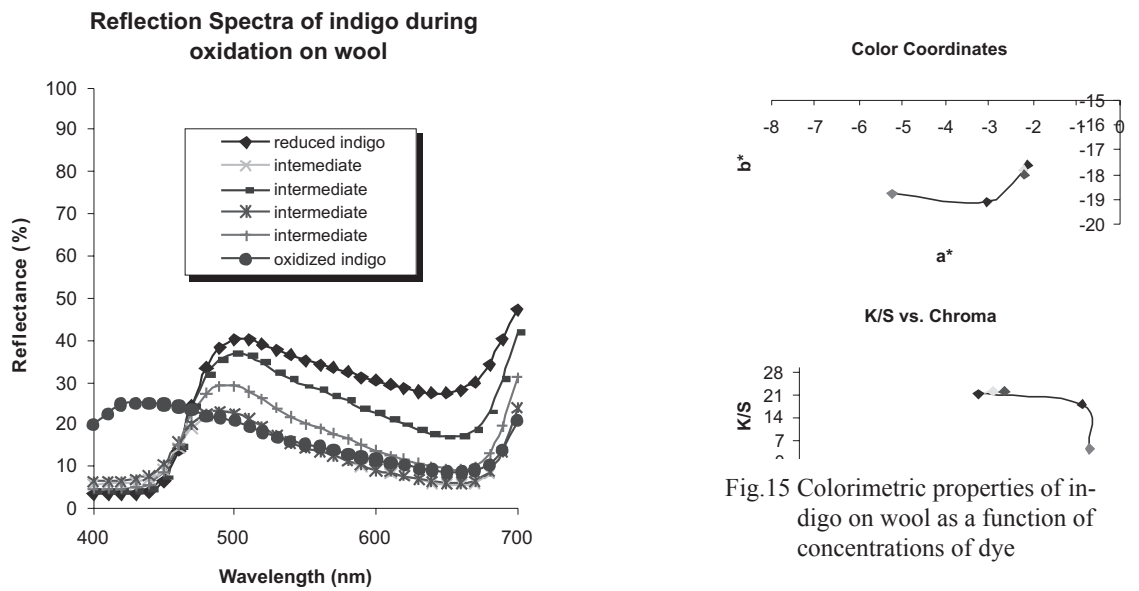


Fig.15 Colorimetric properties of indigo on wool as a function of concentrations of dye

Fig.16 Reflection spectra of indigo during the course of oxidation

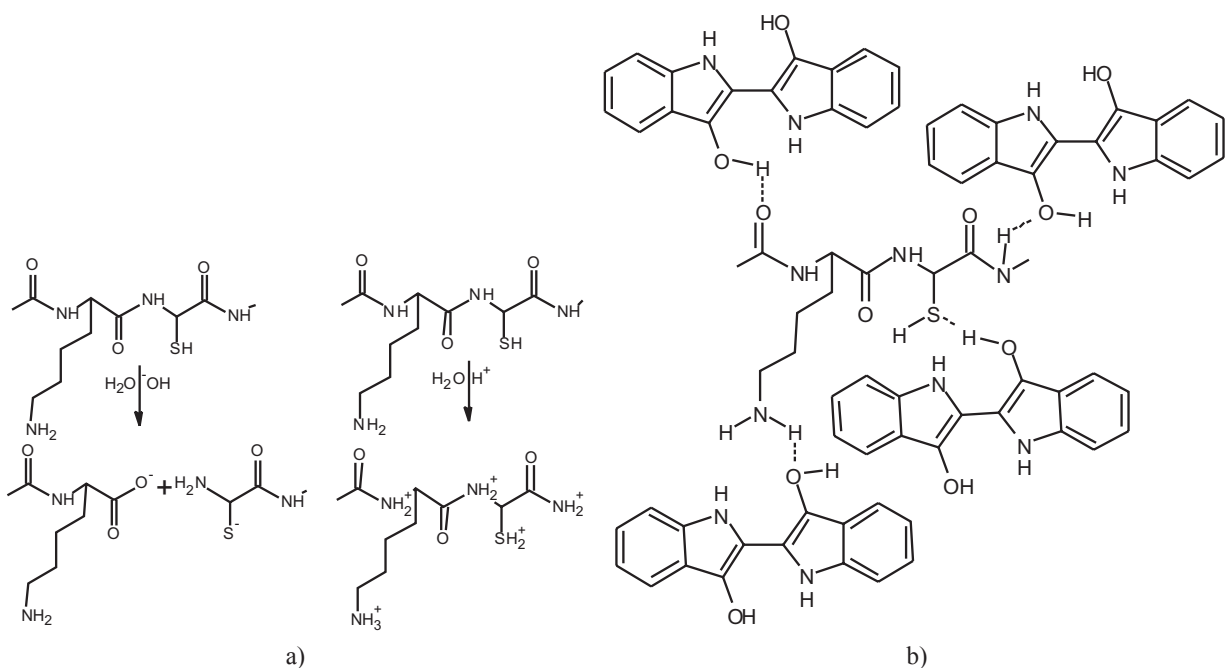


Fig.17 Effect of pH: a) on wool fibers, b) on interaction between wool and dye molecules

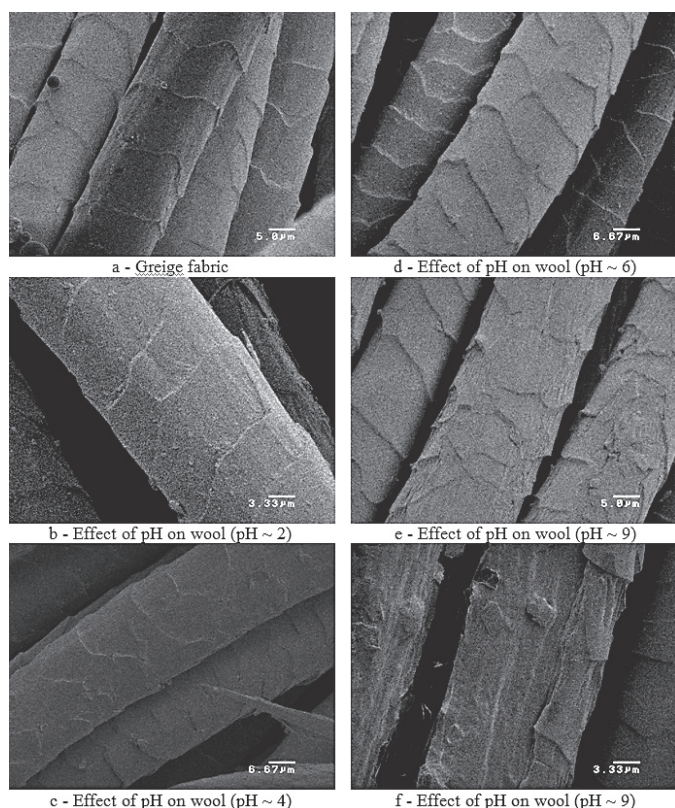


Fig.18 SEM of wool fibres

and that wool fibres were stable in the acidic region. Figures e and f showed wool fibres treated in the alkaline region. It was evident that alkalinity caused severe damage to the wool morphology. Since wool was dyed to a good shade depth in the acidic region, there was nothing to worry about its degradation.

4. Conclusion

Wool fabrics were dyed with indigo through exhaust technique in the carefully controlled pH conditions. The sodium dithionite concentration of 6 g/L is sufficient; when alkali is 0.6 g/L. When reducing agent had been optimized, the alkali concentration should have borne a certain relation-

ship with it. The dyeing pH should be in the acidic range and be monitored strictly. Indigo molecules existed as aggregates within the fiber matrix. The high dyeing temperature and alkaline conditions rendered severe damage to the wool fibres. The wool fibers were damaged and became tendered in the alkaline region while indigo dye molecules were destroyed at 100 °C. Indigo had good build-up on wool fibers. The shades became redder and yellower as the shade depth was increased.

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