DYEING NYLON WITH INDIGO IN VARIOUS PH REGIONS

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Abstract:

Nylon (6.6) fabric was dyed with Indigo dye using an exhaust technique at different pH values. At different pH values different forms of indigo existed in solution, each one having a different substantivity for the fibre. The non-ionic form had the highest, whilst the Ionic ones had relatively less substantivity. The fibres could best be dyed in the acidic to slightly alkaline pH range. The Chemistry of the dyebath and fibre were considered, in order to explain the effect of pH on colour strength. Hydrogen bonding and ionic interactions seemed to be the main reason for the exhaustion of dye onto nylon fibre. Hydrogen bonding occurred between the hydroxyl groups and amide groups, while ionic interactions worked at low pH values between the ionized and end-amino groups of the dye and fibre respectively.

Key words:

Indigo, Nylon, pH, Colour strength, Dye interactions, Fibre hydrolysis.

Introduction

Dyeing of synthetic fibres with vat dyes has been undertaken by a number of researchers in recent times. Synthetic fibers, mainly the polyester, have been dyed with indigo and excellent exhaustion has been reported. In the past such efforts have also been made, but most of them go in vain as indigo has been applied using conventional methods. As the indigo has been applied using conventional methods that use very high pH, in the rage of 12 – 13 that is employed to dye cotton textiles. At this pH range polyester develops a negative potential of -32 ~ -40 mV and moreover since the fibre is hydrophobic in nature, little dye will exhaust onto it [1-9]. In addition to polyester, nylon is also a very important fibre and finds most of its applications in the apparel and hosiery industry. Nylon is mainly dyed, with acid dyes although other dyes for example reactive and disperse are also used; however, their percentage share is much less. The author has already published work on the dyeing of polyester with indigo and the effect of pH on PET dyeing in details [10]. Excellent shade depths, with good washing and rubbing 2/11 fastness have been obtained. However, poor light and sublimation fastness were also noted. The later has been taken advantage of in the production of faded effects on polyester and its blends with cotton [11].

Nylons are polyamides that are manufactured through different techniques but condensation polymerisation of diamines and diacids is the most famous one. This work has been undertaken to dye nylon with indigo using an exhaust technique. Excellent shade depths with overall good fastness properties have been obtained. Unlike polyester, nylon can be dyed in the acidic as well as slightly basic pH regions. Nylon being a polyamide contains many amide groups in its structure. It also contains free amine groups at the ends of its polymeric chains, although the number of these free amine groups is less than the number of carboxylic groups, and therefore, the fibre posesses a negative charge unless in the appropriate pH region. These amide and amine groups provide excellent hydrogen bonding sites and are the main factors contributing to the substantivity of the dye molecules.

Dyebath pH values at the very start as well as at the end of dyeing have been monitored and the results presented. Effects of varying pH on the dyebath composition, colour strength as well as on the structure of the fibre have been discussed. This work finds its potential uses in the hosiery industry where Nylon/ Cotton blends are dyed with Acid/Reactive dye system. These nylon/cotton blends can be dyed in a single bath with a single dye and excellent shade depth can be obtained.

Experimental

Material & Machinery

Tsuji HT dyeing machine 75231-1992 was used to dye nylon samples and the pH measured before and after dyeing using Henna Digital pH Meter PH-210. Reflectance and colour strength were measured on GretagMacbeth ColorEye – 7000A Spectrophotometer. A plain woven nylon fabric having a warp and weft density of 160 and 80 respectively and using nylon filament having a count of 210 denier in the warp and 94 denier in the weft was purchased. This was dyed without any prior pre-treatment because alkaline-reductive treatments followed by soaping were considered enough to remove the impurities present. Indigo dye (85%), granular form, was provided kindly by the DyStar Pakistan. All other chemicals were of laboratory grade.

Dyeing

Samples were dyed with Indigo to 1% o.w.f shade depth. Sodium dithionite 10 gm l-1, temperature 120 oC, time 30 min and liquor to material ratio 40:1 were fixed, while the pH was
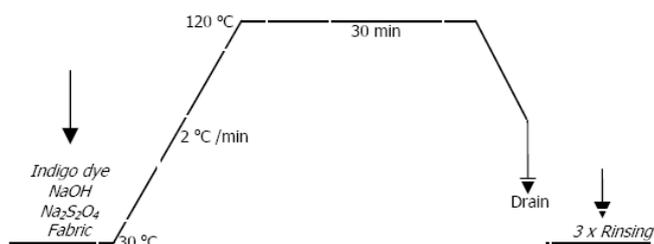

Figure 1. Dyeing Process.

varied from acidic to alkaline regions. After dyeing, all samples were subjected to cold water rinsing. Since nylon fibre has a compact structure, dye was oxidized in hot air at 120 oC for 5 minutes. All of the samples were soaped with Sandopan DTC 5 gm/l at 80 oC for 10 min; air-dried and then tested for colour values. Figure 1 show the complete dyeing cycle while Figure 2 and 3 show the schematic chemical reactions of Indigo reduction and the complete Reduction-Oxidation cycle respectively.
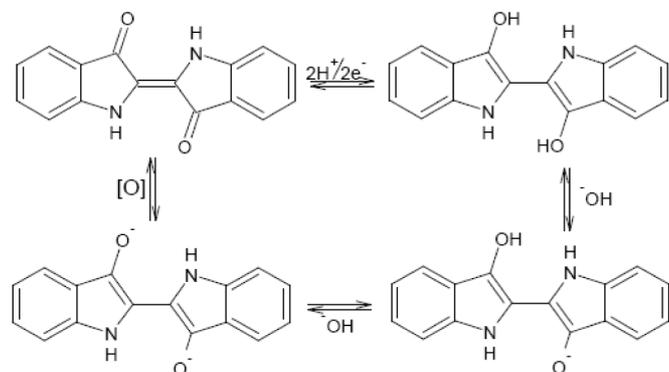

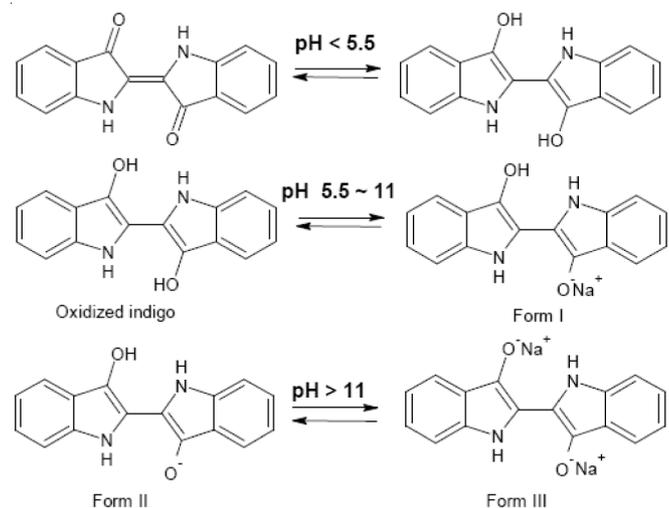**Figure 2.** Schematic reactions of Indigo reduction.

Figure 3. Reduction-Oxidation Cycle of Indigo.

Measurement

pH Measurement

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

Colour Measurement

Colour Strength (K/S) by Single Wavelength method [12] was measured at a specified wavelength (λ) of maximum absorption using the following 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 from 400 – 700 nm at intervals of 20 nm.

Results and Discussions

Bath pH - Start

Figure 4 shows pH values as well as pH change of the fresh dyebath solutions. The graph can be split into thee parts for discussion. It is clear that pH changes very slowly at the start, rises steeply, slows down and finally levels to a constant value. Sodium dithionite is unstable in aqueous solutions, in the presence of air and alkalies. Figure 5 shows chemical reactions of sodium dithionite with these reactants under different conditions. It can be seen that the products are salts of neutral and acidic nature. At the start of dyeing, decomposition of sodium dithionite is slow so that upto 0.6 gm/l pH varies slowly from 5.98 ~ -7.16 and then rises up rapidly in between 0.6 – 1.6 gm/l alkali concentrations. The acidic by-products of sodium dithionite are in high quantities, and therefore, consume all of the alkali present leaving pH in the acidic side despite the addition of alkali into the bath. At and beyond 1.6 gm/l of alkali concentrations, pH remains almost the same.
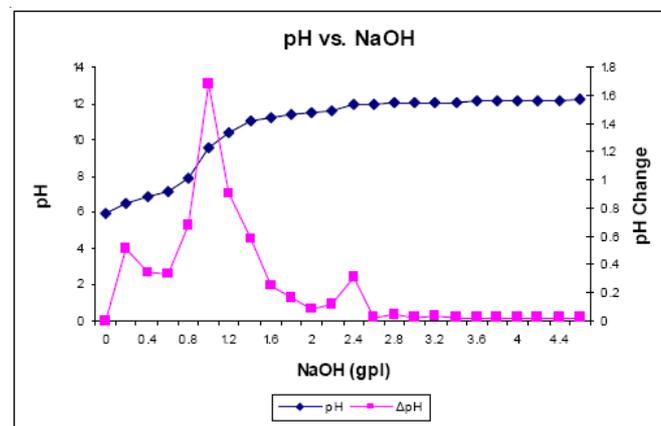

Figure 4. pH & pH change at different alkali concentration – Start (Temp 30 oC, Time 0 min).

As the alkali concentration crosses a certain limit, set by the acidic impurities, a sharp peak can be observed at 1.0 gm/l alkali concentration in figure 4. Further increase in alkali concentrations beyond 1.6 gm/l do not lead to any appreciable

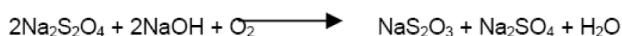**Figure 5.** Chemical reactions of sodium dithionite [13].

increase in pH. The colour of dyebath changes to light green showing that dye has started being converted into the reduced form, however, complete reduction has not occurred because the fully reduced indigo has yellow colour. So the alkali is consumed by Indigo to be converted into the leuco vat acid and to some extent to its ionic forms, mainly mono form. It is not only these acidic by-products that consume the alkali; acidic products can also be adsorbed on nylon. At very low pH it is the amide while at relatively higher pH values but still in the acidic side it is the amine end groups that can be protonated.

Bath pH - Spent

Figure 6 shows pH behaviour of the dyebath solution at the end of dyeing. It seems that two Start-pH curves have been joined together head to tail to form Spent-pH curve. At the very start of the process because of the presence of acidic impurities pH remains in the acidic side and unlike the case with polyester, the length of tail remains almost the same. Nylon is not stable in acidic medium particularly at high temperatures. It is probable that at very low pH values and at 120 oC nylon degrades, thereby producing free amino and carboxylic acid groups.

These groups can consume alkali so that the pH remains in the acidic side for a longer length of time. At the dyeing temperature a complete reaction among the acidic impurities and the alkali takes place so that peak shifts a little toward left.
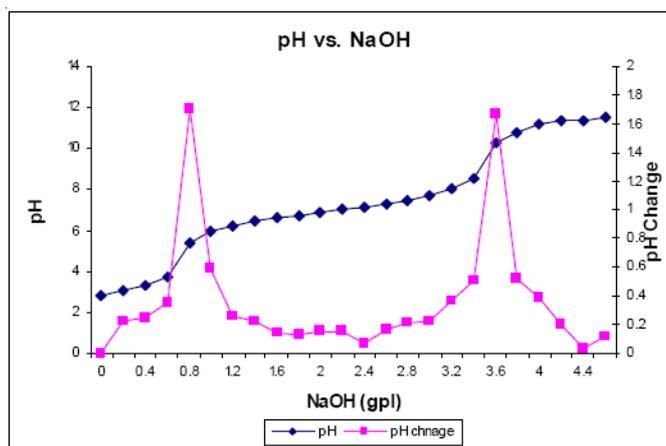

Figure 6. pH & pH change at different alkali concentration – Spent.

After the impurities have been destroyed, a sudden peak at 0.8 gm/l represents the formation of leuco vat acid. From 1.2 to 3.2 gm/l alkali concentrations pH curve rises very slowly and this shows that alkali is again being consumed. Here the leuco vat acid reacts with sodium hydroxide and is converted into the mono-sodium phenolate form. An average value of pH in this region is ≈ 7.047. In the next region from 3.2 to 3.8 gm/l alkali concentrations another hump can be seen to which corresponds the second sharp peak. This sharp peek shows a steep increase in pH which means the leuco vat acid has completely been consumed and now the mono-sodium phenolate solely exists at this point. This mono-ionic form then starts to be converted into the di-sodium phenolate form. It can be seen that the graph starts becoming level once again beyond 3.8 g/l alkali concentrations. During this region the di-ionic from starts appearing in equilibrium with the mono-ionic form. Average value of pH is ≈ 11.23 in the region upto the concentrations that we have studied, but will definitely increase when di-ionic form has completely been formed. It is possible to calculate different fractions of the

leuco vat acid shown in figure 3 which could be present at a particular pH by using the equations 1- 3 [14]. It can be seen from the Figure 8 that vat acid remains as the major moiety upto pH ≈ 5.5 after which its concentration drops down steeply. As the pH increases, di-sodium form also starts appearing. At pH ≈ 9 both the curves of the leuco vat acid and mono-phenolate form cross each other. Beyond this vat acid diminishes steeply and is converted in to the mono-sodium phenolate form. At pH of 9-10, di-sodium form starts appearing, although it is in a minute amount.

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

Where $a = (pH – pK_1)$ and $b = (2pH – pK_1 – pK_2)$.

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

Where $c = (pK_1 - pH)$ and $d = (pH – pK_2)$.

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

Where $e = (pK1 +pK_2 – 2pH)$ and $f = (pK_2 - pH)$.
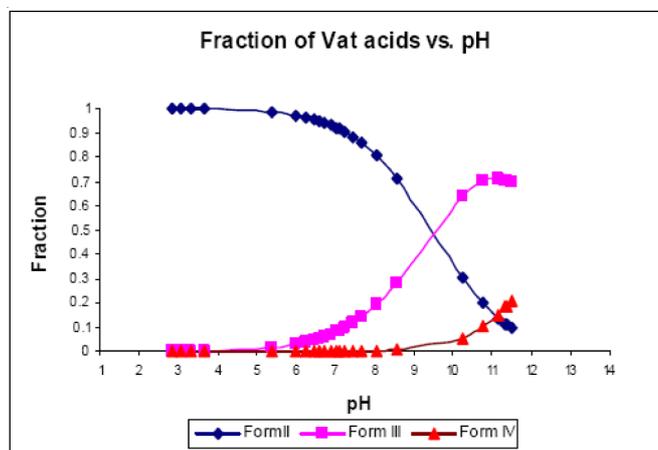

Figure 7. Factions of Vat acid at various pH values.

pH vs. K/S

Figure 11 shows the colour strength of indigo on nylon at different pH values. Comparing it with that of Polyester, it is quite different. The shade depth decreases steeply to the left of pH 5 than on higher pH values. Reduction of sodium dithionite leads to the formation of highly acidic products which are highly soluble in water. Leuco vat acid itself is a very week acid (pKa ~ 6) and so it is only just soluble in aqueous medium. Because of the presence of these highly soluble acidic impurities, the solubility of the vat acid is reduced to a large extent. If these acidic products are not consumed, then according to the Le Chatlier•fs principle the reaction should not proceed further. It is suggested that below pH 4.0 acidity of the dyebath is so high that most of the vat acid is precipitated out. Although in between pH 3 – 5 leuco vat acid is the sole product of reduction reaction because of its poor solubility most of it is thrown away from solution. As pH increases beyond 5 there is a rapid change in pH. It jumps from 3.5 to 5.5 and drive the solubilisation of the vat acid to the forward direction. At pH ≈ 6 leuco vat acid still shares $\approx 97\%$ of the strength in the dyebath solution, as can be seen from figure 5, so a maximum shade depth is produced. As pH increases, the mono-sodium phenolate form also starts appearing in the dyebath but unlike polyester it is also absorbed by nylon. Colour strength forms a flat plateau in between pH 5.40 to
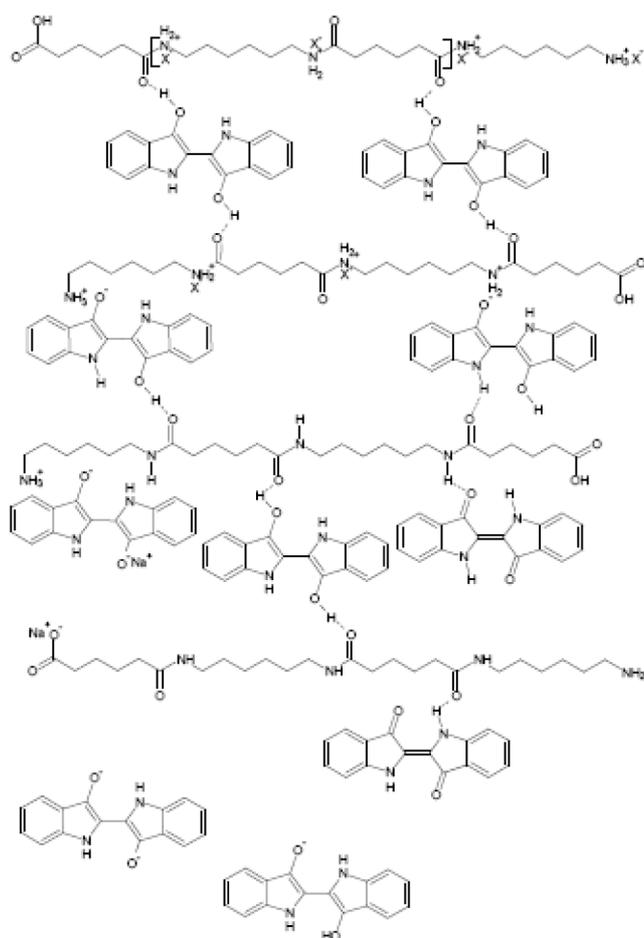
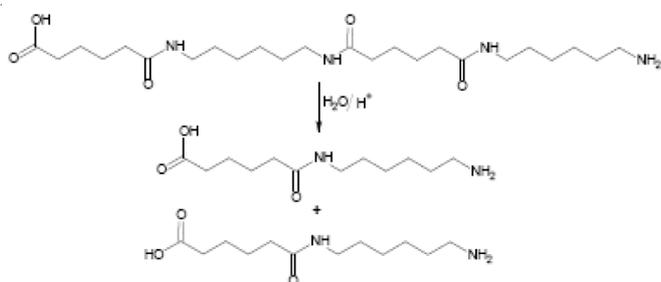**Figure 8.** Schematic Interactions of Indigo with Nylon.

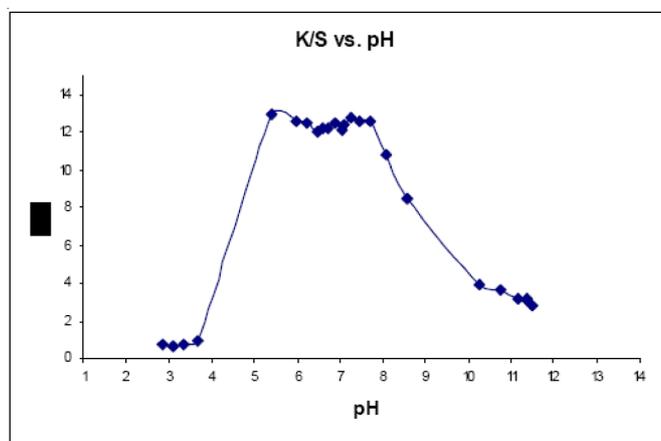**Figure 9:** Schematic Hydrolysis of Nylon.

Figure 10. K/S versus pH (1% o.w.f, 10 gm/l Na2S2O4, 120 oC, 40:1, 30 min).

8.00. In this whole pH region the dye molecules continue to be absorbed by nylon. Above pH 8.00, the nylon fibre is deprotonated thereby leaving the mono-sodium phenolate form in the solution. However, the decreasing quantities of leuco vat acid continue to tint the fibre. It is evident from figure 6 that shade depth increases sharply beyond pH 4 ~ 4.5. It can be calculated that while changing from 4 to 4.5 there is 1400 times more shade depth being produced. The pH should, therefore, be controlled carefully and never be allowed to drop beyond 5.5 otherwise there will be wastage of colorant. Another point from this graph is that pH control is not as crucial as with polyester. Here we have more flexibility in pH control.

Let us consider the interactions in between the fibre and dye molecules. Figure 9 (at the end of paper) shows the schematic interactions of indigo molecules with Nylon while Figure 10 (at the end of paper) shows hydrolysis of nylon. In the acidic region nylon is not that stable as in the alkaline side. In the highly acidic region (pH 3~4) dye does not exhaust well on the fibre probably because most of the sites are blocked due to protonation of the free amine groups at the chains ends as well as the amide groups present in the polymer backbone. In this pH range and at high temperature fibre is very much susceptible to degradation. However, at relatively high pH but still in the acidic side (pH 5~8) amide groups are de-protonated. These groups are now available for the dye molecules to form hydrogen bonding. There could be different forces that constitute to the substantivity between the dye and fibre but hydrogen bonding seems to be the most important one. Polyamides contain both negative as well positive centres so that these can interact with the hydroxyl as well as amine groups of the dye but it is mainly the hydroxyl groups that contribute to the substantivity because they have more polar character.

Like polyethylene terephthalate (PET), since there are no aromatic nuclei in the polymer backbone, no interactions exist between the benzene nuclei and the hydroxyl groups. In the alkaline region, carboxylic groups are ionized so that a negative charge is developed on the fibre. This negative potential repels the ionized species i.e. fractions III and IV away because of its almost ionic as well as non-polar character and thereby remains undyed.

Conclusions

Nylon fabrics can be dyed with indigo through an exhaust technique in carefully controlled pH conditions. When the reducing agent has been optimized, the alkali concentration should bear a certain relationship with it. The optimal pH range is acidic to slightly alkaline regions.

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