

Recent progress in indigo dyeing of cotton denim yarn

J N Erters

The University of Georgia, Athens, GA 30602, USA

During the past several years, significant progress has been made in understanding the important parameters that influence the sorption of indigo dye by cotton denim yarn. It has been observed that dye uptake by cotton fiber and the extent of penetration of indigo dye into the denim yarn cross-section are influenced strongly by the pH-controlled ionic species of both dye and cotton in the dyebath. High dyebath pH results in a high level of ionization of both indigo dye and cotton cellulose, resulting in decreased substantivity and increased penetration of the yarn fiber bundle by the dye, with associated lower color yield. On the other hand, moderate dyebath pH promotes lower ionization of dye and fiber, resulting in increased ring-dyed yarn, greater color yield, and a denim garment that washes down quickly and consistently to produce the current appearance demanded by fashion.

Keywords: Cotton yarn, Denim, Dyeing, Indigo

1 Introduction

Much is yet to be learnt about the various parameters that influence indigo dye uptake by cotton denim yarn. If anything is certain, it is that a complete understanding of all the factors that influence the mechanism of dye sorption is not yet available. Nevertheless, a significant quantity of new information has been uncovered during recent investigations. For example, the influence of dyebath pH on both penetration of indigo into denim yarn and the resulting color yield has been shown to be of paramount importance. Indeed, the importance of dyebath pH was reported as early as 1987 in a BASF technical bulletin¹. The scientific basis of the empirically observed effect was not discussed and detailed quantification of the phenomenon was not given. It was noted in the publication:

"It is most important to ensure that a constant pH is maintained during the [indigo] dyeing process, so that the affinity and dyeing penetration also remain constant and there is no 'ending' within the dyed lot. We recommend dyeing at pH 12; at pH 11.5, the dyeing is less penetrated, whereas above pH 12 the dyeing penetration is better but the dyeing lighter".

The purpose of the present investigation is to review the results of studies at The University of Georgia and elsewhere that have contributed to an increased understanding of the physico-chemical relationships involved in commercial indigo

dyeing. It is hoped that the discussion will reiterate the importance of strict control of dyebath pH on the resulting color yield, extent of ring dyeing of denim yarn, and the associated washdown characteristics of denim fabric. Most of the data that have been obtained in studies made at The University of Georgia was obtained under the experimental conditions given in the following section.

2 Experimental Procedure

2.1 Substrate

100% knitted cotton tubes, prepared from 8s denim yarn and supplied by Auburn University, were used. The tubes had a flattened width of 4.5 cm and a weight of 7.2 g per 30 cm length—the length used for laboratory dyeings. Knitted tubes were used in the laboratory work to facilitate subsequent reflectance measurements. Uniform reflectance measurements on denim yarn are more difficult to obtain.

2.2 Dyebaths

Three-liter infinite dyebaths were employed to assure that the concentration of dye in the bath did not change significantly during the course of the dyeings. Infinite dyebaths are maintained in commercial indigo dye ranges by continuously feeding concentrated stock solutions of dye into the dyebath at a carefully maintained rate.

2.3 Dyeing

Knitted cotton tubes were wet out in a room

temperature solution of 1.5 g/L sodium dioctyl sulphosuccinate wetting agent and passed between the squeeze rolls of a Butterworth's pad mangle at 50 lb/in² pressure. The tubes were rinsed in deionized water, passed through the mangle again, and placed into a fresh deionized water-bath where they were kept until they were dyed.

For dyeings made at each dye concentration and pH, a knitted tube was removed from the deionized water-bath, attached to a lead line of polyester fabric, and passed between the squeeze rolls. The tube was then immersed into the dye-bath at room temperature for 15 seconds, passed through the mangle to about 70% pickup, and air oxidized for 45 seconds. The immersion, padding and oxidation sequence was repeated five times in an attempt to simulate actual commercial dyeing. The dyed tube was then placed on a line and allowed to dry at room temperature. After all dyeings at the various dye concentrations and pH had been completed, the tubes were rinsed together with agitation in a large white, plastic bucket under a faucet of warm running water until the rinse water appeared to be free of loose, unfixed dye, as indicated by the absence of blue coloration. The tubes were then dried on a line at room temperature.

2.4 Reflectance Measurements

Each of the dyed tubes was folded to achieve opacity and reflectance measured over the wavelength range of 400-700 nm, using a LabScan 6000 spectrophotometer. Reflectance values at 660 nm were converted to K/S , using Eq. (1). The selected wavelength of 660 nm has been shown to be the wavelength at which consistently minimum reflectance values are obtained for many different shade depths. Other wavelengths near 660 nm also are appropriate to use. A practical form of the Kubelka-Munk equation can be used to measure depth of shade². The equation is given by

$$\frac{K}{S} = \frac{[1 - (R_c - R_s)]^2}{2(R_c - R_s)} - \frac{[1 - (R_0 - R_s)]^2}{2(R_0 - R_s)} \quad \dots (1)$$

where R_c is the fractional reflectance of the substrate that contains a given concentration of indigo; R_0 , the reflectance of a mock dyed substrate that contains no dye, and R_s , the reflectance of a substrate containing an infinite concentration of dye, i.e. a concentration so high that further increase in concentration does not result in a further lowering of reflectance at the wavelength of minimum reflectance. As is well known that, with-

in a commercially reasonable concentration range, K/S is linearly proportional to concentration of dye in a textile substrate when the dye is uniformly distributed in the cross-section of the substrate. The relationship is given by:

$$\frac{K}{S} = aC \quad \dots (2)$$

where a is the reflectance absorptivity coefficient; and C , the concentration of indigo in the dyed knitted tube. It has been estimated that the value of a for dyeings in which indigo is uniformly distributed in the cross-section of the substrate is approximately 30-40 when the dye concentration is expressed as grams of indigo per 100 g of fiber³.

2.5 Dye Concentration Measurements

Small circular samples were punched out of each dyed knit tube and repeatedly extracted with warm (80°C) pyridine until all the dye was removed. The concentration of indigo in each cotton tube (grams indigo/100 g fiber) was then estimated colorimetrically from known concentration/absorbance curves and the dried sample weights.

3 Results and Discussion

3.1 Shade Depth at Constant Dye bath Concentration but Variable pH

Early in the investigation rather strange results were observed when dyeing cotton tubing in infinite dye baths that contained a constant concentration of dye but were adjusted to different pH. For example, typical results that were obtained from dyeings made in infinite dye baths containing 1.0 g/L indigo but four different dye bath pH are shown in Fig. 1. It is observed from this figure that the shade depth of the dyed tubing, expressed as K/S , increases as the dye bath pH decreases from 13 to 11 and then decreases at the lowest pH of 10. The concentration of dye in the various dyeings was determined by pyridine extraction and is given on the bars in the figure. It is observed that the measured concentration of dye (g/100 g fibre) increases as the dye bath pH decreases. However, when the concentration of dye found for each dyeing is used in Eq. (2) along with the estimated reflectance absorptivity coefficient of 40, the calculated values of K/S are found to be much lower than the measured K/S values. It is now understood that the difference between the measured values of K/S and those calculated by the use of Eq. (2) is due to the fai-

ture of Eq. (2) for substrates in which dye is not uniformly distributed in the substrate cross-section. Microscopy revealed that the extent of ring dyeing of the yarns increased as the dyebath pH decreased from 13 to 11, with the extent of ring dyeing at pH 10 being about the same as that at pH 11. In the case of ring dyed denim yarn, an expression has been found that more accurately describes the relationships between K/S , dye content, and penetration⁴:

$$\frac{K}{S} = a \left[\frac{C}{2p - p^2} \right] \quad \dots (3)$$

where a is the "true" reflectance absorptivity coefficient for uniformly distributed dye; C , the dye concentration in the total cross-section of the denim yarn, expressed as grams of dye per 100 g of yarn; and p , the fractional penetration of the yarn by dye, i.e. a parameter that takes into account the extent of ring dyeing of the denim yarn.

As shown in Fig. 2, when Eq. (3) is used to estimate the shade depth, a much closer agreement with measured values is obtained, at least for dyebath pH of 13, 12 and 11. At pH 10, the agreement is not good. The values of p , roughly estimated by microscopy, for the pH values of 13-10 are respectively 0.65, 0.33, 0.20 and 0.20. Since the measured concentration of dye in the tubing dyed at pH 10 is higher than that made at pH 11, the lower than expected K/S value found for the dyeing at pH 10 must be the result of a lack of contribution to color depth of dye present on the dyed yarn. In fact, microscopy revealed crystalline particles of indigo present between fibers in the yarn interior. Such dye would ofcourse be extracted during the determination of fixed dye content, but would not contribute to shade depth.

3.2 Effect of Dyebath pH on Substantivity

Fig. 1 shows that the substantivity of indigo for cotton fiber is highly pH dependent. Technical sorption isotherms or distribution coefficients found by the use of the disclosed dyeing technique at room temperature are given in Fig. 3. Although the technical values are found to be approximately linear for the dyeing technique used, it is known that true equilibrium sorption isotherms for indigo on cotton fiber follow the Freundlich form⁵. It is clear that the substantivity of indigo for cotton fiber increases as the dyebath pH decreases up to a point. For example, Leupin and Hartmark observed about fifty years ago that a pH of about 9.9 is necessary to maintain indigo in solution form⁶. In addition, the work⁷ of Rus-

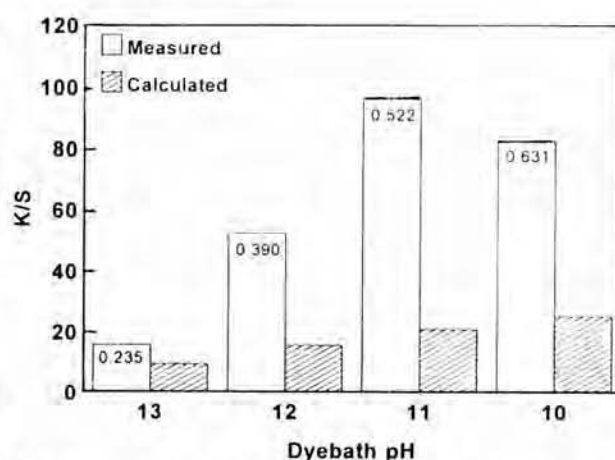


Fig. 1—Measured and calculated values of K/S for dyeings conducted with 1 g/L indigo from infinite dyebaths. Calculated values of K/S made using Eq. (2) and a reflectance absorptivity coefficient of 40

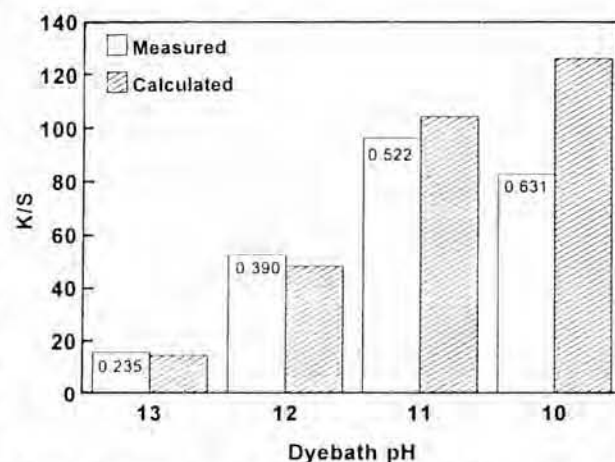


Fig. 2—Measured and calculated values of K/S for dyeings conducted with 1 g/L indigo from infinite dyebaths. Calculated values of K/S made using Eq. (3), measured values of "p", and a reflectance absorptivity coefficient of 40

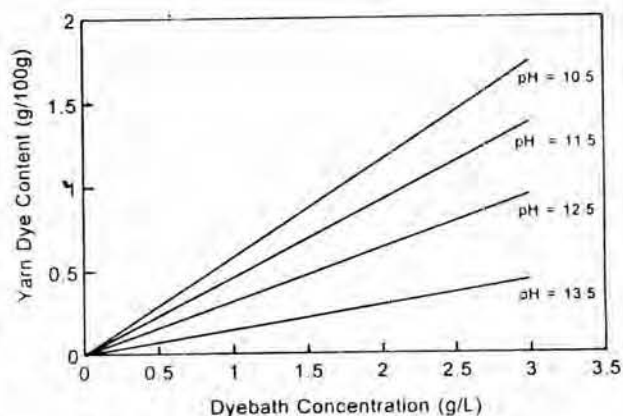


Fig. 3—Technical distribution coefficients for indigo/cotton denim yarn as a function of dyebath pH

sian scientists in the area of dyeing protein fibers at low pH and the work⁸ on the effect of pH on the presence of hydrolyzed indigo suggest that the minimum pH found by Leupin and Hartmark represents only a roughly approximate lower limit. The fractional amount of each ionic species of indigo as a function of pH has been estimated from a knowledge of the apparent pK_a values of the two-step ionization of indigo⁹.

So far, the experimental work has revealed that a dyebath pH of about 11 is optimum from the standpoint of maximizing ring dyeing and color yield. This finding is consistent with the pH reported by Greer and Turner that is present in an innovative Japanese indigo dyeing range¹⁰. According to the authors, the unique quality of the machine is that "five dips and oxidation steps take place in each of the five boxes". The pH of the bath in the unique Japanese machine is a non-conventional 11.2-11.3.

The UGA investigations have established that there is a solid scientific basis for the empirically observed relationship between pH and resulting color yield¹¹. At a pH of about 11, indigo exists as a mono-ionic form having a greater substantivity for cotton than does the di-ionic form of indigo that exists at much higher pH . In addition, at pH 11, cotton cellulose is hardly ionized at all, and this fact minimizes ionic repulsion between negatively charged dye and fiber that occurs at higher pH . The lower level of ionic repulsion between fiber and dye contributes to an even greater substantivity of indigo for cotton. Associated with the increased substantivity that occurs at pH 11 is an increased strike rate of the dye for the fibers in the yarn surface. The increased strike rate results in a more ring-dyed yarn than that which would be obtained with lower strike rates found at higher dyebath pH . With the increasing ring dyeing, there is greater shade depth for a given amount of dye fixed per unit weight of yarn.

Even though modern research has indicated the value of using a dyebath pH of about 11, many indigo dyers continue to employ a dyebath pH range of 12-13 simply because such a pH range is easily obtained by the use of safe concentrations of the conventional alkali sodium hydroxide. Commercial dyers who have attempted to obtain the more desirable dyebath pH of 11 by the use of a NaOH deficiency have experienced difficulty. Many have discovered that the technique is extremely dangerous, producing intense shade variation and streaking. As shown in Fig. 4, the concentration of sodium hydroxide normally used by indigo dyers (2-4 g/L) produces a rather limited

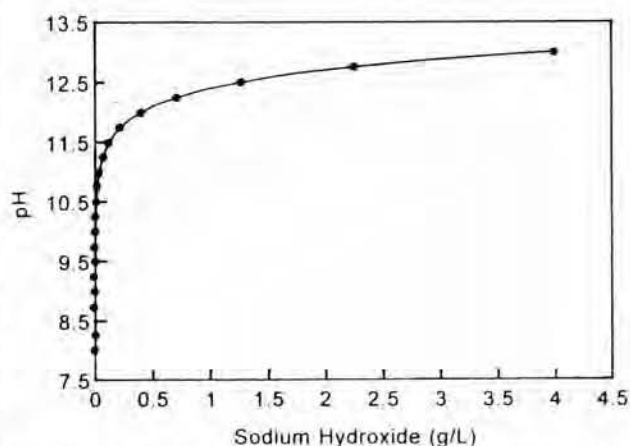


Fig. 4— pH of unbuffered sodium hydroxide solutions as a function of concentration

pH response to small changes in NaOH concentration. However, as shown in the figure, when very low levels of NaOH are used in an attempt to achieve a dyebath pH of 11, small changes in NaOH concentration lead to very large changes in dyebath pH . It is critical that a truly buffered alkaline system be used to achieve the optimum pH of 11. Dyebath alkalinity must be maintained at a safe level, while dyebath pH is controlled at the lower, optimum level. Simply using a deficiency of sodium hydroxide in the dyebath to obtain a pH of 11 is fraught with danger and should not be attempted.

3.3 Washdown Characteristics of Modern Denim

Denim garments that are produced from denim yarn dyed at pH 11 tend to wash down more quickly during "stone-washing" and other laundering processes designed to produce the popular worn or distressed look. It is known that the reason for this behavior is the increased level of ring dyeing found in yarns dyed at pH 11. Such yarns contain much less dye to produce a given initial shade depth than do yarns dyed at conventional pH values. Less dye, therefore, needs to be removed to obtain the desired fashion look.

4 Conclusion

The ancient art of indigo dyeing slowly is being transformed into a much more predictable process. Much progress has been made in understanding the important variables that influence dye uptake, color yield, and washdown characteristics of denim fabric, but much more is to be learnt. Although the modern forms of denim are being made possible through a greater level of technical control of the dyeing process, it must be recognized that dyers have successfully produced

indigo dyed denim yarn for thousands of years. It is hoped that as the art of indigo dyeing is replaced by scientific methods, appreciation of the artistic elements in indigo dyeing and the significant contributions made by traditional dyers will not be forgotten.

References

- 1 BASF, *Technical Information*, T1/T 017, November 1987 (AJM) 13.
- 2 Kuehni R G, *Computer colorant formulation* (Lexington Books, Lexington, Massachusetts), 1975, 11.
- 3 Annis P A *et al.*, *Can Text J*, 108 (4) (May 1991) 20.
- 4 Etters J N, *Am Dyest Rep*, 81 (3) (1992) 17.
- 5 Etters J N & Hou M, *Text Res J*, 61 (12) (1991) 773.
- 6 Leupin O & Hartmark B, *Melliand Textilber*, 24 (1943) 394.
- 7 Golomb L M & Shalimova G V, *Technol Text Ind*, 48 (5) (1965) 105.
- 8 Mishchenko A V & Artym M I, *Text Ind USSR*, 54 (4) (1971) 95.
- 9 Etters J N, *J Soc Dyers Colour*, 109 (7/8) (1993) 251.
- 10 Greer J A & Turner G R, *Text Chem Color*, 15 (6) (1983) 101.
- 11 Etters J N, *Text Chem Color*, 27 (2) (1995) 17.