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Indigo Ring Dyeing of Cotton Warp Yarns for Denim Fabric

Mohammad Gias Uddin

Department of Textile Engineering, Ahsanullah University of Science & Technology, Dhaka-1208, Bangladesh
*Corresponding Author: giasdtt@gmail.com

Abstract Denim is the worldwide much popular form of fabric. A faded stylish look can be achieved due to ring dyeing of warp yarns of denim garments. This effect occurs naturally in the process of indigo dyeing. Stonewashed cotton fabrics with finest washed appearance are generally woven from ring spun yarns which are ring dyed. This paper primarily focuses on the concept of ring dyeing, its depth and significance as well as the important ionic forms of leucoindigo derivatives suitable for uniform ring dyeing. The measurement and control of the dyebath pH is very important in case of achieving desired uniform ring dyeing effect. It has been discussed when the pH of the dye bath is decreased from 13 to 11, the denim yarn progressively becomes more ring-dyed. The paper also focuses on the continuous process of indigo dyeing of denim fabric. Again, the paper emphasizes on the appropriate concentration of dyebath and the dipping time to ensure an even and optimal ring effect by dyeing in several passages. Increasing dye concentration assists in building up shade depth, but the use of too concentrated a dye bath is not effective for deep shades as it results in poor rubbing fastness and more reddish, duller shade. Later, the paper discusses about the typical oxidation-reduction potential (ORP) range, its importance and how it is changed dependent upon the desired final shade. Next, the paper shows how the mechanical parameters such as roller numbers and diameter, squeezing, dyeing speed, flow profile etc. influence on the dyestuff exchange and the dye bath stability. Finally, the paper highlights the indigo dyeing process in a nitrogen atmosphere to reduce the consumption of sodium hydrosulphite in dyeing as it is oxidized by consuming NaOH when atmospheric oxygen is present in the alkaline medium. As shade variation is frequently occurring problems in ring dyeing, this atmosphere is essential to eliminate shade variation throughout the dyeing set and to be able to reproduce the same shade and dye quality on subsequent dye lots.

Keywords Ring Dyeing, Thinner Ring Effect, Denim, Indigo, ORP, Nitrogen Atmosphere

1. Introduction

Indigo dye has been the world's most important and popular dyestuff for almost 5,000 years. "The older, the better look" has been the philosophy of the blue jeans industry. Blue jeans are dark blue when they are first produced. As they are worn and washed, the abraded places become a different color than the rest. The weft yarns of denim fabric are usually white, while the warp yarns are indigo-dyed. The whiteness of the inner weft emerges as the abrasion starts, and the desired 'used effect' is achieved. The 'used effect' is the most important feature of denim fabric. Thus blue-dyed warps wash down to an attractive blue without staining the white weft. This natural worn-out or wash-out effect only happens with denim fabric produced with warp yarns that has ring effect dyeing (i.e., perimeter dyeing), dyed with indigoid vat dye. In general, ring dyeing refers to lack of full penetration of dye all the way to the core of the yarn. Maximum dyes are stained on to the fiber surface that form layer of dyes there while only a few dyes are partially diffused to the interior of fiber [1]. Thus around the fiber a ring-like appearance of the dye can be viewed cross-sectionally, hence the term "ring dyed". This ring-like dye's layer opposes further dye diffusion. The dyed warp yarns are then woven with the un-dyed yarns, which are called filling yarns (or weft). This dyeing leads to poor washing and rubbing fastness of dyed fabric, as well as other staining-related fastness properties. When abraded, either by normal wear or through a garment finishing technique, the white core becomes exposed and affects the overall color and appearance of the garment, giving denim a unique appearance that improves with age. Hence indigo ring dyeing is a unique process that makes denim special and distinguishes denim operations from all other types of cotton fabrics. No other method of cotton textile dyeing generally requires the multiple application of dye to achieve a dark color, thousands of liters of dye bath, slow production speeds and extremes of color variation and color-fastness. Therefore, various aspects of indogo ring dyeing of cotton warps need to be focused accurately.

2. Depth of Penetration

Chemical equilibrium of the dyebath in indigo dyeing is very important which maximizes the attraction between the cellulosic fibers and the dye, leading to optimal ring dyed yarns with clean white centre. Optimal ring dyeing effect can be shown through computer simulated cross-sections (See Figure 1(a) and 1(b)).

2.1. Thinner Ring Dyeing

16-20% penetration i.e., the depth of indigo into the surface fibers of the yarn is at most about 20%, leaving an undyed core of about 80% of the overall cross-section of the yarn [See Figure 1. (a)].

2.2. Deeper Ring Dyeing

30-40% penetration i.e., the depth of indigo into the surface fibers of the yarn is at most about 40%, leaving an undyed core of about 60% of the overall cross-section of the yarn [See Figure 1. (b)].

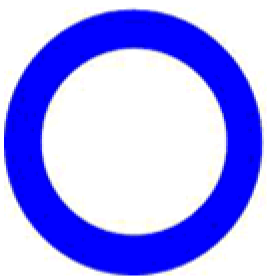


Figure 1 (a). Thinner ring;

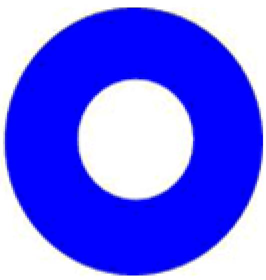


Figure 1 (b). Deeper ring

2.3. Advantages of Thinner Ring Dyeing

A thinner ring dyeing gives the following advantages:

a. Dye savings because of high color yield for a given shade.

b. Savings in wash-down cycle time to match a given wash-down standard.

c. Reduced dye wash-off in the indigo dye house and the laundry due to less dye usage and improved fixation of indigo.

d. The thinner the dyed ring in the fibers and the yarn bundle, the lesser the abrasion is needed to achieve the stonewashed look of dyed areas and white areas where abrasion has occurred. The amount of white undyed fiber showing on the surface of the fabric is directly proportional to the amount of dye and fiber removed by abrasion. The larger white core and the thinner dye ring allowed the abrasion from the stonewashing to more quickly wear away more of the thinner dye ring, permitting more of the undyed core fibers to intermingle with dyed ones to show the lighter shade after stonewashing.

3. Cross-sections of Indigo Ring Dyeing

The computerized mathematical dye bath model provides the correct chemical balance for a given set of dyeing parameters. Optimum wetting and optimum equilibrium conditions are required for the indigo dye bath to achieve maximum dye affinity, consistent ring dyeing and consistent shade, end-to-end, beam-to-beam, and day-to-day.

Cross-section micrographs of the dyed fibers revealed the presence of "ring-dyeing". If the cross-sections of ring dyed yarn are taken at different points along the length of the yarn, then thinner ring dyed yarns show circular rings with even depth of penetration [Figure 2 (a)] whereas in deeper ring dyeing, the rings are elliptical and the depth of penetration varies [Figure 2 (b)]. Variation in the depth of penetration results in non-uniform wash-down.

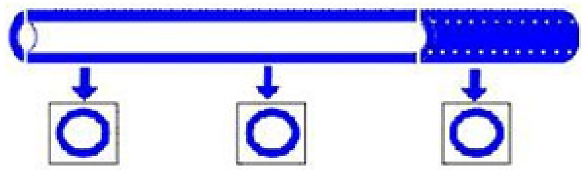


Figure 2 (a). Thinner and Uniform Ring Effect

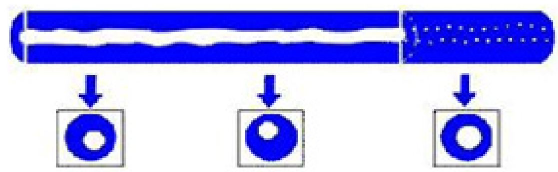


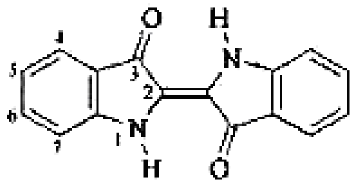
Figure 2 (b). Deeper and Random Ring Effect

4. Suitable Forms of Indigo and Effect of pH For Uniform Ring Dyeing

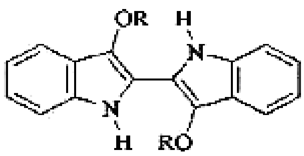
Since leuco indigo is a weak acid, the pH of the medium may greatly affect the extent of its ionisation, so that the substantivity of the dye to cotton fiber changes. It is understood that higher substantivity of dye for cotton fiber can be achieved at about pH 11. Therefore, the degree of ring dyeing of the denim yarn would be higher at this pH than at the more conventional pH region of 12–13.

In order to control the pH values for dyeing, a pH buffer may be used, with the dyebath pH being adjusted with phosphoric acid. Using this method of controlling the pH, the changes in the dyebath pH before and after dyeing with five dips were within 0.15.

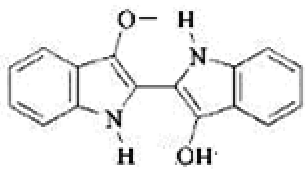
Depending on dyebath pH, reduced indigo can exist in three forms: as nonionic enolic acid leuco compound, the mono-phenolate anion or bis-phenolate anion as shown in Figure 3-7 [1]. Mono-phenolate moiety is much more soluble than the acid leuco form and more substantive than doubly charged bis-phenolate. Its amount reaches a maximum at pH 10.5-11.5 and color yield with the desired ring-dyeing effect correlates closely with its fractional amount [1, 3]. Measurement and control of the dyebath pH can be used to maintain either form of phenolate, in order to produce the desired effect.



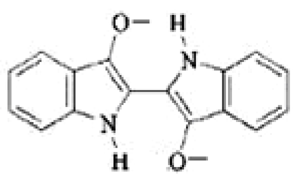
Indigo (3)



R=H: Leuco indigo, indigo white (4)
R=Na: Leuco indigo disodium salt, indigo vat (5)



Mono-ionic form: Soluble/ High substantivity than di-ionic form(6)



Di-ionic form: Highly soluble/Low substantivity than mono-ionic form(7)

Figure 3-7. Forms of Indigo [2]

The higher apparent affinity of the dye at the pH range 11.1-11.3 at 25^0C is correlated with the mono-ionic form of indigo. Mono-ionic indigo has higher affinity for cotton fiber, and therefore produces:

a. Greater ring dyeing effect due to less dye penetration into the fiber resulting into thinner dyed ring.
b. Less dye use due to more surface dyeing and less dye penetration.
c. More uniform dye rings due to lower depth of dye penetration.

Careful buffering of the dye bath pH can be an effective way of conserving indigo and achieving more reproducible dyeing [3]. Microscopy reveals that for indigo dyeing, the cross-section of the resulting dyed cotton yarn depends on the pH of the bath. Generally when the pH of the dye bath is decreased from 13 to 11, the denim yarn progressively becomes more ring-dyed. Associated with the increasing ring dyeing, more color yield is obtained making the wash-down process easier. At pH higher than 11.5, dye penetration will be less and wash down characteristics are also poor. Again, concentrated alkali at elevated temperature leads to decomposition of indigo with formation of aniline, N-methylaniline and anthraanilic acid.

In general, higher pH or caustic concentration results in redder and lighter shades while lower pH or caustic concentration results in greener and darker shades.

5. Yarns Used for Indigo Dyeing

Originally all denim used ring spun (RS) yarns, but in the seventies, a lot of ring spinning for denim was replaced due to the lower cost and faster process of open-end (OE) spinning, called rotor spinning. The ring spun yarn produced is more uneven than OE spun yarn, but it is stronger and smoother to the touch because the fibers are more parallel. Again, OE spun yarn is not as compact as ring spun yarn. It is more difficult to achieve ring effect for the OE spun yarn due to looser in cross section and therefore the indigo dye penetrates into the OE yarn more deeply, increasing the time needed to achieve the desired stone washing result as is obtained more easily with a denim fabric made of ring spun yarn. The yarns in denim are relatively coarse, the count of yarn ranges from 6-16 Ne, most widely 7-12 Ne. For slub yarns, 9-20 Ne. One can have open-end yarn and ring spun yarn in either warp or weft (OE X RS, RS x OE) or both warp and weft (OE x OE) or (RS x RS).

6. Indigo Dyeing Process

The dyeing technique like vat dyeing involves the following three steps:

a. Dissolving of the dye by reduction in alkaline medium;
b. Dyeing in the vat and
c. Oxidation on exposure to air.

The first step, dissolving the dye, is now omitted using stock solutions of pre-reduced indigo (leucoindigo). The dyeing equipment consists essentially of a series of open wash boxes equipped with multiple upper and lower rolls, around which the goods are led in serpentine path, with squeeze rolls between the boxes [4]. Above the middle set 6 boxes skying rolls are provided. After wetting out the goods in first set of boxes, they pass at about 20-30 m/min to the middle set of boxes and are immersed in leuco indigo dye liquors for 20 to 30 seconds, squeezed to about 100% wet pickup and skied for about two minutes after leaving the boxes [1]. A very long air passage (Skying up to two floors high) is necessary to ensure the complete oxidation of dye. These last three steps are repeated in successive boxes, as many times as desired, up to about six. In each box some more leuco indigo is imbibed, followed by air oxidation, and indigo pigment is gradually built up, primarily on the fiber surfaces. Rinsing at ambient temperatures in 2/3 rinsing baths after oxidation is normally adequate to remove alkali and unoxidised leuco compound. The dip tanks are coupled to keep the dyebath composition exactly same.

Though formerly 6 dye boxes were used, now rope dyeing plants are equipped with 8 boxes as for the same depth of shade, the indigo bath concentration is lower. This results in the formation of finer layers of indigo on the yarn. Two advantages [5] are gained from this, i.e.

1. Less indigo penetrates into the interior of the yarns in the first dipping operation which is consistent with the desired high proportion of white in the core of the yarn.
2. The finer layers of indigo result in somewhat better color fastness to rubbing and washing.

A typical recipe for dye-liquor [1, 3]:

Caustic soda (27% by weight), 5 ml/l
Sodium hydrosulphite, 1.5 g/l
Stock vat, 62.5 ml/l

The stock vat is composed of the following:

Indigo Pure (BASF, C.I. Vat Blue 1), 80 g/l
Dispersing agent (Setamol WS), 4 g/l
Wetting agent, 1 g/l
Caustic soda (27% by weight), 130 ml/l
Sodium hydrosulphite, 60 g/l
Sequestering agent (Sodiumhexametaphosphate), 2 g/l

Generally the stock vat is prepared by mixing indigo dye with 0.7-0.8 time's caustic soda (solid) and 0.8-0.9 time's sodium hydrosulphite [1]. The vatting is done at 60-65^{0}C for 15-30 minutes and dyeing is done at room temperature [1]. The content of reducing agent and alkali in the dyebaths must be checked at regular intervals to determine what quantities are necessary.

In their leuco form, most vat dyes are distinguished by a high affinity to the fibers and therefore by high dye bath exhaustion of approximately 70 to 95%. In contrast thereto, leucoindigo is only absorbed by the fiber to approximately 10 to 20% in a single dyeing process. Because of this low dye bath exhaustion, dyeing with indigo by means of a discontinuous exhaustion process (dyeing from the bath) is problematical. As for the poor substantiviity of leuco indigo for cellulose, only pale depths are obtainable by exhaust dyeing procedures.

The difference in method of dyeing with indigo and that of dyeing with other vat dyes is that with indigo the fiber is immersed and oxidised by the leuco several times until the required shade is obtained because of the low affinity of indigo for cotton, but other vat dyes are absorbed in just one phase [6].

7. Effects of Dye Concentration and Number of Dips

In practice, the concentration of indigo dye for dyeing denim yarn varies depending on the requirement of shade depth and the number of dips adopted. In most cases it is in the range of 2 to 6 g/l [7]. Increasing dye concentration assists in building up shade depth, but the use of too concentrated a dye bath is not effective for deep shades as it results in poor rubbing fastness. Dye is applied to the substrate layer by layer to give deep dyeing with a relatively low rubbing fastness. In denim, the final effect is judged after wash down and the effect is achieved by a ring dyeing and not by a full penetration of the yarn by the dyestuff. Generally the more reddish, duller shade of indigo dyeing is obtained from baths that contain a relatively high indigo concentration. Indigo dye is yellow when in its soluble form, as the leuco oxidizes it turns greenish, and then is transformed gradually to blue. If it is not clear and yellow, or if it turns to green very quickly, a small amount of hydrosulphite must be added. This is the simplest method for controlling the vatting of indigo dyes.

8. Reaction Time

Longer the dipping time, more will be the penetration and lesser will be the ring dyeing effect. Again, at very short reaction time, an adequate liquor exchange (i.e. the amount of chemicals consumed and replaced by fresh addition of reduced indigo) is not assured. This has a negative influence on dyeing and depth of dye penetration. In addition to this the time available for diffusion of dyestuff until oxidation commences is too short. To ensure an even and optimal ring effect by dyeing in several passages, the reaction time should be 20-30 seconds for each vat [7] (e.g. at a speed of 20m/min for a reaction time of 10 seconds, the immersion path should be maximum 3.3 meters). A reaction time exceeding 60 seconds should be avoided as the amount of dyestuff again get reduced and released may again supersede that of additionally take up dyestuff, resulting in higher shades.

9. Importance of High Concentration of Hydrosulphite

The clearest shades with minimum reddish streaks are observed by relatively high concentration of sodium hydrosulphite (Sodium dithionite, $Na_2S_2O_4$). After indigo vatting, an extra amount of sodium hydrosulphite should be added to the dyebath to maintain leuco indigo stability because sodium dithionite is sensitive to atmospheric oxygen. Sodium dithionite is oxidized by consuming NaOH when atmospheric oxygen is present in the alkaline medium. On the other side, with lack of hydrosulphite, the leuco indigo is less dissolved and thereby adheres to a greater extent to the fibers. With lack of hydrosulphite furthermore, the amount of unreduced dyestuff by oxidation at the upper level of the liquor and through activation of unfixed dyestuff, gets separated from the fibrous material would constantly rise as the reducing agent for creating leuco form would be missing.

Under these circumstances, a reddish bronze like shade results due to dispersion of not reduced dyestuff in the yarn. The minimum proportion of hydrosulphite for dye liquor should be around 1.3 to 1.5 gpl in case of rope dyeing and 3-4 gpl in case of sheet dyeing. An excess of required hydrosulphite results in irregular dyeing and increases ecological damage.

Also to avoid the lack of hydrosulphite or indigo at certain places in the immersion vat, the whole quantity of the liquor should be circulated 2-3 times every hour.

More hydrose = Greenish effect;
Less hydrose = Reddish effect.

10. Oxidation and Reduction Potential

The oxidation-reduction potential (ORP) must be maintained at a low enough level to keep the indigo dye in the reduced (leuco) form for solubility [8]. The ORP of the bath can also affect the final shade. The typical ORP range is -760 to -860 millivolts, with the actual target ORP dependent upon the desired final shade [8]. The hydrosulphite dosing may be done by controlling ORP of dyebath solution with the mV meter. When all the sodium hydrosulphite has been consumed, the potential undergoes a sudden increase to the point which is at about –695 mV. As indigo is insoluble in the aqueous dyebath, the potential of the solution is therefore the potential of the leuco indigo at this stage, and the potential remains constant for some time. When all the leuco indigo molecules are oxidized, the potential of the solution rises rapidly in the positive direction with the addition of oxidizing agent.

11. Mechanical Parameters

Basically the Denim dyeing process is characterized by a liquor– or dyestuff exchange where a difference is made between

- Dyestuff exchange in textile material (migration)
- Dyestuff exchange in boundary layer field (diffusion)
- Dyestuff exchange in the field of liquor flow between machine and material.

The mechanical parameters which have influence on the dyestuff exchange and the dye bath stability can be determined as follows:

1. The number of rollers

High number of roller = high exchange;
= low exchange of bath concentration.
Small roller diameter = low dyestuff exchange;
= bad material guiding.

2. Immersion time

Long immersion time = high dyestuff exchange;
Short immersion time = low dyestuff exchange.

3. Immersion liquor = intermediate pair of squeezing rollers;

With squeezing = high dyestuff exchange;
Without squeezing = low dyestuff exchange.

4. Dyeing speed

High speed = high dyestuff exchange;
Low speed = low dyestuff exchange.

5. Flow profile

High liquor flow = high dyestuff exchange;
Low liquor flow = low dyestuff exchange

All these parameters have an important influence on material guiding and on the dyeing result.

12. Nitrogen Atmosphere in Indigo Dyeing [9]

12.1 Nitrogen Supply Setup

For an indigo dyeing range installation with 6 dye boxes the nitrogen supply setup including the nitrogen generator may be used. The produced nitrogen generally contains less than 2% oxygen this is sufficiently pure for the dyeing process. The distribution and regulation of the nitrogen flow to the dye boxes, indigo stock solution storage tank and indigo dye mix tank, is controlled by air flow meters with a minimum/maximum capacity from 10-70 l/min. The required nitrogen flow is set with aid of a gaseous oxygen measuring detector. Dyeing indigo in a nitrogen atmosphere has the main advantage of being able to reduce the consumption of hydrosulphite in the dyeing process. This can amount up to 20-40% less hydrosulphite and caustic soda consumption compared to a conventional dye range.

12.2 Shade Stability

The state of the vatted indigo and the required over feed on hydrosulphite during the dyeing process, are kept constant and reproducible at a constant level with the aid of nitrogen flooded baths. This is essential to eliminate shade variations throughout the dyeing set and to be able to reproduce the same shade and dye quality on subsequent dye lots.

12.3 Influence of Environmental Temperature Variations

The nitrogen technology reduces the instability that can be caused by environmental temperature changes. Although the dye liquid temperatures in the dyebaths are kept constant via indirect heating and the storage tanks are equipped with a water cooling ring, the nitrogen ensures a smaller diffusion of oxygen, which can absorb and oxidize the free hydrosulphite in the dyeing solution. In this case the nitrogen stabilizes the dyeing process when serious environmental temperature changes take place, maintaining a constant dye bath quality during the indigo dyeing processes.

In an open uncovered atmosphere the oxidation of the dye liquid would be immense and the dyeing process uncontrollable. The situation in a nitrogen atmosphere permits high liquid turbulences and exchange rates, thus increasing the availability of indigo for the dyeing process, hence increasing the readiness of the indigo to exhaust into the yarn.

13. Conclusions

This paper deals with the basic concept of ring dyeing with indigo dyes for denim fabrics and garments. The concept is much popular nowadays in denim industries but not clears to all. Uniform thinner ring formation leads to savings in dyes and wash-down cycle time as well as reduction of dye wash-off cycle as discussed. As the warp yarn dyeing process using indigo dye often has the problem of color variation [10], the optimum control of different parameters like pH of the dyebath, suitable forms of indigo molecule structure, concentration of dyebath and number of dips, reaction time, concentration of hydrosulphite, ORP range and mechanical settings can produce finer ring effect with no or minimal shade variation. For this purpose, the amount of indigo fixed per dip is important. Most of the shade variations problems can be associated due the change of bath pH. It needs to be remembered that mono-ionic indigo form is more substantive towards cotton and its maximum amount found at around pH 11, which should be carefully controlled. As a result, thinner and uniform ring effect can be possible. Moreover, indigo ring dyeing in a nitrogen atmosphere has the main advantage of being able to reduce the consumption of hydrosulphite in the dyeing process. It can help in getting shade reproducibility as well. Overall, proper pretreatment of warp yarns before dyeing and uniform size pickup after dyeing are necessary for controlled ring dyeing.

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