Advances In Indigo Dyeing: Implications for the Dyer, Apparel Manufacturer and Environment

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Universal win-win scenarios rarely are associated with technological progress in dyeing. It is more likely that a breakthrough in dyeing technology produces an improvement in one area at the expense of some other area. For example, a technological advance may result in an improvement in quality control—but at the expense of dyeing costs. Another technological improvement may result in reduction of dyeing costs—but at the expense of the environment. Technological advancement in another area may result in less environmental contamination—but at the expense of both dyeing costs and quality control. Nevertheless, physicochemical progress that currently is being made at the University of Georgia in indigo dyeing and in associated washdown characteristics of denim apparel reveals that win-win scenarios are indeed possible. These scenarios are evident when the ionic form of both indigo dye and cotton substrate in the dyebath is controlled through effective buffering of the dyebath pH by the use of specially formulated alkalies.

ABSTRACT

Implementation of new technological advances in indigo dyeing can result in improved quality control in both dyeing of denim yarn and laundering of denim garments, lower dyeing and laundering costs and reduced pollution. Advances that are made possible by control of the ionic form of indigo dye and cotton substrate in the dyebath are shown to provide both the denim dyer and the garment manufacturer benefits that previously were not attainable by the use of conventional indigo dyeing techniques.

KEY TERMS

Denim
Dyeing
Indigo
Sulfur Dyes

The present discussion traces the development of the highly successful technique of pH-controlled indigo dyeing of cotton denim yarn from its serendipitous discovery by the writer at Dan River Inc. in the mid 1970s to its present, rapidly expanding international use. It is hoped that the discussion will serve to illustrate how very much the ancient art of indigo dyeing has been transformed into a science. In addition, it is anticipated that the discussion will help to convince those who have practiced the art of indigo dyeing for years that even they can benefit from a more fundamental understanding of the dyeing process. Those who are involved in denim yarn dyeing and denim garment laundering cannot remain complacent. We all have much to learn from the advances that are being made.

Discovery

Discovery often is driven by need, and in the mid 1970s there was a pressing need to find a method for maintaining production of dyed denim fabric in the face of an apparently severe shortage of indigo dye. Dyers who faced the indigo shortage found that by adding inexpensive black or blue sulfur dyes to the dyebath less indigo was needed to produce a given shade. But even the technique of using sulfur dye as an extender was not without at least some disadvantage. Addition of sulfur blue or black dye to the indigo dyebath did permit less indigo to be used, resulting in tremendous cost savings. However, when too much of the sulfur dye was added to the dyebath, the resulting denim garments did not wash down to the attractive blue indigo shade that was desired. It was inevitable that some dyers chose to abuse the use of sulfur dye in the indigo dyebath—to the extent that the resulting denim garments washed down to a completely unsatisfactory grey color.

The use of excessive amounts of sulfur dye became such a problem in industry that a technique was developed for determining the fraction of the total depth of shade that was due to indigo and how much was due to sulfur dye in finished denim fabric. The technique uses *K/S* values that have been integrated over the wavelength range of 400 to 700 nm for reflectance readings obtained on original and on pyridine extracted denim fabric.[1] Since pyridine extraction removes only the indigo—not the sulfur dye, use of the technique permits an evaluation of the indigo/sulfur fractional shade depth ratio for a given overall depth of shade. The technique therefore can be used as part of a larger quality control program.

Although the judicious use of sulfur dye could be effective in attempts to use less indigo, it was decided to study purely empirical indigo conservation research efforts in other areas. Numerous indigo dyeing experiments were conducted using a wide range of alkalies in the dyebath and eventually the discovery was that a combination of sodium hydroxide and sodium carbonate was highly effective.[2] When the two alkalies were used together in place of higher concentrations of sodium hydroxide alone, the indigo concentration in the dyebath could be lowered significantly, producing the same shade at a much lower cost. Indeed, the cost savings were astonishingly high when the newly discovered technique was used in combination with a small amount of sulfur dye in the dyebath.

Even though the alkali system that was empirically developed at Dan River permitted the company to both withstand the apparent indigo shortage and to save hundreds of thousands of dollars in dyeing costs, the system was not stable; the dyebath pH drifted up and down, producing too much shading variation and perhaps even streaking. The fundamental cause of the problem at the time was unknown; yet, a solution to the problem was not pursued in view of even more compelling difficulties in other production areas. The newly developed alkali system was dropped after about one year in production use.

Expanded Research

While the author was research committee chairman of the Southeastern Section of AATCC in 1988-1989, the elementary empirical indigo dyeing research was expanded by the section's research committee into a first place winning ITPC paper.[3] It was revealed that the reason for the instability of the alkali system used by Dan River was nothing more than that the system was not truly buffered at a given level of alkalinity. By the use of specially formulated, buffered alkalies that were provided to the committee by The Virkler Co., the committee was able to conduct a series of experiments that shed much light on the indigo dyeing process. In fact, the work of the committee not only revealed the pH range necessary for the greatest color yield, but also provided a scientific basis for understanding why dyebath pH has such a profound influence on color yield. The scientific work that the committee began is being continued at the University of Georgia.

Distribution of Indigo

Microscopy has revealed[4] that for indigo dyebaths having the same level of alkalinity (e.g., expressed as KOH equivalence) but buffered to different pH's, the resulting distribution of dye in the cross-section of the resulting dyed cotton denim yarn is approximated roughly by the schematic drawing in Fig. 1. While maintaining the same level of alkalinity, Fig. 1 shows that as the buffered pH of the dyebath is decreased from about 13 to 11, the denim yarn progressively becomes more and more ring dyed; i.e., more of the cotton fibers in the exterior regions of the yarn are dyed at the expense of fibers in the yarn interior. Associated with the increasing ring dyeing is more and more color yield; i.e., more shade depth is obtained with a given quantity of fixed dye per unit weight of yarn.

The phenomenon of increasing color yield that is observed with increasing ring dyeing is easy to understand. When a given concentration of dye (expressed as percent on the weight of the yarn) is located in progressively fewer and fewer fibers, the concentration of dye in each of the dyed fibers is increased more and more. Reflectance of light from the surface of the dyed yarn therefore is lowered with increasing ring dyeing so long as the dyed ring of fibers does not become translucent. Translucence will occur only with extremely low concentrations of dye that are associated with pastel shades. The relationship between depth of shade (*K/S*) and ring dyeing for a given concentration of dye may be approximated by the following:[5]

$$K/S=a_t[c/(2p-p^2)] \qquad \text{Eq. 1}$$

where a_t is the true reflectance absorptivity coefficient for indigo that is distributed uniformly in the cross-section of the yarn; *C* is the concentration of dye in the yarn cross-section, and *p* is the fractional penetration of the yarn by the fixed dye.

Eq. 1 makes use of the true reflectance absorptivity coefficient, a_t; however, in practical indigo dyeing processes true reflectance absorptivity coefficients must be replaced by apparent coefficients. Extensive experimental work repeatedly has shown a strong relationship between the apparent reflectance absorptivity coefficient and the pH of the indigo dyebath in which the dyeing is conducted. For a five dip laboratory indigo dyeing process[3] conducted at pH's 11, 12 and 13, the relationship between *K/S* and the actual dye content of the dyed denim yarn is given in Fig. 2. The line slopes in Fig. 2 represent the apparent reflectance absorptivity coefficients or color yields, and are caused by the various levels of ring dyeing that occur at different pH's. It is clear that as the dyebath pH is decreased from 13 to 11 there is more ring dyeing and an increasing apparent reflectance absorptivity coefficient. In fact, it has been found that within the pH range of about 10.8 to 11.2 the greatest color yield is achieved.[2-4] The question to be answered is: Why does ring dyeing increase as pH is lowered?

Source of pH Dependent Ring Dyeing

As discussed elsewhere,[6,7] ring dyeing of fibers can be increased by dyeing conditions that promote a very fast initial strike of the dye for the fiber surface. If the affinity or substantivity of indigo for the cotton fibers in a denim yarn is increased, the strike or rapid exhaustion of the dye onto the fibers in the exterior regions of the yarn will lead to decreased dyeing of the fibers in the yarn interior. Such a phenomenon will result in a ring dyed yarn—even when the fibers in the exterior regions of the yarn are well penetrated.

Affinity or substantivity of a dye for a fiber can be expressed in terms of an equilibrium distribution coefficient; i.e., the ratio of concentrations of dye in fiber to dye in dyebath at equilibrium. Relatively high values of the distribution coefficient indicate relatively high substantivity or affinity of the dye for the fiber. In Fig. 3 the ratio of dye in denim yarn to dye in an infinite indigo dyebath is given for five dip laboratory dyeings conducted at different

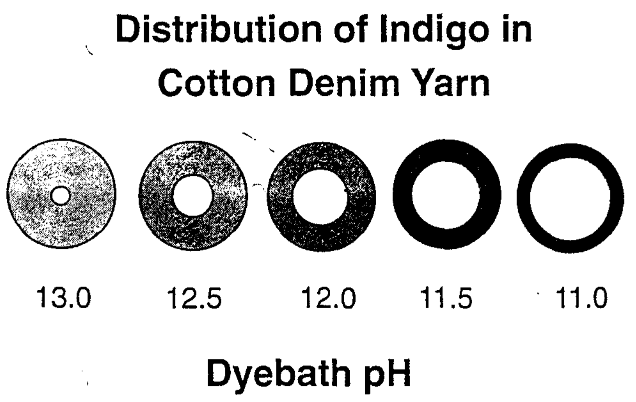

Fig. 1. Simplified schematic of the distribution of indigo dye in the cross-section of cotton denim yarn dyed under different pH conditions.

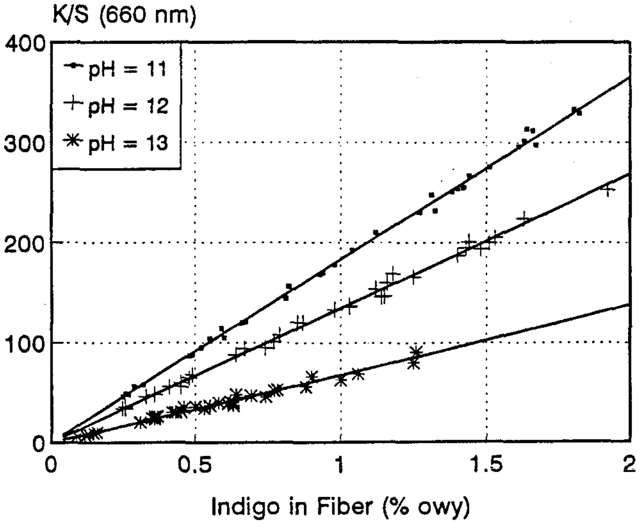

Fig. 2. *K/S* as a function of the denim yarn dye content for dyeings conducted at dyebath pH's of 11, 12 and 13.

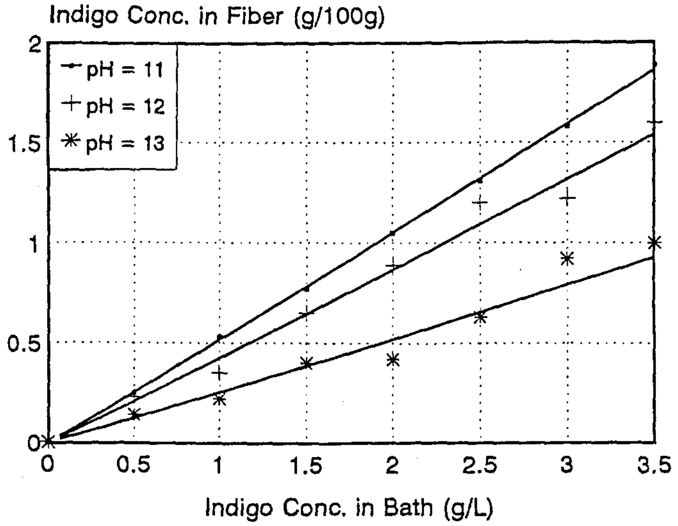

Fig. 3. Technical distribution of indigo between cotton denim yarn (g/100g) and the dyebath (g/L) found for five dip dyeings conducted at different pH's.

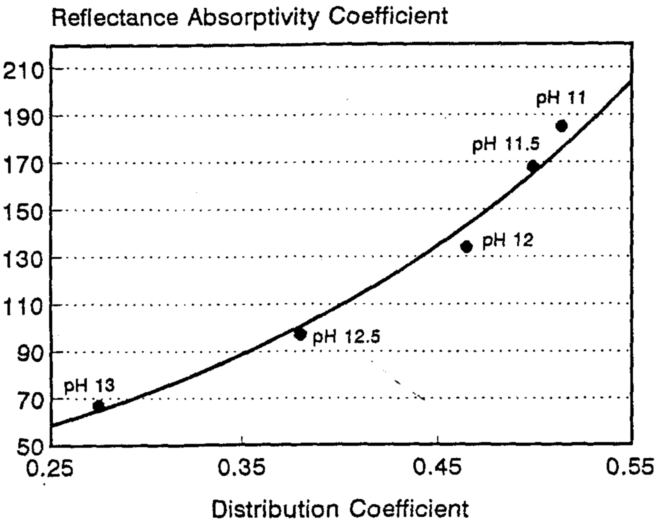

Fig. 4. Apparent reflectance absorptivity coefficients as a function of technical distribution coefficients, for given dyebath pH's.

dyebath pH's, using a previously disclosed experimental technique.[3] The linear sorption isotherms shown in Fig. 3 may be regarded as purely technical quantities, since they were not obtained under equilibrium conditions. Nevertheless the data indicate that pH has a profound influence on the practical substantivity of indigo for denim yarn. As the pH is decreased from 13 to 11, the mean technical distribution coefficients increase. Recent equilibrium measurements confirm that true sorption isotherms of indigo on cotton appear to be of the Freundlich form, with corresponding distribution coefficients that are much higher at lower pH values than they are at higher pH values.[8]

In Fig. 4 the apparent reflectance absorptivity coefficients of Fig. 2 are plotted as a function of the technical distribution coefficients of Fig. 3, including additional data points that correspond to other dyebath pH's. The coefficients of Fig. 4 are shown to be positively related; i.e., as the distribution coefficient increases, the color yield increases. It may be concluded from Fig. 4 that the yarn ring dyeing phenomenon is highly correlated with increasing substantivity and strike of the indigo for the cotton fiber that is associated with lower dyebath pH's. The question remains: Why does the substantivity of the indigo increase at lower dyebath pH's?

Source of pH Dependent Substantivity

Forms of Indigo

Depending on the chemical conditions that are present, there are at least four distinct forms of indigo that can exist in the dyebath. These forms are shown in Fig. 5. Both oxidized and acid leuco forms of indigo have very poor water solubility and substantivity for cotton fiber; however, the physico-chemical properties of the two ionic forms of indigo vary greatly, with the di-ionic form having the higher solubility—but the lower substantivity.

It has been shown repeatedly that the color yield of indigo on denim yarn is greatest within a pH range of about 10.8-11.2, and it is within this pH range that the mono-ionic form of indigo predominates.[2-4] When the activity coefficients are assumed to have a value of unity, the fraction of reduced indigo that exists as the mono-ionic form, I_{mono}, is given by:[2]

$$I_{mono}=1/[1+10^{(pK_1-pH)}+10^{(pH-pK_2)}] \qquad \text{Eq. 2}$$

where pK_1 and pK_2 are the pK_a values associated with the two step ionization of reduced indigo, and pH is self-defined. Mean values of I_{mono} are plotted as a function of dyebath pH in Fig. 6.

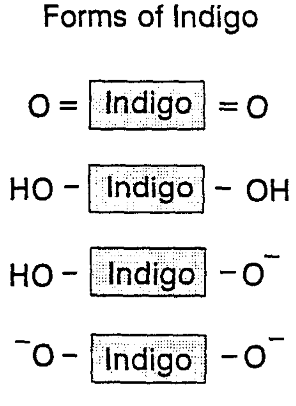

Fig. 5. Simplified representations of the various forms of indigo (from top to bottom): Oxidized or keto form; Reduced or acid leuco form; Mono-ionic form; Di-ionic form.

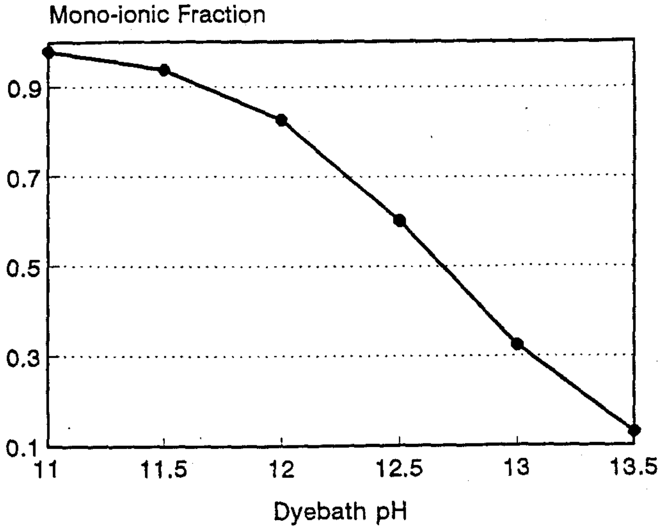

Fig. 6. Mean fraction of the total amount of reduced indigo that exists in mono-ionic form as a function of dyebath pH.

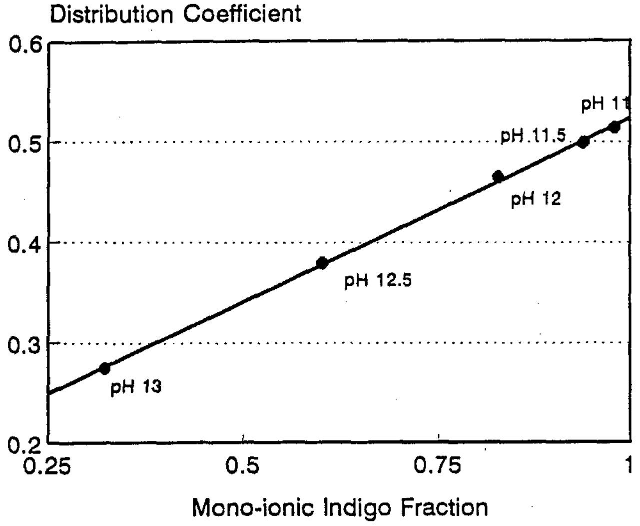

Fig. 7. Correlation between the mean technical distribution coefficient and the mean fraction of reduced indigo that exists as a mono-ionic form at various dyebath pH's.

The mean technical distribution coefficient is plotted as a function of the mean fraction of reduced indigo that exists as a mono-ionic form at various dyebath pH's in Fig. 7. Fig. 7 shows that for a pH range of 11 to 13 there is an exceptionally high linear correlation between the substantivity of indigo for cotton fiber and the fraction of indigo that exists in mono-ionic form. It must be concluded that the mono-ionic form of indigo has much higher substantivity for cotton fiber than does the di-ionic form of indigo. However, not only the ionic form of the indigo must be considered in explaining the substantivity of the dye for cotton—the ionic form of cellulose itself also must be considered.

Ionic Forms of Cellulose

It is well known that cellulose contains alcoholic OH groups that are capable of ionizing if the pH is high enough. The ionic forms of cellulose are represented in simple diagrammatical form in Fig. 8. Vickerstaff[9] has directed attention to the work of Sumner[10] with regard to the ionization of cellulose. As pointed out by Vickerstaff, "From the known ionization constant of cellulose, and making some assumptions as to the proportion of a cellulosic fibre that is accessible to [alkaline] solutions, Sumner has calculated the concentrations of ionized groups in cellulose at various external pH values..." The results of Sumner's computations are given in Fig. 9. It is particularly important to point out that significant ionization of cellulose does not begin to occur until the external bath pH is increased to about 11. At pH's greater than about 11, cellulose ionization occurs more and more strongly. The correlation between the concentration of ionized cellulose and the technical distribution coefficient is given in Fig. 10. It is revealed in Fig. 10 that there is a strong negative correlation between the substantivity of indigo for the denim yarn and the ionization of the cellulose, with substantivity strongly decreasing as the ionization of the cellulose increases.

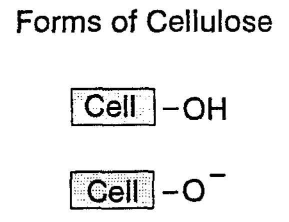

Fig. 8. Ionic forms of cellulose.

Examination of Figs. 7 and 10 leads one to the conclusion that the source of the pH-related substantivity of indigo for cotton fiber can be traced to the ionic form of both the dye and the cellulose. Indeed, it is not coincidental that cellulose ionizes most strongly in the same pH range that the di-ionic form of indigo is produced. It appears that the ionization of the second OH group on the indigo molecule behaves very similarly to the ionization of the alcoholic OH groups of cellulose. Therefore it should not be surprising that substantivity decreases as pH is increased much above 11. At high pH's, ionic repulsion between the di-ionic form of dye and ionized fiber will result in lower affinity, lower strike rate and greater penetration of indigo into the denim yarn. On the other hand, as the dyebath pH is decreased and approaches 11, both dye and fiber are ionized less. Ionic repulsion therefore decreases, leading to higher affin-

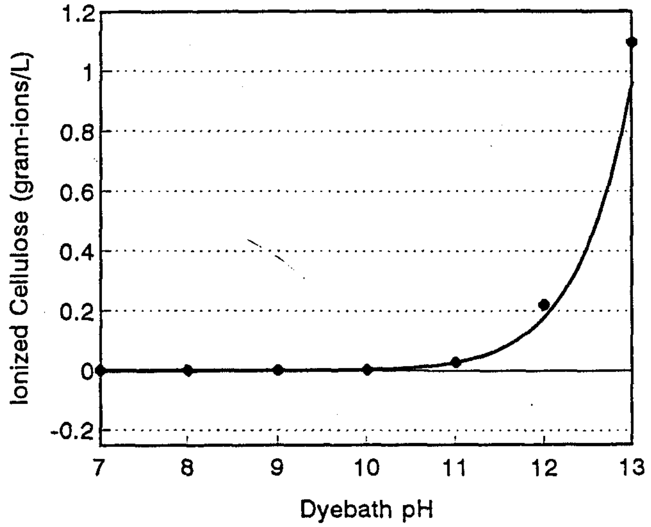

Fig. 9. Concentration of ionized cellulose (gram-ions/L) as a function of the pH of the external dyebath.

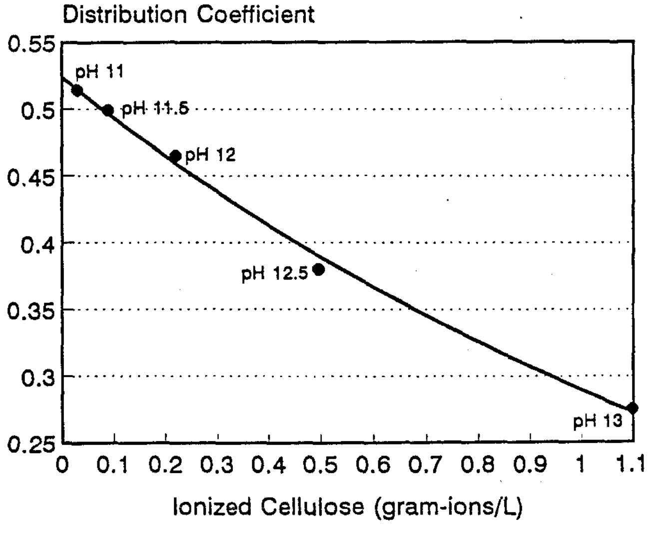

Fig. 10. Correlation between the technical distribution coefficient and the concentration of ionized cellulose for various dyebath pH's.

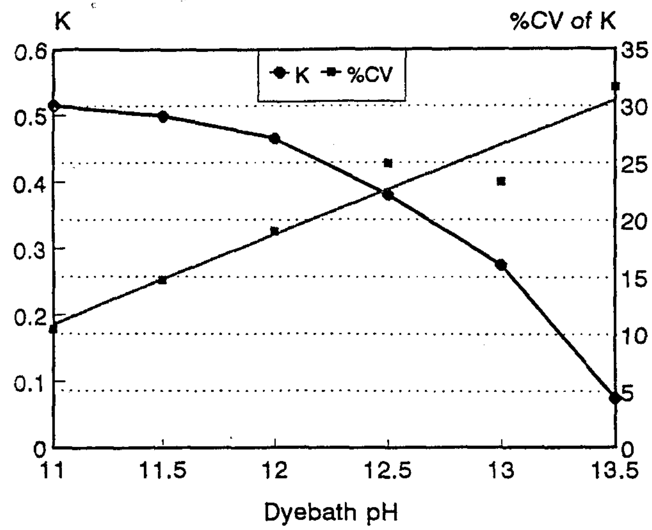

Fig. 11. Mean values of the technical distribution coefficient, *K*, and the associated coefficient of variation, *%CV*, as functions of dyebath pH.

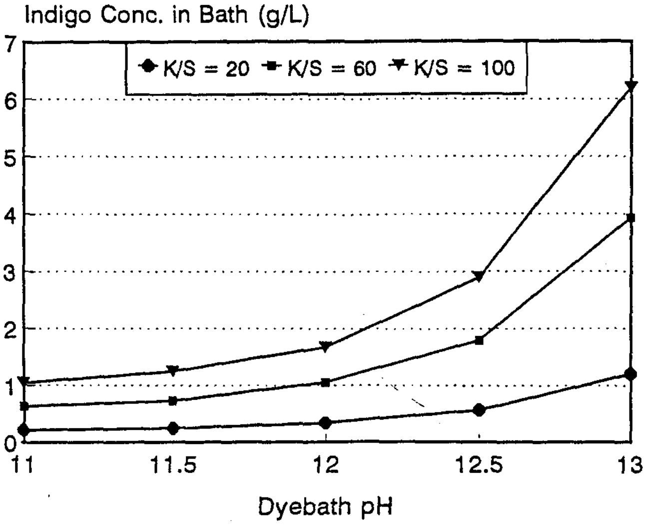

Fig. 12. Mean indigo concentration needed to produce a given shade depth, expressed as *K/S*, at various dyebath pH's for a five dip laboratory dyeing process.

ity, higher strike rate and lower penetration of the denim yarn by indigo.

Implications for the Commercial Dyer

Strict control of dyeing quality is essential for the denim producer to remain competitive in today's international market. Dye substantivity is one of the most important variables that the dyer can regulate in his attempt to maintain quality. As has been shown, substantivity strongly influences not only dye uptake, but also the degree of ring dyeing of denim yarn and related shade depth. Indigo substantivity, expressed as technical distribution coefficient, *K*, and the coefficient of variation of *%CV* are given as functions of dyebath pH in Fig. 11. It is shown in Fig. 11 that as the technical distribution coefficient decreases with increasing pH, the coefficient of variation of the distribution coefficient increases. This fact means that substantivity, with associated extent of ring dyeing and color yield, becomes more variable with increasing pH. Although the data given in Fig. 11 are based on numerous laboratory dyeings, the results of commercial dyeings tend to confirm the constancy of substantivity of indigo for denim yarn when dyebath pH is maintained within a range of about 10.8-11.2.

Control of dyebath pH results not only in dyeing consistency but also in significant cost reduction. In Fig. 12 the mean indigo concentration in the dyebath needed to produce a given shade depth (*K/S*) at various dyebath pH's is given. As revealed in Fig. 12, the concentration of indigo needed to produce a rather dark denim shade (*K/S*=100) is about 3 g/L when the dyebath pH is 12.5, but only about 1 g/L is needed at a pH of 11.0. The reduction in concentration of dye needed to produce the standard shade depth is dramatic.

In addition to cost savings, the use of pH-controlled dyeing at a constant indigo concentration makes possible a reduction in the number of dips in conventional rope ranges necessary to produce a given shade. It is well known in industry that rebeaming of denim yarn cables becomes more and more difficult as the number of dips increases. Furthermore, recent plant trials have shown that even one dip in a slasher dyeing process can produce a reasonably dark depth of shade, with satisfactory fastness. Control of dyebath pH is now making possible methods of indigo application that previously were not viable when only sodium hydroxide was used as the dyebath alkali. These new application methods may even contribute to an increase in the total usage of indigo on a worldwide basis as the world population and demand for denim increase.

For the Apparel Manufacturer

A quality problem that continues to plague the denim garment manufacturer is nonuniformity of washdown of different denim panels within a garment.[11,12] Even when the various garment panels match before the garment is laundered, the panels may not match after laundering. This quality failure often is due to different levels of yarn ring dyeing and dye content that are found in different lots of denim that are otherwise of the same shade depth and hue. It is highly desirable that the manufacturer of denim apparel be confident that each lot of denim fabric of a given shade depth that he receives from the denim manufacturer possesses constant washdown characteristics. As illustrated by the results of a simple computer simulation given in Fig. 13, pH-controlled dyeing can do much to overcome the problem of nonuniform shade depth after washdown. As shown in Fig. 13, the use of pH-controlled dyeing results in swatches of denim all having similar shade depths after laundering. Such uniformity is the result of the unvarying initial level of yarn ring dyeing and dye content for all of the swatches. On the other hand, when the dyebath pH is allowed to fluctuate, the resulting yarn will have different levels of ring dyeing and dye content at the same initial shade depth. Such swatches will not wash down uniformly.

It is paradoxical that, after the dyer has given so much attention to dyeing denim yarn to a uniformly dark depth of shade, the denim garment manufacturer subjects the garments to laundering techniques designed to remove much of the dye from the fabric in a most irregular manner. Stone washing, acid washing and enzyme laundering techniques all are designed to remove expensive indigo dye from denim garments. If most of the dye is going to be removed by the garment manufacturer, it simply makes better economic sense for the dyer to use less dye to achieve a given shade depth. In addition, when less dye is on the denim garment, less concentrated chemicals are needed to remove the dye during laundering. The garment manufacturer therefore can save money on his laundering processing costs—just as the dyer can save on dyeing costs.

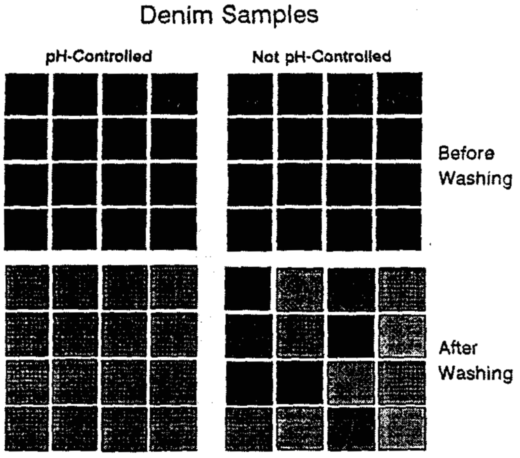

Fig. 13. Before and after laundering simulation of the shade depth of two sets of 16 randomly selected denim samples manufactured from yarn dyed under pH-controlled conditions and under non pH-controlled conditions.

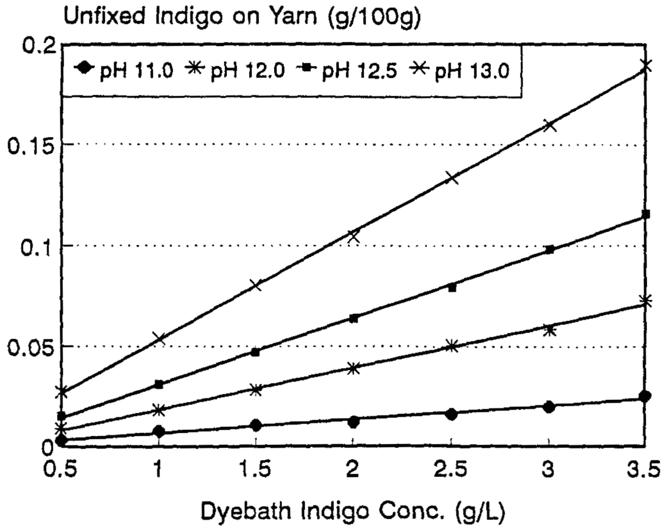

Fig. 14. Estimated concentration of unfixed indigo on denim yarn at the conclusion of dyeing as a function of dyebath indigo concentration and pH.

For the Environment

Since pH-controlled dyeing makes possible the use of less indigo in the dyebath to achieve a given shade depth, less indigo is washed off of the yarn at the conclusion of dyeing.[13] In Fig. 14 the concentration of unfixed indigo is estimated as a function of both concentration of dye in the dyebath and dyebath pH. As the dyebath pH is lowered from 13 to 11, the amount of oxidized indigo that is trapped between fibers in the denim yarn is decreased. Less dye is available to be washed off of the yarn on the dye range and thrown to the drain. In addition, the pH of the wash water is not so high as it is when only sodium hydroxide is used as dyebath alkali. A significant reduction in pollution therefore can be a result of pH-controlled dyeing.

When denim garments that are constructed of yarn dyed by the pH-controlled technique are subjected to one of the various laundering procedures, lower concentrations of the products of decomposition of indigo are produced, since less indigo is on the fabric to be decomposed. Furthermore, lower concentrations of destructive oxidizing agents are needed to remove the indigo. It is easy to appreciate that the use of pH-controlled dyeing can lead to a reduction in pollution not only by the denim dyers, but also by the denim garment launderers as well.

Conclusion

Commercial implementation of pH-controlled indigo dyeing in both North and South America has proven to provide undeniably extraordinary benefits for the denim yarn dyer, denim apparel manufacturer and the environment. When a breakthrough in dyeing technology results in improved quality control, reduced dyeing and laundering costs, reduced pollution and an attractive look in end-use apparel products, the technological advance deserves the close attention of the international dyeing community.

Acknowledgements

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