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Putting Invention into Practice—Conversion of the North American Denim Dyer to a New Form of Indigo

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Introduction

This year, the AATCC Olney Medal Award Committee departed from tradition and selected a textile chemistry advancement, not from the academic sphere, but rather from the unpublicized world of manufacturing. Such an occasional break with tradition can be justified because, after all, product is the ultimate destination of textile chemistry progress. With a production application of a scientific achievement there must be, to a degree, some further research and innovation. From the multitude of advancements that occur constantly in manufacturing textile products, the institution of a new form of indigo was chosen perhaps because of the attention to a popular, intensely marketed product that is blue jeans apparel.

BASF's invention[1] of an improved form of indigo for application was a brilliant accomplishment that required a new manufacturing process and unique logistics; but, establishing the product into mill practice required even more effort. This is the story of how denim mills realized the net benefits of pre-reduced indigo after many years of experiments.

Chemically Reduced Indigo

Indigo dyeing remains principally unchanged from the beginning. The indigotin crystals, with a size distribution of several hundred to several thousand nanometers, cannot fit into cotton's dyeable space of less than 10 nm. Only the leuco ion, with a 1.3 nm dimension, and its various larger micellular arrangements can dye. The dye has such a low affinity[2] (< 10% of other vat dyes) for cotton that it cannot be exhausted to a substantial shade depth. To achieve dark shades with highly-concentrated baths, rinsing before fixation—which is necessary to remove undiffused surface dye—rinses too much of the interior dye. The rinsed result is too uneven and light. Dark shades are achieved by dipping the cotton article into a pit of dilute leuco, removing it, squeezing off excess liquor, and then allowing the air to oxidize and fix the indigo. This process is repeated several times. The principle is the same today as in the original successful dyeings in pre-historic times. Today, the dye bath is still essentially monochromatic indigo; the article or yarn still is dipped, squeezed, and oxidized—all out in the open air. Just as with the old process, darker shades are built by repeating the process several times. It is curious that a dye, only dyeable with such an old process, would be the most widely used* dye for apparel today.

Indigo's unique hue, unaffected by exposure to the destructive elements of use, engenders a lasting appeal; but it is the combination with comfortable, cotton jeans that wins out. Since repeated applications are required to achieve an acceptable depth of shade, each cycle is only seconds in duration to prevent dissolving and removing the previous application. The shortened dip time ring-dyes the yarn, which gradually exposes a light yarn center in wearing and washing. Created with age is a patina that has extra appeal in addition to indigo's unique hue.

Indigo for dyeing cotton, whether derived from plants or benzene, has traditionally been sold as the insoluble blue pigment (Fig. 1). The blue pigment is solubilized by the dyer using a chemical reduction process called "vatting". Sodium hydroxide (caustic) and sodium hydrosulfite powder (hydro) in quantities greater than the amount of indigo must be used to create and maintain the soluble yellow salt necessary for dyeing.

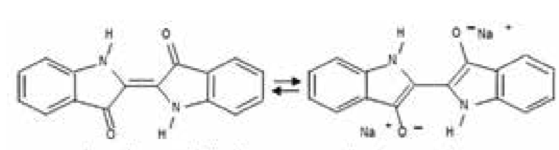

Fig. 1. The two forms of indigo important to the denim dyer.

*According to DyStar, indigo is the individual textile dye used in the greatest quantity on a dry basis; the various sulfur black dyes as a group and the various fiber reactive black dyes as a group are comparable in amount.

The blue pigment powder—700 pounds for a 1000-gallon mix—is manually scooped or dumped into a water vat open to the atmosphere. Caustic liquid is either pumped or manually added to the vat, followed by the manual addition of noxious hydro powder. In very few locations, this dusty, unhealthy operation has been superseded by pre-dispersing the pigment and pre-dissolving the hydro before their introduction to the dye house chemical mix room. After the chemicals are added to the vat, the mix must be allowed to react for at least 2 hours before using. Vatting does not provide the dyer with completely reduced indigo as the exposure of the reduced indigo to air reverses this vatting to a variable degree.

Intense Chinese competition in the early 1990s spurred BASF's textile dye business unit (now DyStar) to introduce an improved form of indigo branded "Indigo Solution," commonly known as pre-reduced indigo or PRI. PRI is a liquid form of indigo that is reduced at the dye manufacturing plant; air exposure is prohibited by reduction and storage in an oxygen-free atmosphere. Hydrogen gas and a recoverable metal catalyst provide the reduction. An excess of hydrogen allows the reduction to be very nearly complete. PRI is ready to be used by the dyer, and only the hydro and its stoichiometric caustic, to counter oxidation loss from air exposure during the open-air process of dyeing, is necessary. Up to 70% of hydro and caustic, and their polluting sulfur salts, are eliminated.

The Challenge

Indigo pigment powder is shipped in 20-kilogram cardboard boxes; PRI is shipped in 20-ton tanks under slight nitrogen pressure. These tanks must be dedicated to PRI and shipped back empty from the US to the manufacturing plant in Germany. This long cycle mandates substantial inventories. At the denim mill, new bulk storage and dyebath injection equipment are required. The added costs of manufacturing, logistics, and equipment made competing with a commodity indigo powder on a cost basis seem impossible. Superior ecology, ease of use, quality, and safety is difficult to translate into savings for the denim manufacturer. In the 1990s, manufacturers could not commit to investment and a higher raw material cost in this period of declining margins for US denim without belief in a monetary return.

Ecology

BASF's PRI rollout touted reduced hydrosulfite and caustic soda, less salt in the waste stream, and easier use. In 1994, Avondale Mills adopted PRI for its Sylacauga operation. There was much excitement about being the first major denim producer to adopt PRI. All production was immediately converted without extensive trials comparing to regular indigo controls. Avondale made a publicity splash, but there was little market effect. We began to learn consumers overall will not pay extra for responsible ecology expected to already be included. This reality quenched any interest from other denim producers. As time passed, DyStar emphasized environmental achievements. Here is a sample of DyStar advertising statements:

- The cleanest and the most ECO awarded indigo on the market
- Cleaner dye house—less dust and odor pollution
- Preferred choice in terms of human and environmental health
- Reduction of major waste water parameters, such as COD, TSS, sulfates, and TDS
- Compliances with environmental certification and standards

To make such statements, DyStar spent much money and effort in improving its indigo manufacturing processes, product testing, and certifications. For years, no US customers beyond Avondale could be convinced to try the product. It became evident, that in a competitive market, price is most important to business, or at least a quantifiable savings. The same lesson holds true today that, if harm is not directly evident, advertising and certifications do not render costly ecological process improvements. This cannot be denied any more than that global warming does not spur pedestrian commuting. Where the public is not directly affected, legal and government penalties drive the improvements. However, eventually public awareness of possible real harm supports the drivers, so one cannot say that the certifications and advertising are irrelevant—just that change is slow.

Before the introduction of PRI, US manufacturers had already invested in automated equipment for producing and handling liquid raw materials to replace manual weighing of unhealthy dusty powders. The second advantage of PRI, easier handling, was not an important issue in the United States.

Converting to PRI

Seven years passed before Avondale adopted PRI in its acquired Graniteville Company indigo dyeing plants. The second and third Avondale plants were converted in much the same way as the first, that is, with no extensive trials. Avondale could have been aware of economic advantages, but such information was not available to DyStar. These conversions did not require much effort from me, which I welcomed at the time; however, I learned nothing about possible cost savings of my product. A sales point at the time was fact that the PRI indigo molecule is the same, and therefore, one should expect the same results. Later in this piece, I explain that this presumption of the result is very wrong. Ironically, the ease of the Avondale adoptions set back progress with other customers for years.

Beyond the two major benefits of PRI for environment and handling, DyStar searched for other advantages. In dye manufacturing, after the dye is made, it undergoes a standardization, which means it is tested and corrected for strength. From strength measurements of several hundred US shipments used from bulk storage, a sample relative standard deviation for DyStar PRI of 0.36% was calculated. Dye house stock vats normally are not tested, but a brief study in one plant demonstrated a relative sample standard deviation of 2.8%. PRI is kept from deteriorating from oxidation by storing under nitrogen. Stock vats normally used from open tanks are continuously changing in hydrosulfite concentration, and pH. Obviously, there are potential savings from the more consistent PRI; but it is difficult to quantify them. Denim producers use an elaborate process of shade grouping and storing a large inventory to overcome shade variations. Realizing savings by eliminating these procedures is risky. Other improvements requiring investment would be necessary to seriously consider such a step.

From its peak in the early 1990s, US denim production steadily declined as NAFTA began in 1994 and WTO in 1995. In 1995, eighteen vertical denim operations (cotton bale to fabric) existed in the US, now only two are left. In addition to declining denim production, cheap Chinese indigo took a share of the indigo dye market. The only US manufacturer of indigo, Buffalo Color, eventually went out of business in 2003. This decline coincided with the 10-year period of no progress in securing additional PRI customers in the US. DyStar struggled to continue a business of cheaper regular indigo dispersion. The handwriting was on the wall that Western economies could not compete with Chinese indigo. Despite distinguishing our DyStar regular indigo product with service, it had become a commodity. DyStar indigo saw that its viability depended on PRI and regular indigo was dropped from its product line. Up to that event, as I serviced our small regular indigo business, I emphasized the variability of stock vats.

Charles Brock, formerly the vice president of sales for Buffalo Color, became my sales colleague after Buffalo shut down. A former loyal Buffalo customer experienced a period of shade control problems in 2003, and Brock persuaded the mill to give PRI a look. But success had to be determined by economics. Proving economics was a different matter from making a single dye run that matched an existing shade of indigo. Desperate times called for desperate solutions and the long-term trial was born. Brock and I parked a 20-ton tank at the plant door that would supply a dye range continuously around the clock for 16 days while we controlled the amount of dye fed to the range with an ad hoc feeding system. This system was crude and spread out on the floor in an out-of-the-way space. Brock and I relieved each other as we monitored this system at all hours. Well-established regular indigo shades were chosen to study. First, we monitored control runs of regular indigo and then many runs of PRI. Brock and I normally made lab measurements ourselves to eliminate operator bias. Reliable data comparing the cost of PRI to regular indigo became available for the first time. The trial shade depths were light and medium, and the cost of using PRI proved equal. So, the added advantages of PRI were essentially free, and the mill made the conversion to PRI.

Long term trials performed in the same way were repeated at plant after plant with the adoption of PRI each time. With each trial I assembled a system in my garage for setup in the mill. Improvements were made with each subsequent system. Fig. 2 shows one of the later systems.

Eventually all US denim mills, for a total of nine, that were in operation during this campaign converted all production to PRI except for one small operation that continued to use regular indigo in some of their long-tradition styles and used PRI in others. These conversions entailed bulk storage and fixed metering systems. Then, I carried the long-term trial method to Latin America. After several

Fig. 2. Temporary indigo metering system. The IBC container of indigo is refilled automatically from a 20-ton ISO container outside the plant.

of my homemade Latin systems, DyStar started purchasing professionally made systems for trials. Now with nearly 100% conversion, PRI is the standard indigo form in Latin America and supplied by DyStar and the chemical company Bann Quimica that dominates the insular Brazilian market.

Tangible Advantages

Hundreds of dyeing runs that my colleagues and I monitored produced data that invariably concluded the favorable economics resulting from the use of a higher-priced PRI product. Why this is so can be explained by the profound salt effect.

Yarn entering the dyebath introduces air, causing oxidative decomposition of hydro in the dye bath. This hydro must be replaced to maintain a constant hydro concentration and the state of reduction of indigo. What results are equilibrium concentrations of the hydro oxidation products of dissolved Na_2SO_4, Na_2SO_3, and $Na_2S_2O_3$.

A mill dyeing experiment demonstrated how important the concentration of the sulfur salts is to the depth of shade after the commercial laundry process. A dyeing of a well-established shade of medium depth was run in the normal manner by feeding regular indigo stock vat. At the end of seven hours, the indigo feed was switched, without stopping the dye range, to PRI at a feed rate of 13% less indigo and then continued 28 hours more. Fig. 3 chronologically charts the average dL* values of the laundered trial fabrics and the bath conductivity as it progressed toward a new equilibrium level. After abrasion laundering the fabrics made from the trial, the difference between start and finish reached 26% based on average K/S over the visible spectrum. A savings of indigo with PRI with this particular shade was greater than the 13% feed rate reduction because the negative dL* values show that the latter hours of running produced shades darker than the standard. PRI's absence of the stock vat salts of oxidation produces a lower equilibrium salt level. A minimum level of salt is required to counter cotton's zeta potential. However, the salt also interferes with diffusion of the adsorbed indigo, resulting in an adverse effect on wash and rub fastness. Sulfur salt levels above 40 g/L when combined with the additional electrolyte from buffers and caustic can produce conductivities above 60 mS as seen in Fig. 3. For very dark shade depths, greater conductivities are produced and up to 30% more stock-vat indigo is necessary to achieve the same laundered shade level possible with PRI. That 30% of regular indigo is not recovered and must be dealt with in waste disposal. It should be noted that when less PRI indigo is applied, the unwashed PRI-dyed jean of course is lighter in shade than the unwashed jean dyed with more indigo. This was an initial issue with some fashion designers, but the market for unwashed jeans is so small that it has little effect.

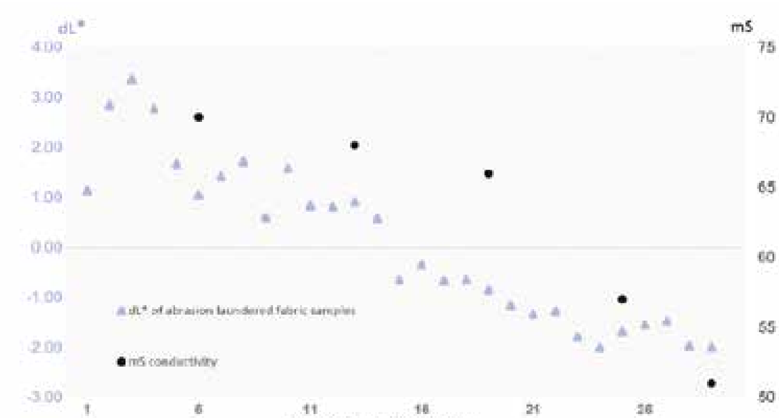

Fig. 3. Salt effect on laundered shade depth.

All regular indigo shades can be acceptably matched in the laundered jean by PRI, but regular indigo cannot achieve the fashionable very dark shades possible with PRI. Etters demonstrated the shade depth limitation caused by electrolytes.[3] The phenomenon occurs, that as more dye is applied, a point is reached where the depth of the laundered shade actually decreases. This is because the hydro requirement increases with dye bath indigo concentration and eventually resultant salt equilibriums reach a ruinous level. The peak shade depth occurs when the bath electrolyte reaches about 25 g/L for the lab dyeings in Fig. 4. This peak is above 50 g/L in industrial continuous range dyeing, but it still becomes a factor in commercial practice. The achievable maximum shade depth varies considerably with the efficiency of the dyeing process. The dyeing variables, which are the number of dye boxes, dye range speed, yarn tension, dye box roller configuration (that is, the number of rollers, roller diameter, and yarn wrap angle that determine dye liquor exchange in the yarn), yarn scouring conditions, and dye bath indigo concentration, pH, conductivity, temperature, hydro concentration, and auxiliary chemicals, when manipulated can produce great differences in maximum shade depth after laundering.

Costly indigo waste resulting from the electrolyte produced by stock vat hydro and a significantly less possible shade depth compared to PRI are the two reasons for mills adopting PRI. This is hard to believe, and each dyer must be convinced in his own element. That can be hard to do. If a condition of an above dyeing variable is not carefully controlled, the economics and the quality of the trial dyeings can be diminished. The long-term trials established the proof, but laboratory experiments set the limits of possibility. For example, altering the indigo concentration some percentage alters several dependent parameters. Learning this on a dye range producing 30 kilograms of dyed yarn per minute is a prohibitive method of learning the scope of effects of the many variables. I had a 2-L dye box built that I used in conjunction with a variable speed laboratory padding mangle. This, with additional redirecting rollers outside of the dye box, facilitated a recirculating loop of yarn to effectively reproduce continuously-running multiple-dip dyeings under tension. Dyeing only 1 g of yarn in a 2-L bath allowed several dips without the necessity of replenishment. Winding the processed yarn on a card facilitated colorimeter measurements. The yarn was wound onto a dowel for Launder-Ometer tests. Dye extraction measurements were made before and after laundering. Hundreds of tests were done, and the information predicted and confirmed what I would learn in the customer's dye house. Each customer's operation produced different results, and often I went back to my laboratory setup to answer questions. Eventually quantitative functions were developed for different dye houses that could predict results and evaluate variation. An interesting result demonstrated an extreme possibility: with PRI alone, a unique ring-dyed blackest of blacks with no bronziness can be produced by manipulating the variables.

The consistency of the PRI feed with respect to indigo concentration, pH, and hydro concentration provided a means of control not available with inconsistent stock vats. The PRI feeding system with a valve-flow-meter-control loop proved to be more precise than even the test results of laboratory spectrophotometric measurements and on-line colorimeters. With PRI's

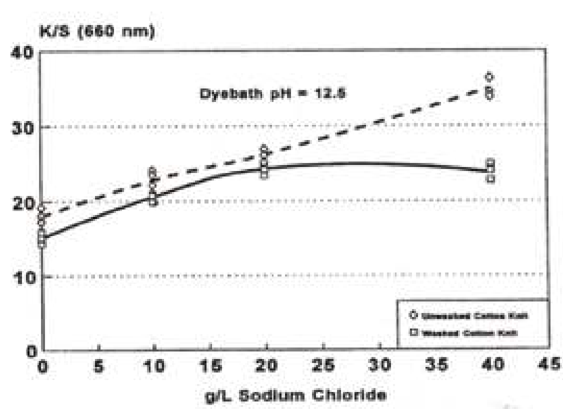

Fig. 4. Effect of salt concentration on resulting indigo shade depth after washing.[3]

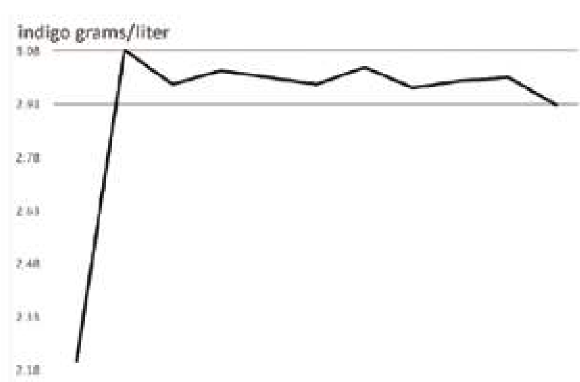

Fig. 5. Indigo concentration vs. time during an actual production dyeing run with PRI.

consistency, indigo feed rates required no adjustment during a dyeing run. Frequently forgotten in continuous indigo dyeing is the objective of applying a specified percentage of indigo onto the yarn just as with all other dyeing methods. At a constant yarn speed, a constant feed rate of indigo applies the same percentage of dye on the yarn if the dye bath concentration is at equilibrium.

Fig. 5 shows measurements of a production dye run with PRI that is typical. A stored dyebath was corrected to the equilibrium concentration before starting the range. The PRI feed rate was maintained constant and the indigo concentration remained within ± 2.5% control limits for the 10-hour run. If the concentration curve were to trend slightly up or down (from most commonly a yarn or atmospheric change), the PRI dyer can let the concentration seek a slightly different equilibrium level, after which concentration would remain within control limits. Then, the dyer would be assured that he was applying the required percent indigo on the yarn. An on-line colorimeter measurement also would seek a slightly different level and remain constant. Adjusting the indigo feed rate to maintain a specified concentration or L, a, b value is incorrect. The stock vat dyer cannot have confidence that his variable stock vat is not causing a trend in his concentration graph or his colorimeter graph, but the PRI dyer can be confident in relying on a constant dye feed rate at equilibrium. It should be qualified that the other bath variables must be at the correct level to assume the equilibrium indigo concentration is properly reached; then, with a flat concentration curve at a constant feed rate, the PRI dyer has immediate assurance of a correct dye run and the eventual garment will be "on shade."

Twenty-five years after its introduction, PRI is now the standard form of indigo. Advantages known intuitively in the beginning eventually became reality and every prospect of mine switched to PRI.

The Future

PRI is now established as the standard form for synthetic indigo; however, there remains significant room for dyeing process improvement for economics and ecology. In 2014, Dr. Dean Ethridge and I submitted a grant to Walmart for US Manufacturing Innovation Research. A joint project was created between Texas Tech University and American Cotton Growers Denim Mill to use PRI applied by foam. In conjunction with Gaston Systems Inc., I experimented with indigo foam dyeing on a single yarn and then provided a patent pending design modifying a Gaston indigo foam dyeing machine. The process uses foam as the medium to transport indigo to a continuous yarn sheet in an oxygen-free environment. This is done with yarn moving through the three chambers: (1) a purge chamber to remove the air from the yarn, (2) a foam application chamber to coat the yarn with indigo foam, and (3) a kinetic chamber to diffuse the indigo into the cotton fiber.

Fig. 6. Indigo-foam pilot range at Texas Tech University.

With the Texas Tech pilot machine (Fig. 6), all the shade depths possible in conventional commercial indigo dyeing have been duplicated. This machine allows, for the first time in commercial indigo dyeing, total elimination of hydro and waste water from yarn preparation and dyeing. Ninety-five percent water and energy savings are realized as no rinsing is necessary to achieve a fastness superior to existing commercial processes. A truly sustainable process is the result because, along with the environmental advances, there are cost savings. Additional benefits are gained with dyeing in a closed, controlled atmosphere, the elimination of dye baths, and the 100% utilization of the applied indigo.

Two Gaston Systems production machines are beginning operations. Indigo dyeing, having been labeled a dirty dyeing process,[4–6] is on its way to becoming the cleanest dyeing process.

Glossary

Abrasion Laundering
The industrial washing of garments with pumice stones or other abrasive materials or enzymes to partially expose the lighter interior of indigo dyed yarn.

Caustic
Water solution of sodium hydroxide with a normal strength of 50% by weight.

Dyeing Range
The continuous dyeing machine unique to denim for dyeing warp yarn through several successive tanks (or boxes) of indigo.

Dyeing Run
A finite quantity of yarn continuously dyed of usually 10-30,000 yards length.

Hydro
Sodium hydrosulfite powder for reducing vat dyes, sometimes used dissolved in water as liquid hydro.

Indigotin
The stable, insoluble blue indigo crystal form of indigo in the powder product and in blue jeans.

Leuco
Technically, the white, insoluble, undissociated form of reduced indigo, but commonly defined as the reduced, yellow, sodium salt of indigo.

Pre-Reduced Indigo (PRI)
Indigo made soluble and ready-to-dye at the indigo factory.

Ring Dyeing
A dyeing where the color does not penetrate completely, leaving a lighter yarn center.

Stock Vat
The preparation for dyeing made at the denim mill by adding unreduced indigotin powder to water, caustic, and hydro for chemical reduction and dissolving.

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Author's Biography

The author's biography is available in the March/April 2019 *AATCC Review* on pages 14 and 15.

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