A Cleaner Way

to Color Cotton

Because of its light weight and natural feel, clothing made from cotton is tremendously popular, especially during warmer weather. But aside from the method used to tie-dye those shirts popular with summer campers and rock band groupies, getting cotton fabric to absorb rich, vibrant colors is not an easy process. And it's one that uses environmentally damaging chemicals and large volumes of water and energy. But now Peter Hauser, a professor in the College of Textiles at North Carolina State University, believes he's found a way around these issues. By tweaking a technology that was originally developed nearly 30 years ago, Hauser believes it's possible to dramatically curtail both the energy and the water requirements of dyeing fabrics.

The Dye Process

Generally, two types of dye are used to color cotton and other fabrics: direct dyes and fiber-reactive dyes. Both types are anionic. Cotton itself develops an anionic charge in water, so without special treatment, getting the fabric to take up the dye is like trying to push the same poles on two magnets close together—it doesn't happen without a lot of work.

Direct dyes create a relatively weak hydrogen bond with fabric's cellulose polymer, forming a semidurable attachment. They can be applied directly from a water bath with a small amount of salt. Direct dyes are easier to use and less expensive, but they are not as washfast as fiber-reactive dyes. However, they exhibit good lightfastness and so are used on textiles that are seldom or never laundered, such as curtains and upholstery.

Fiber-reactive dyes are molecules that combine chromophores (the groups of atoms in a dye molecule that absorb light, which leads to color) with a reactive group that forms strong covalent bonds with the fiber via reaction with hydroxyl groups. These strong covalent bonds provide good washfastness for the color, but they require alkaline pH levels of the dye solution and significant amounts of electrolytes, or salts, such as sodium chloride or sodium sulfate—up to an amount equal to the weight of the fabric—to help screen the anionic dyes from the fiber's charge. The electrolytes also reduce the dyes' compatibility with water.

Before the cotton can be dyed, it has to be cleaned of minerals, waxes, and other impurities. It's also frequently bleached, usually with hydrogen peroxide, which requires repeated rinsings with water to remove. Anywhere from 10% to 40% of the fiber-reactive dye will not form a bond with the fiber, necessitating another washing step to remove the unreacted dye, a process called "scouring." Then too, the large volumes of waste water (containing the waste electrolytes) have to be disposed of, adding a pollution problem to the dye house's other worries.

"Water is the least expensive transfer medium for a dye," Hauser explains. "Dyes go through a water-soluble phase, then individual dye molecules penetrate into the cellulose fibers, and finally the dye attaches to the polymer chain that makes up the cotton fiber. It sounds pretty simple, but it's not."

In addition to water consumption, dye houses have to confront energy use issues as well, says Hauser. For one thing, to dye fabric evenly, the fabric and the dye solution must be kept in constant motion. This requires pumps to keep the solution circulating and some form of mechanical process to pull the fabric through in a continuous motion. Also, scouring is typically done by subjecting the cotton to large volumes of water kept at or near boiling, and Hauser says it can take as long to scour cotton as it does to dye it to begin with. "Three to four hours is not unusual," he says.

According to Hauser, a textile manufacturer that produces 500,000 kg of dyed knit fabric a month will discharge 50 million liters of water containing more than 370,000 kg of chemical solids each month. That same manufacturer will use the equivalent of 3 million kilowatt hours of energy each month. Considering the worldwide shortage of both energy and water, a reliable dye process that cuts down on the use of both commodities should be welcome.

Cationic Cotton

The dye process developed by Hauser uses a cationic reactant called 3-chloro-2-hydroxypropyltrimethylammonium chloride, or CR-2000 (produced by Dow Chemical Company). The reactant is mixed with an alkali, such as sodium hydroxide, to form a substance that permanently changes the charge of the cotton. "One end of the chemical carries a positive charge, while the other has a reactive group that reacts with the cotton," Hauser explains. "[The reactive group] is permanently bonded to the cotton, while the other end is strongly attractive to the dye molecules. Once formed, the bond between dye and cationized cotton is quite strong, leading to outstanding washfastness."

Hauser maintains that the process offers several other advantages in addition to colorfastness. If the process is run properly, nearly all the dye is used, so less dye is needed and very little remains in the wastewater. The process also works without salt. Says Hauser, "No color, no salt, nothing else in the discharge, so you may be able to discharge your wastewater without treatment. And your energy use drops, because you don't have to use hot water to scour, and since you can produce the same amount of dyed goods in less time, your productivity goes up as well."

It's a good solution, but not a perfect one, Hauser admits. For one thing, the chemical used to enhance the dyeability of the cotton is a small, water-soluble molecule, which means it doesn't particularly want to exhaust to the fiber. (Exhaustion rate refers to the amount of dye that leaves the solution and bonds with the fabric. A high exhaustion rate means a good deal of the dye leaves the solution to bond with the fabric, and a low exhaustion rate means less dye leaves the solution.) This requires applying the solution outside of the water process, rather than just mixing it in with the dye.

And the reactant is not without its own issues. "The cationic reagent, as received and used, is completely safe," Hauser says. However, when it's used in the process, it goes through an intermediate reactive stage and forms 2,3-epoxypropyltrimethylammonium chloride, a chemical that flunks the Ames test for carcinogenicity. To ensure that all of the epoxy intermediate is used up before being discharged into the environment, the pH of the water is adjusted. At high temperatures and high pH, the epoxy form of the chemical changes to become biodegradable.

Dyeing to Test the New Technology

Cotton Incorporated, a research and promotional company for the U.S. cotton industry, has investigated cationic cotton technology at various times during the last 20 years. Louis Protonentis, director of Technical Services, Dyeing, and Finishing Research for Cotton Incorporated, says he believes cationic cotton can revolutionize the way cotton is dyed. Protonentis is encouraged by what he has seen of Hauser's work, but he admits there will be some resistance in an industry that tried this approach during the 1970s. "At this point, I've seen two camps with this process," he says. "There are those who know of its

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use years ago and may have had problems. They have a bad taste from before and aren't aware of or confident of the progress that has been made in the chemistry and application knowledge. And there are those who have not heard of it and are somewhat skeptical of this 'great thing.'"

He continues, "Textiles is an old, established business, and anyone who runs a dye house knows their number one job is to get the product out the door without a lot of re-dyes or additions. With a new system like this, you'll need to do a lot of research in the lab and on the floor, to know how to adapt the process to your machinery, fabric, and so on. People in this business shy away from trying new things that may affect the everyday running of their operation. They like the comfort of doing the same thing over and over."

Dow Chemical is sponsoring a research project at North Carolina State University to look at new ways to cationize cotton. Dei Castilleja, Dow's technical services and development manager for CR-2000, says his company will have no issues with sufficient production volume, should the industry come to embrace this technology, but he says the industry will have to recognize certain differences. "The dyeing customer has to realize they can't cationize and dye with the same equipment they've been using all along," he says. "They're forming a whole different kind of cotton, and it's going to take a new way of looking at things. But there were a lot of layoffs in research and development with the industry slowdown, and a lot of companies either merged or sent their operations south to Mexico. It's going to take a more futuristic mindset than the industry is used to. And research is needed at each mill to understand the best process and best economic method to cationize and dye. Industry must accept change."

In addition to changes in attitude, the cationic process faces manufacturing issues as well. For example, earlier versions of CR-2000 weren't manufactured as properly as they should have been, says Hauser. "The raw material left was made from amines, which gives rotting fish its distinctive odor. So you had treated cotton going out with unreacted chemical left in it, and the cotton manufacturers would have had to try and sell shirts that smelled like dead fish."

Another issue is that in the cationic process, the dye reacts with the fabric much more quickly. "In the '70s [when the process was originally attempted] people tried to dye fabric just like they always did," says Hauser. "You need to adjust the procedure, because the dye goes on much more quickly. You could do that by adding the dye more slowly, through a measured rate valve of some sort, spreading the addition out over 30 minutes or so, rather than just dumping it in. If you put in the dye too fast, or before the fabric gets moving properly, you'll get uneven dyeing."

Yet another issue is the exhaustion rate of the cationic reagent to the cotton. The amount of reagent that bonds with the cotton is determined by the application method. Hauser's current process can produce a low exhaustion rate, which makes the cost of cationization higher than it needs to be, despite its overall resource savings.

None of these issues are insurmountable, believes Hauser. "It's important that you add the dye slowly and evenly, so you'll need process controls in place, and there will likely be some trial and error involved in getting the process timed right," he says. "But this is something whose success or failure is going to be driven by economics."

Cotton dye runs around $5.00 per pound, and Hauser says typical use might be 2% dye on weight of fabric, making cost per pound of cotton about $0.10. Add to that the cost of CR-2000 (at a cost of $1 to $2 per pound of reagent, cost per pound of cotton is about $0.15). However, less dye is needed in this process to achieve the same result, so the overall cost per pound to dye is lowered. Though the resulting savings per pound may seem relatively small, consider that some large cotton dye houses are processing millions of pounds a month.

"It's not inexpensive," Hauser admits, "but there are other considerations. For example, you have to factor in the cost of energy, water, and waste disposal. We're spoiled in this country with low cost energy and water, but most parts of the world are not in the same situation. There are dye houses in Mexico where they have to truck in water every day. We've gotten a lot of interest from other countries, like Egypt, India, and throughout Latin America, where water and energy are serious issues."

"It's going to take some willingness to innovate, says Castilleja—some companies in the industry that are willing to look ahead, to think about how they can improve their competitive positions and benefit the environment. It may well be that foreign markets, in areas where water and energy are more scarce and more expensive than here, will be the initial proving grounds for this technology. The textile dyeing industry in North America has to want to do something unique, because I'm not convinced it can survive the direction of the global competitive market."

The question of whether industry will, in fact, embrace this technology remains to be seen. Says Hauser, "Will garment manufacturers request suppliers who use this process, so they can advertise garments dyed with an environmentally benign process? Will GAP be able to sell a T-shirt at 20% more, if they can put on a hang-tag that says it was dyed with a 'green process'? I don't know. We have to look to the market to pull this technology through." If the technology does succeed,es, the result could be a brighter future for the environment.

Lance Frazer

Suggested Reading

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