
Salt Requirements Put Pressure On Wet Processing Plants

Increase of cotton's apparel market share
has caused salinity in textile effluent
streams to become a major issue

In the ancient world, countries that controlled large sodium chloride (salt) deposits also controlled commerce. A vital ingredient in human survival, salt was a valuable trading commodity. Deposited as ancient seabeds, salt mines were worked for millennia by Celts in what is now Western Europe.

In 1884, soon after Bottiger introduced synthetic direct dye for cotton, dyers recognized that addition of concentrated salt to an aqueous dyebath greatly enhanced this dye's substantivity to celluloses. Detailed studies showed that exhaustion level onto the fiber was linked to salt concentration, eventually approaching an upper equilibrium boundary dictated by maximum temperature (Freundlich isotherm behavior).

The first large-volume commercial applications of direct dyes to cotton, such as with the famous Congo Red chromophore early in this century, thus required formulations involving huge quantities of salt. Normal recipes called for 100-150% owg of salt in the formulation: a batch machine dyeing 1000 lb of cotton goods would require up to 1,500 lb of salt in the single dyebath!

Without direct dyebath reuse or separation schemes for segregating salt from the spent baths, and absence of conditions to destroy salt during the process, each bath drop contributed this mass of salt to effluent pretreatment and posttreatment ponds. Only

dilution of salt concentration by streams from the plant containing little or no salt (rinses, prewets, toilets, etc.) offered relief to reduce sodium chloride level to the point that discharge streams into freshwater rivers and creeks from treatment plants would not raise ecological salinity to the point of killing fish and other biological entities.

Many large-volume direct dyes used benzidine, a potent mammalian carcinogen (cancer causing agent) in its free form as the base. With discovery in the late 1970s that the azoic backbone linkages of benzidine-based dyes could be reduced by an enzyme in mammal bodies to release free benzidine in situ, the textile industry quickly converted to other dye classes to color cellulosic fibers.

With conversion in the 1980s when quality was also being stressed, the main winner in the multimillion U.S. dye sweepstakes was the reactive dye class. It gives superior wet and other fastness properties to other dye classes, e.g., sulfurs. Most reactive dyes also allow applications at low or ambient temperature, conserving expensive energy. Also, no noxious reducing agents are required to solubilize chromophores in water.

Unfortunately, reactive dyes do require copious amounts of salt in the dyebath to exhaust to the maximum level in conventional systems. Coupling this fact with the growth of cotton in U.S. apparel markets

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(some 64% of total fiber consumption in U.S. apparel markets in 1992) and decreased Environmental Protection Agency and state limits on salinity levels allowed in stream discharges, many textile wet processing plants are currently faced with an unacceptable dilemma: cut the volume of cellulosic fiber being processed by the plant to correspondingly reduce the salt output (i.e., consumer market denial), or face some combination of fines, government agency-dictated shutdown or curtailment of processing, and/or court suits by environmental groups.

Indeed, one small town in the Southeastern U.S. with two textile wet processing plants whose combined effluents account for about 70% of the municipality's total daily flow through its sewage treatment plant, faces all of the above opportunities.

At this location, the question of simple salt concentration of the discharge stream in the local river has been expanded to the short- and long-term effects of high salt concentrations on the downstream biota, and to the synergistic toxicity of the stream to sensitive test life forms.

The unlisted choice of these plants, of course, is one that would wreak severe economic hardship on the town and surrounding areas: moving the operations offshore where effluent regulations are less strenuous. Unfortunately, this real-world example could become the norm instead of the exception, as regulations continue to tighten and cotton rides its wave of popularity into the next century.

Why not just solve the problem by eliminating salt? Many textile executives are business, management or financial majors, and consequently commonly ask the above question to textile chemists. Unfortunately, you can't easily fight Mother Nature (or the laws of physical chemistry), and the question inherently involves such a fight.

When reactive dyes began developing in the 1930s the approach was to attach a chemical functional group to direct dye chromophores that would be energetic enough to give a facile, statistically appealing reaction with a stationary cellulosic fiber functional group (the hydroxyl, -OH, group of the fiber, or more commonly its derivative alkoxide, -O-Na⁺, derived by reaction with the strong bases sodi-

um hydroxide (caustic soda) and/or sodium carbonate (soda ash) in situ.

When ICI introduced commercial application of reactive dyes in 1956 with its trademarked Procion MXc series, the process called for similar salt concentrations in the formulations as for the direct dye ancestors: 100-150% owg. In essence, these new dyes were applied in two steps: they were exhausted on the fiber to a low level (60-65%) at the low temperatures employed (ambient to 110 F) as direct dyes. In a second step, base was added to convert cellulose fiber hydroxyls to the alkoxide and "fix" the chromophore via reaction between the dye-fiber to form a covalent bond.

Fortunately, the reaction of a reactive dye molecule with the fiber effectively removed that molecule from its inherent equilibrium with its fellows in solution. This resulted in a "step up" in exhaustion, often to the total 80-85% range. Unfortunately, the labile, reactive functional groups on the chromophores of this dye class react with the base as well as the hydroxide ion dissociation product of water, resulting in hydrolyzed ("dead") dye that could not be covalently bonded or otherwise permanently fixed to the fiber in the conventional process. Low temperatures employed with many of these colorants reflect that chemical kinetics favor hydrolysis of reactive functional groups over fixation at higher temperatures, and thus dead dye production is a limiting factor in the process.

The infamous strenuous after-scours and rinses which reactive dyed goods require to avoid bleeding and cross-transfer of colorants in home washing are dictated by this relatively high percentage (1520%) of dead dye that must be removed from the fabric before final finishing, drying and shipping.

But why is so much salt needed in the first step to reach the 60-65% exhaustion level? Without it, exhaustions can be as low as 20-40% at the low temperature employed, unacceptable from both cost (reactive dyes often run \$20-30/lb) and colored effluent treatment viewpoints. Other salts work, but at much higher costs/lb than the plentiful sodium chloride. The need for high salt concentrations relates to three factors:

(1) chemical makeup of the reactive dye chromophores;

(2) water medium used to apply the dye;

(3) hydroxyl group of the cellulosic fiber.

Early in the development of direct dyes, sulphonation of main chromophore to add -SO₃H functional groups to aromatic rings of the colorant was found aided in water solubilization. Conversion of this functional group to its -SO₃Na⁺ ionized form (the sulphonate group) by addition of base at the dye synthesis stage gave the chromophores high, low-clustered solubility in water.

Water molecule clusters have a high affinity for the negatively-charged sulphonate group via hydrogen bonding, accounting for solubility enhancement. Most modern direct dyes (and their reactive dye class descendants) sport one, two or some times even three of these negatively charged sulphonate groups,

The next part of the salt puzzle comes into play when the cotton fiber is placed in the aqueous dyebath. The plentiful hydroxyl groups on the cellulose polymer backbone (six per cellobiose repeat unit) also hydrogen bond extremely well with the water molecules, creating clusters of water around each functional group. The overall charge separation due to hydrogen bonding between fiber and water causes a negative charge to develop at the fiber/water interface (the zeta potential), forming a negative shield around the fiber surface.

What happens when a negatively-charged reactive dye molecule approaches the fiber surface in the critical, first step of an aqueous coloration process is thus obvious: like charges repel each other, and few of the dye molecules approach the anchored hydroxyl group to the proper distance to bring the chromophore to a stop through hydrogen bonding (initial strike, or temporary fixation, of the dye, the distance called the van der Waal's distance where electron clouds overlap).

The result: unacceptably low exhaustions, and an economically and environmentally defunct coloration process. The charge repulsion can be partially overcome by using several tools, e.g., increase process temperature (converting thermal energy to dye kinetic energy, allowing individual molecules to "ram" through the negative barrier) and increase agitation (converting

mechanical energy to molecular kinetic energy). None of these approaches, however, increase the exhaustion to an acceptable level.

Salt, then, becomes a critical auxiliary component to reactive dye formulations. The salt performs two key functions:

- Sodium chloride is fully dissociated in water to loose ion pairs of sodium (Na+) and chlorine (Cl-) ions. The positive sodium ion has the capability of traveling to the fiber/water interface and effectively negating the zeta potential, destroying the barrier to the initial dye/fiber interaction.

- Picturing the water as a lattice structure that has only limited sites for accommodating charged species, and considering the fact that dissociated sodium chloride is more compatible with the water lattice than a large molecular weight, "greasy" dye chromophore with a few sulphonate groups hanging off, the salt is the preferred species to occupy the limited lattice sites.

Dye is thus effectively "salted out" of the bath, with the distribution coefficient of the dye shifted from solution toward the fiber. Both these actions of the sodium chloride lead to the reactive dye exhaustions achieved today in textile wet processing plants.

With the detailed pressures intensifying on textile companies that are processing large volumes of cotton and/or rayon, numerous efforts are underway to minimize the impact of salt in textile operations.

Reactive dye producers are furiously working to reduce the level of salt required in a commercial dyebath while simultaneously increasing total exhaustion of their colorant lines. These goals (and the inherent competitive advantages for the company that first realizes them) require chemically modifying the chromophore bases in long-lived dye lines.

Chemical companies are naturally reluctant to discuss what molecular changes are being tried or even contemplated for their particular lines of reactive dyes. Logical approaches include using fewer sodium sulphonate groups per dye molecule and investigation of ionic functional groups other than sodium sulphonate for dye solubility enhancement that do not carry as tightly concentrated a negative charge, e.g., the ionized organic acid group -COO-.

Both approaches may reduce the net negative repulsive force per molecule of colorant. To increase total exhaustion, chromophores with multiple reactive groups, often of different functionalities, are reported in the patent literature to improve the statistical probability that at least one successful dye-fiber functional group collision will result in a covalent bond (all anchor the chromophore).

The dye molecule modification pathway is at best a long-term, partial solution to the industry's salt problem. Privately, dye producers convey that the targets are chromophores that will require about 60% owg of salt concentration in an aqueous bath, with some 90% total utilization (exhaustion) of colorant on the fiber. Only slight modifications of complex chromophores often shift the wavelength of visible light absorption, e.g., shift the shade in textile terms. Revamping complete dye lines while retaining current shades will take substantial time, both in research and commercial translation.

Meanwhile, the textile wet processing industry doesn't have the time luxury to wait on the chemical industry to solve the salt problem. Other routes are focused toward modifying chemical mixes and processes currently available in innovative ways to reduce the mass and concentration of sodium chloride exiting the plant.

In batch processing, direct dyebath reuse, where multiple batches of textiles are colored from a single standing bath without a drop to drain, has evolved over the past 10 years to the stage of technical feasibility with reactive dyes. For example, High Pressure Liquid Chromatography (HPLC) analyzers, capable of quantifying for direct reuse purposes the concentrations of dead and unaltered reactive dye remaining in a spent bath, has evolved to the point of facile operation. In a severe environment like a textile dyeing facility.

Since the salt is neither exhausted nor destroyed in a normal reactive dyeing process, direct analysis, replenishment and reuse of the dyebath for coloring multiple batches of material is a cost-effective, low-capital route to reducing the mass of salt entering pre- and post-treatment facilities from textile operations.

For continuous dyeing operations, and for those batch dyeing operations not incorporating direct dye-

bath reuse, separation and color kill-off technologies offer promise in the salt reduction effort. For example, Koch Membranes Systems Inc. has recently demonstrated on a pilot scale at Cotton Incorporated's facilities in Raleigh, NC., a polyamide-based nanofilter (NFJ membrane system that retains large organic molecules such as reactive dyes and auxiliaries, but allows the relatively small water and sodium chloride molecules to pass through and be collected for direct reuse (TW, May '93, p. 65).

The spent reactive dyebath is first filtered through a 500-micron bag to remove lint, and then through an ultrafilter to remove colloidal materials, oils and other substances that can foul a NF membrane. After traversing the NF membrane as a final step, the collected brine is analyzed to determine the amount of salt to be added, and the bath is then made up for subsequent dyeing in exactly the same manner as with fresh water, except with less salt added. No difference in fabric quality was determined by using the recycled brine as makeup water for subsequent dyebaths vs fresh water.

The proposed Koch salt recovery system purports to allow 95% salt reuse. With the cost savings manifested in the recycled water and salt, an estimated payback of 0.8 years is projected for installing the system (not including plant modifications). As a bonus, the volume of effluent to be treated by pond digestion or other means (e.g., concentration/incineration) is reduced to less than 5% of the combined, original dyebath and first rinse. At least one large dye supplier is also rumored to be near introduction of a similar type membrane brine/effluent separation system.

Another route is to destroy the color by oxidizing the chromophore to small fragments that do not absorb in the visible region. Both chlorine and ozone gasses appear to be oxidant candidates for reactive dyes in this approach. Once the color is destroyed, treated dyebath containing unaffected salt is then used as makeup water for the subsequent dyeing. One has to be careful with such dye degradation pathways, however, as colorants are highly complicated, aromatic structures that can possibly produce toxic and/or mutagenic/ carcinogenic fragmentation products oxidative breakdown.

Several companies are now promot-

ing electrolytic flocculation processes to physically remove colorant as a solid, followed by direct reuse of the remaining dyebath water. Andco Inc.'s process uses iron plates between which a high voltage is established. Dye flocculates from the system by generated ferrous hydroxide and flocculent then removed by simple gross filtration for solid waste disposal.

Recent research at Georgia Tech by Dr. Wayne C. Tincher and coworkers has indicated that dyes may also be reduced in the electrolytic process. Since the Andco system was first developed to remove heavy metals from metals refining process streams, the possibility also exists that any

such species in the dyebath may also be removed in the flocculent.

A German firm is currently introducing to the U.S. its Hostapura Process, which appears to base on a similar electrolytic principle as the Andco Process, but utilizing copper-based electrodes rather than iron. The process is reportedly in commercial operation in several small European dyehouses. The fate of the salt molecule and its possible interference with such electrolytic processes is currently not well understood or reported in the open literature.

Other more exotic dye cleanup techniques, such as UV-zone combination, are also being investigated,

with the thought of directly reusing the decolorized dyebath (and its inherent auxiliary chemicals, including salt) are also under investigation.

Cost/benefit, of course, will be the determining factor in the fate of all the above recycling technologies, and various combinations may be necessary to handle the wide range of chromophores that a typical dyehouse runs through its processes each year.

The good news is that the technologies appear feasible from a purely technical viewpoint, offering an alternative for companies who do face the wall of forced shutdown or curtailment of operations because of salt (or color) effluent problems. ○