Cleaner Technology Demonstration Site Case Study

Cranston Print Works Company, Webster, MA

TUR Through Process Improvement, Substitution, and Integral Recycling

Summary

As part of their commitment to continuous process improvement, Cranston Print Works Company has used toxics use reduction (TUR) to reduce environmental impact, improve occupational safety, and reduce operational costs. Implementation of in-process acid recycling, process control charting, and carbon dioxide treatment of wastewater has resulted in a 430,000 lb/year reduction in the use of acetic acid and the complete elimination of 2.66 million lb/year of sulfuric acid.

Background

Cranston Print Works provides preparation, printing, and finishing of cotton and polyester/cotton blended fabrics. To achieve the brilliant colors that its customers demand, Cranston Print Works uses azoic, or rapidogen, dyes, which require acid treatment to react the dye molecules so the desired color is achieved. The azoic dye consists of two components. The first component is an aromatic diazo molecule which bonds to the fabric. The second component is a diazonium salt, which only bonds with the diazo molecule to create the desired, brilliant shade in an acid environment. This exposure of the dyed textile to an acidic vapor is
known as "acid aging".

At Cranston, a multi-disciplinary team applying the Deming Quality Process chose to adopt control charting for processes throughout the plant. Control charting is a means of monitoring the state of a process as a function of process inputs by illustrating normal process variability and highlighting extreme disturbances. Analysis of the control chart then allows for improvement of the process such that variability is reduced.

Pre-treatment of fabrics entails repeated exposures to alkaline solutions to scour and whiten the fabric and to prepare the fabric surface for quality printing. Due to these processes, the waste stream at Cranston is highly alkaline and has required large quantities of sulfuric acid for neutralization.

Through toxics use reduction planning and effective engineering, Cranston Print Works has implemented programs that have reduced the quantity of acid required for the acid aging process, and have completely eliminated the sulfuric acid used in waste treatment.

In-Process Acid Recycling

The acetic acid used to bond the two components of the azoic dyes is delivered as a vapor to the printed textile through the use of an acid bath. The bath, a 5% acetic acid solution, is kept at 215F in a vessel called an ager through which the fabric is laced on rollers. In a reservoir, or wet well, at the bottom of the ager, the acid solution is boiled producing the vapor to which the fabric is exposed. Approximately 4% of the acid is either consumed in the dye chemical reactions or
remains as residue on the textile to be washed off in a subsequent operation. The 96% balance of the acid vapor in the ager escapes the vessel and is captured in an exhaust system.

Prior to implementation of the in-process acid recovery system, the entire amount of this acidic exhaust was sent to a scrubber and then to drain as wastewater. Cranston installed the new acid ager with a condenser in-line between the ager and the scrubber. This condenser recovers 90% of the acid steam, and the recovered solution is piped directly back into the ager's wet well where fresh solution is added to make up for losses. Due to the reduced acid content in the exhaust, water flow to the scrubber can be recirculated, significantly reducing discharge.

**Control Charting**

Control charting is used to ensure optimum process efficiency, defined here as achievement of highest product quality with minimum use of acetic acid. The chemical reaction that occurs during the acid aging process is optimal in a 5% acid environment. An environment which exceeds 5% acid introduces excess acid into the process, while an environment of less than 5% acid can result in poor print quality. Historically, the process for the acid agers involved the manual addition of acetic acid to the wet well, resulting in very high variability in acid concentration. In order to ensure a high quality product, the amount of acid added to the system was much greater than the chemical reaction required. The control charts for this process highlighted the extreme variability of the range in acid content and the unnecessarily high mean value of acid concentration.
Once the lack of control which this process exhibited was brought to the attention of management, steps were taken to improve the process. An automated acid feed was added to reduce the variability in acid content by approximately 79%. Tighter control of the process allows the mean concentration of the acid solution to be held closer to the optimal 5% without jeopardizing product quality due to insufficient acid content.

**Carbon Dioxide Substitution in Wastewater Treatment**

The substitution of liquid carbon dioxide (CO₂) for sulfuric acid represents another significant process improvement by Cranston Print Works resulting in substantial reductions in toxic chemical usage. The application of CO₂ in wastewater treatment effectively eliminated Cranston's facility-wide usage of sulfuric acid. Although using CO₂ for the treatment of alkaline wastewater is a technology which is not unique to Cranston, the delivery system which was implemented here is unique.

The wastewater stream at Cranston Print Works has a pH of over 11. This alkalinity must be reduced to a pH of approximately 8 before discharge into the local publicly owned treatment works (POTW). Traditionally this neutralization was accomplished through the use of sulfuric acid, but due to environmental concerns, worker health and safety, and the TUR planning process, Cranston chose to use liquid CO₂ to neutralize their wastewater. In 1992, two methods of CO₂ delivery were available. They were in-line delivery, injecting gaseous CO₂ into wastewater pipes enroute to holding tanks, and diffusion delivery, bubbling CO₂ up through the wastewater in a holding tank. Neither method was suitable because the length of pipe required for in-line delivery and the holding tank depth
required for diffusion delivery were prohibitive at Cranston's facilities.

Cranston Print Works decided to take advantage of the turbulence created by jet aeration headers in the wastewater holding tank which combined 15,000 gal/min of recirculated wastewater with 1,000 ft³/min of air to reduce the biochemical oxygen demand (BOD). Forty nozzles on each header pipe act as aspirators that mix the air and wastewater as they leave the wastewater header. Neutralization is accomplished by injecting liquid carbon dioxide directly into the wastewater header. The turbulence created by the jet aeration system accelerates the chemical conversion of carbon dioxide to carbonic acid. The gaseous CO₂, when mixed with the liquid, converts to carbonic acid and lowers the alkalinity of the waste stream. The CO₂ vendor conducted bench-scale tests with Cranston wastewater to ensure the viability of this new process prior to implementation of the production scale unit. These tests determined that liquid CO₂ would be able to meet the neutralization demands.

**Toxics Use Reduction Assessment**

Process improvements resulting from control charting have reduced annual acetic acid usage in the acid agers by over 128,000 pounds.

The automated feed system has dramatically reduced worker exposure to acetic acid.

Implementation of the acid steam in-line recovery unit with the new acid ager has reduced Cranston’s annual acetic acid usage by more than 302,000 pounds.
Water discharge from the scrubber unit has decreased from 56 gal./min. to 15 gal./min. as a result of recirculation.

The substitution of carbon dioxide for sulfuric acid in the treatment of alkaline wastewater has completely eliminated the annual use of 2.66 million lb. of sulfuric acid.

Due to TUR planning and good engineering, Cranston has reduced its use of TUR chemicals by over 3 million pounds per year since 1992.

Table 1

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**Economic Assessment**

Due to implementation of the acid recovery system, Cranston annually saves approximately $84,000 in acetic acid procurement costs and $200,000 in wastewater treatment costs.
Control charting used in the acid agers has resulted in the reduction of acetic acid procurement costs by over $33,300 annually.

The capital expenditure for the purchase and installation of the acid recycling system was $235,000.

The capital expenditure for the Tytronics unit and the automated feed was approximately $18,000.

Substituting carbon dioxide for sulfuric acid in wastewater treatment has reduced procurement costs annually by at least $70,000 and compliance costs by over $3,000.

The capital expenditure for the purchase and installation of the CO₂ wastewater system was approximately $93,000.

### Economic Summary

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### Transferability

Understanding the extent to which a manufacturing process is "under control" is the first step towards improving that process. All manufacturing processes which involve the use of toxic chemicals can employ control charting as a means to assess the efficiency of toxics use. The information gathered on the control
charts can highlight areas needing improvements and thus reduce toxics use through process improvements. Acid aging of textiles is unique to azoic dyes, however, recovery of acid vapors may be possible in a variety of processes if the properties of the acid are suitable. Manufacturing operations which need to lower process pH may be able to eliminate the need for acid by substituting carbon dioxide to reduce alkalinity.

This case study is part of the Toxics Use Reduction Institute's Cleaner Technology Demonstration Sites Program.