Project Summary

Evaluation of Ultrafiltration to Recover Aqueous Iron Phosphating/Degreasing Bath

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Pollution prevention efforts studied in the report summarized here targeted the hazardous waste generated from a 5000-gal iron phosphating/degreasing bath used by a metal fabricator to clean and precondition steel parts for painting. When oil buildup in the bath began to sacrifice product quality and the discharge levels of oil and grease in the rinse water edged closer to the maximum allowable limit, all 5000 gal were dumped and replaced. Periodic dumping, about three times each year, resulted in at least 15,000 gal/yr of hazardous waste. Several waste minimization alternatives were considered, and ultrafiltration was selected as the most promising technology to recover and reuse the bath and to reduce the total amount of hazardous waste generated.

This project was carried out in four stages: (1) initial assessment of the problem and evaluation of alternatives, (2) bench-scale screening of ultrafiltration membrane candidates, (3) pilot-scale study at the Illinois Hazardous Waste Research and Information Center (HWRIC), and (4) full-scale implementation and testing onsite at the company's facility. Full-scale testing integrated the new waste reduction scheme into the facility's production process by applying ultrafiltration directly to the 5000-gal iron phosphating/degreasing bath. Ultrafiltration successfully removed oil contamination from the bath and returned clean process solution back to the original 5000-gal tank. Ultrafiltration concentrated the hazardous component down to 10 gal of oily waste and reduced hazardous waste generation 99.8%. Permeate flux rates were high enough to compete with the constant input of oil from the production line, and concentrations of oil in the bath were maintained at acceptable operating levels. The estimated payback period associated with implementing ultrafiltration was only 6.9 mo.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objective of the U.S. Environmental Protection Agency (EPA) and the Illinois HWRIC was to evaluate potential technologies and operational modifications that could reduce the amount of hazardous waste generated at a metal fabrication facility. The goal of this project was to find an environmentally responsible means to extend the life of a 5000-gal iron phosphating/degreasing bath and thereby reduce hazardous waste generation. The relative feasibility of ultrafiltration as well as its capability to reduce waste generation were assessed on an engineering and economic basis. Results of this project were used to justify installing a permanent ultrafiltration system and operating practices that would improve product quality.

Industrial Participant

R.B. White, Inc., of Bloomington, IL, operates a sheet metal fabrication facility that manufactures painted steel shelving units. Cold-rolled steel arrives at the plant from the steel mill coated with mill oils to protect the
bare metal from corroding or staining during storage and fabrication operations. During fabrica-
tion, coolants and lubricants are also applied to the metal working surface. Before being painted, the metal surfaces are cleaned to remove the mill oils and metal working fluids and then preconditioned to bond well with the paint coating. Fabricated parts are cleaned and phosphated in a 5000-gal heated, aqueous immersion tank and rinsed with a fresh water spray. The company previously operated separate degreasing and phosphating tanks using trichloroethylene in the degreasing tank and in 1985, switched to a single-stage aqueous iron phosphating/degreasing system to improve worker safety and reduce the generation of organic solvent emissions and hazardous waste. Although the switch eliminated the risks and liabilities associated with organic solvents, it introduced a new waste disposal problem.

Problem Description

Simultaneous degreasing and phosphating in the same bath formed an oil-water emulsion. With extended use, the buildup of oil in the bath reduced cleaning and phosphating efficiency, and product quality was compromised. Additionally, dragout of oil from the bath into the rinse water eventually pushed oil and grease levels in the discharge over the allowable limit. In the past, oil skimmers were used to control oil slicks on the surface and prolong the life of the bath, but the skimmers were only partially effective. When oil in the bath began to sacrifice product quality and the discharge levels edged closer to the maximum allowable limit, the bath had to be replaced. Depending on production rates, the bath typically lasted 3 to 4 mo. Replacing the bath required a full day of lost production time and associated with organic solvents, it introduced a new waste disposal problem.

Process Background

Iron phosphating/degreasing processes are widely used in the manufacture of metal products to clean and precondition ferrous surfaces. Many metal fabricators and others that paint or coat steel choose iron phosphating/degreasing processes because they effectively clean metal parts, provide an excellent surface for paint adhesion, and protect against under-paint corrosion. The goals and mechanisms associated with the degreasing and phosphating processes are discussed below.

The goal of degreasing is to remove mill oils, metal working fluids, and any other shop soils from the steel surface and prepare it for finishing. Degreasing was accomplished using nonionic surfactants in a heated (140°F) air-agitated bath. The surfactants surrounded the oil and dirt particles and formed a stable emulsion that cleaned the parts and prevented the oil and dirt from redepositing on the metal surface.

Phosphating is a common type of pre-paint coating process used to simultaneously provide corrosion resistance and enhance paint adhesion. Phosphate salts chemically bond to the metal surface to produce an amorphous conversion coating. The phosphate conversion coating is non-conductive and it protects the metal surface from electrochemical oxidation that leads to rust and corrosion. The matrix of the phosphate coating forms capillaries that increase the surface area and provide a mechanical interlocking structure on which the paint can adhere.

The 5000-gal bath was charged with Duragard Soke and Tart liquid acid (supplied by DuBois Chemicals),* which contained non-ionic surfactants, phosphate salts, phosphoric acid, and accelerators to promote phosphate precipitation. The concentration of Duragard Soke and the pH in the bath were checked daily with a simple titration kit and litmus paper to ensure that concentrations were maintained between 1.5 and 2.0 oz Duragard/gal and at a pH of 3.5.

Waste Reduction in the Metal Fabricated Products Industry

The EPA's campaign for waste reduction is bringing change to industries through the 1984 Hazardous and Solid Waste Amendments (HSWA) to RCRA, the Toxics Release Inventory (TRI), the 1990 Pollution Prevention Act (PPA), and the more recent 33/50 Program. The HSWA requires industries to set up waste minimization programs and to produce certified manifests demonstrating their waste reduction efforts. The TRI is a computerized data base that tracks the routine and accidental release of approximately 300 toxic chemicals reported by U.S. manufacturers. The 1990 PPA brought about stricter TRI industrial report requirements that include providing information on pollution prevention efforts. The 33/50 Program is EPA's voluntary pollution prevention initiative to reduce the Nation's releases of 17 TRI chemicals 33% by the end of 1992 and 50% by the end of 1995. Backed by federal legislation and economic incentives, EPA's pollution prevention campaign has targeted several operations associated with the metal fabricated products industry. Finding environmentally responsible solutions to the industry's waste disposal problems has focused on source reduction (including process modifications and raw materials substitution) and recycling.

The EPA recommends various strategies for pollution prevention in the metal fabricated products industry. Until now, waste reduction in surface preparation operations has focused on conserving or finding alternatives to organic solvent cleaners. For years, the metal finishing industry has relied on organic solvents for cleaning metal parts. Trichloroethylene, methylene chloride, perchloroethylene, and 1,1,1-trichloroethane account for a majority of the chlorinated solvents used by industry. Recently, however, environmental concerns for health and disposal consequences have increased. Chlorinated solvents were not only targeted by the TRI and 33/50 Program, but solvent wastes were among the first to be banned from land disposal by the 1984 HSWA. More recently, 1,1,1-trichloroethane has been linked to ozone depletion in the upper atmosphere and will no longer be manufactured in the U.S. after 1995. As restrictions increased the cradle-to-grave liability for solvent waste generators, the metal finishing industry began to turn to other options for cleaning operations. Aqueous cleaners, emulsion cleaners, mechanical and thermal methods, and abrasive cleaners emerged as alternatives to organic solvents. These options help reduce emissions of volatile organic compounds (VOCs) and lessen worker exposure. The switch to aqueous cleaners can also reduce the annual reporting required under SARA Title III, Section 313, Toxic Chemical Release Reporting: Community Right-To-Know.

Aqueous cleaners have already replaced solvent degreasers in many industrial surface preparation operations. The water-based cleaners effectively remove protective oils, cutting oils, hydraulic fluids, silicone oils, water soluble coolants, shop dirt, fingerprint, and other soils. Special additives also make the aqueous cleaners versatile coating solutions. Making the switch has even made it possible to eliminate some separate degreasing and coating processes as well as reduce waste generation. Aqueous cleaners are finding success in many industrial surface preparation operations including airplane components, printed circuit boards, advanced composites, fasteners, and automotive parts.

The tank life of the aqueous cleaners is limited by the buildup of the dirt and oils in
the bath. Cleaning effectiveness begins to deteriorate, and the performance of other chemicals in the bath is inhibited. Although the aqueous degreasers do not carry all the risks and liabilities associated with the disposal of waste organic solvent cleaners, periodic replacement of the bath creates a different waste disposal problem.

Current disposal options for spent aqueous cleaning solutions include tankering, incineration, or discharge. The rising costs associated with these disposal and pollution control options are the main incentives to extend the life of the aqueous cleaner baths. Rather than wasting valuable raw materials, the aqueous cleaners have the potential to be recycled again and again. Depending on the physical characteristics of the bath solution, the life of the bath can be extended by skimming contaminants off the top, settling heavier fractions to the bottom, or filtering out suspended species.

Ultrafiltration

Conventional filtration techniques rely on depth or screen filters to remove oil and dirt from a process solution, but conventional filter media clog easily. They require frequent backflushing or disposal, which result in additional wastes. Membrane filtration is a more advanced technique that takes advantage of thin-film membranes and turbulent flow patterns to deliver a more consistent flow rate and a higher quality filtrate than conventional filtration. Ultrafiltration is one class of membrane filtration that uses membranes with pore diameters ranging from 10⁻⁶ to 10⁻⁷ m.

The ultrafiltration process works by producing two separate streams: concentrate and permeate. The permeate stream contains only the components in the feed solution small enough to pass through the membrane pores (water, solubilized species). The concentrate stream contains everything else that is rejected by the membrane (emulsified oil and dirt).

The recent development of more durable membranes, such as PVDF, has expanded the application of ultrafiltration beyond its origins in the food industry to successfully handle industrial process solutions with extreme pHs, high temperatures, and high oil concentrations. Because of its unique capabilities to concentrate oily wastewater and produce a clear filtrate, ultrafiltration has emerged as a promising technology for extending the life of aqueous cleaner baths. Ultrafiltration of oil-water emulsions is a more straightforward method for removing and concentrating oil than are other physical, chemical, or thermal means. Ultrafiltration does not require a stockpile of chemicals and does not produce a chemical sludge that requires special treatment or disposal. Instead, ultrafiltration produces a water phase that requires no further treatment and a concentrated phase only a fraction of the original volume that can sustain combustion or be disposed of efficiently. Ultrafiltration requires no heat input, low energy, and little operator attention.

One of the greatest limitations of ultrafiltration membranes is their tendency to foul. Fouling is detected as the decrease in permeate flux over time, where the flux is defined as the volumetric flow rate of permeate per cross-sectional area per time. Fouling is mainly due to the accumulation of particles on the membrane surface and/or within the pores of the membrane itself. In industrial applications where ultrafiltration could be used to filter aqueous cleaning baths, fouling will typically be due to oils, suspended solids, free surfactants, and metal precipitates. When a membrane shows signs of fouling, the flux can largely be restored by cleaning the membrane, but a portion of the flux may be unrecoverable because of irreversible fouling.

Full-Scale Testing

Results from the bench- and pilot-scale studies were used to develop a full-scale, modified-batch test conducted onsite at the facility. Figure 1 shows how the full-scale test applied ultrafiltration directly to the 5000-gal iron phosphating/degreasing bath. The objective was to directly measure the effect of ultrafiltration on the process solution under actual plant conditions. The full-scale test took into account the constant input of oil from the production line and the daily addition of bath chemicals. Additionally, the full-scale test also helped identify problems with the ultrafiltration equipment and anticipate changes that should be made on a permanent unit.

The full-scale in-plant testing featured an ultrafiltration system provided by Koch Membrane Systems (Model UF-4) equipped with four 1- in tubular PVDF membranes (100,000 MWCO, 4.4 sq ft total area). Data obtained from the full-scale modified-batch test was used to determine whether ultrafiltration would be a viable option for waste reduction at the plant. Technical, operational, and economic aspects associated with the ultrafiltration equipment were examined to evaluate the feasibility of this technology to improve the company's metal fabrication operation.

When field testing began, the iron phosphating/degreasing bath had not been replaced in over 3 mo. The aqueous solution was murky with dirt and oil, and large patches of free oil floated on the surface. The changes that took place over the next 11 days of ultrafiltration testing produced a dramatic effect. Surface oil slicks disappeared and were replaced by a clean, light foam. The bath solution was visibly clearer, and plant personnel testified that it looked like a freshly recharged bath. Results of total organic carbon (TOC) analyses for the full-scale testing showed the change in oil and surfactant concentrations during the test (Figure 2).

Economic Analysis

The costs and benefits associated with installing an ultrafiltration system were analyzed to determine the economic feasibility of this technology. Based on the estimated expenditures and savings, the payback period associated with this technology, was only 6.9 yr. The net present value and interest rate of return indices were $152,143 and 178%, respectively. Therefore, investment in an ultrafiltration system represented a very attractive economic alternative.

Conclusions

The overall evaluation of this pollution prevention project was based on ultrafiltration performance, product quality, and economics. Results indicated that the concentration of oil in the iron phosphating/degreasing bath was substantially reduced and maintained at acceptable operating levels. Virtually all of the unused phosphating agents were conserved although a portion of the unused surfactants was not. Permeate rates exhibited excellent performance during the acidic (pH=3.5), high temperature (140°F) operation and were high enough to process the constant input of oil from the production line. The entire 5000-gal bath was processed in 180 ultrafiltration operating hours. Coating weight, rust creepage, and paint adhesion tests conducted by DuBois Research Laboratory and plant personnel on samples of steel parts indicated that product quality achieved during the full-scale study was good for the plant's application. The payback period for implementing the ultrafiltration system was 6.9 mo. By using ultrafiltration, the company will reduce its hazardous waste generation by at least 15,000 gal/yr, a 99.8% reduction.
This project has successfully demonstrated the ability of membrane filtration to reduce hazardous waste generation and recover valuable raw materials in a metal fabrication operation. This application introduces another innovative waste reduction technique to the metal fabricated products industry that could benefit the many plants nationwide that use aqueous cleaner systems like the iron phosphating/degreasing process at the R.B. White company. The ultrafiltration system implemented in this project saves money, maintains good product quality, and reduces waste generation.

Figure 2. Oil and surfactant in bath vs time.

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Paul Randall is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of Ultrafiltration to Recover Aqueous Iron Phosphating/Degreasing Bath," (Order No. PB93-221 638/AS; Cost: $19.50, subject to change) will be available only from:

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