

EVALUATION OF ULTRAFILTRATION TO RECOVER  
AQUEOUS IRON PHOSPHATING/DEGREASING BATH

by

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## NOTICE

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## FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, Superfund-related activities, and pollution prevention. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report describes the results of laboratory and field testing of an ultrafiltration system to recover and reuse an iron phosphating/degreasing bath. This pollution prevention project supports the emphasis on reducing generation of hazardous waste by encouraging study and development of methods to effectively use and recover aqueous cleaning solutions.

## ABSTRACT

Pollution prevention efforts targeted the hazardous waste generated from a 5000-gallon iron phosphating/degreasing bath used by a metal fabricator to clean and precondition steel parts for painting. With extended use, the buildup of emulsified oil in the bath reduced cleaning and phosphating efficiency. Dragout of oil from the bath into the rinse water also pushed oil and grease levels in the effluent over the allowable limit. When oil in the bath began to sacrifice product quality and effluent levels edged closer to the maximum allowable limit, all 5000 gallons were dumped and replaced. Periodic dumping, about three times each year, resulted in at least 15,000 gallons per year 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. Ultrafiltration has proven successful in similar industrial applications with alkaline cleaning solutions, but the application of new membrane filtration technology to this acidic, corrosive, high temperature bath was an innovative approach to pollution prevention.

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-gallon iron phosphating/degreasing bath. Ultrafiltration successfully removed oil contamination from the bath and returned clean process solution back to the original 5000-gallon tank. Ultrafiltration concentrated the hazardous component down to 10 gallons of oily waste and reduced hazardous waste generation 99.8%. The concentration of oil in the bath was substantially reduced and maintained at acceptable operating levels. Permeate flux rates exhibited excellent performance and were high enough to compete with the constant input of oil from the production line. A significant portion of the unused phosphating agents were also conserved although some surfactant was lost. Product quality tests revealed that quality achieved during the full-scale ultrafiltration study was good for the facility's application. The estimated payback period associated with implementing ultrafiltration was only 6.9 months. Results of this study were used to justify installing a permanent ultrafiltration system and operating practices that would improve product quality.

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## ABBREVIATIONS AND SYMBOLS

### ABBREVIATIONS

ASTM	-- American Society for Testing and Materials
cmc	-- critical micelle concentration
COD	-- Chemical Oxygen Demand
DAF	-- Dissolved Air Flotation
EDTA	-- Ethylenediaminetetraacetic acid + its sodium salts
EPA	-- Environmental Protection Agency
HSWA	-- Hazardous and Solid Waste Amendments to RCRA
HWRIC	-- Hazardous Waste Research and Information Center
IC	-- Ion Chromatograph
IR	-- Infrared Spectrophotometer
IRR	-- Interest Rate of Return
kW	-- kilowatt
L	-- Liter
MEK	-- Methyl Ethyl Ketone
mg	-- milligrams
MIBK	-- Methyl Isobutyl Ketone
mL	-- milliliter
mm	-- millimeter
MWCO	-- Molecular Weight Cutoff
N	-- Normal
NPV	-- Net Present Value
PHC	-- Polyhydrocarbon
POTW	-- Publicly Owned Treatment Works
PPA	-- Pollution Prevention Act
psig	-- pounds per square inch, gage
PVDF	-- Polyvinylidene di fluoride
QAPP	-- Quality Assurance Project Plan
RCRA	-- Resource Conservation and Recovery Act
RPD	-- Relative Percent Difference
SARA	-- Superfund Amendments and Reauthorization Act
TCLP	-- Toxicity Characteristic Leaching Procedure
TOC	-- Total Organic Carbon
TRI	-- Toxics Release Inventory
UF	-- Ultrafiltration
VOC	-- Volatile Organic Compound
WRITE	-- Waste Reduction Innovative Technology Evaluation

### SYMBOLS

Ca	-- Calcium
CaCO <sub>3</sub>	-- Calcium Carbonate
CrO <sub>3</sub>	-- Chromic Acid
Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	-- Iron Phosphate
Mg	-- Magnesium
NaCl	-- Sodium Chloride
NaOH	-- Sodium Hydroxide
Na <sub>2</sub> SO <sub>4</sub>	-- Sodium Sulfate
pH	-- Log of Hydrogen ion concentration
pK <sub>a</sub>	-- Dissociation constant
PO <sub>4</sub>	-- Phosphate

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## **Section 1**

### **INTRODUCTION**

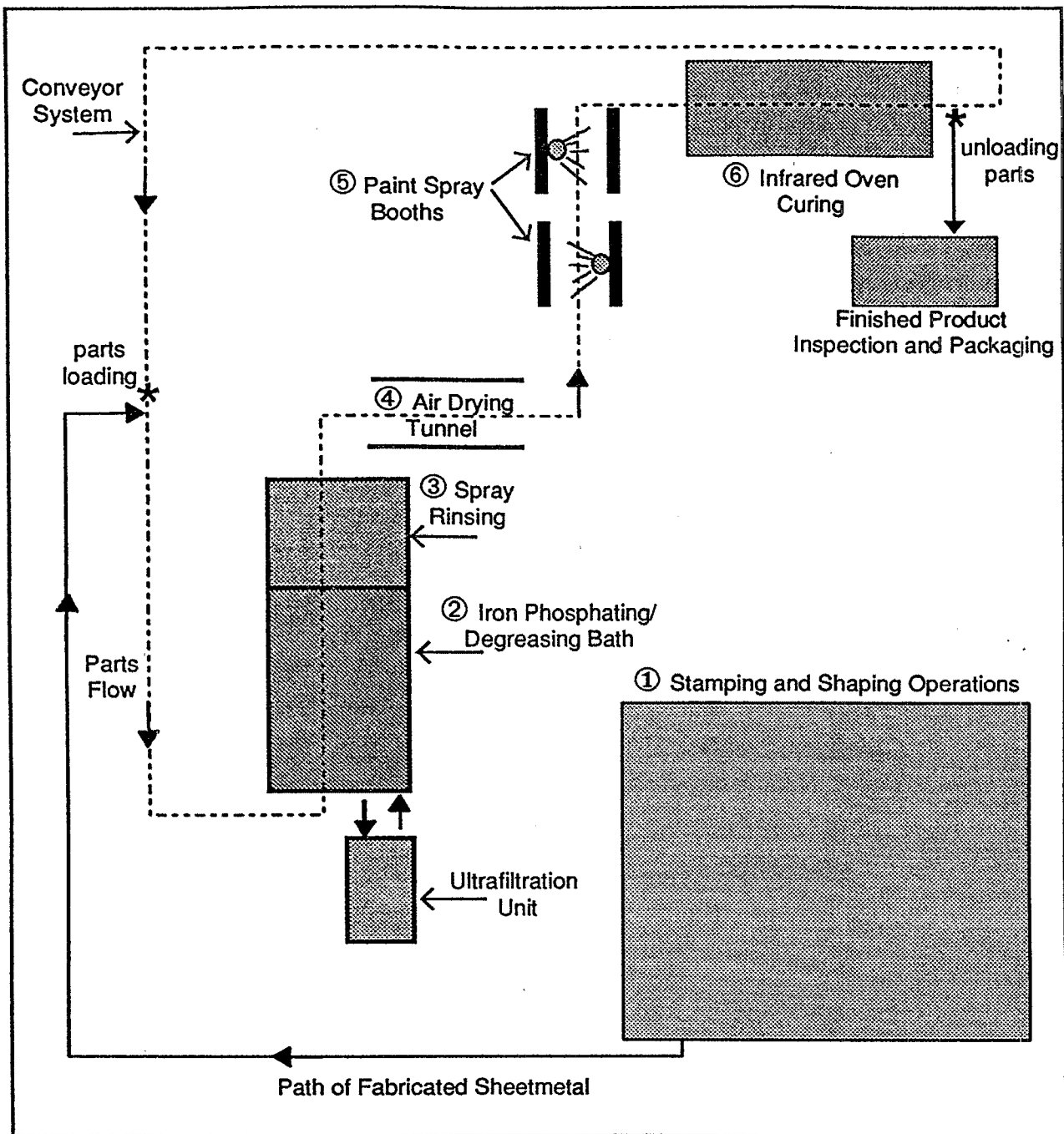
This project is one of five projects conducted under the State of Illinois - U.S. Environmental Protection Agency's (EPA) Waste Reduction Innovative Technology Evaluation (WRITE) Program. It represents a joint research effort of R.B. White, Inc., Bloomington, Illinois; the Illinois Hazardous Waste Research and Information Center (HWRIC), the Department of Energy and Natural Resources, Champaign, Illinois; the Civil Engineering Department at the University of Illinois; and the USEPA Office of Research and Development, Cincinnati, Ohio.

#### **Project Goals and Objectives**

The purpose of this project was to evaluate potential technologies and operational modifications that could reduce the amount of hazardous waste generated at a metal fabrication facility. HWRIC's pollution prevention team worked with R.B. White, Inc., a sheetmetal fabricator, to develop a reduction strategy for hazardous waste generated from operating a 5000-gallon iron phosphating/degreasing bath. The goal of this project was to find an environmentally responsible means to extend the life of the bath and thereby reduce hazardous waste generation. This project was carried out in four stages: (1) initial assessment of the problem and evaluation of alternatives, in which ultrafiltration was identified as the most promising technology to accomplish the project goal, (2) bench-scale screening of ultrafiltration membrane candidates, (3) pilot-scale testing performed at HWRIC labs, and (4) full-scale implementation and testing performed on site at R.B. White. 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. operates a sheetmetal fabrication facility that manufactures painted steel shelving units. Figure 1 depicts a floor plan of R.B. White's metal working, cleaning, and painting operations. 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. The sheetmetal is fabricated using various stamping and shaping operations which apply coolants and lubricants 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 hung on a conveyor system that immerses the steel in a heated, aqueous iron



**Figure 1: Floor Plan of Cleaning and Painting Operations**

phosphating/degreasing bath. Surfactants in the bath clean away the mill oils, coolants, lubricants, and shop soils while phosphating agents simultaneously deposit an amorphous coating that aids in paint adhesion. Quality control in the bath is maintained by performing daily titrations which track the level of chemicals in the bath. When the parts emerge from the bath, a fresh water spray rinses away any oil residue and helps to prevent spotting. Parts are visually inspected to make sure they are free from oil and display a uniform phosphate coating. The cleaned and phosphated parts are dried in a forced-air drying tunnel, coated with enamel paint in a spray booth, and cured in an infrared oven. The parts are then removed from the conveyor, and the adhesion quality of the paint coating is spot-checked using a cross-hatch test. Finally, the finished product is boxed and shipped for distribution. There are various point sources of waste generation in this process. Figure 2 illustrates a flow diagram of the main operations and their associated waste streams. This project focused on the hazardous waste generated from operating the 5000 gallon iron phosphating/degreasing bath and the resulting rinse water discharge.

R.B. White has used the current mode of iron phosphating/degreasing for the past eight years. This process was recommended by DuBois Chemicals (R.B. White's chemical supplier) on the basis that phosphating and degreasing could be accomplished in a single tank by using two of their products: Dura-Gard Soke and Tart liquid acid. Previously, the facility had operated separate degreasing and phosphating tanks using trichloroethylene in the degreasing tank. In 1985, the company switched to DuBois' aqueous iron phosphating/degreasing system to improve worker safety and reduce the generation of organic solvent emissions and hazardous waste. Although switching to a single-stage aqueous system eliminated the risks and liabilities associated with organic solvents, it introduced a new waste disposal problem.

### **Problem Description**

At R.B. White, simultaneous degreasing and phosphating in the same bath formed an oil-water emulsion. With extended use, the buildup of oil and dirt in the bath reduced cleaning and phosphating efficiency, and product quality was compromised. Without a clean surface, residual oil and dirt adversely affected the adhesion and uniformity of the phosphate coating. Additionally, dragout of oil from the bath into the rinse water raised oil and grease levels in the discharge. 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 months. Replacing the bath required a full day of lost production time to take the process off-line, make arrangements with a waste transporter to drain and dispose of the entire contents, and recharge the tank with 5000 gallons of fresh water and raw

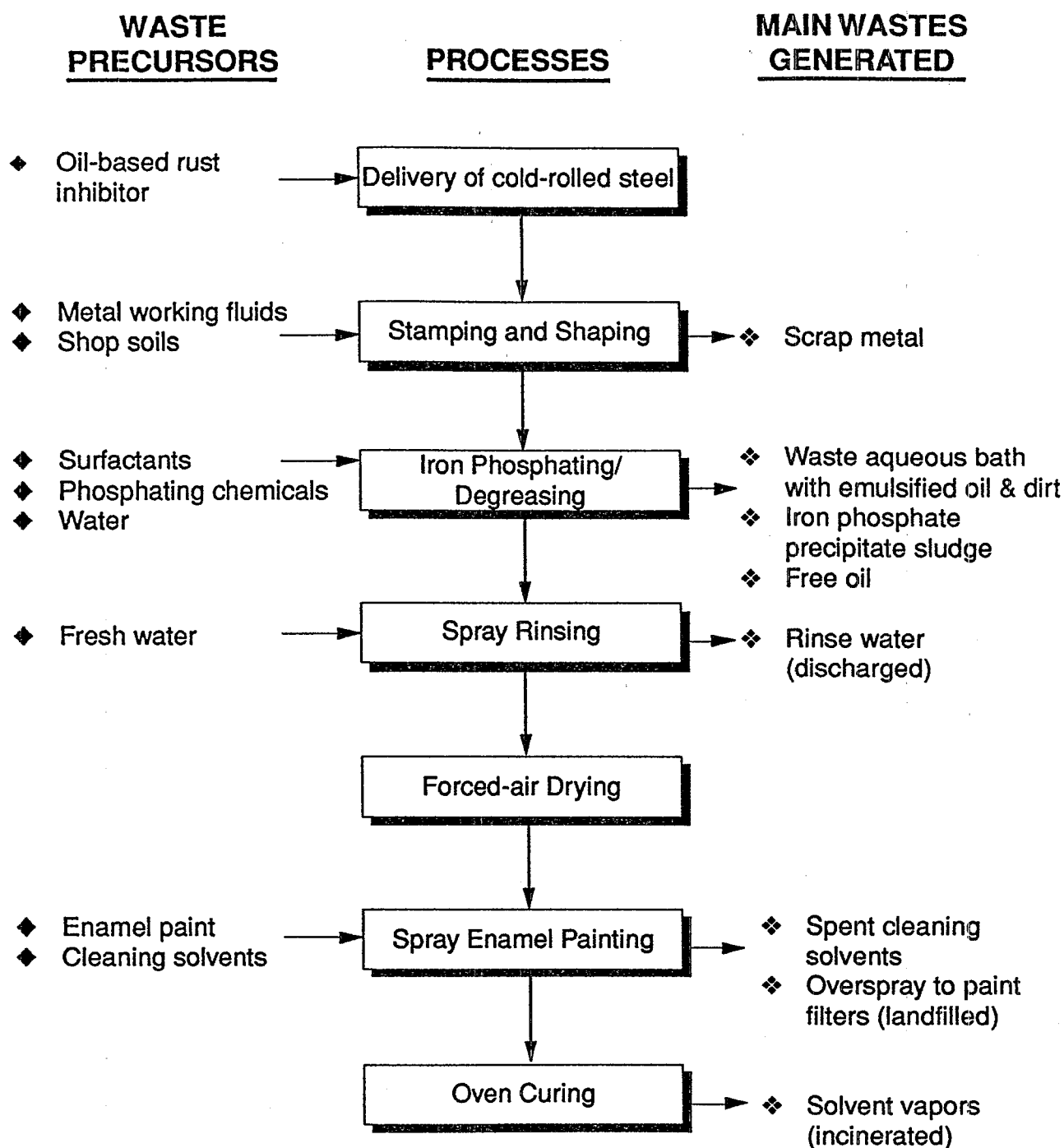


Figure 2: Flow Diagram of Main Operations and Associated Waste Streams

materials. The spent bath was classified as RCRA hazardous waste because it failed Toxicity Characteristic Leaching Procedure (TCLP) tests for xylene. Since land disposal of liquid wastes is prohibited, the bath, sludge, and skimmed oil were incinerated in a cement kiln. Disposal costs including transportation and incineration ran about \$1 per gallon which came to \$5000 per bath, or about \$15,000 per year in addition to the costs associated with lost production time and replacement of water and raw materials.

## Section 2

### 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 (Wittke, 1987). Iron phosphate coatings have become increasingly popular in prepaint applications as existing and projected EPA regulations require more stringent control and more expensive waste treatment methods for other coatings such as chromated seals, zinc phosphate, and chromate conversion coatings (Phillips, 1990). The goals and mechanisms associated with R.B. White's degreasing and phosphating process 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 agents can accomplish this in several ways: detergency, solvency, chemical reaction, or mechanical action (USEPA, 1989). The aqueous cleaning solution in use at R.B. White employs detergency in a heated (140°F), air-agitated bath.

In R.B. White's bath, degreasing is accomplished using nonionic surfactants that act at interfaces between the metal, oil, dirt, and water. The surfactant molecules have hydrophobic "tails" that penetrate the oil and dirt while their hydrophilic "heads" surround the particles and lift them away from the metal surface and into the water phase. Nonionic surfactant molecules owe their "split personality" (Wray, 1992) to long chain, hydrocarbon tails that more readily solubilize in oil than in water and to oxygen-containing heads that rather prefer to hydrogen-bond with water molecules. Surfactant molecules arrange themselves in chemically stable micelle formations, with their hydrophobic tails oriented inward and their hydrophilic heads pointing out. The micelles disperse in the water phase and form a stable emulsion that cleans the parts and prevents the oil and dirt from redepositing on the metal surface (Morrison, Boyd, 1973). Micelles form as aggregates of 50 to 300 or more surfactant molecules depending on the nature, temperature, and concentration of the surfactant. Micelle formation will only occur at or above a very narrow range of surfactant concentration known as the critical micelle concentration (cmc). Below the critical micelle concentration, there is not enough surface activity to provide efficient cleaning (Cutler, Davis, 1972). Studies by Ginn and Harris (1961) have shown that maximum soil removal for nonionic surfactants occurs at concentrations well above the critical micelle concentration. In R.B. White's degreasing application, maintaining sufficient levels of surfactant in the iron phosphating/degreasing bath is an important process control parameter to ensure good cleaning.



**Phosphating** is a type of prepaint coating process used to simultaneously provide corrosion resistance and enhance paint adhesion to a metal surface. Phosphoric acid chemically bonds to the metal surface to produce an amorphous conversion coating. The phosphate conversion coating is nonconductive so it protects the metal surface from electrochemical oxidation that leads to rust and corrosion. The matrix of the phosphate coating forms capillaries which increase the surface area and provide a mechanical interlocking structure on which the paint can adhere (Phillips, 1990). Since the phosphate layers contain surface breaks, immediate painting is imperative or corrosion may begin within twenty-four hours following the phosphating operation (Paul, 1986).

The phosphate coating process chemically reacts in two steps. Phosphoric acid is added to lower the bath pH to between 3.5 and 5 to dissolve a thin layer of metal from the part surface. Solubilizing the metal consumes acid, and the local pH at the metal surface increases. At this higher pH, phosphate salts bond with the solubilized metal ions to form an insoluble phosphate precipitate. The precipitate deposits on the metal surface in an amorphous configuration. The two critical parameters in this process are the solution pH and the concentration of phosphating agents. Maintaining a solution pH between 3.5 and 5 is critical to ensure optimum reaction between the metal surface and the phosphoric acid. Keeping the concentration of phosphating agents sufficiently high is important to provide adequate coating and coverage, but excessive concentrations may produce a coating that is undesirably loose and dusty (Phillips, 1990).

Parameters describing the quality of an iron phosphate coating include: (1) coating weight, (2) rust creepage, and (3) paint adhesion. Coating weight is a measure of the mass of iron phosphate ( $\text{Fe}_3(\text{PO}_4)_2$ ) deposited per unit area. Rust creepage is an indication of coating density and uniformity. Paint adhesion is a measure of the strength of the bond between the phosphate and paint layers. Imperfections in the coating can usually be traced to fluctuations in pH, changes in temperature, or an imbalance of chemicals or contaminants in the bath (Phillips, 1990).

Several system configurations are available for iron phosphating/degreasing processes. Systems may utilize vapor, spray, or immersion applications and range anywhere from one to seven steps. Process designs may include a pickling step to remove rust and scale. Systems also have the option of using distilled water or applying a seal coat in the final rinse. Selection is determined by product quality requirements, soil removal capability, and production load. Traditionally, chemical suppliers have recommended separate degreasing and iron phosphating steps when soils were difficult to remove or when cleanliness was a particularly important quality parameter. Manufacturers would rely on solvents or aqueous alkaline cleaners to degrease the parts, fresh water to rinse, iron phosphate solution to coat, and more water to rinse. In many applications, adequate product quality can be also be achieved by using a system configuration that combines the degreasing and iron phosphating process into one step. This configuration relies on surfactants to function concurrently with iron

phosphating agents in an aqueous solution. Companies like R.B. White switched to the one-step iron phosphating/degreasing bath because it offered an alternative to solvent use and disposal, eliminated separate cleaning and rinsing stages, and reduced water and space usage.

The 5000-gallon bath at R.B. White was charged with Dura-Gard Soke and Tart liquid acid which contained nonionic surfactants, phosphate salts, phosphoric acid, and accelerators to promote phosphate precipitation. The concentration of Dura-Gard Soke was checked daily with a simple titration kit and conversion table to ensure that concentrations were maintained between 1.5 and 2.0 ounces of Dura-Gard per gallon. After the concentration of Dura-Gard was adjusted, pH was checked with litmus paper. If the pH exceeded 3.5, it was adjusted to 3.5 by addition of Tart liquid acid. The bath temperature was maintained at 140°F. During operation, a coarse bubble aeration system was used to prevent bath stratification and provide complete mixing of all but the sludge settled on the tank bottom. Oil skimmers were used to control oil slicks on the surface. Daily operations varied in length from 8 to 16 hours per day, 5 to 6 days per week.

### Section 3

## WASTE REDUCTION IN THE METAL FABRICATED PRODUCTS INDUSTRY

### Waste Generation

The EPA's campaign for waste reduction is bringing change to industries through the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA), the Toxics Release Inventory (TRI), the 1990 Pollution Prevention Act (PPA), and the more recent 33/50 Program. The HSWA require 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 reporting 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 (Hindin, Burch, Fort, 1992). 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 metal fabricated products industry is an integral part of aerospace, electronic, defense, automotive, furniture, domestic appliance, and many other industries. The raw materials used in metal fabrication range from common copper and steel to high grade alloys and precious metals. Typical materials used and types of wastes generated from metal shaping, surface preparation, and surface finishing operations are presented in Table 1.

Wastes generated from metal shaping operations include scrap metal and metalworking fluids. In general, metal working fluids are petroleum-based fluids, oil-water emulsions, or synthetic emulsions. With extended use, these metalworking fluids become spoiled and are often disposed as hazardous waste. The fluids may be contaminated with cadmium, chromium, or lead depending on the metal being tooled. In addition, the fluids may contain chemical additives such as chlorine, sulfur and phosphorous compounds, phenols, cresols, and alkalies (Hindin, 1992).

Surface preparation operations generate wastes contaminated with solvents, heavy metals, and oils. Concentrated solvent-bearing wastes may result from degreasing operations which produce solvent-bearing wastewaters, air emissions, and solid-phase wastes. Chemical treatment operations such as alkaline, acid, mechanical, and abrasive cleaning can generate waste streams contaminated with oils or heavy metals (Hindin, 1992).

Surface finishing operations result in plating-related wastes and painting wastes. Metal plating and related metal deposition processes such as conversion coating account for the largest volume of heavy metal- (cadmium, chromium, lead mercury, nickel) and cyanide-bearing wastes. Painting and cleanup operations result in the direct release of solvents such as MEK, MIBK, toluene, xylene, and many TRI regulated chlorinated solvents (Hindin, 1992).

**Table 1: Typical Materials Used and Types of Wastes Generated in the Metal Fabricated Products Industry (Hindin, Burch, Fort, 1992)**

Operation	Typical Materials Used	Types of Wastes Generated
<b>METAL WORKING</b>	<ul style="list-style-type: none"> <li>. Cutting fluids</li> <li>. Lubricants</li> <li>. Inorganic/organic solvent electrolytes</li> <li>. Heavy metals</li> </ul>	<ul style="list-style-type: none"> <li>. Heavy metal wastes</li> <li>. Solvent wastes</li> <li>. Waste oils</li> <li>. Scrap metal, filings</li> </ul>
<b>SURFACE PREPARATION</b> Cleaning	<ul style="list-style-type: none"> <li>. Acid/alkaline cleaners</li> <li>. Detergents</li> <li>. Organic degreasing and cleaning solvents</li> </ul>	<ul style="list-style-type: none"> <li>. Acid/alkaline wastes</li> <li>. Ignitable wastes</li> <li>. Solvent wastes</li> <li>. Still bottoms</li> <li>. Waste oils</li> </ul>
Chemical Treating	<ul style="list-style-type: none"> <li>. Acid/alkaline cleaners</li> <li>. Etching/Pickling acids</li> </ul>	<ul style="list-style-type: none"> <li>. Acid/alkaline wastes</li> <li>. Heavy metal wastes</li> <li>. Waste oils</li> </ul>
<b>SURFACE FINISHING</b> Electroplating	<ul style="list-style-type: none"> <li>. Acid/alkaline solutions</li> <li>. Heavy metal-bearing solutions</li> <li>. Cyanide-bearing solutions</li> </ul>	<ul style="list-style-type: none"> <li>. Acid/alkaline wastes</li> <li>. Cyanide wastes</li> <li>. Heavy metal wastes</li> <li>. Plating wastes</li> <li>. Reactive wastes</li> <li>. Wastewaters</li> </ul>
Conversion Coating	<ul style="list-style-type: none"> <li>. Phosphate salts</li> <li>. Chromate salts</li> <li>. Acid solutions</li> </ul>	<ul style="list-style-type: none"> <li>. Chromium-bearing wastewaters</li> <li>. Acid wastes</li> </ul>
Painting	<ul style="list-style-type: none"> <li>. Paints</li> <li>. Solvents</li> <li>. Paint carrier fluids</li> </ul>	<ul style="list-style-type: none"> <li>. Heavy metal paint wastes</li> <li>. Ignitable paint wastes</li> <li>. Solvent wastes</li> <li>. Still bottoms</li> <li>. Paint overspray waste</li> <li>. VOC emissions</li> </ul>

#### **Aqueous Cleaners**

The EPA recommends various strategies for pollution prevention in the metal fabricated products industries. 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 (Quitmeyer, 1991). 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 RCRA amendments (Hindin, Burch, Fort, 1992). 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 (Mehta, Besore, 1987). 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 (Quitmeyer, 1991).

The cleaning action of aqueous cleaners relies on water in combination with chemical, thermal, or physical means to lift away dirt, oils, and scales from surfaces. Aqueous cleaning systems may be designed for soak cleaning, spraying, ultrasonic cleaning, electrocleaning, or steam cleaning operations. The cleaning process is then usually followed by rinsing and drying. Typically, aqueous cleaners come in acidic or alkaline formulations to remove or deposit a variety of coatings. Alkaline cleaning solutions may contain builders, surfactants, anti-oxidants, stabilizers, and small amounts of solvents. Alkaline cleaners and strippers are effective in removing dirt and oil from metal parts, as well as old paint or plated metals. Antioxidants can also provide protection against rust and corrosion (USEPA, 1989). Acidic cleaning solutions may be formulated with mineral acids, organic acids, surfactants, coating reagents, chelating agents, and small amounts of solvents. Acid cleaning is most often used to remove rust, scale, and smut; but surfactants and coating agents can also be added to remove dirt and oil as well as apply a conversion coating to a metal surface (USEPA, 1990).

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, finger prints, 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 (Quitmeyer, 1991).

Aqueous cleaners are finding success in many industrial surface preparation operations including airplane components, printed circuit boards, advanced composites, fasteners, and automotive

parts. In one case study, a major U.S. aerospace manufacturer successfully made the switch from a 1,1,1-trichloroethane vapor degreaser to an aqueous cleaning bath with only slight modifications and little capital investment. In another case, a large plating firm replaced a two-stage solvent degreaser and caustic bath with a single-stage, heated (140°F), aqueous cleaning bath (Quitmeyer, 1991). In 1985, R.B. White also made the switch from trichloroethane to a single-stage, heated (140°F), aqueous degreasing/phosphating system and eliminated separate degreasing and rinsing operations.

In all these applications, the tank life of the aqueous cleaners is limited by the buildup of dirt and oil in the bath. Cleaning effectiveness begins to deteriorate as dirt and oil accumulate in the water, and the performance of other chemicals in solution is inhibited. Although the aqueous degreasers do not carry the risks and liabilities associated with the disposal of waste organic solvent cleaners, periodic replacement of the bath creates a different waste disposal problem. Aqueous degreasers form stable oil-water emulsions that work well in cleaning but make them difficult to treat for disposal. The emulsions contain levels of dirt, metal particles, and oil that are not acceptable to pour down the drain. When pretreatment limits for wastewater discharge are exceeded, high oil content and chemical oxygen demand (COD) keep the waste process solution from being treated at a publicly owned treatment works (POTW) by conventional biological treatment methods (Bailey, 1977).

Current disposal options for spent aqueous cleaning solutions include tankering to an offsite treatment facility, incineration on or offsite, or discharge to a POTW. Tankering the waste process solution to another site is a convenient but expensive option since more than 90% of the waste is actually water. Tankering is also not a pollution prevention solution since it only transfers the problem from one location to another. Incineration is another disposal option that can be used to burn the waste oil despite its high water content. Incineration is commonly used, but the process requires supplemental fuel and leaves no room for reuse or recovery of the spent bath (Bailey, 1977).

Discharge to a sanitary sewer is another option for disposal only as long as the wastewater meets with effluent standards. An industrial facility may operate an end-of-pipe, wastewater pretreatment plant before discharging spent cleaning solution to the POTW. A conventional wastewater pretreatment plant might employ the following unit processes to remove oil from water prior to discharge. Skimming can remove free oil from the surface, but sulfuric acid or lime may be required to adjust the pH and help release free oil. Coalescing can separate water and dispersed oil droplets that do not float to the surface, but this technique is only effective when surfactants are not present. Additional chemicals are required to overcome surface active agents and release the oil. Chemical emulsion breaking can be used when coalescing is not effective. Chemical emulsion breaking begins by adding aluminum sulfate (alum) as a coagulant to destabilize the emulsified oil droplets. Lime or caustic soda is used to raise the pH and form an insoluble aluminum hydroxide floc. Cationic polymers may also be used with alum to eliminate the need for pH adjustment. The destabilized oil

droplets then adsorb onto the alum floc surface. Dissolved air flotation (DAF) employs tiny bubbles of air to carry the alum floc to the surface and over a clarifier weir (Springborn Laboratories, 1982).

The primary goal of this type of conventional, end-of-pipe pretreatment is compliance. Treated water is discharged to the sewer while sludge produced during the process creates a new waste disposal problem. With increasing environmental restrictions, landfilling the chemical sludge is becoming less and less attractive as a disposal option. Alternatively, the sludge can be incinerated or treated on site to recover the oil. Thermal oil recovery relies on heating the waste sludge to nearly the boiling point to separate the oil, water, and sludge phases. The process may require a heat exchanger, centrifuge, evaporator, acid, and additional chemicals (Springborn Laboratories, 1982). Since waste emulsified oil solutions typically contain less than 10% oil, it usually does not pay to install such an extensive oil recovery system (Cheng, 1983).

The rising costs associated with these disposal and pollution control techniques are the two main incentives to extend the life of the aqueous cleaner baths (Wahl, 1979). 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 (Quitmeyer, 1991). R.B. White found skimming only marginally effective, and no amount of settling time would break the stable oil-in-water emulsion, but filtration did have potential for extending the life of their aqueous cleaning bath.

### 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. One way that membrane filtration differs from conventional filtration is that the direction of feed flow is tangential to the filter media rather than perpendicular to it. Turbulent cross-flow across the membrane means oil and dirt are less likely to build-up on the surface of the filter media and clog the flow (Bailey, 1977). The membranes themselves are also revolutionary. Instead of thick beds of filter media, membranes are cast as thin films with designated pore sizes ranging from atomic to macroscopic levels. Ultrafiltration is one class of membrane filtration that uses membranes with pore diameters ranging from  $10^{-9}$  to  $10^{-6}$  meters. This is smaller than the size of an emulsified oil droplet but much larger than the water molecules and other dissolved species in an aqueous cleaning solution (Cheryan, 1986).

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. For an aqueous cleaning bath like R.B. White's, the permeate would contain water, phosphating agents, and solubilized raw materials that did not react with the membrane surface. The *concentrate* stream contains everything else that is rejected by the membrane. At R.B. White, this would include emulsified oils, dirt, and water associated with the emulsion.

The recent development of more durable membranes, such as polyvinylidene di fluoride (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 cleaners. Ultrafiltration of oil-water emulsions is a more straight-forward method for removing and concentrating oil are than any of the chemical or thermal techniques mentioned earlier. Ultrafiltration does not require a stockpile of chemicals such as sulfuric acid, alum, lime, caustic soda, polymers, and other proprietary chemicals. 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 (Wahl, 1979).

Each ultrafiltration application calls for a specific membrane type. Membranes used in ultrafiltration are characterized by material of construction, pore size statistics, rejection, and flux. The *material of construction* determines the acceptable range of chemical and physical parameters (resistance to pH, temperature, pressure, solvents) that the membrane can withstand. *Pore size statistics* describe the membrane's structure in terms of nominal pore size, pore size distribution, and percent porosity. These parameters determine the minimum molecular weight cut-off (*MWCO*) which is the minimum weight of a typical molecule that would be rejected by the membrane. *Rejection* describes the degree to which ultrafiltration prevents components from passing through the membrane. The rejection may change with use or aging of the membrane, but the % rejection may always be determined by the following equation:

$$\% \text{ Rejection} = (C_F - C_P)/C_F \times 100\% \quad (\text{Eq. 1})$$

where  $C_F$  = concentration in feed solution  
 $C_P$  = concentration in permeate stream

*Flux* is defined as the volumetric flow rate of permeate per cross-sectional area per time. Flux is a function of pressure, feed concentration, temperature, flow rate and turbulence in the feed channel, and the tendency to foul (Cheryan, 1986). Flux determines the membrane surface area and pump capacity requirements for a given wastewater flow rate or volume. Therefore, capital and operational



costs are directly related to flux characteristics.

Membranes are cast in a variety of module configurations, each having particular advantages and limitations. Spiral wound, hollow fiber, and tubular membranes are the most popular cross-flow configurations. These configurations are designed to supply the greatest amount of surface area per unit volume and flow channels that will accommodate the nature of the feed stream. Illustrations of each are provided in Figure 3. The wide-channel tubular configuration is usually preferred for high strength oily wastewaters. Although tubular membranes do not have the high surface area to volume ratios that the other configurations do, the wide-channel tubular membranes provide good resistance to cake formation and clogging by oil and particulates (Cheryan, 1986).

One of the greatest limitations of ultrafiltration membranes is their tendency to clog or foul. *Fouling* is detected as the decrease in permeate flux over time and is a result of changes in the membrane structure or interactions between the components of the feed stream and the membrane surface. Fouling is mainly due to the accumulation of particles and adsorption of foulants on the membrane surface and/or within the pores of the membrane itself. Almost all feed solutions will foul a membrane to some extent, but optimizing the chemical compatibility of the feed stream and the membrane material will help to reduce the effects of fouling. When a membrane shows signs of fouling, the flux can largely be restored by cleaning the membrane to remove accumulated foulants like oil, suspended solids, and metal precipitates. Mechanical cleaning employs sponge balls to remove chemically precipitated species. Detergents work to breakup deposits on the membrane surface and disperse them into solution. Solubilizing uses acids and chelating agents to dissolve stubborn foulants like metal hydroxides or other chemical deposits (Pinto, 1978). Even with regular cleaning, a portion of the flux may be unrecoverable because of irreversible fouling. The extent of irreversible fouling determines the useful life of the membrane, which is also part of the operational cost associated with the process (Cheryan, 1986).

The rate of fouling depends not only on the type of membrane and the nature of the feed stream, but on the operating conditions as well. Fouling can be minimized by controlling pretreatment, temperature, pressure, velocity, configuration, and concentration. *Pretreatment* of the feed stream protects the membrane surface by straining out debris like suspended solids, grit, metal filings, and cigarette butts. *Temperature* controls the viscosity of the feed stream and the adsorption of foulants to the membrane surface. Increasing temperature within the recommended range for a membrane may increase flux and decrease foulant adsorption. Transmembrane *pressures* are usually specified by the membrane manufacturer to deliver optimal flux without compressing or changing the membrane structure. Increasing the pressure within a certain limit will yield an increase in flux. *Velocity* in the flow channel determines the degree of turbulence and, therefore, the likelihood of cake formation at the membrane surface. High velocities at the membrane surface tend to shear off deposited material

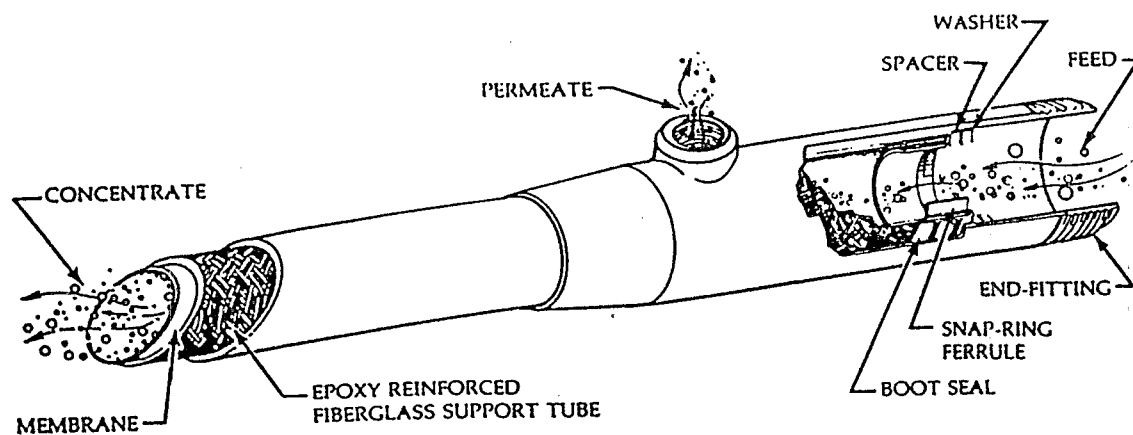


Figure 3a: Tubular Membrane Module (Cheryan, 1986)

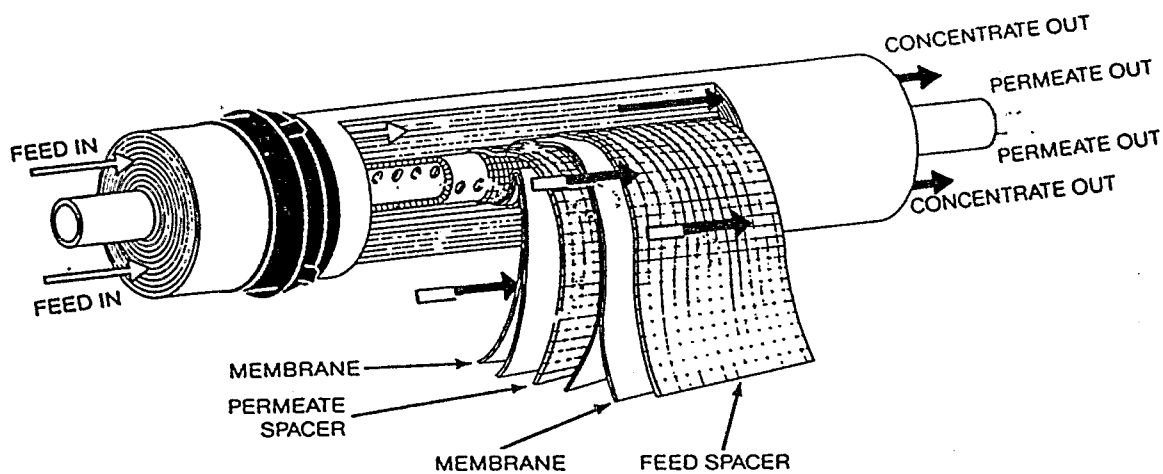


Figure 3b: Spiral Wound Membrane Module (Cheryan, 1986)

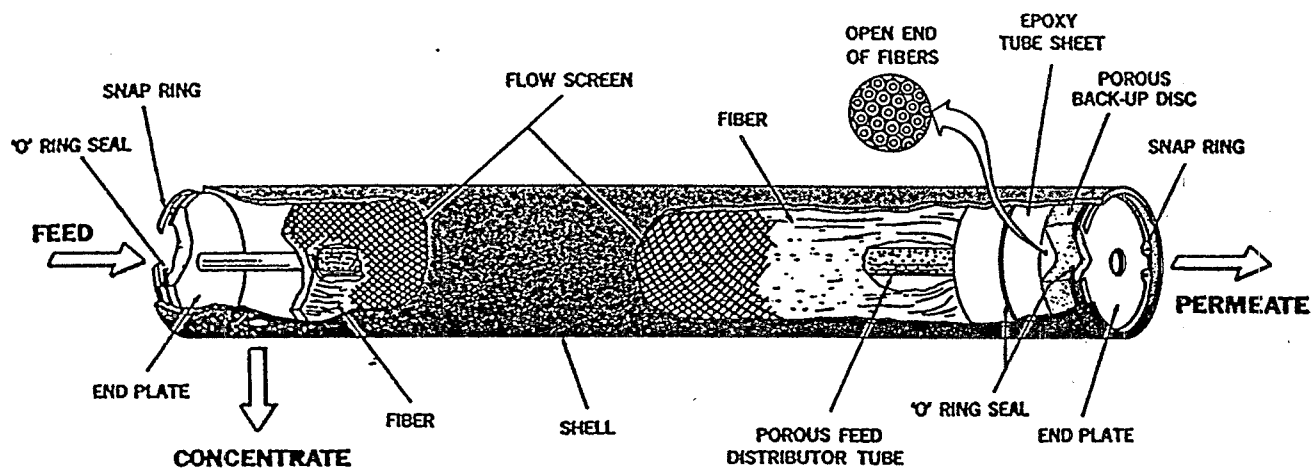


Figure 3c: Hollow Fiber Membrane Module (Donnelly, Goldsmith, McNulty, 1976)

and prevent the formation of a fouling layer. Membrane *configurations* establish flow patterns to minimize fouling from different types of feed streams. Choosing the best membrane configuration will depend on the nature of the feed stream, the type of application, and the economies of scale. *Concentration* of the feed stream determines the rate of permeate flux and the potential for cake formation at the membrane surface. While it is possible to achieve 40 - 75% oil in the concentrate, it may be more economical to settle for 40 - 50% since the rate of permeation decreases rapidly as feed stream concentration rises. Higher feed stream concentrations also have a greater potential to foul the membrane, which leads to higher membrane cleaning and replacement costs (Bailey, 1977).

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 (Pinto, 1978). Research by Bhattacharyya, et. al. (1979) predicted fouling phenomena for oil-surfactant-water conditions similar to those at R.B. White. Bhattacharyya experimented with ultrafiltration of oily-surfactant waters using tubular, non-cellulosic membranes. The study was used to determine the feasibility of using ultrafiltration aboard Navy ships to treat "bilge waters" to meet marine discharge standards. The bilge oil Bhattacharyya used to mix the samples consisted mainly of fuel oil, lubricating oils, and hydraulic oils. The experimental formulations were prepared at a neutral pH using distilled water or river water and nonionic surfactants. Bhattacharyya worked at temperatures of 25 and 40°C (77 and 104°F) and tested different combinations of feed streams: oil-water, surfactant-water, and oil-surfactant-water.

From the test results, Bhattacharyya attributed fouling and flux decline to a combination of gel formation and adsorption of foulants on the membrane surface. In the oil-river water samples, Bhattacharyya found that the interaction between oil and suspended solids resulted in the formation of a gel layer that restricted permeate flux. Gel formation occurs when the interactions between the oil droplets are strong enough to produce aggregates that eventually develop into a gel layer on the membrane surface (Lee, 1984). With the dirt and other particulates in R.B. White's bath, the formation of a gel layer was a possible source of fouling. In the surfactant-water samples, Bhattacharyya found that free nonionic surfactants contributed to fouling and inhibited flux by physical adsorption and micelle formation within the membrane pores. In R.B. White's application, this type of surfactant stripping by the membrane was a concern for preserving the concentration of raw materials in the bath. In the oil-surfactant-water systems, Bhattacharyya found that there was less flux decline than in the other two systems. With the surfactant and oil tied up in an emulsion, there was decreased adsorption of free surfactant and oil on the membrane surface. However, since less free surfactant was available, surfactant rejection was enhanced in the presence of oil. This scenario most closely represented the actual conditions at the R.B. White facility. In general, the degree of adsorption depends on the type and concentration of surfactant, other materials present in solution, and the type of adsorbent (oil,

membrane, etc.). Adsorption of surfactant tends to decrease as temperature increases and as concentrations rise above the critical micelle concentration (Cutler, Davis, 1972). By raising the temperature to 40°C (104°F), Bhattacharyya found that flux increased due to lower viscosities and less adsorption of oil and surfactants on the membrane without sacrificing oil rejection (Bhattacharyya, Jumawan, Grieves, 1979). For the warmer operating temperatures (140°F) at R.B. White, this observation was encouraging.

## Section 4

### BENCH-SCALE MEMBRANE SCREENING

#### Methods and Materials

The laboratory bench-scale activities served as an initial screening of candidate membranes to assess their respective flow rates and chemical compatibility. The key parameters for membrane evaluation focused on flux and fouling characteristics and permeate quality.

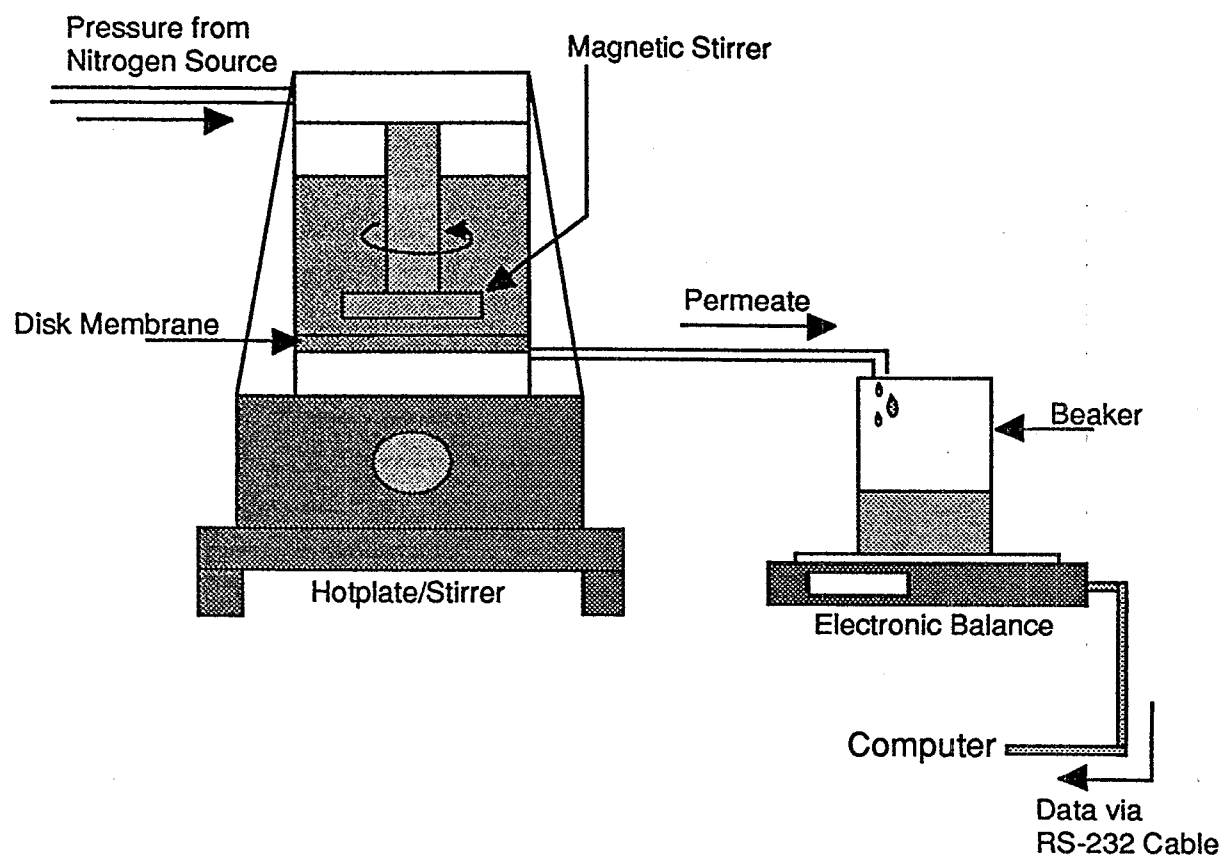
Ultrafiltration equipment used in this study was provided by a variety of well-known equipment and membrane manufacturers. The laboratory bench-scale study utilized an Amicon dead-end, stirred-cell ultrafiltration assembly (Model 8200, 180 mL capacity) with a nitrogen pressure source. The bench-scale apparatus was used to screen a variety of 62 mm diameter disk membranes for flux rates and chemical compatibility. A summary of the disk membranes tested is presented in Table 2, and a diagram of the bench-scale apparatus appears in Figure 4. Permeate flux rates were determined by weighing the permeate as it filtered through the stirred cell over time. Permeate was collected in a beaker located on a Sartorius analytical balance (Model LC 12000s). The balance was connected to a computer via a RS-232 cable, and mass measurements were sent in prescribed time intervals to a Lotus 1-2-3 spreadsheet.

**Table 2: Membrane Candidates and Material Specifications**

MODEL NO.	VENDOR	MATERIAL OF CONSTRUCTION	MWCO	MAXIMUM PRESSURE (psi)	MAXIMUM TEMPERATURE (°C)
HG05	Osmonics	Polysulfone	2,000	400	100
SNO4	Osmonics	Cellulose Acetate	20,000	150	60
PM10	Amicon	Polysulfone	10,000	70	100
PM30	Amicon	Polysulfone	30,000	70	100
M2	Enviro-Process	Teflon	20,000	80	* No limit specified
M3	Enviro-Process	Teflon	500	200	* No limit specified

#### Bench-Scale Activities

Samples for the bench-scale study were collected from the iron phosphating/degreasing bath while it was relatively dirty. Samples were drawn from twelve locations in the tank along the surface, middle, and bottom using a Scienceware polyethylene dipper. The dead-end, stirred ultrafiltration cell



**Figure 4: Bench-Scale Ultrafiltration Apparatus**  
(Laine, Hagstrom, Clark, 1989)

was used to test six different membranes for clean water flux, process solution flux, and flux recovery at consistent transmembrane pressures in triplicate. First a clean water flux test was run with 180 mL distilled/deionized water to establish an initial flux. The process solution flux test directly followed to characterize a representative flow rate of process solution through the membrane. Flux recovery was determined by rinsing the membrane and filtering a second 180 mL aliquot of distilled/deionized water. The deterioration of process solution flux with time and the net difference in initial flux and flux recovery were used as a measure of fouling that occurred during filtration.

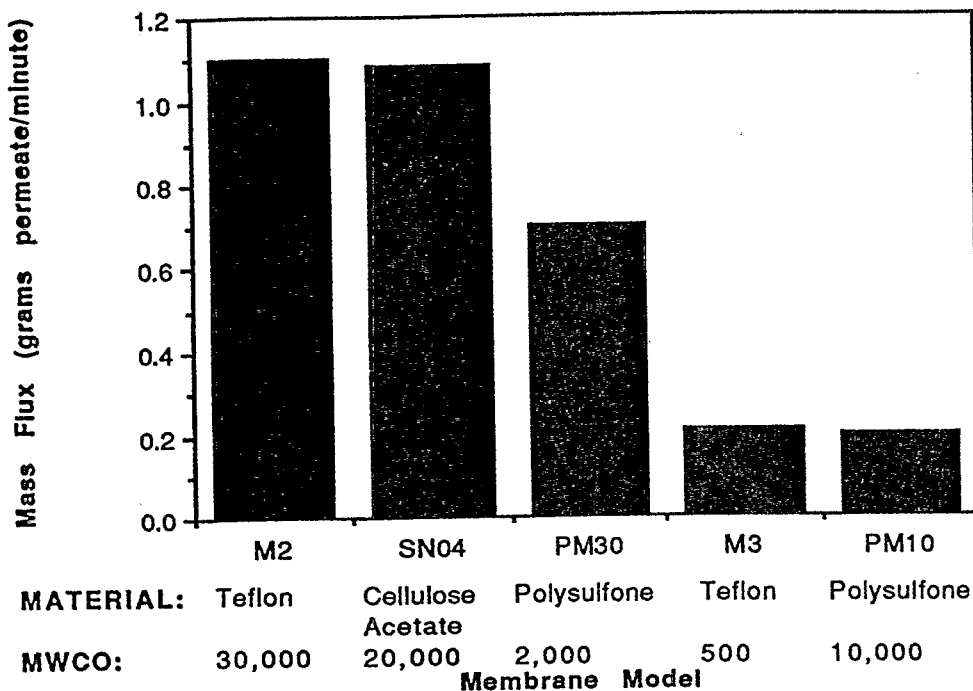
Sample quality for the bench-scale testing was defined by the partition-gravimetric method for oil and grease (USEPA Method 413.1). At this stage, oil and grease tests were performed without sufficient analysis to actually differentiate between oil/grease and non-ionic surfactants because the contract lab used was unaware of the importance of specifying these components separately (see Quality Assurance section). Oil and grease analyses were performed on permeate, concentrate, and unfiltered process solution samples. Results are still considered valid to the extent that they were used to determine the relative efficiency of each membrane to remove emulsified oil contamination in the process solution and last without fouling.

## Results and Discussion

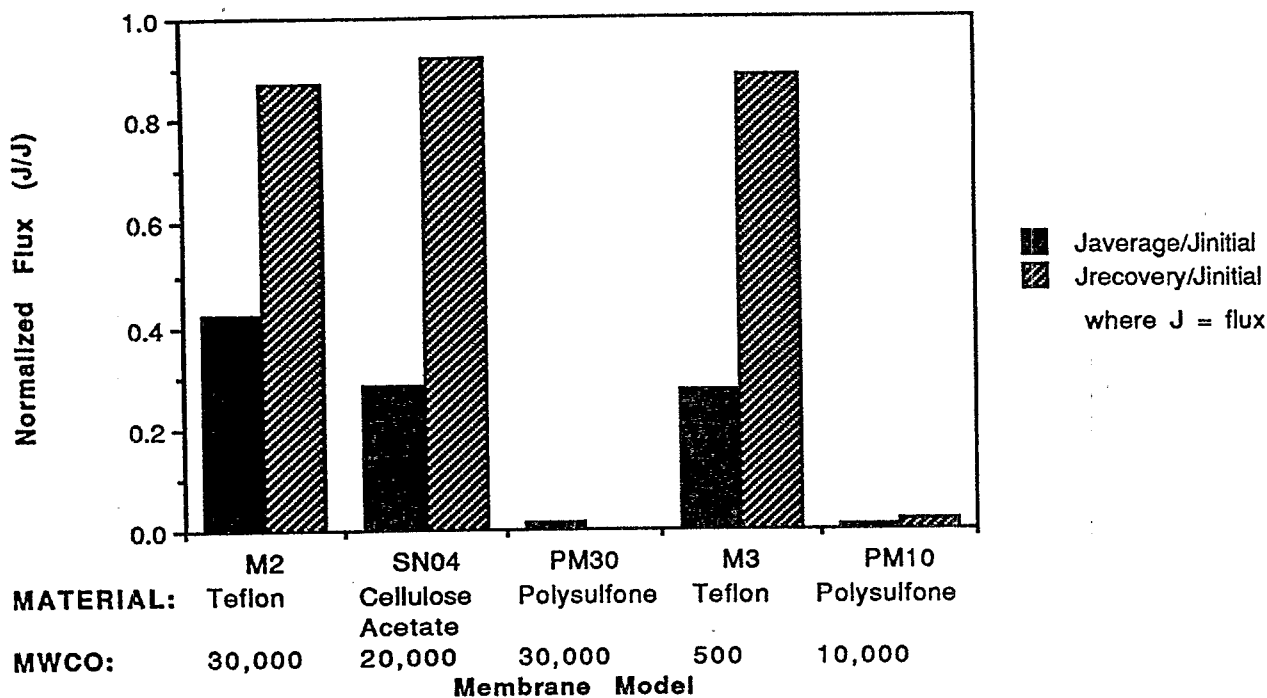
The results of the bench-scale flux tests are summarized in Figures 5a and 5b. Figure 5a compares the relative wastewater flux rates of each membrane candidate. Model M2 (Teflon 30,000 MWCO) produced the highest flux rates with Model SN04 (Cellulose Acetate 20,000 MWCO) running a close second. Figure 5b shows that both candidates displayed competitive flux recovery, but  $J_{\text{average}}/J_{\text{initial}}$  values set the M2 Teflon model out front.  $J$  represents the permeate flux, and the value of  $J_{\text{average}}/J_{\text{initial}}$  is an indicator of the loss in permeate flux from clean water to wastewater. The relative loss was much less for the M2 Teflon model than the SN04 Cellulose Acetate which indicates the M2 Teflon membrane underwent the least fouling in the bench-scale test.

Oil and grease levels in the permeate as measured by the USEPA Method 413.1 were consistently low, typically less than 40 mg/L for all membrane candidates. As discussed in the Quality Assurance section of this report, a portion of the oil and grease measurements was attributed to the presence of free surfactant in the permeate.

The overall best performance was given by the M2 Teflon 30,000 MWCO membrane from Enviro-Process Systems. Even though the SN04 Cellulose Acetate membrane appeared to be a close competitor, manufacturer's ratings indicated that the cellulose acetate would not have withstood the extreme conditions at the R.B. White facility with long-term use. Attractive features of the M2 Teflon model for this application were its resistance to extreme pH, its ability to withstand high temperatures, and its durability in the presence of industrial wastewater components.



**Figure 5a: Comparison of Wastewater Flux Rates During Bench-Scale Testing**



**Figure 5b: Comparison of Normalized Flux Rates During Bench-Scale Testing**



## Section 5

### PILOT-SCALE TESTING

#### Methods and Materials

Although dead-end filtration is useful for bench-scale screening, pilot- and full-scale membrane cartridges typically use hollow fiber, spiral wound, or tubular configurations (see Figure 3, Sect. 3). Due to the high concentration of suspended solids and other impurities associated with the process solution, a tubular configuration was chosen for the pilot- and full-scale tests. Although tubular membranes do not have the high surface area to volume ratios that other configurations do, the wide-channel, cross-flow nature of the tubular membranes provides good resistance to cake formation and clogging by particulates. Additionally, tubular membranes offer the advantage of being able to use rubber sponge-balls in cleaning. A pilot-scale, tubular module made of the Enviro-Process M2 Teflon was not available, so other membrane suppliers were contacted to find a suitable replacement. Koch Membrane Systems' 5'HFP-276-PNO PVDF 100,000 MWCO membrane was recommended in the one-inch tubular configuration with 1.1 square feet of membrane area. Like Teflon, PVDF is capable of withstanding high temperatures and extreme pHs. The PVDF 100,000 MWCO was greater than the 30,000 MWCO tested for the Teflon membrane, but the PVDF surface was negatively charged to repel emulsified oil droplets. The larger nominal pore size would also permit higher permeate flux rates and permeation of unused surfactants and phosphating agents. The pilot-scale ultrafiltration unit utilized the Osmonics PES/OSMO-O5T-SSXX model capable of operating at pressures between 40 and 60 psig within a pH range of .5 to 13.

Three types of large-scale operating schemes can be used in pilot- and full-scale applications: continuous, batch, and modified-batch. Scheme selection depends on the size of the operation, the availability of space, and the nature of the process solution.

The continuous scheme implies a dead-end filtration configuration or a system with internal recycle (see Figure 6). Permeate is returned directly to the bath as contaminants continuously accumulate at the membrane surface and within the system plumbing. This scheme does not bear the additional capital cost of a separate holding tank for the permeate, but continuous or dead-end filtration is likely to significantly shorten the useful life of the membrane due to the rapid accumulation of foulants.

The batch scheme filters process solution one tank at a time. Figure 7 illustrates a schematic of the batch set-up. When process solution is pumped from the feed tank through the UF system, some of the flow permeates through the membrane into a separate tank while the majority of the flow is recirculated back to the feed tank for further concentration. As the flow is recirculated, more and more solution is permeated through the membrane until only a fraction of the original solution volume

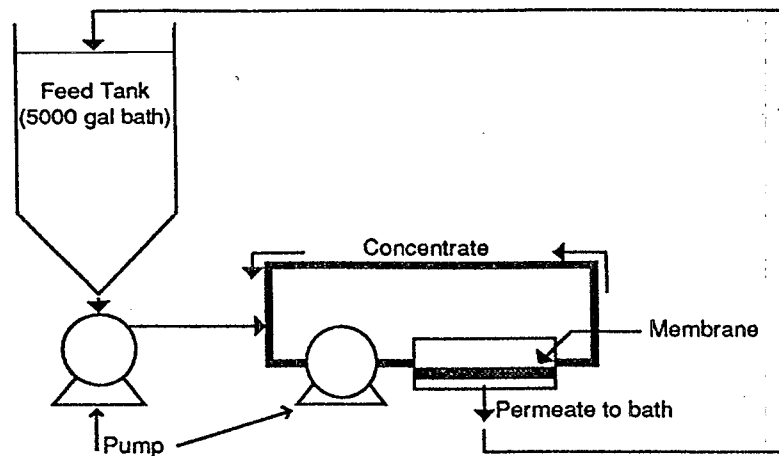


Figure 6: Continuous Scheme Ultrafiltration

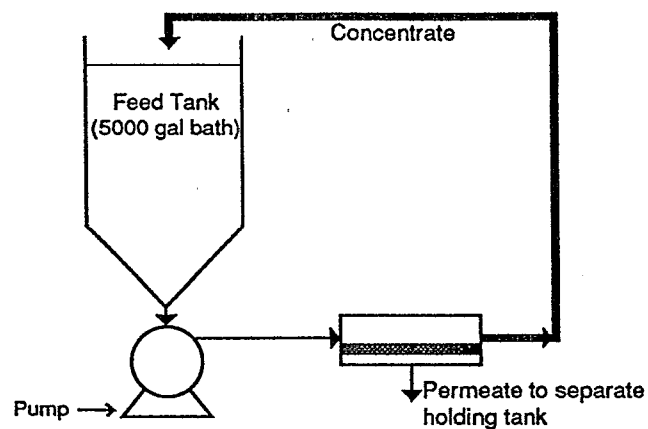


Figure 7: Batch Scheme Ultrafiltration

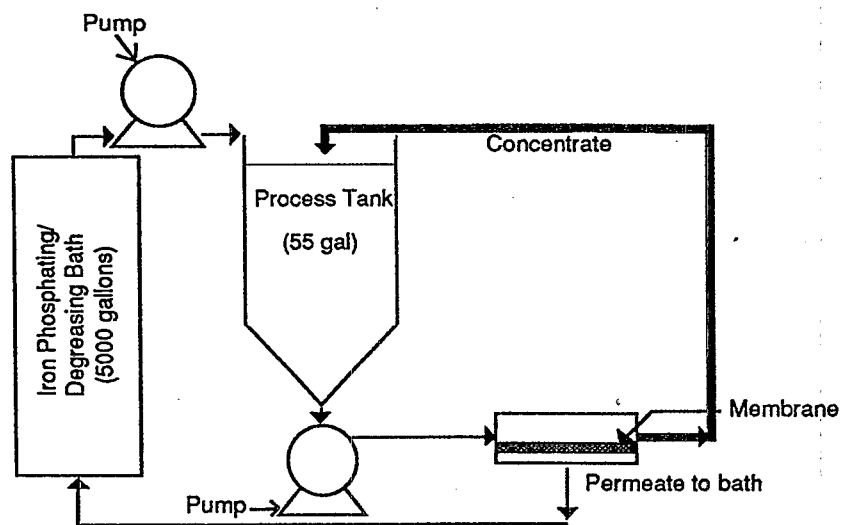


Figure 8: Modified-Batch Scheme Ultrafiltration

remains in the feed tank. This type of set-up was tested in HWRIC's pilot lab facility using a 55-gallon feed tank. For a batch scheme to work on a full-scale operation, the entire bath would have to be filtered into another 5000 gallon holding tank and then returned to the operating tank all at once. Periodic batch filtration uses membranes more efficiently and helps to prolong the useful life of the membranes. However, this option involves down time as well as the additional capital costs associated with a separate holding tank and greater membrane capacity.

The modified-batch scheme is a cross between the batch and continuous schemes. This scheme utilizes an intermediate process tank which is only a fraction of the size of the primary feed tank. A schematic of the modified-batch scheme is depicted in Figure 8. The oily bath is first fed into the process tank and then sent through the ultrafiltration system. The clean permeate is continuously returned to the bath while the concentrate is recirculated back to the process tank for further concentration. As the permeate is filtered into the bath and the process tank gets low, solution is pumped from the bath into the process tank to keep it full. When levels in the process tank reach sufficient concentration, a batch-down procedure can be used to further concentrate the contents of the process tank. During a batch-down, flow to the process tank is stopped, and the contents of the process tank are allowed to concentrate down as described for the batch scheme. The modified-batch scheme was chosen in the full-scale testing for its cost efficiency, lack of disruption to the production process, and limited space requirements.

#### **Pilot-Scale Activities**

A batch scheme ultrafiltration system was set up at HWRIC's pilot lab facility to filter bulk samples of process solution. The pilot-scale system was intended to model the flux and fouling characteristics that might be expected in a full-scale operation.

A preliminary pilot test was conducted on clean process solution to determine the selective permeation of raw materials through the PVDF membrane. Since the two essential components of Dura-Gard Soke are phosphating agents and surfactants, it was important to monitor the fate of these chemicals under the influence of ultrafiltration. Twenty gallons of clean process solution were prepared with distilled water at 2.5 ounces Dura-Gard/gallon and filtered through the UF pilot unit.

A second pilot-scale test was used to evaluate the effectiveness of the UF equipment regarding removal of emulsified oil and raw materials from the waste process solution. A 50-gallon sample was collected from R.B. White's iron phosphating/degreasing bath and shipped to HWRIC by a DOT licensed hazardous materials transporter. This solution was filtered through the UF pilot-scale unit, and transmembrane pressure, concentrate flow, permeate flux, and influent temperature were monitored during the test.

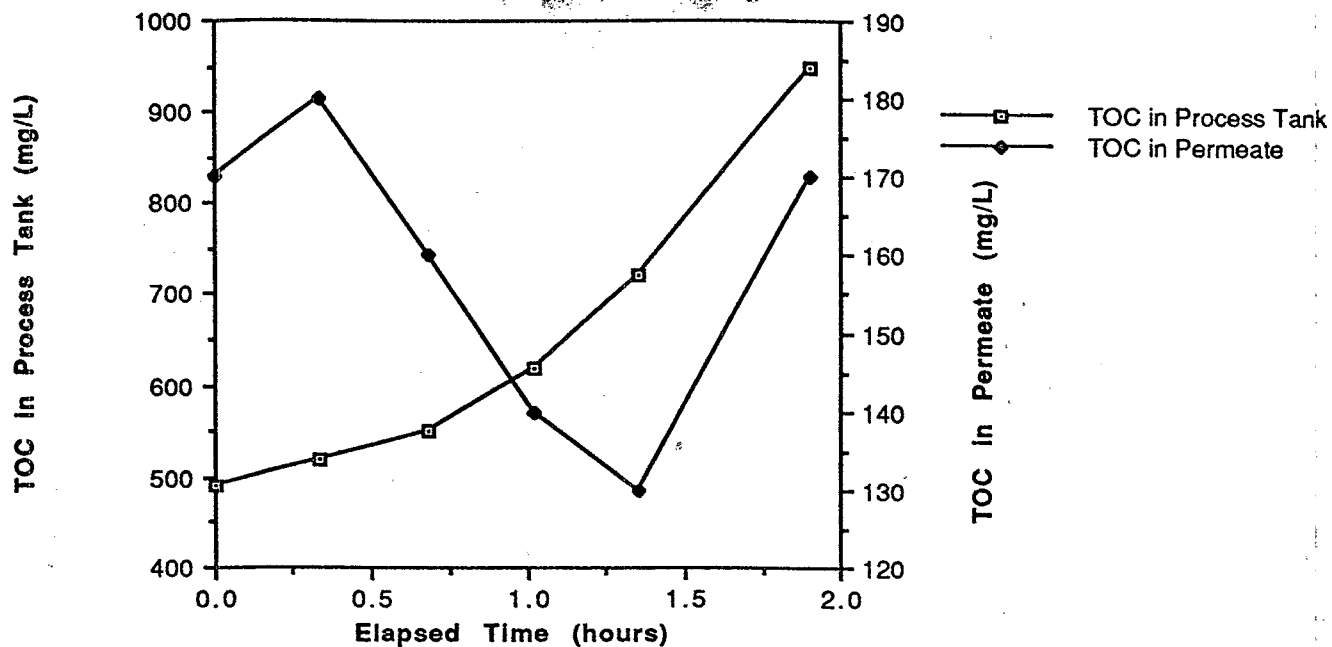
In both pilot-scale tests, one-liter samples of permeate and inflow were collected in glass

bottles at 1-hour intervals. Permeate flux and temperature were measured every 15 minutes. Samples of the concentrate, permeate, and unfiltered process solution were analyzed for oil/grease and surfactant by TOC (Standard Method 5310 B) and for phosphate by titration (Standard Method 2310 B).

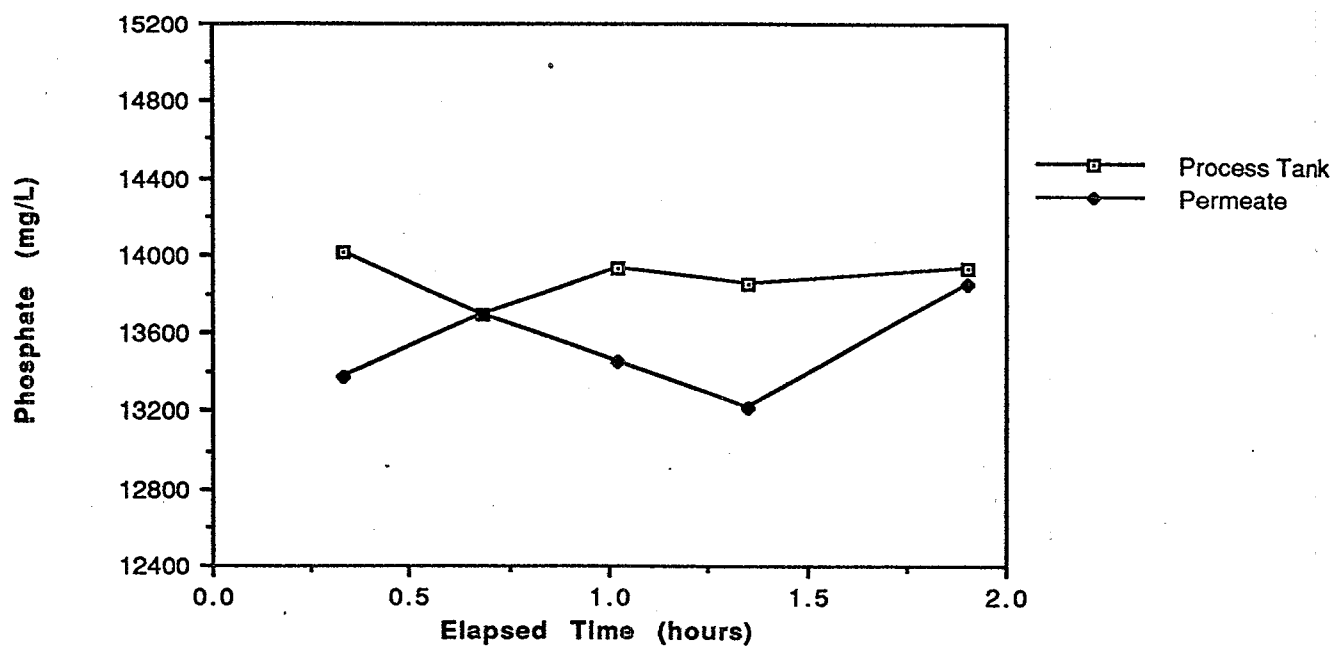
## Results and Discussion

Results of the preliminary pilot test with clean process solution helped to identify the extent of selective permeation of raw materials through the membrane. Since the process solution was clean and uncontaminated by oil, Dura-Gard surfactants accounted for the only TOC contribution to the system. Figure 9 shows that during the course of the test, surfactant TOC levels steadily rose in the process tank while levels in the permeate showed a predominantly downward trend with the exception of the last sampling point. Without emulsified oil in the process solution, all the surfactants were free and able to interact with the membrane structure. The build up of free surfactant TOC in the feed tank indicated that the PVDF membrane was selectively filtering out some free surfactant from the process solution. As less and less surfactant permeated through the membrane, it appeared that the surfactant molecules were adsorbing to the membrane surface and forming micelles in the membrane pores. Interactions between free surfactant and membrane structures were described by Bhattacharyya, et. al. and are summarized in the Waste Reduction section of this report. It is interesting to note, however, the sudden increase in TOC/surfactant for the final permeate data point. During the preliminary pilot test, the temperature of the feed stream rose from 25 to 51°C (77 to 124°F) and concentration nearly doubled from 490 to 950 mg/L TOC. As predicted by Bhattacharyya (1979), adsorption of free surfactant on the membrane was reduced as temperature and concentration increased. For the full-scale testing, this was encouraging, and an increase in surfactant permeation was expected due to the warmer operating temperatures (app. 140°F) at R.B. White. As illustrated in Figure 10, phosphate levels in the process tank and the permeate remained relatively constant during the course of the test. Phosphate values for permeate were only slightly lower than in the process tank, indicating that the phosphating agents were not selectively removed by the PVDF membrane to a significant degree. On the other hand, the surfactant component did show signs of selective removal by the PVDF membrane.

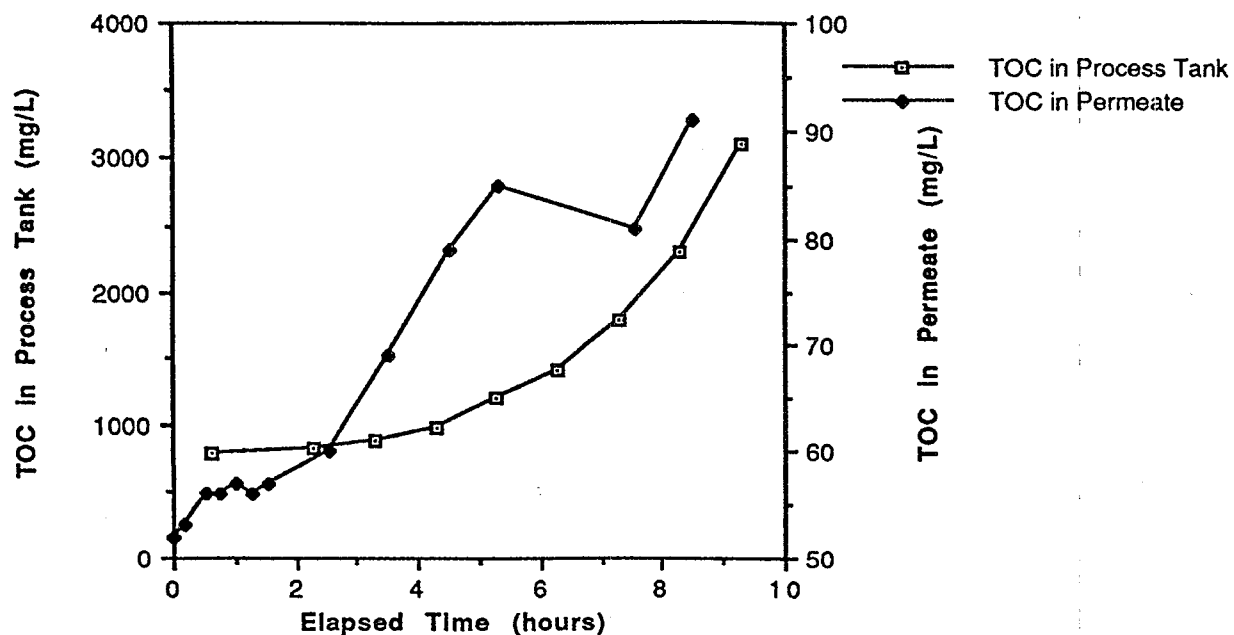
Results of the second pilot-scale test conducted on the 50-gallon sample of waste process solution are presented in Figures 11 and 12. Figure 11a depicts the steady increase of TOC in the process tank and permeate with time. As TOC levels built up in the tank, more and more clean permeate was filtered out and the oily process solution concentrated down. During the test temperatures rose from 24 to 54°C (75 to 130°F) and paralleled the rise in permeate TOC (see Figure 11b). Exactly what percentage of the TOC could be attributed to oil/grease or surfactant was unclear,



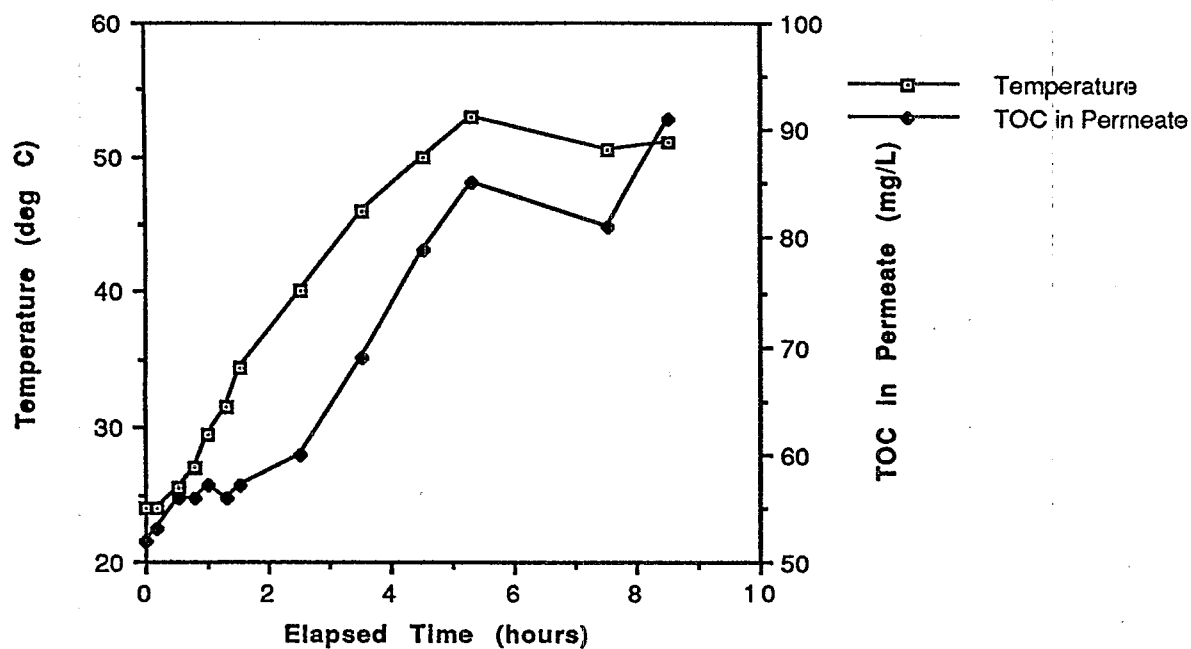
**Figure 9: TOC in Process Tank and Permeate vs Time Using Clean Process Solution**



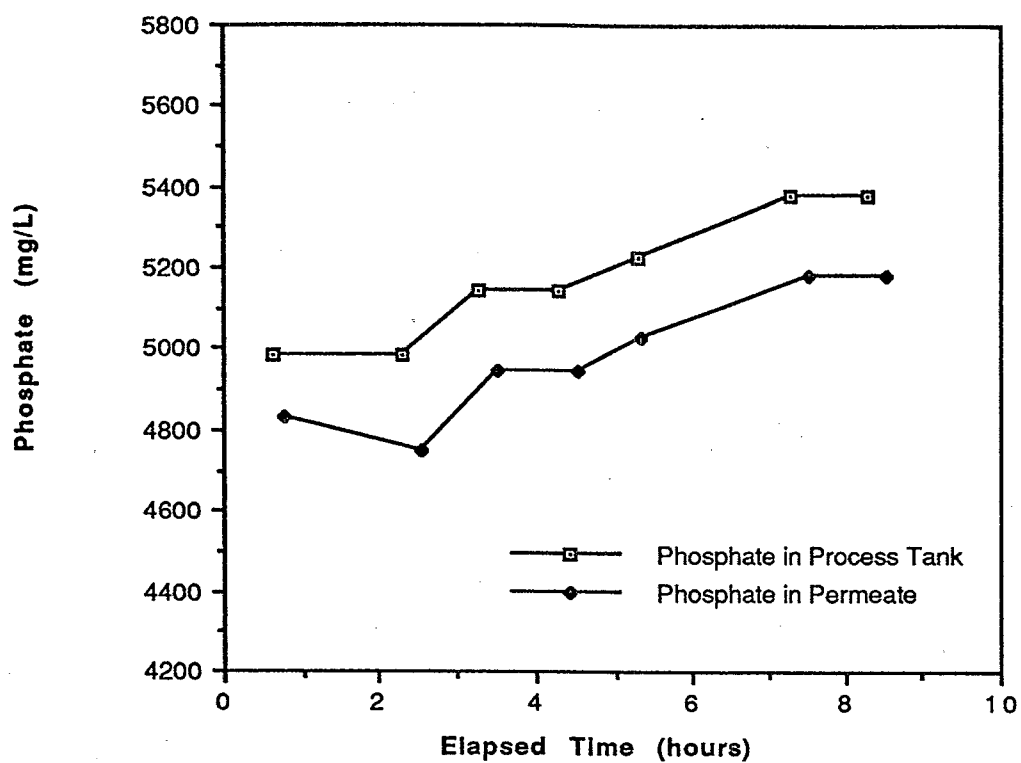
**Figure 10: Phosphate in Process Tank and Permeate vs Time Using Clean Process Solution**



**Figure 11a: TOC in Process Tank and Permeate vs Time Using Waste Process Solution**



**Figure 11b: Temperature Effect on Permeate TOC vs Time Using Waste Process Solution**



**Figure 12: Phosphate in Process Tank and Permeate vs Time Using Waste Process Solution**

but research by Bhattacharyya and results of the first preliminary pilot test led to the assumption that perhaps increasing levels of surfactant TOC were passing in the permeate along with some oil.

As demonstrated by the two pilot-scale tests, the interactions of free and combined surfactant with the membrane surface are completely different. The preliminary pilot test with clean process solution demonstrated that free surfactant tended to foul the membrane, increasing surfactant rejection. When temperature and concentration in the feed tank increased, surfactant adsorption occurred to a lesser extent. In the second pilot-scale test with the waste process solution, more surfactant was tied up with the emulsified oil droplets and was not available to adsorb onto the membrane surface. Only a small fraction of free surfactant was actually present in the waste process solution; most of it became physically associated with the oil during the rigorous mixing in the process tank. With the waste process solution, less fouling was attributed to adsorption of surfactants and formation of micelles on the membrane, and an increase in temperature seemed to encourage permeation of surfactant.

Figure 12 illustrates the relationship between phosphate levels in the process tank and corresponding levels in the permeate in the second pilot-scale test with the waste process solution. The graphs show an upward trend in phosphate levels for both concentrate and permeate with time. Values for both data sets were relatively close, confirming the free passage of phosphating chemicals through the PVDF membrane. The increasing levels of phosphate with time were not anticipated in the preliminary pilot test with the clean process solution. This may be an indication that the phosphating agents were somehow associated with the emulsified oil or other rejected components in the feed tank and passed through as concentrations rose in the feed tank.

Results from both pilot tests indicated that UF would be effective in removing emulsified oil contamination while conserving some valuable raw materials. Data confirmed that phosphating agents were conserved during ultrafiltration. Levels in the permeate were only slightly less than the levels in the feed stream. The interactions of free and combined surfactants with the membrane surface indicated that some free surfactant was selectively removed by the PVDF membrane, but the presence of oil in the full-scale application was expected to minimize fouling caused by surfactant adsorption and micelle formation within the membrane structure.



## Section 6

### FULL-SCALE IMPLEMENTATION AND TESTING

#### Methods and Materials

The full-scale in-plant testing featured an ultrafiltration system provided by Koch Membrane Systems (Model UF-4) equipped with 4 of the same 1" tubular PVDF membranes (100,000 MWCO, 4.4 sq. ft. total area) utilized in the pilot phase. The modified batch scheme was chosen for the full-scale in-plant test (see Fig. 1, Sect. 1 and Fig. 8, Sect. 4).

#### Full-Scale Activities

Results from the pilot study were used to develop a full-scale, modified-batch test conducted onsite at R.B. White's facility. The full-scale test applied ultrafiltration directly to the 5000 gallon 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 and develop solutions to problems with the ultrafiltration equipment and anticipate operating changes that should be made on a permanent unit.

Transmembrane pressure, flux, and temperature were monitored during the test as samples were taken. A daily log sheet was utilized to keep records of chemical additions to the bath. Samples of inflow (from the intermediate process tank) and permeate were collected daily in 1-liter glass bottles and stored in a 4°C cold room. Samples of the bath were collected every third day from five different locations 1 foot deep along the length of the tank using a transfer pump. All samples were collected in the morning prior to production start-up. This helped to nullify any fluctuations in process solution quality that occurred during the day under actual production conditions. Rinse water samples were also collected every third day from the catch basin located downstream of the iron phosphating/degreasing tank. These samples helped to determine whether oil was clinging to the parts as they emerged from the bath and if UF would help to control compliance problems with the discharge. All samples from the full-scale study were analyzed for oil/grease and surfactant by TOC and for phosphate by titration (see Quality Assurance section). A representative group of 20 full-scale samples were analyzed for orthophosphate by IC and for oil/grease and surfactant by the extraction/infrared technique (Standard Method 5520C). A sample of the make-up water supply was also tested for Ca/Mg hardness to identify hardness levels that might contribute to higher surfactant usage.

To determine the impact of the UF system on product quality, DuBois Chemicals ran a series of 6 steel test plates through the iron phosphating/degreasing bath during the UF experiment. The test

plates were analyzed for coating weight, rust creepage, paint thickness, and paint adhesion as described in the Quality Assurance section.

Permeate flux rates were recorded daily, and the time required for the UF unit to filter the entire 5000 gallons of process solution was calculated. When it had been determined that the UF unit had processed 5000 gallons of permeate, a batch down of the contents in the intermediate process tank was performed. The feed line from the 5000-gallon bath to the process tank was shut off, and the UF unit concentrated down the 55-gallon process tank to approximately 10 gallons of oily waste.

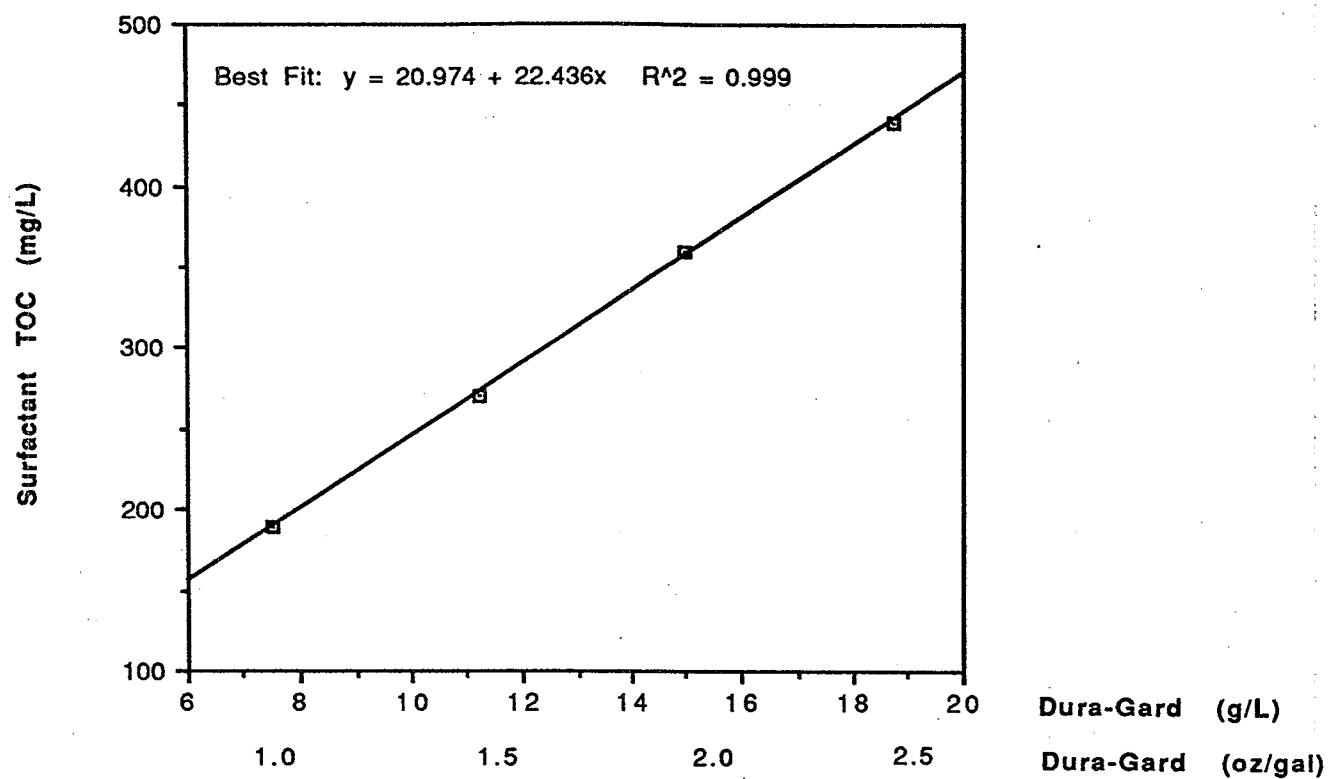
Data obtained from the full-scale modified batch test was used to determine whether UF would be a viable option for waste reduction at the R.B. White plant. Technical, operational, and economic aspects associated with the UF equipment were examined to evaluate the feasibility of this technology to improve R.B. White's metal fabrication operation.

## **Results and Discussion**

Results of the full-scale testing on site at R.B. White provided a more complete picture of how ultrafiltration impacted the 5000 gallon iron phosphating/degreasing bath and the quality of the parts it produced. For the scope of this report, the time frame for experimental data was limited to the time that was required to filter the first 5000 gallons of permeate and to proceed to batch down. This covered a test period of 11 days. A total of 180 UF operating hours was required to process 5000 gallons of bath solution.

When field testing began, the iron phosphating/degreasing bath had not been replaced in over 3 months. 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. Product quality tests also revealed that quality of the steel parts was improved significantly as a result of the cleaner process solution maintained by the ultrafiltration system.

In order to quantify this exceptional improvement, results of the full-scale testing were analyzed one-step further than the bench- and pilot-scale tests, paying particular attention to the separate TOC contributions of oil and surfactant. Since standard analytical test methods were not adequate to make the important distinction between oil/grease and surfactant for reasons detailed in the Quality Assurance section of this report, analysis of the field data took a new approach. A mass balance was developed to provide a more realistic representation of the events that took place over those 11 days. The mass balance utilized TOC data, records of chemical additions, and an estimation of the daily production load. The analytical information on TOC provided a base line for total oil/grease and surfactant levels in the bath, process tank, permeate, and rinse water. Daily records of the chemical



**Figure 13: Calibration Curve for Dura-Gard TOC**

additions of Dura-Gard Soke provided an accurate measure for the amount of TOC added as surfactant to the bath during the course of the full-scale test (see Figure 13 for calibration curve of Dura-Gard TOC). An estimation of the daily production load provided a practical and realistic value for the amount of oil that was washed off in the bath during 8 full days of production.

The daily production load was calculated by dividing the oil TOC in the bath at the start of the test by the number of working days since the bath had last been dumped. The oil TOC in the bath at the start of the test was extrapolated from titration data that was used to determine Dura-Gard concentrations in the bath. The titration was actually a measure of the level of phosphating agents in the bath, but this method was also valid for tracking the level of surfactant before ultrafiltration began. According to DuBois, both the phosphating agents and surfactants are consumed at the same rate under normal operating conditions. On the morning of the full-scale start-up, the bath titrated at 0.80 ounces Dura-Gard per gallon. Using the titration data, the level of surfactant was computed from the calibration curve in Figure 13 as 155 mg/L, and the level of oil was calculated as the difference between total TOC (422 mg/L) and surfactant TOC (155 mg/L). This value of oil TOC (267 mg/L) was converted to mass units (267 mg/L x 3.785 L/gal x 5000 gal) and divided by 71, the number of working days since the bath had last been dumped. The estimated production load was computed as 0.0712 kg oil/day.

Once UF testing was implemented, the titration was no longer a reliable indicator of surfactant or oil levels. The selective rejection and permeation of surfactant and phosphating agents by the UF membrane resulted in different consumption rates for each component, so the mass balance was developed to characterize the levels of oil and surfactant in the bath thereafter.

$$\text{MASS IN} - \text{CHANGE IN MASS} = \text{MASS OUT} \quad (\text{Eq. 2})$$

$$\text{where } \text{MASS IN}_n = \{n(\text{O}) + m(\text{S})\}_{\text{added}} + \{(\text{O} + \text{S})_{\text{bath}} + (\text{O} + \text{S})_{\text{rinse}}\}_{n=0}$$

$$\text{CHANGE IN MASS}_n = \{(\text{O} + \text{S})_{\text{process tank}} + (\text{O} + \text{S})_{\text{sludge}} + (\text{O} + \text{S})_{\text{skim}}\}_n$$

$$\text{MASS OUT}_n = \{(\text{O} + \text{S})_{\text{bath}} + (\text{O} + \text{S})_{\text{rinse}}\}_n$$

$n$  = number of working days ( $n = 0$  to 8)

$m$  = number of Dura-Gard additions (90 lbs) in  $n$  days ( $m = 0$  to 5)

$\text{O}$  = oil TOC mass

$\text{S}$  = surfactant TOC mass

Known Values:  $m(\text{S})_{\text{added}}$  TOC added as Dura-Gard surfactant

Measured Values:  $\{(\text{O} + \text{S})_{\text{bath, process tank}}\}_n$

Estimated Values:  $\{(\text{S})_{\text{bath}}\}_{n=0}$  Initial surfactant TOC mass  
 $\{(\text{O})_{\text{bath}}\}_{n=0}$  Initial oil TOC mass  
 $n(\text{O})_{\text{added}}$  Daily production load

Unknown Values:  $\{(O + S)_{\text{rinse, sludge, skim}}\}_n$   
 $\{(O + S)_{\text{rinse}}\}_{n=0}$

Ratio of O to S

The known, measured, and estimated values of TOC mass account for the major contributions to the mass balance equation. The unknown values of  $\{(O + S)_{\text{rinse, sludge, skim}}\}_n$  and  $\{(O + S)_{\text{rinse}}\}_{n=0}$  made up a smaller fraction of the mass balance and were difficult to determine analytically. The TOC mass in the rinse was not calculated due to lack of consistent measurements for the volume of rinse water; the mass of sludge produced was not possible to measure under field conditions; and the skimmed oil did not lend itself to a homogeneous sample that could be analyzed by the HWRIC's TOC analyzer. These unknown values of  $\{(O + S)_{\text{rinse, sludge, skim}}\}_n$  and  $\{(O + S)_{\text{rinse}}\}_{n=0}$  were combined into a single loss factor,  $k$ , to complete the mass balance. Still, one key assumption had to be made for the unknown ratio of O to S. A quantitative relationship needed to be defined for the ratio of oil/grease to surfactant in each facet of the mass balance equation: bath, process tank, and rinse. Without analytical laboratory data to affirm the relative concentration of each component in the separate test streams, insight into the physical chemistry of nonionic surfactants was used to fit together the final pieces of the puzzle.

Surfactant molecules associate with an oil phase in an amount proportional to the concentration of oil present and the conditions of mixing. Hundreds of surfactant molecules may surround a single droplet of oil to form a micelle, but the amount of surface area on the oil nucleus determines the number of bonding sites for the surfactant's hydrophobic tails. When sufficient surfactant is available, the critical micelle concentration (cmc) is reached, and the surfactant molecules effectively emulsify the oil in an aqueous phase. There is a direct and consistent correlation between the amount of surfactant and the amount of oil in an emulsified solution (Cutler, Davis, 1972). Of course, the presence of free surfactant or oil not associated with the emulsion would bias the balance between the oil to surfactant ratio. Based on field observation during the full-scale testing, the only times free oil was visible were on the first day in the bath and in the process tank there after. At all other times, the absence of free oil indicated that the balance of oil to surfactant favored excess surfactant. In terms of the mass balance, this observation led to a conservative estimate for reporting the amount of surfactant, attributing a higher percentage of the total TOC to oil.

The mass balance assumed that the ratio of oil/grease to surfactant in each test stream (bath, process tank, rinse) was equivalent to the ratio of oil to surfactant in the total system at time  $n$ . The ratio of O to S was defined using the daily production load, surfactant additions, and initial bath conditions. An example calculation follows.

# **MASS IN - CHANGE IN MASS = MASS OUT**

$$\{n(O) + m(S)\}_{\text{added}} + \{(O + S)_{\text{bath}}\}_{n=0} - \{(O + S)_{\text{process}}\}_n = \{(O + S)_{\text{bath}}\}_n + k$$

$$\text{where } k = \{(O + S)_{\text{sludge}} + (O + S)_{\text{skim}} + (O + S)_{\text{rinse}}\}_n - \{(O + S)_{\text{rinse}}\}_{n=0}$$

For  $n = 8$  days

$m = 5$  additions

$(O)_{\text{added}} = .0712$  kg oil/day (daily production load)

$(S)_{\text{added}} = .989$  kg surfactant

$\{(O)_{\text{bath}}\}_{n=0} = 5.06$  kg oil TOC (initially)

$\{(S)_{\text{bath}}\}_{n=0} = 2.94$  kg surfactant TOC (initially)

$\{(O + S)_{\text{process}}\}_{n=8} = 3.96$  kg TOC

$\{(O + S)_{\text{bath}}\}_{n=8} = 6.43$  kg TOC

Substituting these values and solving for the loss factor,  $k$ , gives:

$$8(.0712) + 5(.989) + (5.06 + 2.94) - 3.96 = 6.43 + k$$

$$(.570 + 4.94) + (5.06 + 2.94) - 3.96 - 6.43 = k = 3.12 \text{ kg TOC}$$

Grouping the O and S terms of the first two quantities separately and adding gives the total measurable TOC in the mass balance system at  $n = 8$ :

$$O_{\text{Total}} = (.570 + 5.06) = 5.63 \text{ kg oil TOC}$$

$$S_{\text{Total}} = (4.94 + 2.94) = 7.88 \text{ kg surfactant TOC}$$

Calculating the ratio of O to S at  $n = 8$  gives:

$$O/S = 5.63/7.88 = .714/1 \text{ or } O = 41.7\% \text{ and } S = 58.3\%$$

Following the assumption that the ratio of oil/grease to surfactant is equivalent for each test stream (bath, rinse, process tank, permeate) gives:

$$\{(O)_{\text{bath}}\}_{n=8} = 41.7\% (340 \text{ mg/L TOC}) = 142 \text{ mg/L oil TOC}$$

$$\{(S)_{\text{bath}}\}_{n=8} = 58.3\% (340 \text{ mg/L TOC}) = 198 \text{ mg/L surfactant TOC}$$

$$\{(O)_{\text{rinse}}\}_{n=8} = 41.7\% (11 \text{ mg/L TOC}) = 4.58 \text{ mg/L oil TOC}$$

$$\{(S)_{\text{rinse}}\}_{n=8} = 58.3\% (11 \text{ mg/L TOC}) = 6.42 \text{ mg/L surfactant TOC}$$

$$\{(O)_{\text{process}}\}_{n=8} = 41.7\% (19000 \text{ mg/L TOC}) = 7918 \text{ mg/L oil TOC}$$

$$\{(S)_{\text{process}}\}_{n=8} = 58.3\% (19000 \text{ mg/L TOC}) = 11082 \text{ mg/L surfactant TOC}$$

$$\{(O)_{\text{permeate}}\}_{n=8} = 41.7\% (160 \text{ mg/L TOC}) = 66.7 \text{ mg/L oil TOC}$$

$$\{(S)_{\text{permeate}}\}_{n=8} = 58.3\% (160 \text{ mg/L TOC}) = 93.28 \text{ mg/L surfactant TOC}$$

Figures 14a and 14b show the change in TOC levels of oil and surfactant in the bath and rinse water over the course of the 11-day experiment. When the field testing began, the bath had not been replaced in over 3 months and free oil could be seen floating on the surface. At the start of the field

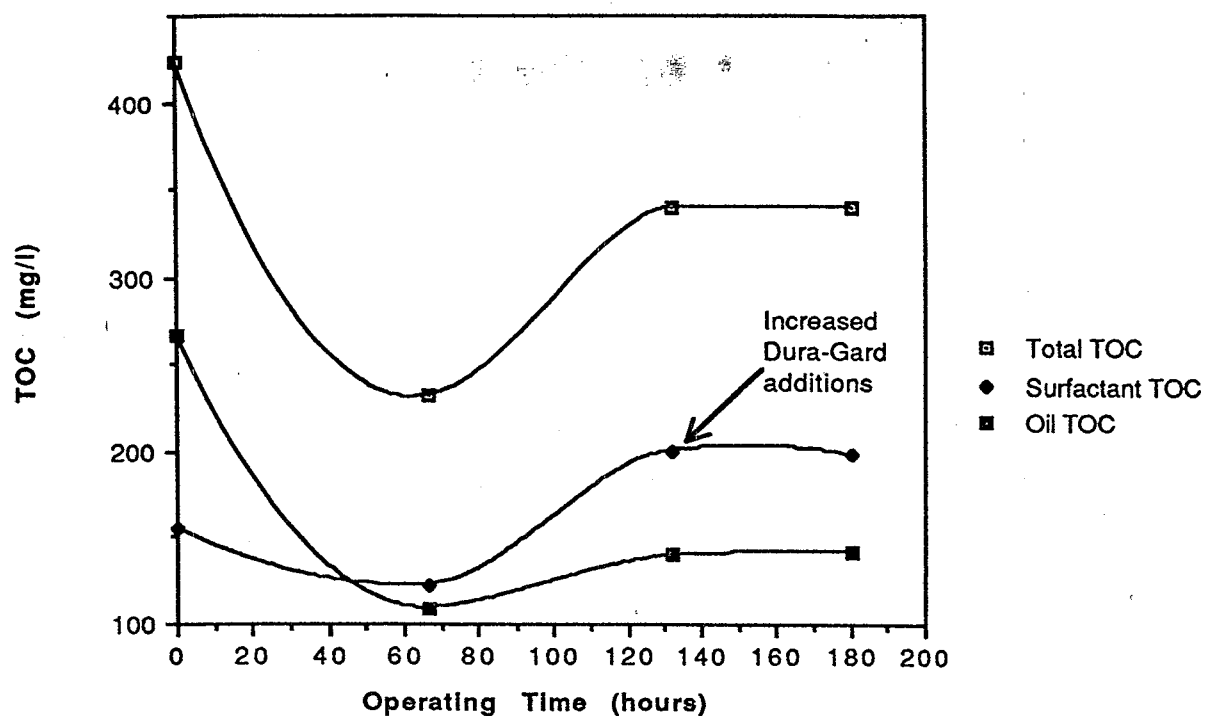


Figure 14a: Oil and Surfactant TOC in Bath vs Time

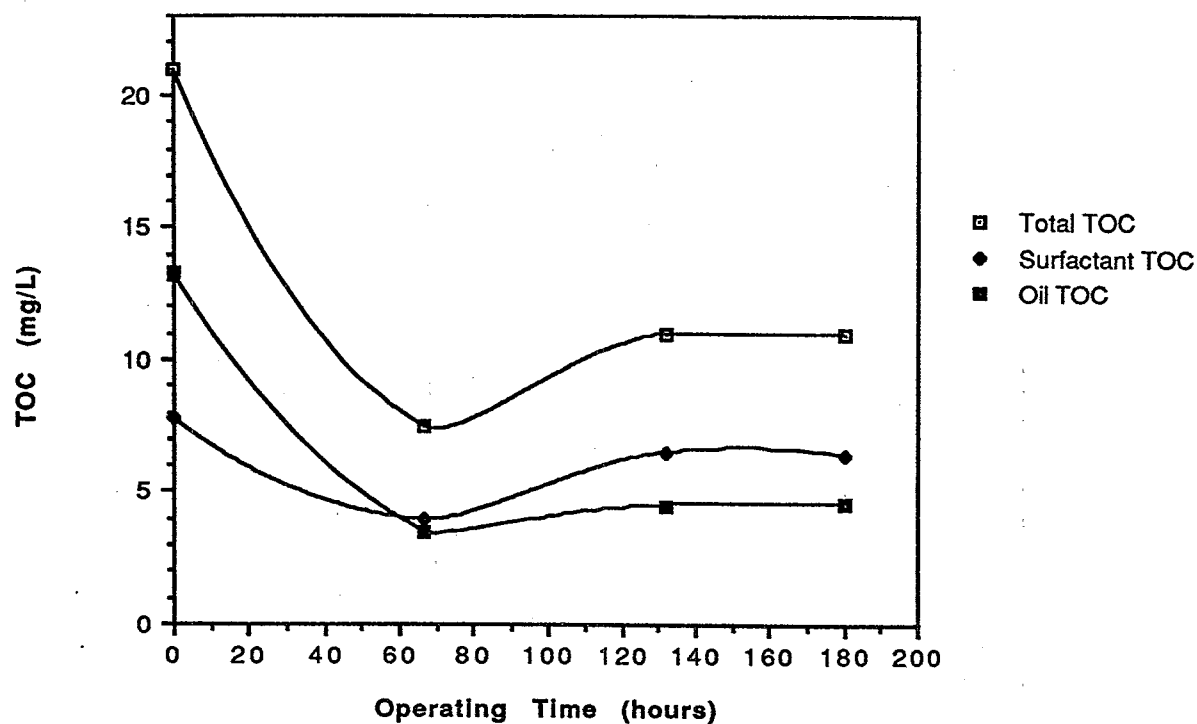


Figure 14b: Oil and Surfactant TOC in Rinse vs Time

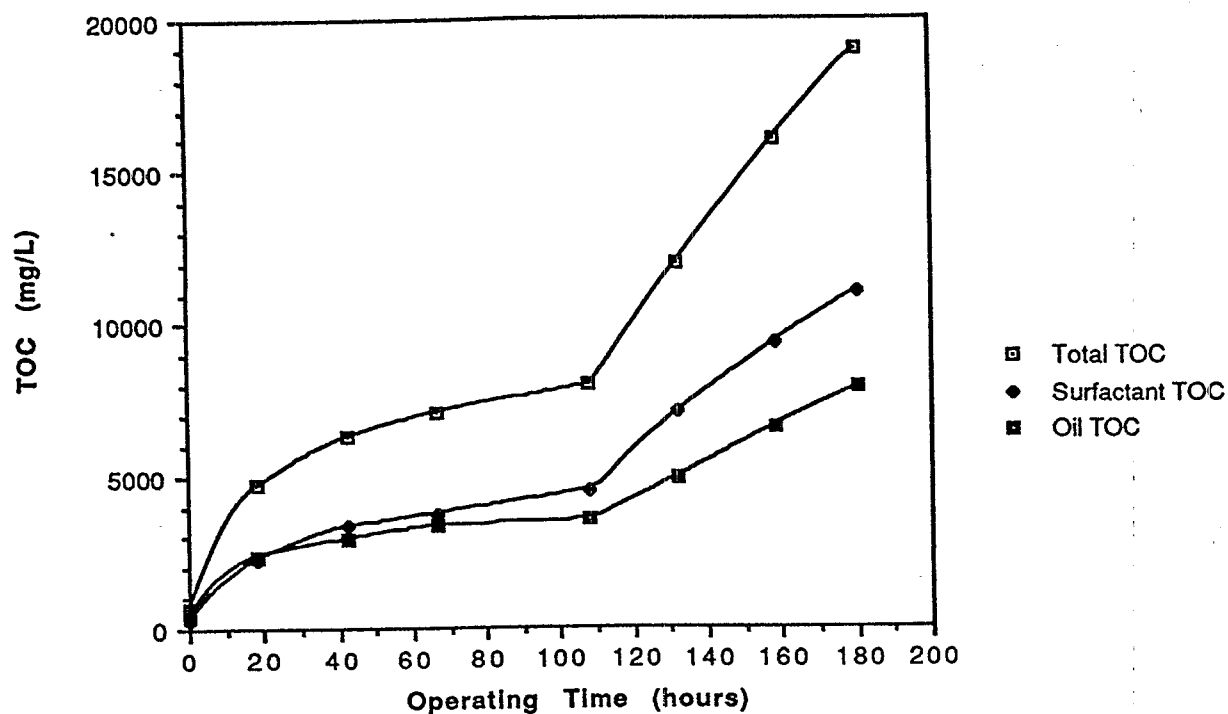


Figure 14c: Oil and Surfactant TOC in Process Tank vs Time

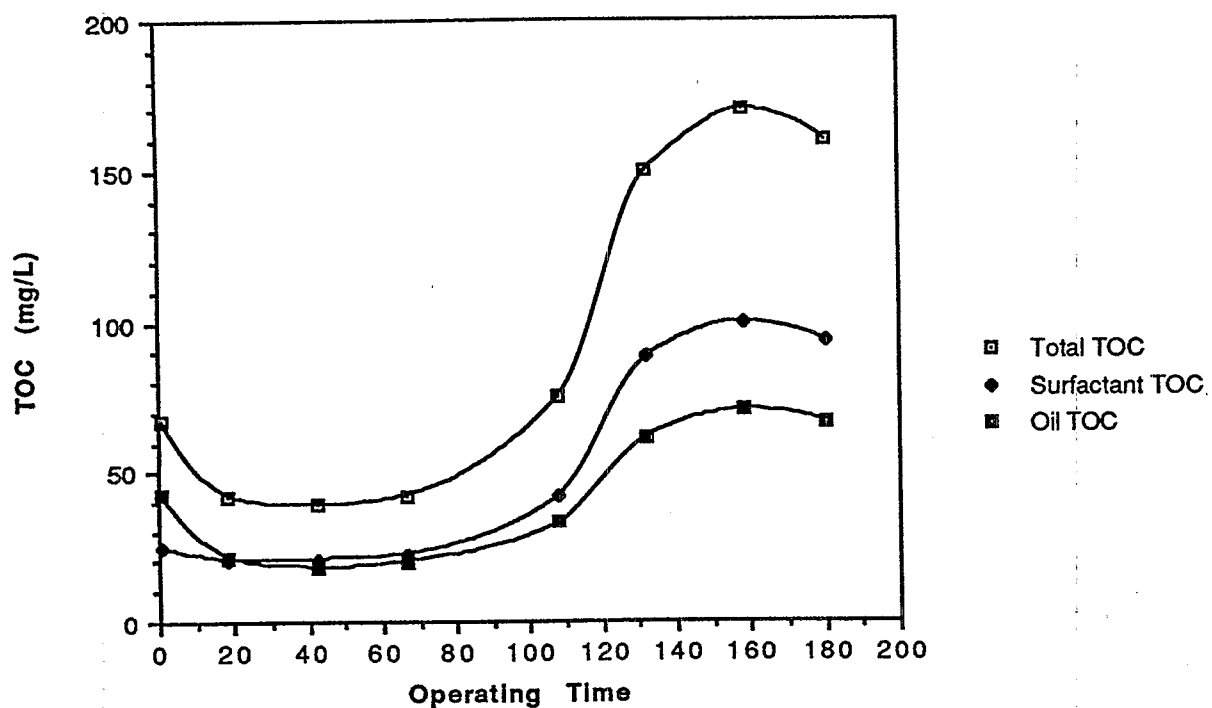


Figure 14d: Oil and Surfactant TOC in Permeate vs Time

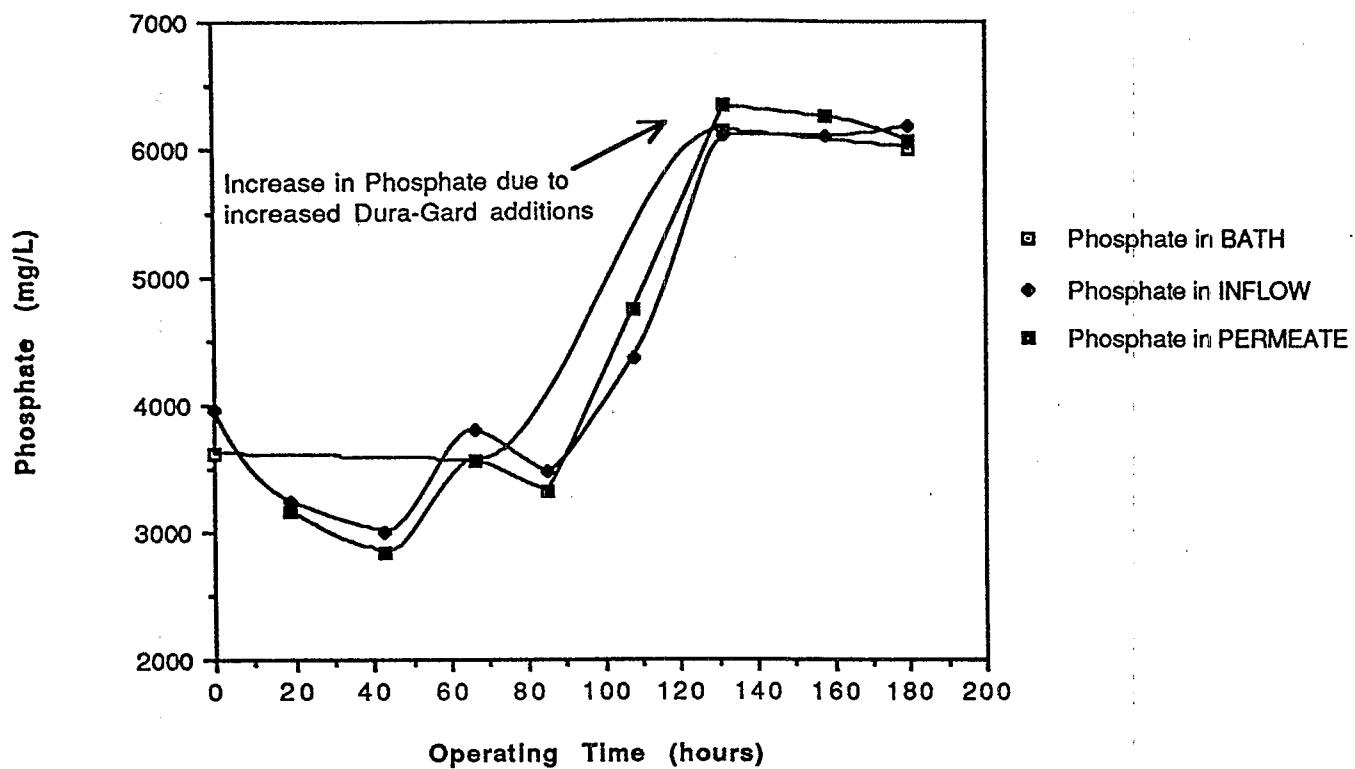


test, levels of oil/grease averaged 267 mg/L TOC and surfactant levels averaged 155 mg/L TOC. The bath titrated at 0.80 ounces Dura-Gard per gallon which was well below normal operating parameters. Under normal conditions, the bath is maintained at a Dura-Gard concentration of 1.5 to 2 ounces per gallon. On the third day, oil TOC in the bath had dropped by 157 mg/L to 109 mg/L. On this day, the bath composition was still low at 0.79 oz. Dura-Gard/gal as measured by titration in HWRIC's laboratory. Apparently, R.B. White's simple colormetric test kit was not very precise in measuring Dura-Gard levels in the bath. HWRIC field personnel alerted plant operators and provided R.B. White with a more precise titration apparatus for testing the level of raw materials in the bath. The new test apparatus included a pipette, buret, and pH meter for more accurate sampling and pH measurements than the simple test kit could provide. The same titration procedure used in the lab was also used in the field and is described in the Quality Assurance section of this report.

After ultrafiltration testing began, R.B. White personnel began adding more Dura-Gard to the bath, and phosphate levels and surfactant TOC concentrations increased substantially. The rise in phosphate levels in the bath shown in Figure 15 confirmed this surge in raw chemical addition. Phosphate levels in the bath, permeate, and process tank rose simultaneously with the increase in bath concentrations. The close correlation between phosphate levels in the separate test streams demonstrated that virtually all the phosphating agents were recovered by the ultrafiltration equipment. However, only a fraction of the unused surfactants managed to permeate through the membrane. Figures 14c and 14d reveal the discrepancy of surfactant TOC in the process tank and permeate. As predicted by the two pilot-scale tests, ultrafiltration was preferentially removing surfactant.

In addition to the effects of ultrafiltration, increased surfactant consumption may have been aggravated by high calcium and magnesium levels in the make-up water supply. Results of the hardness analysis on the make-up water identified 158 mg/L as  $\text{CaCO}_3$ , which qualified the make-up supply as a very hard water. High levels of Ca and Mg precipitate soaps and surfactants like those in R.B. White's bath and increase surfactant consumption although low pH levels help to minimize the effect. For R.B. White a water softening system might be beneficial, but the expense of purchasing such a system would outweigh the cost of additional surfactant usage that R.B. White had already become accustomed to before ultrafiltration was implemented.

Since Dura-Gard Soke only contained 2-3% surfactant by weight, compensating for surfactant lost to ultrafiltration by adding more Dura-Gard could have resulted in excessively high phosphate concentrations that would have contributed to loose and dusty coatings. At this point, it became clear that Dura-Gard and Tart alone could not maintain the chemical balance in the bath. DuBois Chemicals recommended a neutral cleaning additive, IPI-27, that contained the surfactant component found in Dura-Gard Soke along with very low levels of phosphates. Since there was no good way to detect levels of surfactant in the bath without laboratory analysis, it was suggested that plant operators



**Figure 15: Phosphate Levels in Bath, Inflow, and Permeate vs Time**

develop their own gage for adding the surfactant component, IPI-27, on an as-needed basis. Operators could even add excess surfactant as a safety factor to ensure clean part quality. Koch Membrane Systems representatives indicated that excess surfactant would not irreversibly harm the membrane, and DuBois Chemicals representatives saw no danger in excess surfactant interfering with the phosphating process. The only loss seemed to be the extra money spent on adding too much surfactant. Relative to the cost of the other raw materials, this added cost would be minimal.

Results of the coating weight, rust creepage, paint thickness, and paint adhesion tests conducted by DuBois Research Laboratory and R.B. White personnel on samples of steel parts indicated that acceptable product quality was achieved during the UF full-scale test. No previous product quality records were kept on file, but conversation with DuBois laboratory personnel and R.B. White plant operators confirmed that the product quality achieved during the UF full-scale test was good for R.B. White's application for controlled indoor air environments. Product quality test results appear in Table 3.

**Table 3: Product Quality Test Results**

PRODUCT QUALITY TEST	RESULTS (averages)
Coating Weight	50.4 mg/ft <sup>2</sup>
Rust Creepage 1/8" Salt Fog 5% Humidity 96%	Passing at 24, Failed at 48 hrs Passing at 504 hrs
Paint Thickness	1.6 mil
Paint Adhesion	Good*

\* Only qualitative data available from R.B. White personnel.

Permeate flux rates exhibited excellent performance during the full-scale operation. Figure 16 shows the change in permeate flux with time and the approach to steady-state. According to Koch Membrane Systems representatives, R.B. White's acidic iron phosphating/degreasing bath produced much higher permeate flux rates than alkaline cleaning baths in similar UF applications. The combination of acidic conditions (pH = 3.5 to 4.5), high temperature (140°F), relatively low oil concentrations (267 mg/L in a dirty bath), and surfactant usage contributed to a very favorable performance. High temperatures functioned to lower water viscosity and reduce free surfactant adsorption while encouraging higher flux rates. The presence of surfactants also helped to keep the membrane surface clean by tying up the oil and dirt in an emulsion.

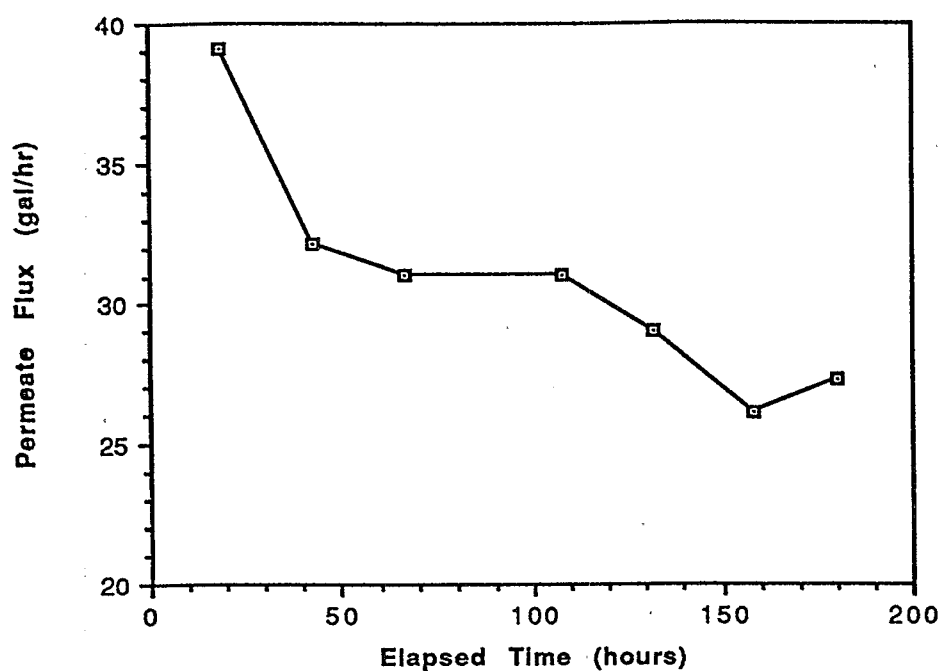


Figure 16a: Permeate Flux Rate vs Time

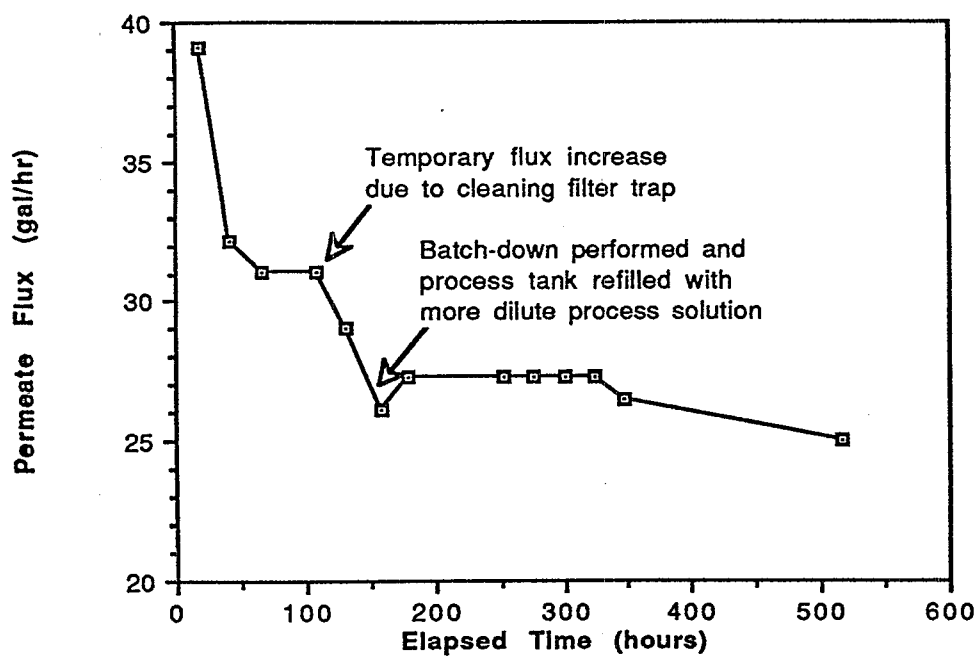


Figure 16b: Permeate Flux Rate vs Time (Extended Study)

During the 180 hour operating period of the full-scale UF test, permeate flux rates remained steady and the membranes were never cleaned. Data collection was completed, but the UF system was kept on line to evaluate the equipment's long-term performance. After several weeks the permeate flux began to decline rapidly. Attempts to clean the membranes with alkaline cleaner (KLD-Koch Liquid Detergent), diluted Tart (phosphoric acid plus surfactant), and rubber sponge balls were not effective in restoring flux. These cleaners were designed to remove oil, but apparently the oil was not the primary cause of fouling and flux decline. The other major component in the bath that had the potential to foul the membranes was the iron phosphate precipitate. A two-stage cleaning regime with rubber sponge balls was prescribed. Sodium bisulfite was used in the first stage to reduce the iron species to its more soluble state. Citric acid in the second stage acted as a chelating agent to combine with the iron and prevent it from redepositing on the membrane surface. After lime pH adjustment, the spent sodium bisulfite and citric acid cleaners were acceptable to pour down the drain. This cleaning regime provided excellent flux recovery, but the high flux rates only lasted a few hours.

About this time, the centrifugal pump on the full-scale UF system began to show accelerated signs of wear and tear. At least one pipe plug had been completely eaten away, and the pump casing was leaking badly. The pump was made of cast iron and did not fare well under the corrosive conditions of the bath and cleaning chemicals. The pump was taken off-line and replaced with a stainless steel pump. When the interior of the old cast iron pump was examined, the inside had severely corroded and the impeller had almost completely disintegrated. The bath and cleaning chemicals had dissolved the iron from the pump and precipitated an iron phosphate coating on the membrane surface. The accelerated iron corrosion and deposition from the cast iron pump kept the membranes from staying clean for longer than a few hours. When the pump was replaced with a stainless-steel one and the membranes were cleaned weekly, permeate flux rates were restored and maintained.

In addition to membrane life, another long term concern pertained to regular maintenance on the 5000 gallon tank. Since ultrafiltration had been implemented, periodic emptying of the tank was eliminated. Previously, emptying the tank allowed plant personnel to recover lost parts from the tank floor and remove the scale and sludge that had accumulated on the tank and heating element surfaces. The scale and sludge consisted mainly of iron phosphate precipitate and undissolved Dura-Gard Soke powder. DuBois recommended that the scale and sludge be removed periodically to reduce contamination and improve heating element efficiency. Without emptying the tank, R.B. White needed an alternative means of performing regular tank maintenance.

Plant personnel found that they could recover lost parts just by running a long pole with a hook at one end along the bottom of the tank and fishing out the steel parts and hangers. The heating elements were removable and could be cleaned without emptying the tank. With slight design

modifications, the sludge that settled on the bottom of the tank could be removed using a slow-moving sludge scraping mechanism and a sludge pump at a low point in the tank. Another alternative for regular tank maintenance might involve renting or purchasing a 5000 gallon holding tank to use every other year to store bath solution from the 5000 gallon process tank while regular tank maintenance is performed. This way R.B. White could empty the tank, clean away sludge and lost parts, and still save the bath solution. For the meantime, R.B. White has chosen to go with a third alternative. DuBois Chemicals has recommended a liquid form of Dura-Gard Soke known as Secure Soke. This was intended to reduce the amount of sludge accumulated in the tank by eliminating the undissolved Dura-Gard component.

## Section 7

### QUALITY ASSURANCE

A Quality Assurance Project Plan (QAPP) was prepared and approved by the U.S. EPA before testing began (Miller, Lindsey, 1992). The QAPP contains a detailed design for conducting this study. The experimental matrix, sampling and testing procedures, and laboratory analytical procedures are delineated in the QAPP. The analytical objectives of the QAPP are discussed below. With the exception of analytical difficulties involved in the oil/grease analysis, QA objectives for this project were not only met but expanded to include more complete sample characterization.

The original intent, as outlined in the QAPP, was to analyze all samples for oil and grease in order to determine the proficiency of ultrafiltration to remove oil contamination from the iron phosphating/degreasing bath. As the project progressed, it became apparent that samples should also be analyzed for concentrations of surfactant and phosphating agents to determine if valuable raw materials were being filtered out along with the oil. Additionally, steel test panels were analyzed for product quality during the full-scale study. Analysis of samples from the bench-, pilot-, and full-scale studies included tests for oil/grease, polyhydrocarbons (PHC), total organic carbon (TOC), orthophosphate, EDTA hardness, coating weight, rust creepage, paint thickness, and paint adhesion. Table 4 presents a summary of sample types and analyses.

**Table 4: Sample Summary**

PHASE	SAMPLE TYPE*	SAMPLES	ANALYSIS
Bench Scale	Process Solution	19	Oil/Grease
	Concentrate	18	Oil/Grease
	Permeate	18	Oil/Grease
Pilot Scale	Inflow	18	TOC, Phosphate
	Permeate	22	TOC, Phosphate
Full Scale	Process Solution (Bath)	20	Oil/Grease, PHC, TOC, Phosphate
	Inflow (Process Tank)	10	Oil/Grease, PHC, TOC, Phosphate
	Permeate	10	Oil/Grease, PHC, TOC, Phosphate
	Rinse Water	5	Oil/Grease, PHC, TOC, Phosphate
	Raw Water Supply	1	EDTA Hardness, TOC
	Phosphated Steel Panels	3	Coating Weight
	Painted Steel Panels	3	Rust Creepage, Thickness, Adhesion

\* Liquid samples were stored at 4°C in glass bottles with Teflon-lined caps; holding times did not exceed 2 months.

Laboratory analyses of the samples collected during this three-phase project were modified as new information came to light. Oil and grease analysis as prescribed by USEPA Method 413.1 (Methods for Chemical Analysis of Water and Wastes, 1983) was complicated by the presence of nonionic surfactants in the process solution. As the project progressed, it became evident that the nonionic surfactants in the process solution would interfere with the accuracy of this analytical procedure. The surfactants contributed to a persistent, stable emulsion layer in the separatory funnel that inhibited complete solvent extraction. Attempts to break the emulsion were time-intensive and only partially successful. Glass beads, glass wool,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ , heating, freezing, pH adjustment, centrifugation, and continuous solvent-solvent extraction were not effective in breaking the emulsion or achieving complete extraction.

In addition to the problems associated with the emulsions, the surfactants also contributed false readings regarding the amount of oil and grease present. No known solvent will selectively dissolve only oil and grease. With the USEPA partition-gravimetric method (Method 413.1), freon extraction not only dissolved oil and grease but other organics as well (Clesceri, Greenberg, Trussell, 1989). In this case, biodegradable nonionic surfactants were extracted along with the oil and grease in the process solution. When the extract was distilled, the residue reflected the combined total mass of oil/grease plus surfactant. Since each component carried a different meaning, measuring the quantity of the two components separately as oil/grease and surfactant was important.

Standard Method 5520 C extraction/infrared technique (Standard Methods for the Examination of Water and Wastewater, 1989) goes one step beyond the USEPA partition-gravimetric method to differentiate between oil/grease and other organics. This method utilizes solvent extraction plus infrared spectroscopy. Analysis of the solvent extract by infrared spectrophotometer is capable of discerning oil and grease as polyhydrocarbons (PHC) apart from nonionic surfactants. A representative group of 20 full-scale samples were analyzed using this method, but the same problems associated with the extraction procedure kept these samples from providing any conclusive data.

During the course of this study, laboratory personnel found that standard methods would not be adequate for analyzing the industrial process solution. Following standard protocol for defining and reporting levels of oil and grease provided false and misleading information. In-house laboratory staff worked on new methods and combinations of methods that would give a more accurate indication of the samples' make-up. Their research went beyond the scope of this pollution prevention project, but HWRIC staff will continue to research the analysis of similar industrial solutions in hopes of establishing a more complete and accurate procedure for analyzing oily-detergent wastewaters.

Due to the complications involved in the oil and grease analysis, another analytical test was developed for the complete set of pilot- and full-scale samples. Analysis for total organic carbon (TOC) was used as a surrogate test for combined levels of oil/grease and non-ionic surfactant. Analysis by



TOC provided an accurate, efficient, and repeatable test for combined oil/grease and surfactant concentrations. Under the circumstances, TOC provided the best indicator of the ability of ultrafiltration to remove organic species, whether oil or surfactant, from the process solution. A mass balance was then developed to describe the fate of each component. Analysis for TOC was conducted by the Rosemount Analytical Dohrmann DC-190 TOC Analyzer according to the Combustion-Infrared Method (Standard Method 5310 B). The TOC Analyzer was calibrated with 1000 ppm potassium hydrogen phthalate (KHP) giving a reference standard of 999.7 ppm C as KHP with a typical recovery of  $986.4 \pm 25.57$ , standard deviation = 2.592 %. Method blank results were below the 10 ppm detection limit. Samples were diluted according to strength.

In addition to testing for oil/grease and surfactant, samples were analyzed for phosphate concentrations to determine whether ultrafiltration might selectively remove the valuable phosphating agents from solution along with the emulsified oil. Concentrations of  $\text{PO}_4$  were determined by Ion Chromatograph (IC) analysis using the Dionex Ion Chromatograph. The IC was calibrated with potassium phosphate. Samples were prefiltered with a solid phase extraction cartridge (C18) to remove oil that might interfere with the IC equipment. Due to the time and expense involved with the IC testing, only a representative group of 20 full-scale samples were analyzed for orthophosphate by IC. The remaining samples were analyzed for  $\text{PO}_4$  by using the same titration procedure R.B. White plant personnel relied on for checking levels of phosphoric acid (free and combined) in the bath. Samples were titrated with .1 N NaOH to the second  $\text{pK}_a$  endpoint of 9.2. For the 20 representative samples, a consistent ratio was defined between the volume of titrant required to reach the endpoint and the known  $\text{PO}_4$  values determined by IC. This ratio was used to calculate concentrations for all remaining samples.  $\text{PO}_4$  data and data reduction procedures from the titrations and IC testing are presented in the Appendix.

For the onsite, full-scale testing, the make-up water supply for the iron phosphating/degreasing bath was also tested for calcium/magnesium hardness. Hardness testing was used to determine the potential for surfactant loss due to precipitation caused by calcium or magnesium in the water. The EDTA titrimetric method (Standard Method 2340 C) was used to determine the level of water hardness. These results were utilized to determine if a water softening system would be beneficial in conserving surfactant in the long run.

Besides waste reduction, the primary objective of this study was to preserve product quality by ensuring the steel parts were being cleaned and a good phosphate coating was being formed. Quality control tests were performed by the chemical supplier and R.B. White personnel while the full-scale ultrafiltration system was in operation. Standard tests included coating weight, rust creepage, paint thickness, and paint adhesion. Coating weight was determined using DuBois Research Laboratory's own method (Gortsas, 1993). Briefly described, steel test parts were processed through

the iron phosphating/degreasing bath during normal operation. The parts were dried, weighed, and measured. The phosphate coating was stripped with chromic acid ( $\text{CrO}_3$ ), and the parts were reweighed. The net difference in weight gave milligrams phosphate coating weight per square foot. Rust creepage was determined according to ASTM methods B117 and D2247-87. For these tests, steel test parts were processed through the complete production line. Painted test parts were scored and subjected to either a 5% salt fog or 96% humidity. Rust creepage from the score was reported as passing/failing for 1/8" creepage at 24, 48, and 504 hours. Paint thickness was measured by the Zorelco 757 coating gage and calibrated with a standard film thickness. Paint adhesion was checked by R.B. White plant personnel using the cross-hatch test which involved scoring the paint and applying a piece of tape to the scratch. Adhesion quality was observed as the tape was pulled away, and results were qualitatively reported.

Tables 5 and 6 present the precision and accuracy data for the full-scale sample analysis performed by HWRIC and DuBois labs. Due to the complications discussed earlier, data from the oil/grease and PHC analyses was not used in the final evaluation.

**Table 5: Precision Data for Full-Scale Sample Analysis (Typical values)**

PARAMETER	NO.	REGULAR SAMPLE	LABORATORY DUPLICATE	FIELD DUPLICATE	PRECISION
TOC	2	440 mg/L	430 mg/L		RPD = 2.3%
	13	42 mg/L		39 mg/L	RPD = 7.4%
Oil/Grease*	Data from the oil/grease and PHC analyses were not utilized due to complications in laboratory procedures.				
PHC**					
Orthophosphate	46	6055 mg/L	6095 mg/L		RPD = 0.7%
	14	3641 mg/L		3799 mg/L	RPD = 4.2%
EDTA Hardness	100	158.144 mg/L	158.144 mg/L	N/A	RPD = 0%
Coating Weight	114	53.2 mg/ft <sup>2</sup>	N/A	51.6 mg/ft <sup>2</sup>	RPD = 3.0%
RUST CREEPAGE Salt Fog 5%	111	1/8" at <48hr	N/A	1/8" at <48hr	RPD = 0%
Humidity 96%	113	1/8" at >504hr	N/A	N/A	N/A
Paint Thickness	112	1.6 mil	N/A	1.4 mil	RPD = 13%

\* Oil and Grease analysis (USEPA Method 413.1) measures oil plus surfactant.

\*\* PHC analysis (Standard Method 5520 C) differentiates between oil and surfactant.

**Table 6: Accuracy Data for Full-Scale Sample Analysis (Typical values)**

PARAMETER	ID NO.	REGULAR SAMPLE	MATRIX SPIKED SAMPLE	MATRIX SPIKED VALUE	ACCURACY (% RECOVERY)
TOC	No data was obtained for spiked samples because oil would not stay emulsified or remain in solution.				
Oil/Grease*	Data from the oil/grease and PHC analyses were not utilized due to complications in laboratory procedures.				
PHC**					
Orthophosphate	3 <sup>a</sup>	3905 mg/L	1154 mg/l	1018 mg/l	88.3%
EDTA Hardness	100 <sup>b</sup>	158.144 mg/l as CaCO <sub>3</sub>	1000 mg/L as CaCO <sub>3</sub>	1004 mg/L as CaCO <sub>3</sub>	100.4%
Coating Weight	114	53.2 mg/ft <sup>2</sup>	N/A	N/A	N/A
RUST CREEPAGE					
Salt Fog 5%	111	1/8" at <48hr	N/A	N/A	N/A
Humidity 96%	113	1/8" at >504hr	N/A	N/A	N/A
Paint Thickness	112	1.6 mil	N/A	N/A	N/A

\* Oil and Grease analysis (USEPA Method 413.1) measures oil plus surfactant.

\*\* PHC analysis (Standard Method 5520 C) differentiates between oil and surfactant.

<sup>a</sup> Bath

<sup>b</sup> Raw water supply

## Section 8

### ECONOMIC ANALYSIS

The costs and benefits associated with installing an ultrafiltration system at the R.B. White facility were analyzed to determine the economic feasibility of this technology. Assumptions regarding inflation rate, discount rate, federal tax rate, depreciation schedule, project life, and various operating expenses were entered into a LOTUS spreadsheet program (General Electric, 1987) which calculated a number of economic indices. The assumptions utilized in these calculations and their sources are presented in Table 7.

**Table 7: Assumptions for Economic Calculations**  
(based on 1992 conditions)

ITEM	FACTOR	SOURCE
Inflation Rate	4%	Consumer price index
Discount Rate	7.72%	10 year treasury bill rate + 0.5%
Federal Tax Rate	34%	General Electric, (1987)
Labor Rate	\$15/hour	R.B. White
Power Costs	\$.10/kw	Illinois Power
Depreciation Schedule	7 years	General Electric, (1987)
Project Life	20 years	Koch Membrane Systems, Inc.
Raw Materials Costs*	\$900/bath	R.B. White
Down Time Costs**	\$1000/bath	R.B. White
Salvage Value	\$0	Koch Membrane Systems, Inc.
Waste Disposal Costs	\$1/gallon	R.B. White

\* Raw Materials Costs include phosphating and degreasing chemicals required to charge a fresh bath.

\*\* Down Time Costs include costs associated with lost production incurred during bath cleaning activities.

Table 8 provides estimates of the capital and operating expenses as well as the cost savings that could be anticipated as a result of investment in an ultrafiltration system. These estimates assume that the phosphating/degreasing bath would have to be disposed of and recharged at a frequency of once every 2 years following installation of the ultrafiltration system. This contrasts with the schedule utilized prior to installation of the ultrafiltration system which involved disposing of and recharging the

**TABLE 8: CASH FLOW SUMMARY**  
(Dollar Amounts before Taxes and Depreciation)

YEAR	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
<b>CAPITAL EXPENDITURES</b>																					
Koch Ultrafiltration Unit	12000	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
<b>OPERATING EXPENDITURES</b>																					
Clean Membranes	75	156	162	169	175	182	190	197	205	213	222	231	240	250	260	270	281	292	304	316	329
Chemicals	390	811	844	877	912	949	987	1026	1067	1110	1155	1201	1249	1299	1351	1405	1461	1519	1580	1643	1709
Labor (52 hrs./year)																					
Equipment Maintenance								987							1299						
Replace Pump											740										
Replace Pump Motor											296										
Miscellaneous	0	104	216	225	234	243	253	263	274	285	296	308	320	333	346	360	375	390	405	421	438
Replace Membranes (2/year)	500	1040	1082	1125	1170	1217	1265	1316	1369	1423	1480	1539	1601	1665	1732	1801	1873	1948	2026	2107	2191
Power Consumption (23 kw/day x 80% availability)	337	700	728	757	787	819	852	886	921	958	996	1036	1077	1121	1165	1212	1261	1311	1363	1418	1475
Waste Disposal																					
400 ga./year sludge	200	416	433	450	468	487	508	528	547	569	592	616	640	666	693	720	749	779	810	843	876
30 ga./year oil emulsion	15	31	32	34	35	36	38	39	41	43	44	46	48	50	52	54	56	58	61	63	66
<b>TOTAL EXPENDITURES</b>	<b>13517</b>	<b>3258</b>	<b>3497</b>	<b>3637</b>	<b>3782</b>	<b>3933</b>	<b>4091</b>	<b>4241</b>	<b>4425</b>	<b>4602</b>	<b>4777</b>	<b>4977</b>	<b>5176</b>	<b>5383</b>	<b>5597</b>	<b>5822</b>	<b>6055</b>	<b>6298</b>	<b>6549</b>	<b>6811</b>	<b>7084</b>
<b>SAVINGS</b>																					
Raw Materials																					
(recycled phosphating/ degreasing chemicals)	1350	2808	1947	3037	2106	3295	2278	3553	2463	3943	2664	4157	2882	4496	3117	4863	3371	5259	3646	5688	3944
Reduced Plant Down Time (associated with cleaning process tank)	1500	3120	2163	3375	2340	3650	2631	3948	2737	4270	2960	4618	3202	4995	3463	5403	3746	5844	4052	6321	4382
Waste Disposal (15000 gallons/year spent bath solution)	7500	15800	16224	16873	17548	18250	18980	19739	20529	21350	22204	23092	24015	24976	25975	27014	28095	29219	30387	31603	32867
200 gallons/year skimmed oil	100	208	216	225	234	243	253	263	274	285	296	308	320	333	346	360	375	390	405	421	438
<b>TOTAL SAVINGS</b>	<b>10450</b>	<b>21736</b>	<b>20550</b>	<b>23510</b>	<b>22227</b>	<b>25428</b>	<b>24041</b>	<b>27503</b>	<b>26003</b>	<b>29747</b>	<b>28125</b>	<b>32175</b>	<b>30420</b>	<b>34800</b>	<b>32902</b>	<b>37640</b>	<b>35587</b>	<b>40711</b>	<b>38491</b>	<b>44033</b>	<b>41631</b>
<b>CASH FLOW</b>	<b>-3066</b>	<b>18477</b>	<b>17053</b>	<b>19872</b>	<b>18445</b>	<b>21494</b>	<b>19950</b>	<b>22261</b>	<b>21578</b>	<b>25145</b>	<b>22598</b>	<b>27197</b>	<b>25243</b>	<b>29416</b>	<b>26004</b>	<b>31817</b>	<b>29531</b>	<b>34413</b>	<b>31941</b>	<b>37221</b>	<b>34547</b>

bath at a frequency of at least 3 times per year. Additionally, it was assumed that the wasted bath could be discharged directly to the sanitary district (following neutralization of its acidic conditions for a minimal cost) as a result of ultrafiltration processing. This is appropriate since the bath would no longer contain significant quantities of emulsified oil which had prevented discharge of the spent bath prior to utilization of ultrafiltration.

As shown in Table 8, installation of an ultrafiltration system would require significant capital expenditures (approximately \$12,000) associated with purchasing and installing the equipment. Additionally, significant operating expenses associated with cleaning and replacing the membranes, equipment maintenance, and power consumption would be incurred over the projected 20 year life of the equipment. However, substantial savings associated with reduced raw materials usage, reduced plant down time, and reduced waste disposal costs would repay the capital and operating expenses several times over.

Based on the estimated expenditures, savings, and economic conditions described above, the financial analysis program (General Electric, 1987) was utilized to calculate the economic indices described in Table 9. As shown, the economics associated with installing an ultrafiltration system at the R.B. White facility are very favorable. It is estimated that the payback period associated with this technology is only 6.9 months. The net present value and implied rate of return indices are \$152,143 and 178%, respectively. Therefore, investment in an ultrafiltration system at the R.B. White facility represents a very attractive economic alternative.

**Table 9: Economic Summary**

Capital Invested	\$12,000
Payback Period	6.9 months
Net Present Value (NPV)	\$152,143
Interest Rate of Return (IRR)	178%

## **Section 9**

### **CONCLUSIONS AND RECOMMENDATIONS**

#### **Conclusions**

The overall evaluation of this pollution prevention project was based on ultrafiltration performance, product quality, and economics. Results of the full-scale ultrafiltration study 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 flux rates exhibited excellent performance during the acidic ( $\text{pH}=3.5$ ), high temperature ( $140^{\circ}\text{F}$ ) operation and were high enough to continuously process the constant input of oil from the production line. The entire 5000 gallon bath was processed in 180 ultrafiltration operating hours. Coating weight, rust creepage, and paint adhesion tests conducted by DuBois Research Laboratory and R.B. White plant personnel on samples of steel parts indicated that product quality achieved during the full-scale study was good for R.B. White's application. Based on the estimated expenditures and savings, the payback period associated with this pollution prevention technology was only 6.9 months.

By using ultrafiltration, the R.B. White will reduce its hazardous waste generation by at least 15,000 gallons per year, a 99.8% reduction. In addition, the company will no longer have periodic problems exceeding allowed oil and grease levels in their rinse water discharge to the sanitary district.

This project has successfully demonstrated the ability of membrane filtration to reduce industrial waste generation and recover valuable raw materials in a metal fabricating 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 facility. The ultrafiltration system implemented in this project saves money, maintains good product quality, and reduces waste generation.

#### **Recommendations**

Many industries are facing tougher laws and tighter restrictions on solvent use and hazardous waste generation. Along with the environmental concerns come the rising costs of liability, compliance, and waste disposal. Developing cleaner production techniques will call upon innovative ideas and creative engineering to build the environmentally responsible industry of the future.

The metal fabricated products industry needs to examine its present methods of operation and set goals for cleaner production. Using iron phosphate and alternative coating chemicals can modernize a metal coating operation as existing and projected EPA regulations require more stringent

control and more expensive waste treatment methods for chromated seals, zinc phosphate, and chromate conversion coatings. Making the switch from solvent to aqueous cleaners holds the potential to reduce solvent waste, improve worker safety, and avoid stricter environmental regulations. Learning to extend the life of aqueous process solutions opens the door to recovery technologies like ultrafiltration that could save money in raw materials and waste disposal. In-plant evaluation and testing can provide useful information for customizing a recovery scheme to fit an industry's specific needs. Developing and implementing new ideas can bring about innovative solutions, but the industry should be aware of limitations and special concerns. The issues of membrane fouling, sludge build-up and disposal, regular tank maintenance, proper chemical balance, and raw material substitution need to be dealt with on a case-by-case basis.

When industry cooperates and works with the EPA and equipment dealers, environmentally responsible solutions to generating hazardous and industrial process wastes can be found. With the advent of water-based cleaners, waste minimization and pollution prevention have become realistic and attainable goals for the metal fabricated products industry.



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**GLOSSARY**  
(Cheryan, 1986)

- Concentrate** : the portion of the feed solution that is rejected by the membrane
- Flux** : the volumetric flow rate of permeate per cross-sectional area per time
- Fouling** : detected as the decrease in permeate flux over time and is a result of the changes in the membrane structure or interactions between the components of the feed stream and the membrane surface
- MWCO** : molecular weight cut-off, the minimum weight of a typical molecule that would be rejected by the membrane
- Permeate** : the portion of the feed solution that passes through the membrane
- Rejection** : describes the degree to which ultrafiltration prevents components in the feed solution from passing through the membrane

## APPENDIX Numerical Data from Figures in Text

**Figure 5a: Comparison of Wastewater Flux Rates During Bench-Scale Testing**

MEMBRANE MODEL	MASS FLUX (grams permeate/minute)
M2 Teflon (30,000 MWCO)	1.100
SNO4 Cellulose Acetate (20,000 MWCO)	1.080
PM30 Polysulfone (2,000 MWCO)	.704
M3 Teflon (500 MWCO)	.209
PM10 Polysulfone (10,000)	.198

**Figure 5b: Comparison of Normalized Flux Rates During Bench-Scale Testing**

MEMBRANE MODEL	NORMALIZED FLUX	
	$J_{\text{average}}/J_{\text{initial}}$	$J_{\text{recovery}}/J_{\text{initial}}$
M2 Teflon (30,000 MWCO)	.423	.869
SNO4 Cellulose Acetate (20,000 MWCO)	.284	.921
PM30 Polysulfone (2,000 MWCO)	.017	.001
M3 Teflon (500 MWCO)	.275	.886
PM10 Polysulfone (10,000)	.009	.020

**Figure 9: TOC in Process Tank and Permeate vs Time Using Clean Process Solution**

ELAPSED TIME (hours)	TOC (mg/l):	
	Permeate	Process Tank
0.00	170	490
0.33	180	520
0.68	160	550
1.02	140	620
1.35	130	720
1.90	170	950

**Figure 10: Phosphate in Process Tank and Permeate vs Time Using Clean Process Solution**

ELAPSED TIME (hours)	PHOSPHATE (mg/l):	
	Permeate	Process Tank
0.00		
0.33	13376	14010
0.68	13693	13693
1.02	13456	13930
1.35	13218	13851
1.90	13851	13930

**Figure 11a: TOC in Process Tank and Permeate vs Time Using Waste Process Solution**

Permeate		Process Tank	
ELAPSED TIME (hrs)	TOC (mg/l)	ELAPSED TIME (hrs)	TOC (mg/l)
0.00	52		
0.18	53	0.63	790
0.52	56	2.28	810
0.77	56	3.28	870
1.02	57	4.28	980
1.28	56	5.28	1200
1.53	57	6.28	1400
2.53	60	7.28	1800
3.53	69	8.28	2300
4.53	79	9.28	3100
5.32	85		
7.53	81		
8.53	91		

**Figure 11b: Temperature Effect on Permeate TOC vs Time Using Waste Process Solution**

ELAPSED TIME (hrs)	TOC (mg/l)	TEMP (°C)
0.00	52	24.0
0.18	53	24.0
0.52	56	25.5
0.77	56	27.0
1.02	57	29.5
1.28	56	31.5
1.53	57	34.5
2.53	60	40.0
3.53	69	46.0
4.53	79	50.0
5.32	85	53.0
7.53	81	50.5
8.53	91	51.0

**Figure 12: Phosphate in Process Tank and Permeate vs Time Using Waste Process Solution**

Permeate		Process Tank	
ELAPSED TIME (hrs)	PHOSPHATE (mg/l)	ELAPSED TIME (hrs)	PHOSPHATE (mg/l)
0.77	4828	0.63	4986
2.53	4749	2.28	4986
3.53	4947	3.28	5144
4.53	4947	4.28	5144
5.32	5026	5.28	5224
7.53	5184	7.28	5382
8.53	5184	8.28	5382

**Figure 14a: Oil and Surfactant TOC in Bath vs Time**

OPERATING TIME (hrs)	Total	TOC (mg/l):	
		Surfactant	Oil
0.0	422	155	267
66.5	232	123	109
132	340	200	140
180	340	198	142

**Figure 14b: Oil and Surfactant TOC in Rinse vs Time**

OPERATING TIME (hrs)	Total	TOC (mg/l):	
		Surfactant	Oil
0.0	21	8	13
66.5	8	4	4
132	11	7	4
180	11	6	5

**Figure 14c: Oil and Surfactant TOC in Process Tank vs Time**

OPERATING TIME (hrs)	Total	TOC (mg/l):	
		Surfactant	Oil
0.5	710	261	449
18.5	4700	2301	2399
42.5	6300	3351	2949
66.5	7100	3752	3348
85.0	5900	3325	2575
108.0	8000	4482	3518
132.0	12000	7078	4922
158.0	1600	9387	6613
180.0	19000	11088	7912

**Figure 14d: Oil and Surfactant TOC in Permeate vs Time**

OPERATING TIME (hrs)	Total	TOC (mg/l):	
		Surfactant	Oil
0.5	67	25	42
18.5	42	21	21
42.5	39	21	18
66.5	42	22	20
108.0	75	42	33
132.0	150	88	62
158	170	100	70
180	160	93	67

**Figure 15: Phosphate Levels in Bath, Inflow, and Permeate vs Time**

OPERATING TIME (hrs)	PHOSPHATE (mg/l):		
	Bath	Inflow	Permeate
0.0	3617	3958	.
18.5		3245	3166
42.5		3007	2849
66.5	3562	3799	3561
85.0		3483	3324
108.0		4353	4749
132.0	6142	6094	6332
158.0		6094	6253
180.0	6008	6174	6055

**Figure 16: Permeate Flux Rate vs Time**

ELAPSED TIME (hrs)	FLUX (gal/hr)
18.5	39.1
42.5	32.1
66.5	31.0
108.0	31.0
132.0	29.0
158.0	26.1
180.0	27.3
252.0	27.3
276.0	27.3
300.0	27.3
324.0	27.3
348.0	26.5
516.0	25.0



# **Data Correlation for Phosphate Analysis by Titration and IC**

<b>SAMPLE</b>	<b>TYPE</b>	<b>Volume Titrant (mL)</b>	<b>PO<sup>4</sup> (mg/l) by IC</b>	<b>RATIO</b>
3	Bath	4.4	3937	894.8
6	Permeate	5.2	4091	786.7
7	Inflow	5.0	4028	805.6
17	Bath	4.5	3455	767.8
21	Permeate	4.6	3642	791.7
22	Inflow	4.8	3736	778.3
30	Bath	7.9	6333	801.6
34	Permeate	8.0	6161	770.1
33	Inflow	7.7	5129	666.1
42	Inflow	7.8	5588	716.4
43	Permeate	7.6	6248	822.1
46	Bath	7.6	6357	836.4
53	Bath	7.8	5760	738.5
54	Inflow	7.8	5428	695.9
55	Permeate	7.6	6145	808.6
67	Bath	9.7	8011	825.9
70	Permeate	9.4	7790	828.7
71	Inflow	9.3	6909	742.9
<b>AVERAGE</b>				<b>782.1</b>

(Volume of Titrant, ml) x (Ratio = 782.1, mg/l/ml) = PO<sub>4</sub> mg/l

