Molten Salt Oxidation Reuse and Phosphate Reduction Projects

MnTAP Intern Project Report

Associated Finishing, Inc.

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Summer 2002

MnTAP Provided a student intern and staff assistance free of charge to identify useful changes that reduce waste, emissions, and/or hazards, to increase efficiency at the company. However, the company decided whether to implement suggestions based, among other things, on its own evaluation of the project, including its own evaluation of the work performed by the intern under the company's supervision. THE COMPANY ACCEPTED THE SERVICES "AS IS" AND WITHOUT WARRANTY, INCLUDING EXPRESSLY WITHOUT WARRANT OF MERCHANTABILITY OR WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE.

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Abstract:

Molten salt oxidation is an excellent method to remove paint through an oxidation reaction in an 800-1000°F salt bath. Unfortunately for the paint-stripping industry, this method also produces large amounts of solid waste. Associated Finishing, Inc. (AFI) in Mankato, Minnesota developed the innovative idea to reuse the salt waste as a supplemental source of potassium hydroxide for their caustic chemical bath. This idea could reduce the waste stream from the molten salt oxidation process (MSO) and reduce the amount of raw KOH needed. The secondary project was to reduce the phosphates in the wastewater.

It was determined that the molten salt waste was somewhat water-soluble with about 35% KOH in solution. Stripping experiments performed showed that using a solution of the molten salt waste had no adverse effect on stripping time or quality when compared to the current caustic bath. Although chemically possible, it is not currently economically feasible to use the salt waste as a source of potassium hydroxide for the caustic bath. The salt is being reclassified as nonhazardous and, pending approval, can be sent to the industrial landfill in Buffalo, Minnesota. Reclassifying the molten salt waste as nonhazardous changed AFI's standing of "Large Quantity Generator", reduced their taxes, and lowered their disposal and transportation costs.

Six main sources of phosphorus were identified within the AFI plant. Phosphates are used in metal preparation to improve paint adhesion, minimize corrosion, and protect the metal surface. The Mankato Wastewater Treatment Plant (MWTP) has set the current allowable level for phosphates in wastewater without an additional fee at 1 kg/day. The Mankato Treatment Plant tested Associated Finishing at 1367 total kilograms of phosphorus in 2001. It is suggested that Associated Finishing arrange more frequent testing of the phosphorus levels as well as review the results themselves.

Chemical precipitation and evaporation systems to remove the phosphorus were researched, but they are more expensive than the fee from the MWTP. A weak solution of sulfuric acid is recommended to replace the phosphoric acid in the descale tank and for pH adjustment around the plant. Further reduction can be achieved by replacing the missing stop valve on the chemical line to the spray washer. It is recommended to replace the chemical in the inline washers with a lower phosphorus alternative. These actions will reduce the phosphorus in the wastewater by an estimated 500 kg/year and reduce the final surcharge from the treatment plant by an estimated 50-80%. The total phosphorus reduction will depend on the concentration at which the new washer chemical is used.

Waste Reduction Option	Waste Reduced	Raw Material saved	Cost Saving	Status
Reuse MSO waste in caustic bath	11,000 pounds	800 gallons	($3,000)	Not recommended
Use bulk chemical additive in place of name brand product	N/A	N/A	$5,300	Implemented
Reclassify salt waste as nonhazardous	11,000	N/A	$600	In progress
Dispose of salt waste as nonhazarous	N/A	N/A	$4,000	In progress
Replace phosphoric acid with sulfuric acid in descale tank	233 kilograms of phosphorus	N/A	$1,100	In progress
Replace stop valve on spray washer	16 kilograms of phosphorus	220 gallons	$1,300	Implemented
Lower phosphorus cleaner for in-line washers	186 kilograms of phosphorus	N/A	($5,000)	Suggested
		higher concentration required, but lower phosphorus		
Regular phosphorus testing	500 kilograms of phosphorus	N/A	$4,000	Suggested

Background

Company description:

Associated Finishing Inc. (AFI) is an employee-owned paint and metal prep job shop located in Mankato, MN. The paint stripping techniques available include a caustic or acidic bath, burn-off oven, or molten salt oxidation (MSO). Stripped production parts are then cleaned and phosphatized. Powder or liquid paint coatings are applied to the clean parts. AFI also does glass etching, pad printing, and silk-screening. They provide a full spectrum of finishing services. AFI is concerned about the environmental impact of their business and is always interested in economically attractive reduction options; that is why they contacted MnTAP for assistance. Already, they have repiped many of their operations to reuse and recycle water and they use an in-house reverse osmosis system. AFI currently employs approximately 65 people in the Mankato area. Their SIC codes are: 3479, 3471, and 2759.

Associated Finishing's Permit Numbers:
M.P.C.A Air Emissions Permit #01300067
M.P.C.A. Hazardous Waste License MND 006219919
S.A.R.A. Section 312 Tier Two E.R.C. I.D. 07-100-0076
City of Mankato Wastewater Discharge Permit #4001

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Molten Salt Oxidation Project:

One of the methods used by AFI to strip off paint is the molten salt oxidation process. Associated Finishing installed a molten salt oxidation machine from the Kolene Corporation in 1989. Combustible organic waste is oxidized in a bath of potassium hydroxide/sodium nitrate salt heated to 800-1000°F. At this temperature, the salt becomes liquid. Organic components react with oxygen to produce water, carbon dioxide, and nitrogen. The inorganic components retained in the salt build up over time and must be periodically removed. This residue consists mainly of carbonates, nitrates, and hydroxides. In 2001, there were 11,200 pounds or 16 barrels of salt waste generated with a disposal cost of $4,800. Associated Finishing has been under the impression since 1989 that the salt waste was hazardous based on incorrect information from a landfill and so they followed hazardous waste disposal procedures. Associated Finishing did not want to just dump the waste in a landfill so Vice President of Engineering Joe Appelhof found the opportunity to recycle the salt waste at a disposal facility in Wayne, Michigan as a neutralizer. This action saves them about 50% on their disposal costs- $0.43/lb as opposed to \$0.86/lb for other methods of hazardous waste disposal- while reusing the material in an environmentally friendly way.

Associated Finishing wanted to find a way to further reduce their costs for disposing of the molten salt waste. Quality controller Alan Baer started doing some benchscale tests in November of 2001 and discovered that the salt residue was water-soluble and that the solution was very basic. Company president William Klammer theorized that the salt waste contained a large concentration of usable potassium hydroxide in solution. He proposed the idea to reuse a solution of salt waste as a source of KOH for the caustic bath. Being able to extract some of the potassium hydroxide would reduce the amount of raw material needed for the caustic tank. His proposal had the possible benefits of eliminating a hazardous waste stream, reducing the caustic bath raw materials costs, and instigating the first "green" project using the Kolene process. Associated Finishing personnel had become familiar with MnTAP and their intern program through various coatings expos and professional meetings. Since the initial results with the salt waste solution were favorable, a summer intern was requested to verify the initial results, do scale-up of the process, and evaluate other possible options.

Phosphate Reduction Project:
Reduction of the phosphates in the wastewater was a secondary project. Phosphatizing is necessary for increased paint adhesion and corrosion protection for the metal. Unfortunately, phosphates in wastewater are becoming a big problem. They increase the growth of algae in lakes and rivers and rob water of oxygen. They can also make water unfit for drinking.

The phosphorus limit set by the NPDES (National Pollutant Discharge Elimination System) for the Mankato Wastewater Treatment Plant (MWTP) is 20,000 kg/year. Each company in the Mankato area is allowed 1 kg/day of phosphorus in their effluent without any additional treatment fees.

The MWTP treats all the wastewater with ferric chloride as a primary step to precipitate out the phosphorus. In 2001, they treated over 144,000 pounds of phosphorus with more than 100,000 gallons of ferric chloride solution. At least 70% of the influent phosphorus is removed in the treatment plant before the effluent is discharged into the Minnesota River.

In 2001, the treatment plant determined that Associated Finishing's wastewater contained approximately 5.3 kg/day or 1367 total kilograms for the year. After the 260 kilogram credit for each working day, the MWTP charged Associated Finishing \$4.56 per kilogram treated for a total cost of \$5,045, which was later reduced to \$4,362 after some negotiation. This figure was significantly higher than an earlier estimate of the treatment surcharge. The average level of phosphorus in 2001 was determined by one 48-hour composite sample. The final amount of phosphorus was an estimate based on the product of the average phosphorus level and yearly water usage.

Associated Finishing also requested that the MnTAP intern research possible phosphorus reduction and treatment options to help decrease the phosphorus treatment surcharge from the Mankato Wastewater Treatment Plant. The MWTP volunteered their assistance and lab space to the project at no cost.

Project Incentives:

The primary reason that options for the molten salt and phosphorus waste streams were considered is the cost. Together, disposal and treatment of these two streams is a $10,000 annual expense for Associated Finishing. Any business would like to see if they could put some of that back into their pockets. Waste disposal costs come right off of their bottom line. A close secondary concern is the environmental impact of their business. The nature of the paint and metal treatment business means that AFI will produce industrial and hazardous waste and they strive to manage these wastes properly. Associated Finishing received a Hazardous Waste Compliance Recognition award from the MPCA in 1994 and an Environmental Leadership Award from Minnegasco in 1997. The job shop business is highly competitive and those who stay stagnant will find their business in trouble very quickly. Environmental laws will continue to become stricter and more widely enforced. Preemptive action on the part of Associated Finishing will help them to prepare for regulations in the future which will help them to be a competitive business in the paint and metal prep industry.

Plant Process Descriptions

Stripping:

When customers bring in parts to have the paint stripped off, metal prep and stripping supervisor Cal Schultz decides which of the several methods of paint stripping- molten salt, caustic bath, or burn-off oven- would be best suited to each particular part.

Figure 1: Kolene Molten Salt Oxidation Unit

The MSO machine from Kolene is shown in the picture above. A steel basket of parts to be stripped is lowered into a bath of molten salt at 800-1000°F. An interesting property of molten salt is that it conducts electricity. The salt oxidizes the organic components and forms byproducts such as carbon dioxide, metal hydroxides, and water. Gases that are released are captured in a vacuum and put through a water scrubber.

After the paint has been removed by the salt- usually in about 5 minutes- the basket is dipped into two subsequent tanks of cooling rinse water to remove any salt residue. Parts painted with epoxy paint and the company's paint hooks are usually stripped in this machine. Over time, inorganic byproducts of the oxidation reaction- resins, binders, and metals from the paints- build up in the salt tank. These are removed periodically by pulling a pan up from the bottom of the tank and dumping it into a 55-gallon waste barrel. Fresh salt is added after dredging to replace the volume of sludge removed- usually about 1-3 bags of salt. As the molten salt waste cools, it forms exceptionally hard chunks of material. This material is inorganic in nature and somewhat water-soluble.

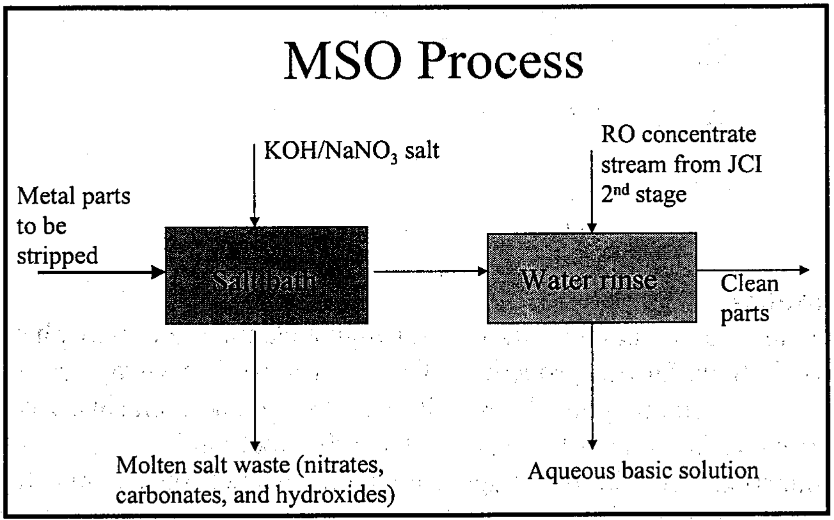

Figure 2: Schematic of MSO Process

The Kolene machine is very expensive to operate and there are significant utility costs to keep the salt molten. It is used about 90% of the time to strip the company's own paint hooks. Most customers prefer a more economic method of paint stripping for production parts since the MSO is charged out at about $75 per hour.

Another method used to strip off paint is the caustic chemical bath. The caustic stripping tank is a 1200-gallon solution of 40% potassium hydroxide, 0.5% stripping additive and 59.5% water run at approximately 200°F. Parts painted with polyester and polyurethane are usually stripped in this bath. The KOH is an activator and the Stripping additive is the primary stripping agent. This bath is rarely completely changed out, but is only topped off to compensate for evaporative losses. A titration schedule analyzes the KOH concentration and determines how much potassium hydroxide should be added. The operators add 5 gallons of the additive almost every day.

Parts to be stripped are dipped in the tank and left for several hours. The chemicals weaken and soften the paint itself as well as dissolving the adhesive bond between the metal part and the paint. Then the parts are sprayed off with a high-pressure spray to remove the paint residue. This high-pressure spray can be just water or a water/phosphatizing chemical blend. There is also an immersion tank containing a phosphoric chemical that parts can be dipped in after they are stripped to protect the metal and prevent rusting.

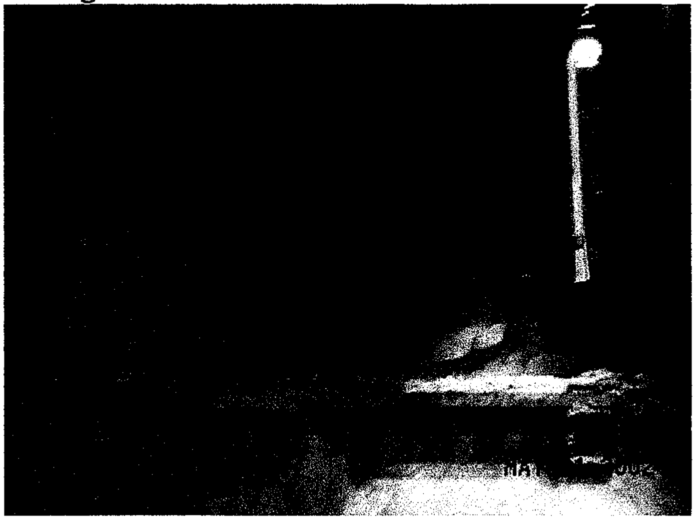

Figure 3: Side view of caustic tank

Metal Preparation:

Before metal parts can be painted, they go through a cleaning and phosphatizing process. AFI uses two methods for this procedure. The belt washer is a 3-stage conveyor belt in which parts are cleaned and phosphatized in the 1st stage and then rinsed with reverse osmosis (RO) water in the next two stages. The other method is a larger 5-stage in-line cleaner and phosphatizer. The first stage is an acidic cleaner, the second stage is a rinse, the third stage is a phosphatizer, and the last two stages are rinses with RO water. Phosphatizing is a chemical reaction in which the steel is etched and iron or zinc is deposited on the surface. This helps paint adhesion and protects the metal should the paint chip or scratch. These washers are one of the main sources of phosphates in AFI's wastewater stream. Batch chromating, aluminum brightening, rust removal, and descaling are other areas of metal prep.

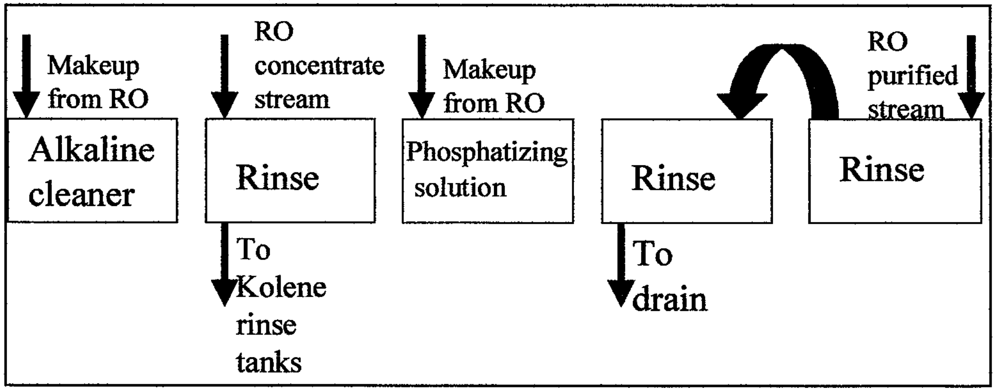

Figure 4: Schematic of 5-stage JCI washer

Molten Salt Oxidation Waste Project

Amount of waste produced:

The job shop business is highly irregular so waste production is not a steady-state operation. When the workload is heavy and many parts are stripped in the MSO bath, the tank might get dredged every couple of days. When there isn't much stripping to do, there might be weeks or even months between desludging. Additionally, the Kolene machine is expensive to operate so many customers prefer cheaper stripping options. In 2001, there were 11,200 pounds of molten salt waste discarded. Typically this byproduct is not reused; however, Associated Finishing has been sending the salt waste to Michigan Disposal in Wayne, Michigan through Onyx Environmental Services where it is used to neutralize acidic waste streams. Cooperating with Onyx and Michigan Disposal was a good first step on Associated Finishing's part toward a more environmentally friendly disposal. Typically the cost in the industry to dispose of the salt waste as hazardous is $0.86/lb plus transportation costs. The cost to AFI in 2001 was $4,800 or about $0.43/lb.

Current management practices:

Right now, Bill Muldoon or one of the other operators pulls a submerged pan out of the salt tank every few days to every few weeks, depending on usage. Waste from the pan is dumped into a hazardous waste barrel stored in a compartment between the molten salt tank and the first water rinse. This is a very hot, dangerous procedure. The waste barrel is stored in a compartment between the salt tank and first water rinse. When the barrel is full, it is sealed and stored until ready for transport to the disposal site in Wayne, Michigan. The molten salt waste has historically been treated as a hazardous waste by Associated Finishing because they received incorrect information years ago from a landfill. Apparently they were told that since it had a high pH in solution, the salt waste was considered to be a D002 waste. A D002 is a waste that carries the corrosivity characteristic. A full definition of this characteristic can be found in Appendix VII.

Experimentation:

I began by repeating the small-scale experiments done by Alan Baer and researching the chemistry to understand the interactions between the potassium hydroxide and the stripping additive. I found that heat above 160°F and agitation is absolutely necessary to dissolve the salt waste. Once the salt waste is in solution, it has a pH range of 12-14, a 30-45% potassium hydroxide content, and about 25% undissolved solids. The potassium hydroxide content was found by titration with 1.0N hydrochloric acid. Data from an assay done by Kolene in 1993 revealed that the material was 20 wt% alkali hydroxides, 50 wt% alkali carbonates, 20 wt% alkali nitrates, and the balance miscellaneous paint components and trace amounts of various metals. Measurable levels of heavy metals were not detected.

The Toxicity Characteristic Leaching Procedure or TCLP test exposes material to a leachate similar to what would be encountered in a landfill- usually acetic acid or a mixture of nitric, acetic, and sulfuric acids. It determines the mobility of metals, volatile organics, pesticides, and herbicides; the levels of 39 components are tested. If certain analytes are detected in great enough quantities, the material being tested may be deemed hazardous. There were several TCLP tests done on the molten salt waste from 1990-

1992. All of those tests indicated metal leaching far below the prescribed limits and there were no VOCs (volatile organic compounds) detected. Since it had been 10 years since the last TCLP test, Pace Analytical Labs in Minneapolis was contracted to perform a TCLP test for metals on a current sample. The test for VOCs was not performed since by generator knowledge of the process, there would be no VOCs present at such high temperatures. Pace found that only four of the eight metals tested were present in detectable amounts: barium, mercury, arsenic, and chromium. The full results of this TCLP test can be found in Appendix IIIA.

The inorganic components of the molten salt waste- the hydroxides, carbonates, and nitrates-are all water-soluble to some degree. The nitrates and hydroxides are more soluble than the carbonates. However, a large percentage of the carbonates are sodium and potassium carbonates, which are Group I carbonates. Group I carbonates are soluble in water. This means that the undissolved solids are metals, resins, and binders from the paints, for the most part.

Research on the chemical interactions indicated that the potassium hydroxide is the activator and the stripping additive is the primary stripping agent. Historically, methylene chloride has been used as the primary stripping agent but it has been nearly completely replaced in industry due to health and environmental concerns. A few less hazardous alternatives to methylene chloride have been found such as benzyl alcohol and dimethyl sulfoxide, but they do not work as well as their more hazardous counterpart. The stripping additive used by Associated Finishing is a very expensive element; the maintenance cost is around $100/day.

I ran scanning experiments at the beaker size examining the bath composition and a few different stripping additives. I determined that the percentage of stripping additive had the most effect on stripping time and quality. The percentage of potassium hydroxide did not have much of an effect until the level dropped below 25%.

Once I was fairly comfortable with the performance of the beaker-sized runs I dissolved a 55-gallon barrel of the molten salt waste using a barrel belt heater and a Lightning mixer. This took approximately two days to dissolve. Then I made up a 40-gallon bath at 35% KOH, 0.5% Stripping additive, and 64.5% water. This was given a full day to heat up. I put some pieces in when the temperature was around 140-150°F, but there was very little to no stripping. Once the barrel came up to around 170°F, I began stripping several pieces. I did scrap pieces, some production parts that had been brought in to be stripped, and various other parts around the plant. I found that the bath was performing as well as the current caustic tank. There were large evaporative losses and keeping the temperature up was an issue. Stripping times ranged from 30 minutes to 6 hours depending on the type of paint and how many layers were on the part. The stripping supervisor, Cal Schultz, said that the time and quality were comparable to the 1200-gallon caustic tank.

I reviewed the MSDS sheet for the stripping additive and discovered that it had one main ingredient listed at 90-100%. I ordered a quantity of this ingredient in bulk and evaluated its performance in beaker and barrel-sized stripping runs. I found that it performed as well as the current additive at a 40% cost reduction. The other stripping additives that I tested were benzyl alcohol, *n*-methyl pyrrole (NMP), or dimethyl sulfoxide-based (DMSO). They did not strip as completely or as quickly as the current stripping additive. Benzyl alcohol performed the best of the additives tested. All of the additive experiments were run by heating a beaker of solution up to 180°F, putting in a steel part painted with epoxy or polyester paint, and checking the stripping progress every 30 to 60 minutes. Another chemical that might have potential as a stripping additive is phenol. I did not have the opportunity to test this chemical so some benchscale experiments should be done to test its effectiveness.

I stripped many parts over the course of several weeks and the bath never died or failed to strip as long as the additive was replenished periodically, about every 3-4 days. It became apparent that little or no stripping would occur unless the bath was agitated and heated to about 170°F. The heat appeared to have more significance than the agitation on stripping performance. I continued to add water periodically, as there was a good deal of evaporation and occasionally tested the KOH level by titration. The removed paint, dirt, and oils began to build up in the barrel after about 4 weeks, but the silt did not seem to negatively affect the stripping time or quality.

Hazardous Waste Rules:
One very important point about the salt waste is the waste classification. It has been historically treated as a hazardous waste by Associated Finishing, apparently because of the corrosive nature of the material in an aqueous solution. It is not wrong by any means to treat a waste with more caution that it legally requires. However, in this situation the special handling may have caused some undue expense. It is the generator's responsibility to determine whether a waste is hazardous or not by a combination of generator knowledge of the process, reviewing relevant MSDS sheets, and comparing the materials to listed wastes on the F, K, P, and U lists of the Minnesota Rules. The Minnesota Rules section 7045.0131 gives the characteristics of a hazardous waste. A waste is hazardous if it is a listed waste in the Minnesota rules section 7045.0141, or if it exhibits one of these characteristics: ignitability, corrosivity, reactivity, toxicity, lethality, or is an oxidizer.

The components of the salt waste are not listed, it does not exhibit any of the hazardous characteristics and it is a solid. Historically the D002 corrosive label has been applied to the molten salt waste. Subpart 4 of the Minnesota Rule 7045.131 states that for the corrosivity label to apply, the waste must be liquid or aqueous. The Federal RCRA law regarding corrosive waste is worded the same way. The salt is neither liquid or aqueous so it is not a hazardous waste. The federal RCRA guide states that "physically solid, nonaqueous wastes are not evaluated for corrosivity". However, this is a material that should be handled with care and disposed of properly.

Julia Rantala of the MPCA in St. Paul stated in an email in April to MnTAP senior engineer Paul Pagel that she does not believe the salt waste to carry the D002 characteristic. Copies of the Federal and Minnesota Rules can be found in Appendix VII and Ms. Rantala's email is enclosed in Appendix VIII. The results of the TCLP test performed by Pace Labs were sent to Ms. Rantala along with a letter contending that the test was performed on a representative sample. A copy of the test results can be found in Appendix IIIA and the letter sent to Ms. Rantala is in Appendix VIII.

Project Challenges:

One of the potential snags in this procedure is the time and energy required to dissolve the salt waste. The smaller the pieces, the more quickly and easily they will dissolve. The pieces might be reduced in size if they were forced through a steel screen as the salt tank was being dredged or put through a grinder. Applying water very quickly after dredging might also reduce the dissolving time. It might be possible to dissolve the salt by applying water and letting the solution sit for several weeks. There would have to be a constant source of heat for any method of dissolution. Before use in the caustic bath, the solids must be filtered out from the salt solution. During my experiments, sediment from the salt solution collected around the metal part and inhibited the stripping. The cleaner the bath is the better and longer it will strip and raw materials will have to be added less frequently.

Another challenge is the potassium hydroxide content of the salt waste. In the course of my experiments, I found a range of 30-45% KOH content. If the caustic bath is to be run at 35% KOH, a batch of salt waste solution at 30% will not be adequate to supply the necessary concentration of potassium hydroxide. Supplemental KOH will have to be added. When the barrels of 45% KOH are purchased, there is very little variability in the amount of KOH present, so the current titration schedule is applicable. Using the salt waste solution in the caustic would also require a completely new and variable titration schedule.

Additionally, storage for the salt solution would be required since it takes a few days to dissolve the salt. Floor space at Associated Finishing is hard to come by. A lesser concern is that some carbonates can form scale at high temperatures in hard water. The salt solution does contain carbonates that might scale the caustic tank.

Filter Bags:

In the course of my research I came across the "Waste Water Sludge Dewatering" bags from a company called Aquamark in Ohio and distributed by Water Concepts in Rochester, Minnesota. These bags were originally designed to help drain lagoons, but they have many applications. As was stated earlier, the cleaner a chemical bath is, the longer that it will last. We got a sample of these polypropylene bags and I put pieces in the descaling tank, the immersion phosphate tank, and the caustic tank. The material did not dissolve in acidic, basic, or hot conditions. Chuck Klammer suggested using the bags to filter the tanks.

A sample 200-gallon bag was ordered and a trial run was done on the descaling tank. The bag had handles that were suspended above the tank with a forklift. A pump pushed the liquid from the tank into the bag and then filtrate just passed through the bag back into the tank. The mesh in the bag was too large to catch most of the sludge. A few particles were retained in the bag, but most of it just went right back into the tank. If a bag were available with smaller mesh, it would be worthwhile to make another attempt.

Reclassification:
As was mentioned before, by the state and federal law, the salt waste is not hazardous. Even though the virgin salt is a hazardous material since it is an oxidizer, once the reaction has taken place between the salt and the paint, the salt waste is not an oxidizer. Therefore, contact with Julianne Rantala from the MPCA was initiated by MnTAP senior engineer Paul Pagel. I talked to her on the telephone a few times and a telephone conference was arranged with Associated Finishing's Alan Baer, Joe Appelhof, Ms. Rantala, and myself on July 30, 2002. In the course of that conversation, Ms. Rantala stated that she did not think that the salt waste was hazardous, but requested a copy of the most current TCLP results for review and a letter stating our position. I drafted a letter asserting that the TCLP was performed on a representative sample of the salt waste. The letter also requested permission to remove the salt waste stream from the hazardous waste combined bill and to reclassify Associated Finishing as a Small Quantity Generator.

A copy of this letter can be found in Appendix VIII. A Large Quantity Generator is defined as an industry that produces more than 2200 pounds of hazardous waste per month. Once the salt waste stream is removed from the hazardous waste manifest, Associated Finishing will be well within the bounds of the Small Quantity Generator limits.

Possible Options:
I found two main options for the molten salt waste stream. First of all, it is chemically possible to use an aqueous solution of the salt waste as a source of KOH for the caustic bath. Secondly, the waste can be disposed of either in a landfill or by recycling at the disposal facility in Wayne, Michigan.

The following tables show the 2001 raw materials, disposal, and hazardous waste costs for the caustic bath and molten salt processes. The cost for disposal includes transportation costs and the $25/drum cost.

Table 1: Raw materials costs for 2001

Chemical	Cost/Unit	Yearly Use (Approx)	Yearly Cost
Salt	$.68/lb	20,000 lb	$13,600.00
Caustic Potash	$0.3295/lb	15 drums x 660lb/drum	$3,270.00
Stripper Additive	$21/gal	12 drums x 55gal/drum	$13,860.00

Table 2: Annual disposal cost for the molten salt waste and MPCA hazardous waste fees for 2001

Fee Description	Amount
Salt residue waste stream	$292.90
LQG flat tax	$500.00

Waste Stream	Amount	Disposal Cost
molten salt waste	16 barrels: 11,200 lb	$5,200

Option 1:
Based on my experimentation and research, dissolving the salt waste and using an aqueous solution as a source of KOH works chemically. In fact, the additional carbonate, nitrate, and hydroxide salts contribute to the basicity of the solution and probably promote the stripping capabilities of the bath. However, the cost to make up a useable bath of solution is not economically feasible at this time. First of all, the salt waste must be dissolved. The hardness of the waste makes dissolution difficult. Secondly, the pieces of salt cannot easily be broken up to facilitate the dissolving process. Also, high heat and agitation are absolutely required to dissolve the salt waste. A tank with heating and stirring capabilities would be required as well as a possible method of size reduction such as a grinder or hammer mill.

Alan Baer estimated that to find and place a tank, mixer, and pumps for this process would be a one-time expense of $1,500. Associated Finishing has a supply of tanks and pumps in storage so no new equipment would be required. He also estimated the heating cost for each 525-gallon or 3 drum bath to be $1,500 and the labor cost to make up one useable bath to be $280 for 6-8 hours of work. The heating cost is based on their current cost to heat other comparable tanks in the plant. By these estimates, each 525-gallon bath would cost $1,780. In 2001, 15 drums of potassium hydroxide solution were used in the caustic tank. This means that about 5 batches of the salt waste solution would be required to replace the potassium hydroxide and possibly more if the caustic tank were emptied. The solution would also have to be filtered before it could be used, so that would add more labor expense. I estimated 3 more hours of labor per 525-gallon batch at $105/batch for filtration.

Table 3: Estimated Costs for Producing Salt Solution

Process	Approximate Time	Estimated Cost
Dissolving 15 barrels of salt	3 days/3 barrels	$8,900 (heat and agitation)
Filtering solution	3 hours/3 barrels	$500 (labor)
Find and place holding tank & pump	40 hours	$1,500 (labor)
Disposal of filtrate	N/A	$500

The cost to make the salt solution is around $9,900 in addition to the $1,500 installation cost for the tank, mixer, and pump. The solution is approximately 25% insoluble so there would still be a few drums of filtrate that would have to be disposed of in some manner. The total cost to use the salt solution as a replacement for the potassium hydroxide would be more than $10,000. If an efficient, inexpensive method of dissolving and filtering the salt could be found, at some time it might be economical to use it as a source of hydroxide for the caustic bath, but not at this point.

Option 2:
Another option is to continue operating the caustic bath as usual and substitute the bulk chemical for current stripping additive. Now that the salt waste does not have to be handled as hazardous, there are more disposal options. It would be possible to continue sending the salt waste to Michigan for recycling, transported as nonhazardous industrial waste. The Onyx representative is still putting together a cost scenario for that option. A

Superior-owned landfill in Buffalo, Minnesota could take the salt waste for $40/ton plus a $55 application fee. This means that the yearly disposal cost (based on the amount of salt waste discarded in 2001) would only be around $300 including the transportation costs of $35-40 for each drop-off. The DOT drums that the salt waste is transported in cost $25 each, so the total yearly disposal cost would be $700. Associated Finishing is licensed as a hazardous materials transporter so they would take the salt waste to Buffalo themselves. Approval for sending the salt waste to Buffalo is still pending.

Unfortunately, the salt waste cannot be sent to the same landfill in Rosemount as the paint filters. This landfill is in Dakota County and is subject to very strict landfill requirements. One of these requirements is a pH test even on solids with a limit of 12.5. Since the salt waste has a pH of 13 to 14 in solution, it cannot be sent to the Rosemount landfill.

Recommendations:
First of all, I recommend that Associated Finishing handle the salt waste as nonhazardous industrial waste from this point on. They can be reclassified as a Small Quantity Generator, which would take effect in 2003. This classification will be applicable unless process changes are made that bring them up to a waste generation rate of more than 2200 pounds per month.

The most economically sound suggestion is to continue running the caustic chemical bath as normal, with the potassium hydroxide solution. I contend that the concentration of the KOH can be dropped to around 35%, which might save a little bit on the raw materials cost. When I occasionally titrated the caustic tank, it was consistently below 40%, so this change might not have to be actively implemented.

Additionally, I would suggest buying just the main component of the current stripping additive in bulk at a cost of approximately $13/gallon as opposed to $21/gallon. Based on experimentation, it will not affect the stripping time or quality and will save about 40% annually. Because of the evaporation rate and solubility characteristics of the additive, I would suggest trying 4 gallons per day instead of 5 and possibly try to skip a day when the tank is lightly loaded. This could possibly reduce the raw materials usage. Also, I would recommend not adding chemical on days that nothing will be stripped in the tank or over the weekend. That would just be a waste of chemical. The current stripping additive has a moderate solubility in water; it is possible that only a small percentage of the chemical is actually being consumed. It has a boiling point of 204°F, a flash point of 214°F, and a solubility of 40 g/L at 68°F.

For disposal, I recommend that Associated Finishing utilize the landfill in Buffalo, Minnesota- their acceptance of the salt waste is still pending approval. I advocate recycling and reduction wherever and whenever possible but shipping the salt waste out to Michigan uses fossil fuel and costs 10 times more than sending it to the landfill in Buffalo will. The Onyx representative is still putting together a cost scenario if they would take it to Michigan as nonhazardous but I strongly suspect it will not be as cost-effective as the Buffalo landfill. It does not make good business sense to spend much more money to recycle a waste 2 states away when landfilling instate is an option. A site visit and confirmation of the proper permits is still necessary before a final decision to send the salt waste to Buffalo is made can be made. Vice President of Engineering Joe Appelhof and I are planning a site visit later on this month.

Another suggestion is to list the salt waste with the MnTAP Materials Exchange Program. It is possible that another company might have acidic waste streams and be able to use the salt waste in solution to neutralize these streams.

I would also suggest periodically filtering out all the big tanks. The cleaner the bath is, the longer the chemicals will be active. This could reduce the raw materials usage and thus slightly reduce operating costs. The filter bags from Aquamark, distributed by Water Concepts are one option if they are available in a slightly smaller mesh size. The forklift and pump method seemed to work well enough for a rough filtration, but Associated Finishing could install a more sophisticated system at their discretion.

Benefits of these recommendations:
First of all, reclassifying the waste as non-hazardous will remove Associated Finishing, Inc. from the "Large Quantity Generator" status. This means that the salt waste stream will no longer be subject to a hazardous waste tax and there will be no $500 flat tax for large generator size. Also, there will be fewer inspections, which will save a good deal of time and paperwork for the Associated Finishing staff. They will also be able to store the molten salt waste for a longer period of time and will no longer have to weekly inspect the drums as required by hazardous waste laws. Additionally, the hazardous satellite accumulation signs on the Kolene machine are no longer necessary.

As a Small Quantity Generator (SQG), Associated Finishing is no longer required to prepare a Pollution Prevention Plan, file annual progress reports, and pay a $500 annual fee to the MPCA. They also no longer need to update and distribute a contingency plan to the MPCA and their employees; only an emergency contingency plan is required. Associated Finishing is still required to be registered with the USDOT and MnDOT and pay fees as a hazardous materials transporter.

Using the bulk chemical instead of the brand name additive will give Associated Finishing more freedom to choose suppliers. The bulk chemical is easier find than the brand name additive. Also, the bulk chemical will save about 40% annually in raw materials costs.

There are several more disposal avenues for a nonhazardous industrial waste than for a hazardous waste. Now Associated Finishing has more flexibility to decide how to dispose of the molten salt waste. It might be advantageous to have a TCLP test performed on the salt waste every 4-5 years. In the event that Associated Finishing wanted to change disposal companies, they would have a fairly recent analytic test to submit for approval.

Filtering out the baths could slightly reduce the raw materials costs since the baths will work longer before being changed out. The solids can be disposed of in the same manner that they are when the tanks are dropped, either sewered with the tank or sent to landfill.

Economic analysis:
Over the course of this project, Associated Finishing approved a major test- the TCLP test done by Pace Analytical Labs in Minneapolis, Minnesota. This test was very helpful in analyzing the best disposal options. Most, if not all, landfills require analytical test results before they will accept a waste stream into their landfill. It is valuable to have these tests done by a reputable third party so that the data is unbiased. The cost for the TCLP test for metals including the extractions was $150 plus a $100 courier fee. Pace Analytical billed the test at a reduced rate since the project was indirectly connected to the University of Minnesota.

The tables below give the 2001 raw materials and disposal costs and the projected costs for the two possible options. These costs are based on Associated Finishing's purchase records from 2001.

Table 4: 2001 Molten Salt and Caustic Bath Raw Materials and Disposal Costs

Raw Materials	**Yearly Cost**
Kolene salt	$13,600
Rostrip	$13,860
Caustic Potash	$3,270
Disposal of salt as hazardous	$4,800
Cost of Processes	**$35,530**

Table 5: Cost for using Molten Salt Waste in the Caustic Bath

Raw Materials	**Yearly Cost**
Kolene Salt	$13,600
Bulk Chemical Stripping Additive	$8,500
Caustic Bath Solution	$11,000
Disposal of salt filtrate	$500
Cost of Processes	**$33,600**

Table 6: Disposal of the salt waste as nonhazardous

Raw Materials	**Yearly Cost**
Kolene salt	$13,600
Bulk chemical Stripping Additive	$8,500
Caustic Potash	$3,270
Disposal of salt as nonhazardous	$500
Cost of Processes	**$25,870**

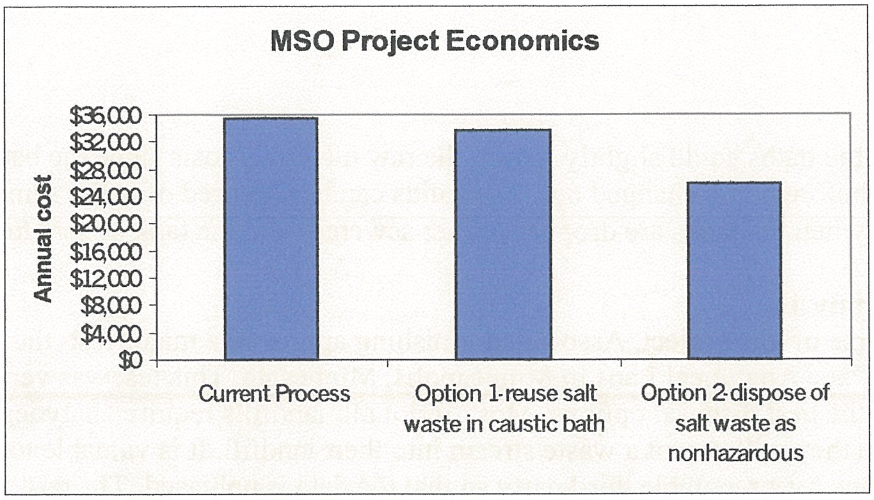

Figure 5: Graphical representation of options for MSO project

In my estimations of the cost, I did not change the raw materials price, the usage of the salt or the caustic potash, or the amount to be discarded. The biggest area of saving is using the bulk chemical in place of the current stripping additive. The suggested changes will not add any labor costs, new equipment, or process organization. The only new process for the operators might be the filtration of the baths, but that procedure will most likely require minimal training and labor time. The payback time for this project is less than a year since the only monetary outlay was for the analytical test. Additionally, the cost for the TCLP test and the landfill application fee were one-time costs. The table below shows the projected 1st year savings.

Table 7: Annual projected savings

Molten Salt Oxidation Project	
Expenditures	
TCLP test	($250)
Landfill Application Fee	($55)
Savings	
Raw Materials	$5,400
Hazardous waste taxes & fees	$600
Disposal costs	$4,000
Total 1st Year Savings	$9,695

Where the project is now:

As of the writing of this report, I am still waiting on approval from the Buffalo landfill to take the salt waste. They were sent a copy of the most recent TCLP test and a waste profile stream. The profile and analytical data for the salt waste goes to the main office in Fond du Lac for final approval. However, the Buffalo landfill manager didn't think that there would be any problems and they should be able to take the salt waste. I am also still waiting for a few price estimates from Onyx Environmental Services for transporting the salt waste to Michigan as nonhazardous and for disposal in one of their industrial landfills. Joe Appelhof and I are making a site visit to the Buffalo landfill on August 26.

Ms. Julie Rantala has been sent the letter requesting confirmation that the salt waste is nonhazardous and a petition to provide a letter from an agent of the MPCA to Associated Finishing stating that fact. Once she replies the hazardous waste labels can be removed from the salt waste drums and the satellite accumulation signs around the Kolene machine can be removed.

The bulk chemical in the current stripping additive will be ordered as soon as a supplier is chosen. Once it arrives, the operators will begin using it in the caustic tank after the current barrel of the current stripping additive has been used up.

Reducing the Phosphorus Emissions

Amount of waste produced:

The Mankato Wastewater Treatment Plant lab technicians test water from Associated Finishing's manhole with grab samples or a composite 24-hour sampler. In 2001, there was only one 48-hour composite test run. Based on this sample, they determined that AFI was emitting 5.3 kg/day of phosphorus into their wastewater. The total amount of phosphorus billed to Associated Finishing was 1367 kilograms, but they received a 260 kilogram credit-1 kilogram for each working day. The initial fee assessed to AFI was $5,046 for 1106 kilograms. After some negotiation, this was reduced to $4,362. A wastewater survey done by Minnesota Valley Testing Labs out of New Ulm estimated the phosphorus level to be at 88.2 mg/L from a 24-hour composite sample. It cost the Mankato Wastewater Treatment Plant $4.56/kg to treat the phosphorus in 2001. They remove around 70% of the phosphorus in the wastewater. Four companies in the Mankato area were assessed fees for their phosphorus emissions in 2001.

Current management practices:

The only pretreatment performed on wastewater from Associated Finishing is neutralization of the caustic stripping bath and stages 1 and 3 from the 5-stage washer.

Why changes were necessary:

Phosphorus has become a problem in Minnesota's lakes, rivers, and streams. This element is essential for plant and animal growth, but there can be too much of a good thing. Excess phosphorus can cause algae to spread wildly, absorbing all the oxygen, and choking out other aquatic life. In essence, the lake or river can die. Detergents, fertilizers, and cleaners are common sources of phosphorus. A phosphatizing process is used in Associated Finishing's metal preparation area to increase paint adhesion, minimize corrosion, and protect the metal.

The regulations for phosphorus are not going to get any more lenient. Besides contributing to the pollution of the Minnesota River, the expense of treatment is something that Associated Finishing very much wanted to address. Phosphatizing is critical to their business so until a satisfactory alternative is found, they will not be able to eliminate phosphorus completely, but the discharge to the wastewater can be reduced.

Research and Testing:
I began by identifying all the sources of phosphorus around the plant. There are six main sources of phosphorus: a high-pressure spray washer, an aluminum brightening tank, a descaling tank, an immersion phosphating tank, the 3rd stage of the large inline washer, and the 1st stage of the belt washer along with the rinsing stages which follow the 3rd and 1st stage on the two washers. There are five main chemicals used in these processes, each with a different concentration of phosphoric acid. The immersion phosphating tank is very infrequently dumped, so the sprayer, the washers, and the descale tank are the main sources of phosphorus in the wastewater.

I reviewed Associated Finishing's wastewater permit issued in June of 1999 and set to expire in 2004. The table below shows the allowable limits for certain metals and other contaminants. Most of the analytes are usually tested quarterly with a 24-hour composite sample, but based on previous data, the Treatment Plant decided that monitoring was not necessary at Associated Finishing unless process or production changes were made. There is also a provision in the permit stating that sludges generated by the permitee shall not be placed in the City's Wastewater Treatment System.

Table 8: Allowable levels of contaminants in wastewater as of 1999

Contaminant	pH	Suspended solids	BOD	Grease/Oil	Phosphorus	Cadmium	Chromium
Allowable level	>6.0, <10.0	280 mg/L	260 mg/L	50 mg/L	1 kg/day	1.03 mg/L	5.23 mg/L

Contaminant	Copper	Cynaide	Lead	Mercury	Nickel	Zinc	Silver
Allowable level	2.86 mg/L	1.09 mg/L	1.05 mg/L	0.01 mg/L	3.65 mg/L	8.10 mg/L	2.14 mg/L

Minnesota Valley Testing Laboratories was hired to do a wastewater survey. This test involves measuring the flow rate and taking samples every 15 minutes for 24 hours. Since Associated Finishing has two pipes coming into the manhole, a weir had to be built to make one composite flow out the two pipes. An ISCO sampler and an ISCO 4230 Flow Meter were used for the survey.

Figure 6: MVTL workers placing weir in manhole

The last such survey was done in 1995 and Associated Finishing has made multiple procedural and process changes since that time. The new survey from 2002 suggested a daily outflow of approximately 8,000 gallons of combined industrial and sanitary wastewater. Water meter readings taken during the same time as the wastewater survey showed that only about 60% of the incoming water was being sewered. Some of the water loss is certainly due to evaporation and drag-out with the production parts. Analytical tests showed that the levels of everything except BOD (biological oxygen demand) and Total Suspended Solids were well within the published limits for the Mankato Water Treatment Plant. The test was performed June 27th to June 28th, 2002. Some of the testing results are shown below. A copy of the full results is found in Appendix IIIB.

Table 9: Results of MVTL testing

~2.8 Kg/day

Contaminant	pH	Suspended Solids	BOD	Grease/Oil	Phosphorus	Cadmium	Chromium
Tested Level	Not Tested	740 mg/L	271 mg/L	18.6 mg/L	88.2 mg/L	<0.001 mg/L	0.035 mg/L
Allowable Level	<10.0, >6.0	280 mg/L	260 mg/L	50 mg/L	1 kg/day	1.03 mg/L	5.23 mg/L

Contaminant	Copper	Cyanide	Lead	Mercury	Nickel	Zinc	COD
Tested Level	0.302 mg/L	<0.02 mg/L	<0.008mg/L	<0.06 µg/L	0.121 mg/L	4.990 mg/L	804 mg/L
Allowable Level	2.86 mg/L	1.09 mg/L	1.05 mg/L	0.01 mg/L	3.65 mg/L	8.10 mg/L	N/A

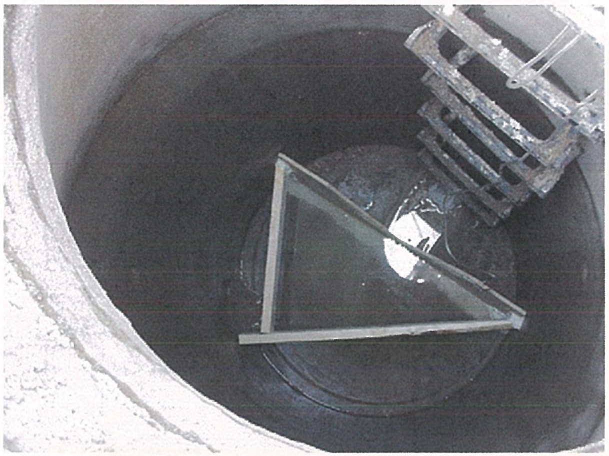

Figure 7: Weir in manhole after placement

During the period that MVTL tested, the suspended solids and phosphorus were significantly above the allowable levels. The rest of the analytes were far below the acceptable limit. Even though this was a very worthwhile test, since sump pumps remove all the process water from the two pits at random intervals during the day, it cannot be assumed that the test results present a steady state picture. On another day, the phosphorus could be a quarter of the level that MVTL tested or the water flow could be several thousand gallons more. However, this wastewater survey does give a good rough guide as to the current levels of controlled contaminants in Associated Finishing's wastewater.

Wastewater Treatment Plant:

South Bend Township puts 2 ppm of phosphorus into the water before it is distributed to homes and businesses. Barb Pikal from the Mankato Wastewater Treatment Plant tested three days worth of samples; one for each day of the water coming into the plant and one from the reverse osmosis (RO) output. The incoming water had an average of 0.438±0.05 mg/L of phosphorus and the RO purified stream contained 0.192±0.03 mg/L. Based on the water usage from 2001, this means that the incoming water adds about 8-10 kilograms per year of phosphorus to the wastewater. This is an insignificant amount considering the total amount of phosphorus in the wastewater. However, it was a valuable exercise to eliminate possible large sources of phosphorus.

The Mankato Treatment Plant supplied me with their test data from 2001 and 2002. Interestingly enough, the entire phosphorus treatment bill for 2001 was based on 2 samples taken over a 48-hour period. These two samples gave an average of 62.55 ppm. Starting in February of 2002, they began testing approximately weekly and the testing levels ranged from 5.25 ppm to 250 ppm. The testing range for 2002 is more than 200 ppm which calculates out to an estimated difference of more than 4000 kilograms for the year when multiplied through by the water usage. Additionally, the three highest samples on April 11, May 13, and May 29-30, of 2002 were marked as "over". This means that the spectrophotometer did not give an actual number and the sample should have been diluted and retested. The results of the phosphorus testing are shown in the table below.

Table 10: 2001 and 2002 Phosphorus Testing by Mankato Wastewater Plant

2001 Testing

Date	Type of Sample	Total Phosphorus (ppm)
4/25-4/26	Composite	59.70
4/26-4/27	Composite	65.40
	Average	**62.55**

2002 Testing

Date	Type of Sample	Total Phosphorus (ppm)
2/26/02	grab	54.35
3/13/02	grab	36.45
3/18/02	grab	48.6
3/27/02	grab	66.25
4/3/02	grab	34.4
4/11/02	grab	125
4/17-4/18	composite	34.85
4/18-4/19	composite	87.35
5/2/02	grab	5.25
5/10/02	grab	10.88
5/13/02	grab	250
5/20/02	grab	19.4
5/29-5/30	composite	125
6/5/02	grab	32.3
6/11/02	grab	26.1
6/19/02	grab	49.2
6/25/02	grab	16.7
7/3/02	grab	21.7
	Average	**57.99**

The test to find the amount of phosphorus in a sample is based on the absorbance of light. A sample is diluted and sulfuric acid and potassium persulfate are added. The test tube is heated to 150°C for about 30 minutes. Then sodium hydroxide and a PhosVer 3 reagent pillow packet are added after the tube has cooled off. The PhosVer 3 pillow turns the sample blue in the presence of phosphorus. The sample is inserted into a spectrophotometer and a reading in mg/L of phosphorus is given depending on the absorbance of the sample. A blank and a standard are prepared with each sample. Associated Finishing's water samples are usually diluted by a factor of 50.

I looked at stripping supervisor Cal Schulz's maintenance records from the past two years to try and correlate high testing levels with dumping the tanks. The high level on May 29th and 30th can be explained by the fact that the belt washer was dumped on May 28, 2002. That was the only obvious direct correlation.

Associated Finishing has a computer program that tracks all chemical usage in the plant. The amount and price of each chemical containing phosphoric acid is shown in Table 11 below. I used those records and the content of phosphoric acid to calculate the theoretical maximum amount of phosphorus that could have been sewered in 2001 assuming that everything that was purchased eventually went down the drain. I also calculated the amount of phosphorus that was put into the effluent every time a tank was dumped. Table 12 shows these results. Additionally I calculated that the spray washer gun used 21 kilograms of phosphorus in 2001. The details of these calculations can be found in Appendix V. I found that in 2001 the most phosphorus that Associated Finishing could possibly have put down the drain is 414 gallons of phosphoric acid or 833 kilograms of total phosphorus. This is 500 kilograms less than the amount cited by the MWTP.

Table 11: Chemical usage and cost in 2001

Chemical	Use	Price/Unit	Amount Used in 2001	Cost in 2001	Phosphorus Content	
Phosphoric Acid	Descale tank	$.56/lb	2876 lb	$1,611	466 kilograms	5
207-3	dip tank	$7.84/gal	30 gal	$235	6 kilograms	
209-3	spray wands	$6.30/gal	275 gal	$1,733	21 kilograms	
1007-004	washers	$10.08/gal	1,300 gal	$13,104	295 kilograms	3
1009-1001	aluminum brightening	$8.75/gal	60 gal	$525	42 kilograms	
				Total Phosphorus	833 kilograms	

Table 12: Kilograms of phosphorus sewered for each tank

Tank Emptied	Chemical Concentration	Phosphoric acid content	Total Phosphorus
JCI line 3rd stage 600gal	1.50%	11%	2 kilograms
Belt washer 1st stage 400gal	1%	11%	1 kilogram
Descale tank	15%	77%	233 kilograms
Immersion phosphate tank	10%	10%	24 kilograms
Aluminum brightening tank	100%	35%	1 kilogram

I also calculated an estimate of Associated Finishing's 2002 total phosphorus bill based on the testing so far by the Treatment Plant, AFI's water usage so far, and their purchase records. I assumed 350,000 gallons of water per month and a surcharge of $5/kilogram from the Mankato Treatment Plant. I found a range of 577-922 total kilograms depending on if the high numbers were thrown out of the average and a fee for 2002 of $1,585 to $3,310. Depending on the actual water usage and the final average concentration of phosphorus, these figures could fluctuate.

Source Reduction:

There are two approaches I took to the phosphorus problem: reduction and treatment. I identified a few areas where reduction might be possible: the descale tank, the spray washers, replacing the phosphatizing chemical which is used in the JCI 3rd stage and the 1st stage of the belt washer, and replacing the aluminum brightening chemical.

I talked to the Dubois representative, Gary Hess, about low phosphorus options to replace the phosphatizing chemical. He suggested a new chemical, which is very low in phosphoric acid: 1-5% with superior salt spray performance. Associated Finishing is very concerned about the salt spray hours since some of their customers have very stringent requirements. The new chemical uses sodium chlorate to produce excellent paint adhesion and salt spray resistance hours. This chemical has an operating concentration range of 2-4% by volume. The 3rd stage JCI line is currently operating at 1.5% concentration of chemical and 130°F. The temperature would have to be bumped up to about 140°F according to Mr. Hess. However, even at a slightly higher concentration of chemical, the phosphoric acid content is so low that the phosphorus will still be reduced. Mr. Hess also suggested a seal rinse for the last stage. The products Epoxy Link and Polyester Link contain no phosphorus, but they are paint-specific. Another seal product, ICA 503, works on all types of paint, but it does add a very small amount of phosphorus.

Before the phosphatizing chemical is replaced, the tank should be cleaned out. Proper maintenance dictates that the washer tank should be cleaned and descaled at least once per year. Mr. Hess also mentioned that Associated Finishing would be well advised to clean out their cleaning and phosphatizing tanks a little more often. Clean tanks mean that the chemical works better and longer. A dirty tank will just continue to absorb the chemicals without enhanced performance.

I also talked to the W. D. Forbes representative, Ray Holford, about a replacement for the aluminum brightening chemical. Unfortunately, he said that there is no other alternative that works as well for aluminum brightening since it is a very particular chemistry tailored to the needs of Associated Finishing's metal prep work.

The spray washers are supposed to have stop valves in the line to reduce the amount of chemical coming through the line. The valve decreases the flow of chemical in the spray from about 3% down to 0.5%. This valve was missing on the spray washer near the burn-off ovens. The spray washer in the caustic tank area doesn't have a line running to chemical, so it was irrelevant whether it had such a valve or not. The immersion phosphate tank is used instead of hooking chemical up to the spray gun in the caustic tank area.

The descale tank is a 12% by volume solution of phosphoric acid used to remove rust and clean metal parts, especially after they have been in the burn-off oven. After talking with Alan Baer and other plant operators, it was determined that sulfuric acid was previously used in this tank and no one was quite sure why it had been replaced with phosphoric acid. They said that it might have gotten too concentrated and posed a health concern to employees.

Treatment:

Once options for phosphorus source reduction were identified, there was still the issue of treatment. Research indicated that precipitation with ferric chloride is one of the best ways to remove phosphorus from the wastewater. Sometimes a floculant can be added to increase the size of the precipitate and a polymer can be added to assist in dewatering the sludge. Dave Walsh from Water Concepts in Rochester sent me some information about sludge dewatering bags that are currently used to remove the floc from precipitating out phosphorus. He made a site visit and took several jar samples. There was one composite sample made from the two drainage pits, a sample from the JCI stage 3 tank, and one from the belt washer stage 1 tank.

He then did a series of tests to determine the best combination and concentration of chemicals to precipitate out the phosphorus. The phosphorus precipitated easily out of the pit sample, but he had a good deal of trouble precipitating the phosphorus out from a combined sample made up of water from each of the washer tanks and the pits. Once he had added flocculent and coagulant, I took samples of the treated water down to the Mankato Treatment Plant and ran the test for phosphorus. The water from the pit had 28 mg/L of phosphorus and the composite sample had a phosphorus content too high for the spectrophotometer to read. Mr. Walch said that the maintenance cost for the chemical alone would be around $25/day for 166 pounds of ferric chloride solution. This works out to $6,500 per year. That figure does not include any pumping or settling tank equipment that would most likely be necessary.

A further complication with chemical precipitation is the sludge that is formed. Since Associated Finishing is a metal prep and painting job shop that applies chemical conversion coatings, they need to take into account the F019 rule. This rule, found in the MN Rule 7045.0135 Subpart 2, states that, "wastewater treatment sludges from the chemical conversion coating of aluminum, except from zirconium phosphating in aluminum can washing when such phosphating is an exclusive conversion coating process" are considered to be hazardous from nonspecific sources. Since chemical precipitation is considered treatment, the sludge would be subject to the F019 rule. Some members of the chemical coating industry argue that aluminum does not get a conversion coating from iron phosphatizing, which Associated Finishing uses, at certain pH and temperature levels. However, at this point, it appears that no one from a regulatory agency is willing to support that view and so these sludges must be presumed to be hazardous. Karl DeWahl at MnTAP is continuing to examine this issue and its interpretation.

Another idea that company president Chuck Klammer suggested was to evaporate the wash tanks from the JCI 3rd stage and belt washer 1st stages thus eliminating a major source of phosphorus. I found that it takes about 14,000 BTUs to evaporate a gallon of water. According to their website, Minnegaso's current price for natural gas is \$0.54/therm. Based on these figures, to evaporate the JCI 600-gallon tank would cost about \$45 and the 400-gallon belt washer tank would be about \$30. However, there will be sludge left over in the bottoms of the evaporator. The question arises then of how to handle the sludge. Most likely it would have some fuel value, but by the same F019 rule it may be labeled as hazardous because of the aluminum parts that go through the washers. There would also be the capital equipment investment and the floor space requirement.

Recommendations:

I would focus on reduction at the source and insuring accurate testing. Treating wastewater in-house can be difficult and expensive so the first thing to do is reduce the fee from the Mankato Wastewater Treatment Plant.

The stop valve in the spray washer should be reinstalled. This will bring the flow of chemical down from 3% to 0.5%. In 2001, 275 gallons of chemical were used by the spray washer. Re-installing the stop valve will bring the chemical usage down to an estimated 50 gallons. This will also save \$1,400 in raw materials costs. Also the operators should be instructed to make sure the chemical line is closed if phosphatizing is not necessary.

The descale tank uses a 12% solution of phosphoric acid to clean up paint hooks and remove rust. A 10% solution of sulfuric should fulfill the same purpose. In the opinion of Gary Hess, sulfuric also does a better job of pickling and removing rust than phosphoric acid. There is the possibility of rust from the vapors, but since an exhaust system is already in place above the tank, it shouldn't be a significant problem. Additionally another acid such as sulfuric should be substituted for phosphoric when used for pH adjustment in the plant. The health and safety hazards for sulfuric are not significantly different than for other chemicals used around the metal prep and stripping area. Sulfuric acid is significantly less expensive than phosphoric acid and will eliminate another major source of phosphorus in the wastewater.

Based on discussions with Gary Hess, the Dubois representative, I would suggest switching from the current phosphatizing chemical, which is 11% phosphoric acid, to the newer chemical which is only 1-5% phosphoric acid. The new low-phosphorus chemical will provide the same quality of metal prep and salt spray resistance with significantly lower phosphorus content. The utilities cost for the washers would increase very slightly because of the higher temperature requirements. The raw materials cost will increase since the newer phosphatizing chemical is slightly more expensive then Associated Finishing's current product and a higher concentration might be necessary.

If it has not been done recently, I would also suggest looking at the nozzles on the JCI line washer and the belt washer. Clogged nozzles can give an uneven coating and use more chemical than necessary. Associated Finishing has already eliminated all the phosphorus-containing janitorial supplies in the plant.

Finally, I would suggest setting up at least bi-weekly testing of the phosphorus levels with the Mankato Treatment Plant. Even if they require Associated Finishing to pay for the testing, it would only be $220 per year at $8.50 per test. The accurate testing and resulting yearly savings will more than cover the price of the testing. I would also ask for a copy of the testing every quarter or so for monitoring purposes.

Benefits of these recommendations:
There is a direct correlation between phosphorus level and additional treatment fee from the Mankato Treatment Plant. In 2001, it cost Mankato $4.56/kg to treat the phosphorus. Honeymead was the largest contributor to the additional phosphorus in the water. A source from the Treatment Plant mentioned that Honeymead has now hired an engineering firm to come in and help them reduce the phosphorus in their wastewater. With the largest contributor removing the majority of their pollution, Associated Finishing is the next largest contributor in the area. The fewer companies there are to share the financial burden of phosphorus treatment from the MWTP, the larger the cost will be to each company.

More frequent testing and reviewing the results of that testing will give Associated Finishing assurance of a more accurate bill for 2002 and the years beyond. Having access to the test results will also give Associated Finishing some warning about how expensive their treatment surcharge will be- rather than an unexpected $5,000 charge. Associated Finishing will be reducing their phosphorus emissions and the costs for wastewater treatment with these changes.

Economic Analysis:
Associated Finishing approved the funds for a major test- a wastewater survey by MVTL labs. This was a very thorough evaluation, including flow rate and analytical data. The test showed a great variation in flow rate depending on the day, since there was three days worth of flow data. The cost for this survey was $950, which included all the equipment rental and analytical testing.

The tables below show the estimated chemical usage and cost with the suggested changes. The total possible amount of phosphorus calculated based on the phosphoric acid content of each product is also shown. Amounts used and prices are subject to change.

Table 13: Chemical usage and cost with reductions using new phosphatizer

Chemical	Use	Price/Unit	Projected use	Estimated Cost	Phosphorus Content
Sulfuric Acid	Descale tank	$.56/lb	2876 lb	$430	0 kilograms
207-3	dip tank	$7.84/gal	30 gal	$235	6 kilograms
209-3	spray wands	$6.30/gal	55 gal	$350	4 kilograms
new phosphatizer	washers	$10.20/gal	1,800 gal	$18,360	181 kilograms
1009-1001	aluminum brightening	$8.75/gal	60 gal	$525	42 kilograms

Total Phosphorus	233 kilograms

Table 14: Chemical usage and cost with reductions using current phosphatizer

Chemical	Use	Price/Unit	Projected use	Estimated Cost	Phosphorus Content
Sulfuric Acid	Descale tank	$.56/lb	2876 lb	$430	0 kilograms
207-3	dip tank	$7.84/gal	30 gal	$235	6 kilograms
209-3	spray wands	$6.30/gal	55 gal	$350	4 kilograms
current phosphatizer	washers	$10.08/gal	1,300 gal	$13,104	288 kilograms
1009-1001	aluminum brightening	$8.75/gal	60 gal	$525	42 kilograms
				Total Phosphorus	340 kilograms

The chemical precipitation system that was available from Dave Walch would have a $25/day maintenance cost for the chemicals alone. This would be about $6,500 per year- which is more than the treatment fee. This figure does not include any holding tanks or pumps that would be required. The same principles apply for the evaporation idea. The JCI line 3rd stage would be about $45 to evaporate and the belt washer 1st stage tank would be about $30. These numbers themselves do not seem to be very expensive, but there would also be a large capital equipment cost. The biggest drawback to these two alternatives is the production of hazardous waste sludge by the F019 rule. If a ruling were made to exempt these sludges from the F019 rule, it would be worthwhile to take another look at pretreatment alternatives. Until the fee from the treatment plant becomes more expensive, it appears to be more cost effective to sewer all the water without in-house pretreatment.

The tables below show the estimated 1st year savings.

Table 15: Phosphate Project 1st year Savings using new phosphatizer

Phosphate Project	
Expenditures	
Wastewater survey	($950)
Savings	
Raw Materials	($2,693)
Disposal fee	$4,000
Total 1st Year Savings	$357

Table 16: Phosphate Project 1st year savings using current phosphatizer

Phosphate Project	
Expenditures	
Wastewater survey	($950)
Savings	
Raw Materials	$2,563
Disposal fee	$3,000
Total 1st Year Savings	$4,613

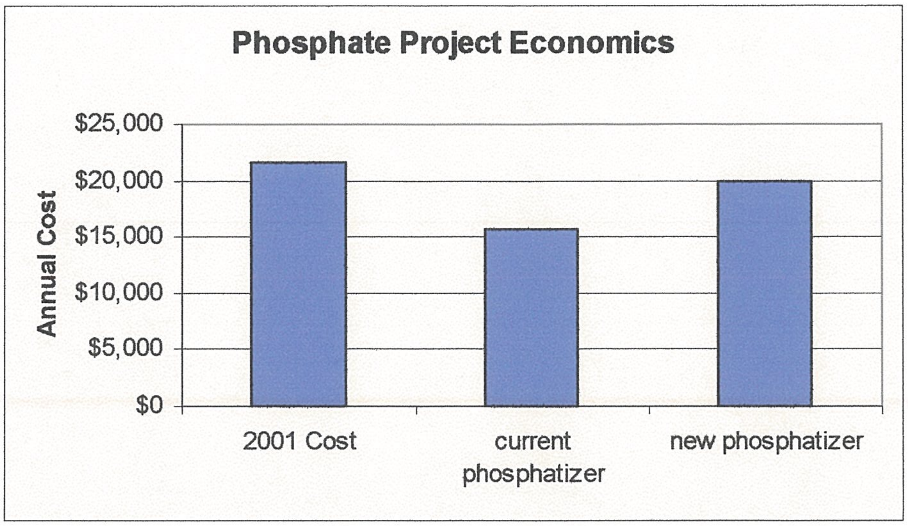

Figure 8: Graphical Representation of Phosphorus Reduction Options

Where is project is now:
As of the writing of this report, the stop valve has been replaced on the spray washer. The Mankato Wastewater Treatment Plant is already testing the phosphorus level in the water almost weekly, but once the phosphorus study is over they will most likely abandon such frequent testing. Associated Finishing should find out when the study will be over and request testing to continue biweekly beyond that date. They might also want to examine further how much of their incoming water is actually going to sewer. It might be financially advantageous of them to do some further studies. It is up to Associated Finishing whether they want to switch over to the new phosphatizer or stay with their current product.