Proceedings

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Frank Clay, recently retired from U.S. EPA, Raleigh, NC

Beyond Awareness: Effective Outreach to the Metal Finishing Industry

Linda Darveau, US EPA New England, Boston, MA
Dr. Ihab Farag, University of New Hampshire, Durham, NH

Through funding provided by the Strategic Goals Program, EPA New England has launched an outreach program to industry that includes sponsoring Best Practices for Dragout Reduction Workshops and measuring the results of these workshops, conducting an internship program that provides hands on assistance, and obtaining corporate sponsorship for the Strategic Goals Program in New England. The outreach program focuses on nontraditional projects that go beyond simple awareness workshops to include workshops conducted in plating shops, interns working directly for members of the Strategic Goals Program, and encouraging large contractors to use financial incentives to improve subcontractor environmental performance. This paper will include detail on the National Pollution Prevention Roundtable (NPPR) research on outreach effectiveness, the results of the three projects undertaken by EPA New England, and the transferability of these projects to other regions.

For more information contact:

Linda Darveau
Environmental Scientist
US EPA New England
One Congress Street
Boston, MA 02114
Darveau.Linda@epa.gov

Introduction

From 1995 to 2001 EPA Region I implemented a metal finishing initiative involving both enforcement and assistance. The goals of the initiative were:

1) To assist metal finishers in complying with basic regulatory requirements,
2) To give metal finishers pollution prevention information that may allow them to go beyond compliance, and
3) To enforce against those metal finishers who did not meet regulatory requirements.

The assistance part of this initiative included outreach to partners such as trade associations, state regulatory and technical assistance agencies, interstate organizations, and colleges and universities. Most of the assistance involved workshops, conferences, meetings and tools developed with one or more of those partners. The enforcement efforts of this initiative included the formation of an Industrial Sectors Team consisting of a representative from each media and from the assistance division. This team worked together using various media specific databases and general industry knowledge to target poorly performing metal finishing facilities for inspections.

During the period of this initiative the Strategic Goals Program was developed as a partnership between industry and regulators to bring the metal finishing industry beyond compliance. The Strategic Goals Program (SGP) fit into Region I's ongoing initiative. Region I's established relationship with the metal finishing industry helped to get SGP programs in Massachusetts and Rhode Island off the ground quickly. Through SGP, Region I received funds from Headquarters that helped to support outreach activities. Region I would then use those outreach activities to recruit new SGP members.

Over the 6 years of this initiative Region I tried many different ways to reach metal finishers. Our experience and data shows us that the projects that were successful in changing behavior were the projects that went beyond awareness.

What is "Beyond Awareness" ?

Although Region I began to produce many workshops on different topics and they were usually well attended, they did not seem to have any effect on the compliance issues our inspectors were finding at facilities. Early in the initiative EPA decided to target workshops at the problems that inspectors were finding in the field. One such issue was Hazardous Waste Determinations. RCRA inspectors complained that the metal finishers they visited were not looking at their waste in any systematic way. Metal finishers were not sending samples of waste out for TCLP testing, and keeping the records on file as they were suppose to. As a result hazardous waste was often found in the dumpsters at metal finishing facilities. Workers were not trained to know what was hazardous waste and why because in many cases the facility owners did not know. Region I organized a half day classroom style awareness workshop on Hazardous Waste Determination. The workshop included information on hazardous waste classification, how to determine whether waste is hazardous, and how to document the findings. RCRA Inspectors presented what they would like to see when they do an inspection. The workshop was held at three different locations around the state of Massachusetts, and attendance was high and workshop evaluations were very positive. A few months after the workshops a RCRA inspector was on an inspection and someone at the facility said to her " Oh, I recognize you, I went to the workshop on hazardous waste determination". But, when the inspector asked to see the facility records, the facility had not done any hazardous waste determinations. As this story illustrates, it was the experience in Region I that awareness workshops often do not change behavior in the metal finishing industry.

The 2000 Summary White Paper by the National Pollution Prevention Roundtable's Research and Technology Transfer Workgroup(1) reiterates this point. This paper states " Most P2 Technical Assistance Providers focus the bulk of their technology-related efforts on educating businesses about P2 technologies. However technology education alone does not usually provide the site specific information required for implementation. Consequently, companies that receive only P2 information still have a low rate of adopting these technologies. " Although this paper is focused on Pollution Prevention Technology, experience in Region 1 attests to the fact that many of these observations hold true for compliance assistance as well. This paper goes on to say "Most Technical Assistance Providers focus the bulk of their efforts on education. This approach includes practices such as workshops, seminars, case studies, fact sheets, and internet resources, etc. that distribute large amounts of information to many customers at relatively modest cost. However, technology education alone does not usually provide the site specific information required for implementation." Region I conducted 21 workshops over three years, along with fact sheets, mailings, videos, and other traditional tools, and saw very little impact on compliance rates among metal finishers.

Beyond Awareness Projects

The following projects were successful in changing behavior. These projects are targeted not at what EPA wants the metal finishers to know, but at what EPA found out the metal finishers need. After working with metal finishers for several years EPA began to understand the challenges that face this industry. The biggest problem at metal finishing facilities and probably at most small businesses was the lack of time on the part of owners and operators. These people wore many hats, and ran a business that was technologically challenging. The other need that was recognized was lack of resources. Most metal finishers could not afford to hire consultants or to make major investments in new technology. The third issue faced by many small businesses is the lack of trust in government agencies. Even when free on site assistance was available many facilities did not take advantage of it because they did not want government agencies on their site. In order to try and address these needs the following programs were developed.

1) Internship program.

Working with the already established Pollution Prevention Consortium's Internship program at the University of New Hampshire, Region I began to hire summer interns to work with metal finishers. During the first summer of this project two interns were hired to sign companies up to the Strategic Goals Program. Signing up to this program is a critical step for many facilities, because the SGP is the beginning of an environmental management system. It was the experience of the interns this first year that many of the facilities did not know how much water they used, how much energy they used or what it cost, or how much waste they shipped off. The interns had to contact utilities and disposal firms to get much of the information. Without this knowledge it is hard to imagine a company making any investment, whether it is money or effort, in change. During the second year of the internship, one intern worked full time at a job shop developing an environmental management system. This project gave Region I valuable insight into how an environmental management system can help a small job shop. It also proved very valuable to the participating company when they were coincidentally inspected by the state at the end of the summer. The second intern signed six additional companies up to the SGP and also conducted projects at various SGP plating shops that were intended to assist these shops in meeting their goals. These projects included designing a rinse system that would save one metal finisher over $30,000.00 a year in water costs, testing a fume suppressant used in a chrome tank, and developing a database to track VOC emissions from paints and coatings. On the third year of this project Region I received enough funding for only one intern. This intern spent time at eight different SGP shops. Two shops were new to SGP, so the intern filled out their reporting forms. The remaining shops were already members, so the intern worked on various projects including compliance related activities such as reviewing the facility RCRA program and filling out a water permit as well as testing rinse water and investigating close loop systems. It is hoped that Region I will be able to continue to offer the help of interns to SGP companies as a benefit to signing up and staying in the program.

2) Best Practices Workshops

The Best Practices Workshop focusing on drag out reduction was developed by Michael Keefe and Patrick Wooliver of Tetra Tech E. M. Inc. These workshops were different from previous workshops offered by Region I because they were conducted in plating shops. Designed for line operators, the workshops consisted of hands on experiments done by the participants. The results of the experiments were then graphed, so that participants had a dramatic display of the amount of drag out that could be saved by racking parts properly, using proper hang time and spray rinsing techniques. Tetra Tech has developed a spreadsheet so that cost savings can be calculated from this data. Evaluations immediately after the workshop found that 90% of attendees planned to bring information back to their facilities and use it. A follow up phone survey three months after the workshops found that 80% of the participants could point to actual changes they had made in their shops based on information from the workshop they attended. These changes included training, focus on parts racking, addition of spray rinses, and addition of drip pads and bars. These are changes that will lead to less dragout, less hazardous waste, lower water and chemical bills, and a more efficient and hopefully more economical processes. (See Graph titled Good Technique Matters!)

3) SGP Corporate Sponsorship

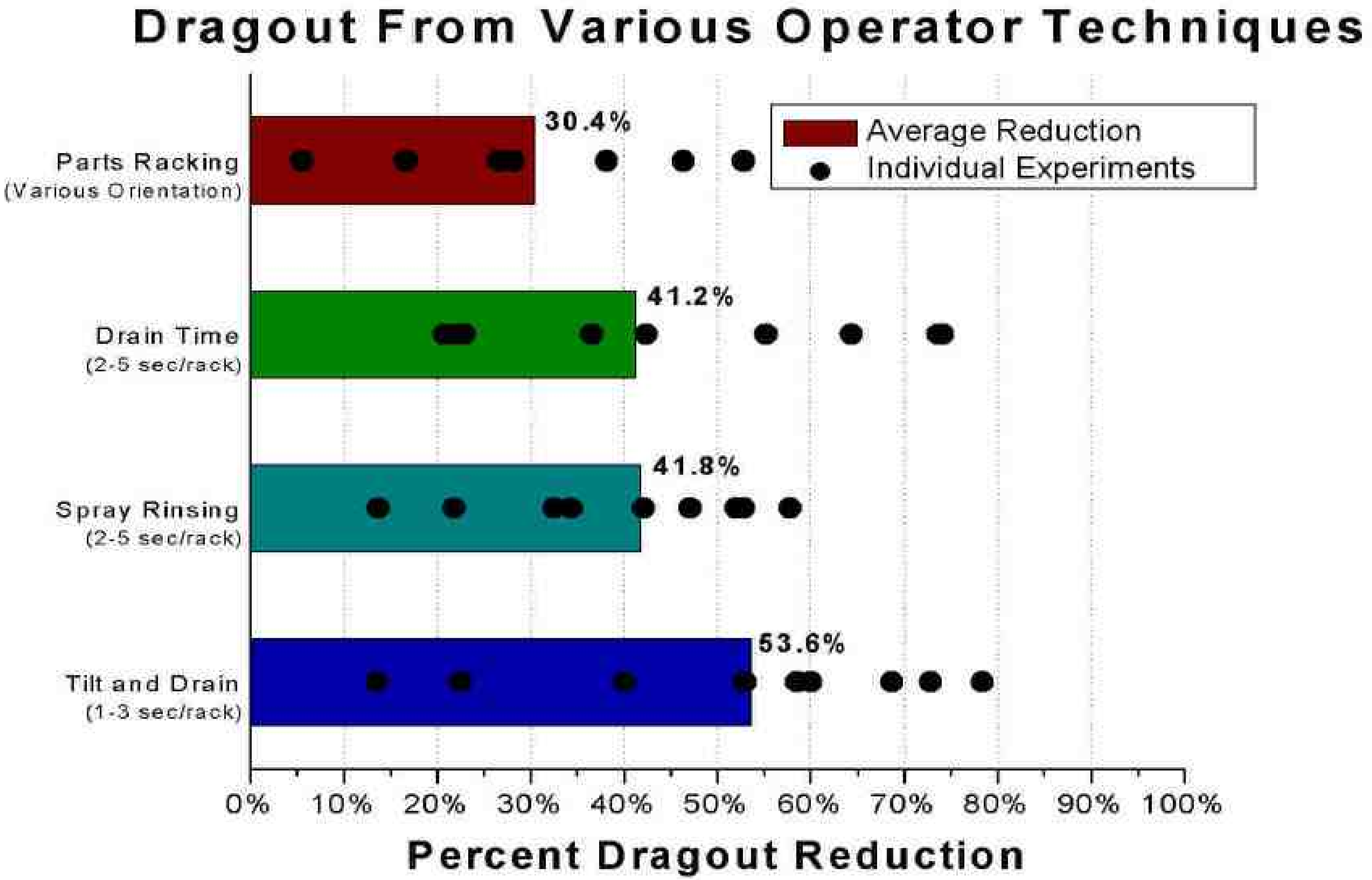
The third project on going in Region I is aimed at the issue of trust. Many facilities have resisted joining the SGP because it is perceived as an EPA program. In order to get more industries involved, EPA began to work with Raytheon Company. Raytheon, like many large contractors, subs out most of its plating to approximately thirty local platers. Raytheon does quality audits of its subcontractors, but does not have any institutionalized way of dealing with environmental issues among its subcontractors. They became interested in the Strategic Goals Program as a way to monitor subcontractors and track their environmental progress. Raytheon has a great deal of knowledge and expertise on environmental health and safety issues that they are willing to share with their smaller sub contractors. Raytheon signed up as the first SGP Corporate Sponsor as a way to develop a mentoring relationship with small job shops. The SGP workgroup meetings formerly organized by EPA are now being held at the Raytheon facility in Lexington, and it is hoped that this will be perceived as an industry program, not a government program. During the first workgroup meeting the attendees brain stormed a list of areas where Raytheon could help them, and these are being addressed at future meetings. So far two new companies have joined SGP as a result of Raytheon sponsorship. The workgroup members are now exploring developing a chemical management system for their facilities with Radian Corporation. Raytheon has a chemical management contract with Radian and has saved millions of dollars in chemical management costs over the past two years. Radian will be meeting with the smaller shops on November 13, 2001 to determine the feasibility of a similar program for small shops. Quarterly meetings of this workgroup are planned for the future. Raytheon is also starting a similar project for painting sub contractors.

Conclusion

EPA Region I found that the keys to effective outreach were developing creative assistance programs that went beyond awareness and even beyond what traditional technical assistance providers offered. This was done by developing an ongoing, long lasting relationship with the metal finishing industry, and good communication between enforcement and assistance staff at EPA Region I. It is hoped that we will be able to continue these relationships and become even more effective in the future. It is also hoped that other regions and states can learn from our mistakes and replicate our successes while developing their own successful programs.

(1)
White Paper, “Pollution Prevention Technology Diffusion: Role of Technical Assistance Providers.”
National Pollution Prevention Roundtable’s Research and Technology Transfer Workgroup 2000 Summary.

Good Technique Matters!



Revised Method 306-A: A Simplified Way for Finishers to Do Certification Testing

Frank R. Clay, Formerly U.S. EPA, Raleigh, NC USA

On October 17, 2000, revised versions of Method 306 and 306-A were published in the *Federal Register*. These methods are used to determine hexavalent chromium emissions from electroplating tanks. Do changes in the methods improve them, and will the changes be of benefit to the plating industry? This presentation will focus on Method 306-A, a simplified method that allows the plater to do his own certification testing.

On October 17, 2000, the FEDERAL REGISTER published changes to Methods 306 and 306-A. Are these changes improvements to the methods and will they be of benefit to the electroplating industry? There is not enough time in this presentation to discuss both methods so this paper will concentrate on Method 306-A.

Before answering the questions about method improvement and industry benefits, let us review briefly Method 306-A. The method was developed as an inexpensive and simple way for electroplaters to show compliance with the U.S. EPA concentration standard of milligrams per dry standard cubic meter. It could be used by the platers, control device suppliers, consultants, or anyone who was willing to assemble the sampling apparatus and collect a sample. It offered an alternative to having only one choice which was to use consultants exclusively.

Does the revised version of Method 306-A actually improve it? Are the revisions of benefit to the plating industry? The answer to both questions is “No.” The method is still useable, but corrections to the calculations will have to be made to the October 17, 2000 version in the FEDERAL REGISTER before the method is published in the Code of Federal Regulations if accuracy and correctness are desired. Revising the method created areas that increase the effort required in collecting and handling a sample while adding nothing that benefits the sampling method or the electroplating industry. If the additions found in the most recent version of Method 306-A were removed, it would make no difference in the method at all, except that it would be easier to use, and would contain no superfluous material or errors.

The first clue that there might be problems with Method 306-A can be found on page 62260 of the Federal Register /Vol. 65, No.201/Tuesday, October 17, 2000/Rules and Regulations. The note at the top of the page says that in order to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306. One of the purposes for developing Method 306-A was to eliminate the need for having a thorough knowledge of isokinetic methods (Methods 5 and 306). Although the two methods will give the same results in concentration per dry standard cubic meter, the sampling principles of Methods 5 and 306 do not apply to Method 306-A. If this were an actual requirement, the only people who could perform 306-A would be consultants who would probably opt for the more expensive and profitable Method 306.

One of the problems with the latest version of Method 306-A is the lack of experience with the method of the people who made the changes. An obvious example of this inexperience is on page 62270 which shows a drawing of the sampling train with an optional by-pass valve. Based on my own experience, never in 127 sample runs, (381 mason jars), has a train failed to pass the leak check test at full vacuum. The difference between sample vacuum and maximum vacuum is about 5””, and even though the by-pass valve is optional, it would add nothing but labor and expense to the sampling train. If a train will leak check at the higher vacuum, what is the point of performing a leak check at the lower vacuum? The drawing also shows a main valve on the train for starting and stopping the sample run. This is unnecessary, and the train can be more easily started and stopped with an inexpensive power strip. The by-pass valve should not even be considered

Another example of inexperience with the method is the note found in the middle column of page 62262 that talks about high concentrations of acids and sulfur dioxide in the stack gas and the need to use 0.5N reagent to maintain the pH level above 8.5 for sodium hydroxide and 8.0 for sodium bicarbonate if the first run using 0.1 N reagent did not meet the pH requirements. This requirement was taken from the boilers and industrial furnaces standard where there would be high concentrations (10% to 12%) of carbon dioxide and high percentages of acids. Plating facilities have no combustion sources producing high concentration of carbon dioxide and acids. Experience with the method shows that 0.1 N sodium hydroxide would have a pH of 12 at the end of the test run and sodium bicarbonate would be at least 8.0. Measuring the pH level at the end off each run is unnecessary and increases the possibility of contaminating the sample, or losing it entirely.

The next item concerns paragraph 8.1.1.3.1 and 8.1.1.3.2 on page 62262, saying that to demonstrate that the flow rate is constant over several days, perform velocity traverses at the beginning and end of each day’s test effort. Nobody cares what the flow rate is. The standard is a concentration standard in milligrams per dry standard cubic meter. The control equipment should be in good working order, but measuring the flow rate over several days is not the job of EPA. If the EPA had looked at its own test data, it would have realized that the flow rates of ventilation systems in the plating industry are virtually constant and these two paragraphs probably would not have been written. An analysis of test data for 54 sampling runs for 10 plating facilities tested by the EPA was done by ratioing the average volumetric flow rate for all the sample runs at a particular site with the individual runs at that site. The values were converted into an absolute value average %, (all positive numbers). The average of these 54 runs was 1.7%. To get a higher average, the highest flow rate from a site was ratioed with the other values and the highest flow rate per cent (which would have been zero) was omitted from the average. In this worst case calculation, the average was 2.7%.

Paragraph 8.1.1.3.2 says to record only the delta p (velocity pressures) for the duct. Comparing just the velocity pressures is no way to determine flow rate. The square roots of the velocity pressures would be a less inaccurate way to do this. The last sentence says to determine an average stack velocity pressure to get a mass emission rate. This too, is in error. Velocity should be determined for each point and averaged, not from an average velocity pressure. How to determine the deviation is not specified. All of this certainly does not enhance the plater's desire to do his own testing. The best way to avoid these problems is to do all the sampling on one day.

The first column on page 62263 gives a procedure for cleaning glassware. Glassware is found in the train in the Mason jars and possibly the nozzle. Glass tubing could be used in fabrication of the impingers, but the glass tubing is easily broken and difficult to repair. The most trouble free sampling train uses glass in the Mason jars only. Paragraphs 8.1.1.8. and 8.1.1.8.1 are unnecessary. Cleaning two brand new Mason jars with nitric acid makes no sense. The effect of a 10 per cent nitric acid solution on the plastic components has not been determined, and was never done when Method 306-A was being developed. Recent analysis of the rinse solutions (tubing, nozzle, and Mason jars) has shown that the positive hexavalent chromium bias is very close to the minimum detectable limit of the analytical method. Since the Mason jars are already rinsed before collecting the sample, the plater can live with a reagent rinse of then nozzle and tubing. Even the mention of nitric acid cleaning of the train components does nothing but make the Agency look foolish.

Paragraph 8.1.1.9.2 on page 62263 says to use a small cotton ball in the outlet tube of the third impinger. In over 127 sample runs in more than five years of chromium sampling, this has not been necessary. The reason that the cotton ball is in the method is that someone called the Agency and said that the desiccant in the third impinger was going out the impinger, through the critical orifice, and damaging the pump. Since the orifice tubing is 3/32 inches in diameter, it is obvious t the desiccant size was smaller than the 6 to 16 mesh recommended in paragraph 8.1.1.9.1. The Agency should have told the source sampler to make sure his desiccant was the correct mesh size and left the cotton ball out of the method.

On page 62264, a procedure is given for sample recovery. It is incorrect. Paragraph 8.2.1.3 says to position the nozzle, probe, and connecting plastic tubing in a vertical position so that the tubing forms a "U". The nozzle, probe, and connecting tubing will be very difficult to recover unless the nozzle and tubing are removed from the sheath (usually a piece of steel conduit). The nozzle/tubing should be rinsed three times, not two as is written in the latest version of the method. Thus, there are 6 rinses for the nozzle/tubing (3 in each direction) and the same is true of the short tubing that connects the first and second impingers.

On page 62265, paragraph 8.3.2 says to refrigerate the samples at 4 degrees C or –40 degrees F (-40 is an error). Whether this is necessary or not is unknown since the EPA has no such data on chromium samples from electroplaters. When I was at the Agency, I saw either a letter or a memo that said that if samples were refrigerated prior to analysis, some of the chromium would adhere to the walls of the glass container and not be analyzed. Since we never refrigerated samples at that point in time, I paid little attention to a possible problem with refrigeration of samples. Now refrigeration is in the method in order to maintain consistency with the sample handling specifications of the boilers and industrial furnaces standard. Recent samples collected from electroplaters seem to suggest that part of the sample (if refrigerated) may be lost to the walls of the collection jar, but whether or not this is actually true is still indeterminate.

Page 6f2265, paragraph 10.1 says the pitot tube shall be calibrated. During the development of the chromium standard, no pitot tubes were calibrated and the pitot tube coefficient was assumed to be 0.84. Since this is a concentration standard, it is not necessary to calibrate the pitot tube, nor is calibration necessary for an approximate (and optional) mass emission rate. Experience shows that the stack temperature will remain constant across the duct and before and after velocity traverses are redundant. The pitot coefficient will make no difference in calculating point sample times since the square roots of the velocity pressure readings are used for that purpose. All that is necessary is that the pitot be properly constructed.

A serious problem exists on page 62267 in calculating the chromium concentration in milligrams per dry standard cubic meter (12.5, 12.6, and 12.7). Determining this concentration is the whole point of Method 306-A. The revised method has made this determination more difficult and also is incomplete. Paragraph 12.7 goes to the trouble to tell how to convert micrograms to milligrams by dividing by 1000, but there is no conversion of cubic feet to cubic meters. Dry standard cubic feet should be divided by 35.31 to get cubic meters. Most sampling in this country is done in cubic feet, but the allowable concentration is in milligrams per dry standard cubic meter for electroplaters. Paragraph 12.7 also mentions micrograms per dry standard cubic foot. This is a mixture of English and Metric units, and this policy was dropped in 1977 by the Emission Measurement Branch. There is also a half page wasted on calculating a volumetric flow rate. The standard is a concentration standard, not a pounds per hour standard. Paragraphs 12.8 through 12.11 are non-productive and show a lot of effort put into something that is completely unnecessary.

The preceding discussion has presented some (but not All) of the problems with revised Method 306-A. It is one of the poorest documents to be written by the Emission Measurement Center of the Office of Air Quality, Planning, and Standards, in Research Triangle Park, NC. It is filled with needless material, calculation mistakes, and shows a lack of knowledge of both the method and the standard. This version of the method should be replaced with the original version until personnel who are qualified could make some additions that are improvements.

It is not difficult to criticize a piece of work that is as poorly done as the latest version of Method 306-A. Aside from correcting the multitude of flaws in the October 17, 2000 version, what improvements could be made in the method? Here are four:

First, the use of Method 306-A for systems that have dilution air should be approved. This was supposed to have been done back in 1997 but the Agency never got around to it.

Second, the method for sampling multiple ducts to a control device where some of the ducts contained dilution air was cumbersome to use and required extra long sampling times. Is there another way to sample these systems without the excessively long sample times?

Third, there are processes such as reverse etching that produce chromic acid mist and the mist is also routed into a control device that controls plating emissions. Should the reverse etching gas streams be considered process air or dilution air?

Fourth, how should a cyclic process be sampled? An example would be a process where the plating time to finish a part was less than the time required to change the finished part for another part to be plated. Is it possible to sample this type of cyclic operation without using an excessively long sampling time?

It is difficult to say how long the EPA will take to correct the current version of Method 306-A. If the need arises to perform a test using Method 306-A before the method is corrected, the following recommendations may help:

1. Work with state or local regulatory personnel.
2. Forget the by-pass valve; it is useless. Use a power strip with a rocker switch to start and stop the train.
3. Perform all runs in a single day.
4. Use laboratory grade 0.1N sodium hydroxide to rinse the nozzle, tubing and Mason jars.
5. Omit the cotton ball from the third impinger and fill the Mason jar about half full using 6 to 16 mesh silica gel.
6. When recovering the sample, rinse the tubing and nozzle 3 times in each direction. Use the same procedure on the connecting tubing from the first to the second impinger.
7. As soon as each sample is collected, refrigerate it until it reaches the laboratory. This may help the platers.
8. Construct the pitot tube properly but do not bother with calibration.

9. When doing calculations to determine the milligrams per dry standard cubic meter, be sure to divide dry standard cubic feet from the dry gas meter by 35.31 to get dry standard cubic meters if sample collection involves using a meter that records volumes in cubic feet.

CONCLUSION

Hexavalent chromium is one of the deadliest carcinogens in the environment. If the plating industry is to be regulated by U.S. EPA standards, it has the right to expect sampling methods that are fair, accurate, and have been developed by qualified personnel. This is the AESF/EPA Conference for Environmental Excellence. The current version of Method 306-A does not qualify as excellent. The general public, the platers, and the American taxpayers deserve better than the current version of Method 306-A found in the October 17, 2000 FEDERAL REGISTER.

AESF WEEK

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A Study of Wear Resistance of a New Cr Replacement: An Electrodeposited Ni-Co-X Alloy
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Overview of U.S. HCAT Technology Insertion Program on Qualification of Thermal Spray Coatings as Replacement for Hard Chromium Plating on Aircraft Components
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Improving Ion Vapor Deposition of Aluminum
Lisa Cato & Melissa Klingenberg, Concurrent Technologies Corp. (CTC), Edgefield, SC & Johnstown, PA, respectively

Alternative Coatings for Wear & Corrosion: The Electrospark Deposition Process
Roger N. Johnson, Pacific Northwest National Laboratory, Richland, WA

Designing Environmentally Safe Compounds for Mass Finishing

Andrew Kuuttila, Chemist, Hammond Roto-Finish, Otsego, MI

Mass finishing compounds have very specific functions. These include cleaning and degreasing, burnishing, surface improvement, deburring, descaling and inhibiting. To carry out these functions, mass finishing compounds must have certain chemical and physical properties. Many times, however, compounds can be designed with environmentally safe components that can offer characteristics comparable to traditional compounds. In addition, some compounds can be designed to be recycled or reused, while others still can be designed to be treated more easily than traditional compounds.

For more information contact:
Andrew Kuuttila
Hammond Roto-Finish
610 S. Platt St.
Otsego, MI 49078

INTRODUCTION

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There are many concerns when designing compounds. Is the compound biodegradable? Is the compound water soluble? What is the pH of the compound? At what concentration is the compound used? What is the compound used for? What contaminants might be in the compound that would cause the effluent to be out of compliance with local municipality regulations? Can the compound be dumped down the sink?

The best way to answer these questions is to explain how compounds are used and why compounds need certain raw materials formulated into them. Once we know why a certain compound is designed the way it is, we can ask, “Is there a more environmentally friendly way to formulate the compound?”

COMPOUND FUNCTIONS

Of the functions compounds carry out, cleaning and degreasing is the most important since the part must be clean to successfully carry out other functions such as burnishing or deburring. There are two basic types of cleaning compounds – organic and aqueous. Organic cleaning compounds are those found in traditional solvent systems such as mineral spirits, chloroethanes, MEK, and acetone. These types of cleaning compounds are not soluble in water which offers great environmental and treatment concerns. Indeed, most of these organic cleaning compounds must be hauled away as hazardous waste.

Aqueous cleaning compounds are those that are water-soluble. These types of cleaning compounds usually are formulated with surfactants (Surface Acting Agents). Surfactants are usually large molecules with a hydrophilic (aqueous – water soluble) part and a hydrophobic (organic – oil soluble) part. The hydrophilic part allows the substance to be water-soluble while the hydrophobic end helps pull the oil soluble contaminant into the aqueous phase. Aqueous cleaning compounds can often be treated on site or sent to a municipal treatment center to be treated as water.

Aqueous cleaning compounds offer another advantage over organic cleaning compounds. They can be built with caustic raw materials which help clean oils from dirty parts. Some animal and vegetable fats and oils will react with a highly alkaline material to form a soluble soap. This is known as saponification. Many recent developments in synthetic oils make them react as animal or vegetable fats and oil and they can become saponified also. Not only is the oil gone, but soap is formed in the process adding extra cleaning ability. One downfall of saponification is that many soaps that are formed add extra foam to the system. The only cleaning mechanism offered by organic solvents is that of the solvent nature of the compound in dissolving organic contaminants.

Abrasive cutting, of which deburring, radiusing, and preplate refinement are major operations is another very important function of mass finishing. These compounds must be designed with lubricity and part impingement in mind. Many deburring compounds contain chelating agents to quicken the cut down process. Chelating agents chemically react with metal atoms to form complex, water-soluble ions. This is good for the deburring process but not good for the treatment process since once the chelating agents react with the metal atom, they don't like to let go.

Along with chelating agents, many abrasive cutting compounds contain lubricants or high-foaming surfactants to help cushion the mass to help the media produce a smooth mirror-like finish. In the abrasive cutting process the media acts like a grinding wheel or file to cut down the surface of the part. The compound must keep the media and part clean, while carrying the contaminants (oil, broken down media, and metal chips) away before they have a chance to redeposit on the part. Foam helps accomplish this.

In burnishing, like deburring, the compound and media work in unison to provide a smooth and shiny surface of the part. Most burnishing processes utilize steel media and acidic compounds. Metals tend to get brighter, the more acidic the compound. However, if the compound is too acidic, the process becomes too reactive and an oxide of the metal can occur causing tarnish or darkening of the part.

Finished parts usually are very susceptible to rusting and oxidation processes. As a consequence an inhibiting compound must be used to slow down the damaging reaction. Many inhibiting compounds work by either slowing down the oxidation process or by redirecting it. Organic inhibiting compounds coat the part to keep moisture off. Parts must be dry for organic inhibiting compounds to work optimally; if water is trapped under the oil, rust can occur. Aqueous inhibiting compounds are more affected by humid conditions. Organic inhibiting compounds usually give longer protection but must be removed before any subsequent processes are performed on the parts.

COMPOUND CONCERNS

The biggest concern of vibratory compounds is the pH of the solution. Most vibratory compounds are designed to be used at 1-10%. In addition, for some processes a very low pH or a very high pH is required to carry out the function. To get a compound to have a pH range of 4-4.5 at 1%, the concentrate may have a pH reading of 3 or below. Likewise, to get a cleaning compound to have a pH of >10 at 1% the concentrate pH may approach 14. Most municipalities require that effluent streams be between pH 6 and pH 9. It is obvious then that many waste streams would have to be neutralized to be sent to the waste municipal treatment facilities even if no other contaminants were present.

Another concern of vibratory compounds is the foam level of certain compounds. As stated before, many deburring compounds are built with high foaming surfactants to help cushion the mass to provide a smooth finish. The foam in the waste stream can cause excess air into the water adding to treatment woes for the municipal treatment facility as well as cause general cleanup problems if the foam spills over the machine onto the floor.

Chelating agents are added to many vibratory compounds. Chelating agents hasten the deburring, cleaning, and burnishing processes by chemically reacting with metal atoms to form water-soluble complex molecules. The concern of chelating agents is at the treatment step for the waste stream either onsite or at the municipal treatment center. Some compounds can be formulated with nonchelating agents and be very effective. However, generally, nonchelating compounds do not work as quickly or give as good luster or shine.

Another concern of vibratory compounds is their form. Compounds come in three forms solid, liquid and paste. Solid compounds are formulated as comparable formulas to liquid compounds or as a mix of compound and an abrading species. The biggest concern of solid compounds is that they add particulate matter to the waste stream. Also, they can plug drains and lines as they build up with extended use.

Pastes are in between solids and liquids. They are designed as a mixture of liquid and solid and contain suspended abrasives or emulsified polishing agents. Pastes are normally used in fine polishing operations. Pastes, like solids, add considerable particulate matter to the waste stream and tend to plug drains and hoses.

Most liquid compounds are designed as pure, homogeneous solutions, while some liquid compounds are emulsions or dispersions. Liquid compounds are the most popular form of vibratory compounds because of their ease of handling and the lack of their interference in waste streams. The challenge is to design homogeneous liquid compounds that are effective for the desired end result.

WASTE TREATMENT

All vibratory processes generate wastewater. The process, in conjunction with the various government guidelines and regulations determines how the spent fluid must be handled. The vibratory compounds, with the exception of their pH level cause minimal influence on the waste stream. It is the presence of dissolved metals, dissolved solids, and emulsified oils which can make the effluent stream out of compliance of discharge codes.

The treatment of a waste stream can vary from very simple as evaporation or settling to very complex including chemical treatment and ultra filtration. Settling tanks allow a given retention time for the spent fluid to release either oils, which can be skimmed or solids which fall to the bottom of the tank. Settling tanks are usually a part of every waste treatment setup. Sometimes, however, if there are a large number of solids, the entire waste stream can be handled as a slurry and the entire stream can be treated without settling out the solids beforehand.

There are several onsite treatment options depending upon level of treatment desired and end use of the treated water. The type of media used in the process also has a significant impact on the treatment process. For example, if a process is utilizing ceramic media, the particles added to the waste stream from the wear of the media would have to be calculated into the waste treatment procedure. There are additives that can be added to the waste stream and coagulate the particles. The coagulated particles could then be more easily filtered from the stream leaving a clearer fluid. The coagulated material many times is non hazardous, but would have to be tested to make sure it could be sent to a landfill or handled as hazardous waste.

Waste streams containing dissolved metals are more complicated to treat than waste streams with particulate matter in them. Most metals however, will drop out of the solution when the pH is adjusted to an appropriate level and an additive which precipitates and flocculates metals is added.

If a higher level of purity is desired, sub micron filters can be used. These filters can be as fine as molecular weight levels and actually separate the solids as well as emulsified oils from the effluent stream. This is known as ultra filtration and is quite common in the reuse technology. Membrane filtration can be expanded even farther to reverse osmosis in which the filter media will only allow a molecular weight of water or less through the system. The system is used primarily to treat water to drinking standards and is usually not required at the industrial level.

CONCLUSION

Vibratory compounds are necessary in many industries to help deburr, clean, burnish, and improve surfaces. All vibratory processes produce waste streams. It is through selection of vibratory compounds and treatment processes that the negative effective of vibratory compounds can be minimized. Many vibratory compound waste streams can be treated with standard treatment procedures. Many times with appropriate treatment procedures and pH adjustment the waste stream will be compliant with government regulations and guidelines.

Organic compounds are still used somewhat-mostly in solvent cleaning systems. Sometimes organic compounds are necessary to carry out the specific task. Organic compounds, however, are harder to handle as waste. Many times the only alternative is to have them hauled away as hazardous waste. Aqueous compounds are finding more uses in industries as cleaning/degreasing, deburring, descaling, or inhibiting compounds. They can be very effective while still remaining environmentally friendly. Many times, aqueous waste streams can be treated onsite to be reused or sent to municipal treatment centers. Another option is to evaporate the water out of the waste stream to reduce the volume by 90% and send the remaining out to be disposed of as hazardous waste.

The Road to a Cyanide Free Plating Shop

Glen H. Graham, Oklahoma City Air Logistics Center, Tinker AFB,OK

Beginning in May of 1989 a plan was initiated to eliminate the use of cyanides in the Plating Shop at Tinker AFB, OK. We were using cyanides in cleaners, stripping solutions, cadmium plating, copper plating and silver plating. We have successfully accomplished the last hurdle this year silver plating. This paper will detail the implementation of each successful substitution along the road to a cyanide free plating shop.

For more information, contact:
Glen H. Graham, Chemical Engineer
OC-ALC/LPPEE
3001 Staff Drive 2B93
Tinker AFB, OK 73145 – 3034
Tel: 405-736-2018
E-mail: Glen.Graham@tinker.af.mil

The Oklahoma City Air Logistics Center (OC-ALC) at Tinker AFB, OK maintains a large family of aircraft and gas turbine engines and operates one of the largest plating shops in the Department of Defense. Finishing services include hard chrome, nickel (hard and soft), electroless nickel, silver, copper, abrasive particle and zinc/nickel plating. We have chromate conversion coating of aluminum, magnesium, Ion Vapor Deposited Aluminum (IVD), Type I, II and III anodizing, and black oxide coatings. Also, we have a large stripping process line for plating and plasma spray coatings and some specialty etching solutions.

In May of 1989 the DoD held a joint workshop in Dayton, OH of all Armed Services engineers and chemist involved in repair / overhaul processes that used chemicals. The intent of the workshop was to identify those steps necessary to reach an absolute minimum usage of hazardous materials in plating, cleaning and stripping processes and to eliminate duplication of pollution prevention among the Services by sharing in our efforts. These substitutes were to be equivalent or superior to the current processes and result in at least a fifty percent reduction in three years (1992) or elimination if possible. The plating processes group came up with three areas of environmental concern; cadmium, chrome, and cyanide.

We did a survey of how much cyanide, cadmium, and chrome we had used in 1988. We decided to start on the cyanide reduction first. We were using cyanides in alkaline cleaners, in strip solutions, and cadmium, copper, and silver plating. The results for the cyanide use are shown in Table 1 and it was the beginning of our road to cyanide elimination on our shop. Our ultimate goal was to continue reducing cyanide until it was all eliminated even though our initial challenge was a 50% reduction. Since our immediate goal was to reach a 50 % reduction, we began our road in the areas that would result in the biggest reductions the fastest; alkaline cleaning and stripping.

The first step down the road was the biggest impact, alkaline cleaners. In working with our vendors we had already reduced the cyanide in our electrolytic alkaline cleaners from 14 ounces per gallon to 8 ounces per gallon. One of our vendors had a cyanide free alkaline cleaner which was normally used at 190° to 200° F as a soak cleaner, but they felt it could be used at 130° to 140° F as an electrolytic alkaline cleaner. We consider our sulfamate nickel line to be our most sensitive process so we replaced one cyanide cleaner tank with the non-cyanide. We keep close record of parts going through the nickel plating tanks using the non-cyanide. We processed the parts with our normal process for 6 months without any plating failures. Since we could not tell any difference in performance or quality of the end nickel plating, we decided to replace the remaining cyanide cleaner tanks. As our other 6 tanks became ready for a new make up, they were then replaced with the non-cyanide cleaner. One of the big facts that contributed to us being able to make this change is that the gas turbine engine parts that we plate are initially cleaned when they first come in for overhaul. The success of this change was reported to other Air Logistics Centers, DoD repair centers, and Original Equipment Manufactures (OEM). The non-cyanide cleaner was added to the Qualified Products List (QPL) in the Technical Orders (T.O.) for repairs. Since our first non-cyanide cleaner was proven satisfactory, we have found other suppliers that meet the performance requirements, however they were more difficult to maintain for our Solution Maintenance crew and have not been used. AESF policy does not allow vendors products to be mentioned in papers presented at their conferences. Anyone interested in specifics will have to contact me later. This step down our road to being cyanide free gave us a 49.3 % reduction.

The next step was rather a small one. We had a few tanks with a low amount of cyanide in rinses. We simply eliminated the cyanide in the rinse water and rinsed more thoroughly before going to next process step. Since this step was mainly to keep from contaminating an alkaline bath with acid, good rinsing accomplished the purpose.

Our third step, the replacement of the cyanide nickel strippers, was our second largest step. These strippers are used to remove nickel/alumunide and tungsten carbide plasma sprays, nickel/cadmium and nickel plating. It was made relatively easy for us though since San Antonio Air Logistics Center had just received the final report on a project that they funded to find non-cyanide nickel strippers. Their report showed several strippers that worked successfully, but they were unable to use them since they were not approved alternates in their T.O.'s. Since our Material Management Engineers had authorized Process Engineering to make changes in T.O. solutions that did affect the form, fit or function of the parts, we were able to try some of the candidates from the report. We found that some of the strippers required additional steps and the personnel on the strip line did not like the additional work. After 6 months of production processing of parts, we were able to select one meet all our requirements and most closely gave results similar to a cyanide stripper. We completed our implementation of our first three steps down our road by the end of 1990. At that time we had surpassed the DoD's initiative of 50 % reduction by achieving a 73.8 % reduction. Since our initial qualification we have one solution that is equivalent or superior to our first source.

Our fourth step, cadmium cyanide, was much more difficult to take than our previous steps. This step meant that we could achieve two goals by eliminating cadmium and cyanide at the same time. The difficulty lay in the long-term use of cadmium and nickel/cadmium by the DoD for corrosion control. This meant coming up with an alternate or alternates that would meet low temperature (below 400°F) as well higher temperatures (up to 900°F).

The Air Force began looking for cadmium and nickel / cadmium alternatives in the mid 1980's. Ion Vapor Deposited (IVD) aluminum is a process where aluminum wire is melted in a vacuum and catholically deposited on the parts. LVD aluminum was found to be superior to cadmium in corrosion tests. Many of the Air Logistics Centers installed the IVD aluminum units. We began operating ours in 1987, but we found a lot of resistance to change. Also, the IVD aluminum could not be used on tread items or internal diameters. We were able to get engineering approval for IVD aluminum on several parts. With cadmium plating also being approved we found that the parts ended up going back to plating instead of the IVD aluminum. We really were not able to reduce the cadmium usage this way.

We have used electroless nickel plating on several parts for years for corrosion protection. These were primarily non-rotating and non-threaded parts from aircraft. These applications gave us ample experience in using electroless nickel for corrosion control on parts. This provided us with another option for complex part corrosion control.

In 1991 the use of alkaline zinc / nickel coatings as cadmium replacement in automotive applications was spreading in Europe, Japan and the United States. A lot of testing was done, which showed that it was very superior to cadmium or nickel cadmium coatings.

We had meetings with several engineers responsible for aircraft and turbine engine parts, but they felt that there were too many engineers involved for them to get the changes authorized for all parts even though we could show equal or superior coatings to cadmium or nickel / cadmium coatings. We came to the conclusion that the only way to get out of any type of cadmium plating was to eliminate the option. At OC-ALC we were able to obtain upper management authorization to depose of our cadmium plating capabilities and offer the responsible engineers for parts require cadmium plating coatings four options; (1) IVD aluminum; (2) zinc / nickel, (3) electroless nickel, and contracting out.

In November of 1991 we deposed of our cadmium plating tank capability and by February 1992 all parts had been converted to one of the first three items. All our test data obtained a year later showed that in every respect the alkaline zinc / nickel exceeded cadmium and most of the nickel / cadmium requirements and our three coating options provide superior corrosion protection for the parts. Thus we eliminated cadmium usage and reduce our cyanide by 79.4 % of our 1988 level.

Our fifth step down, copper plating, our road was another small one and relative easy to implement. A new alkaline non-cyanide copper plating solution came on the market in 1993 and was proving to work well in production environments. We were able to depose of our copper cyanide bath, leach the tank, bring up the new solution and use the same rectifier. We have used the solution as a copper strike or copper plating without having to change our plating parameters. The solution has been found to be long lasting with our normal solution maintenance procedures.

Our sixth step, silver stripping from steels not stainless, proved to be a little more complex than the previous steps. Here again we had the benefit of some work done at SA-ALC since they had implemented a non-cyanide silver strip and were operating it. We obtained the same solution and tried to use it. We found excessive smutting on the parts and it was unacceptable for production. The supplier was unable to help us since they manufactured it for chrome stripping. Until we were able to talk to the man actually using the strip at SA-ALC, we could not figure out how to make it work. We found that there were a few simple changes that had to be made that were different from the way we operated our cyanide strip. Once the correct procedures were put into production we able to eliminate one more cyanide solution. By the end of 1995 we had traveled down our road to being cyanide free to a 91.6 % reduction from our base line.

Our last step, silver plating, proved to take the longest to accomplish. Initially we minimized our operating tanks to one silver strike and one silver plating solution which reduced our cyanide usage to about 3000 pounds a year and brought to a total of around 95 % reduction from the 1988 baseline. After this accomplishment in the early 1990's, we ran into difficulty in finding a non-cyanide silver plating solution that would operate on a daily basis. A testing program run for us showed one solution which meet all our physical requirements, but production could not maintain the solution as needed for daily plating. At that time we came to a stand still on final elimination of cyanides.

In 1999 when the manufacturer of the copper strike / plate solution that we are using began marketing a non-cyanide silver solution. We tested it and found it to work satisfactorily, however we did not implement into production because of renovations being done on the silver plating line. In June of 2001 we began using the non-cyanide silver plating solution. It does not plate as simply as cyanide silver and it has a slightly different appearance, but it is manageable to obtain 99 + % silver on a daily basis. The main problem encountered in switching to the non-cyanide solution was the difficulty in plating thickness over 0.001 inches per side. We worked on this for sometime and came up with a very involved process, which extend our plating time. However on inventorying the parts that we plate we found only two (2) parts that had this requirement. We requested an engineering change to the Technical Order requirement to allow build up using soft nickel or copper plating with less than 0.001 inches of silver plating. This allowed the functional surface of silver plating while restoring the dimensional requirements. Another is the anode to cathode ratio is important. The solution works better with an even or higher ratio of cathode to anode. The component that regulates dissolving of the anode must be added daily to maintain the silver concentration. The solution is more conductive than a silver cyanide solution so lower amps per area have to be used and different times. It is enough different to cause some operator resistance at first. As we use it, daily we are becoming more proficient in obtaining consistent good plating from this solution and the operators are able to produce parts satisfactorily.

So twelve years after beginning our journey down the road to a cyanide free plating shop, we have meet and exceed the goals given us in Dayton in May of1989. We have met our personal goals for cadmium plating and cyanide usage by eliminating both. What is next for us is the third component of the Dayton workshop, chrome plating. We have met the 50 % reduction goal mainly through a reduction in workload, but the complete elimination of chrome plating will be a difficult task. We expect to see a further reduction by implementing HVOF plasma spray coatings. These coatings are limited to line of sight applications. This could result in a 60% reduction of our current chrome plating workload. A task has been undertaken to try and find a plating solution for the remaining non line of sight parts.

This has been an interesting journey for us. Even though we know the cyanide technologies are simpler to operate and more forgiving of operator errors, we have found equivalent or superior products to do the same function. We have seen our plating and finishing industry lead in all environmental areas. Great strides have been made in pollution prevention, environmental controls, and water use minimization. As we continue our journey, it will be interesting to see where the road to future leads us.

TABLE 1

CYANIDE USAGE BEFORE FY89

USE	IN TANKS	USEAGE FOR YEAR	TOTAL/USE
1. Alkaline Cleaners	7,800 lbs.	5,000 lbs.	32,800 lbs.
2. Nickel Strippers	4,700 lbs.	11,300 lbs.	16,000 lbs.
3. Silver Stripping	1,500 lbs.	6,600 lbs.	8,100 lbs.
4. Silver Plating	2,350 lbs.	2,750 lbs.	5,100 lbs.
5. Cadmium Plating	1,700 lbs.	2,000 lbs.	3,700 lbs.
6. Copper Strike/Plate	200 lbs.	300 lbs.	500 lbs.
7. Cyanide Rinse	100 lbs.	200 lbs.	300 lbs.
TOTALS	18,350 lbs.	48,150 lbs.	66,500 lbs.

A Study of Wear Resistance of a New Cr Replacement: An Electrodeposited Ni-Co-X Alloy

Wenhua Hui Shining Surface Systems, Inc, Shining Surface Systems, Inc. NJ USA
Fanjuan Meng, Tsinghua University, Beijing, P. R. China
Kaiyuan Ji, Tsinghua University, Beijing, P. R. China
Lei Li, Tsinghua University, Beijing, P. R. China y

Abstract

Friction and wear tests have been conducted to determine the wear characteristics of a new chromium replacement, an electrodeposited Ni-Co-X alloy, without lubrication at the contact surface. The results show that the wear resistance of this alloy layer was superior to that od an electrodeposited chromium layer under the same conditions. The microstructure and surface morphology of this allay before and after the wear process were analyzed by transmission electron microscopy and scanning electron microscopy. The mechanisms of its excellent wear resistance are discussed.

Keywords: Wear resistance, without lubrication, chromium replacement

For More Information, contact:
Wenhua Hui
Shining Surface Systems, Inc.
20 Lexington Avenue
Suite 2
Ewing, NJ 08618
Tel: 609-883-8910
Fax: 609-883-4470
hui@surface-systems.com

1. Introduction

Chromium plating coating has been widely used to increase the surface wear resistance of materials. In the chromium plated coating, atoms are bound closely together owing to the relatively small radii of chromium atoms and the strong interactions between 4d electrons and 3d electrons. These mechanisms create a relatively high level of hardness and wear resistance. However, as the temperature increases, thermal motion of atoms weakens the bounding strength, and thus the hardness and wear resistance of the plated coating decrease. In order to overcome this disadvantage, and more importantly, to avoid harm of electrodeposited chromium for human health and environment, we developed a new chromium replacement coating, - Ni-Co-*X* Alloy. This coating has a beautiful appearance and excellent corrosion resistance. In this paper, we conducted comparison experiments of wear under high speed and heavy load without lubricant. By microstructure analysis before and after wearing, the mechanism of excellent wear resistance of Ni-Co-X alloy coating will be discussed.

2. Experimental details

We carried out dry rolling-sliding wear tests on an Amster wear test machine. The counterpart materials were a 52100 bearing steel with a hardness of Hv750 and roughness Ru=0.17ìm. The test sample wheels were 50 mm in diameter and the counterpart 38.5 mm, with 10 mm wheel thickness, and its surface roughness is 0.16-0.18ìm. During wear testing, the test sample rotates at 200 rpm against the counterpart upper wheel at 180 rpm. This gave a sliding ratio of 30% at contact motion. The applied loads were 98, 157 and 392 N, respectively, corresponding to a maximum Hertzian stress of 157, 199 and 315 Mpa.

We weighed the samples after each period of testing using a balance accurate to 0.1 mg. The results given here are the average of three tests.

The torque induced by the frictional force was indicated by the swung angle of a pendulum and was recorded from a scale during testing. The coefficient of friction was calculated from the measured value of torque.

We analyzed the worn surface of the test samples and the counterpart steel wheel, transverse and longitudinal sections of the test samples, and the collected wear debris using scanning electron microscopy (SEM) with energy dispersive x-ray analysis (EDAX), and x-ray diffraction analysis (XRD) with copper K2 radiation. Transmission electron-microscopy (TEM) was employed to study the change in the microstructure alloy plated coating before and after wearing testing.

Micro-hardness indentations were made into the surface and cross-section. The measurement was performed with a 50g load for 15 seconds along the wear track and the hardness was calculated by averaging five measurements.

3. Results

Fig. 1 shows the wear rates of both the electrodeposited chromium coating and the electrodeposited Ni-Co-*X* alloy coating under different applied loads. It can be seen that the wear rate has been reduced for Ni-Co-*X* alloy in all the cases. The wear rate for electrodeposited chromium increased quite significantly with increasing applied load, while that of the Ni-Co-X alloy coating increased only slightly. It appears that at heavy load, the wear resistance of this alloy coating is much better than that of a chromium-plated coating.

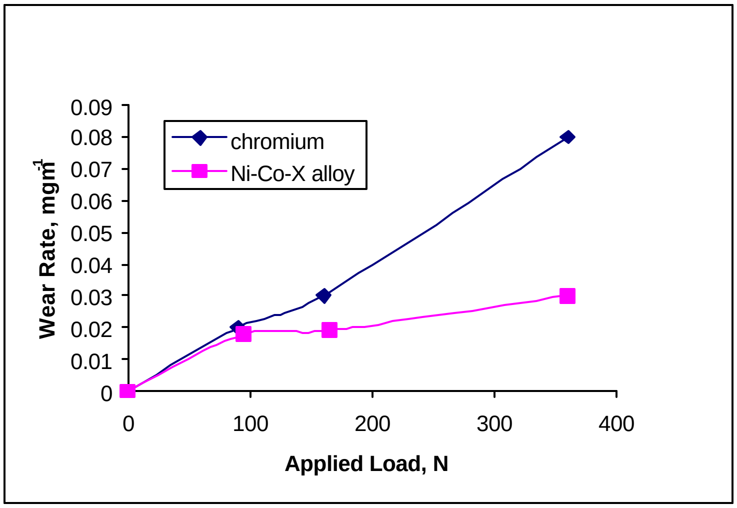


Fig.1- Wear Rate of Chromium and Alloy Coating Samples under Different Loads

Fig. 2 shows that the friction coefficients of the electrodeposited chromium and electro-deposited Ni-Co-*X* alloy against the wear distance under the loads of 98 and 392 N. Generally, the friction coefficient of the alloy was close to constant throughout the wear testing, only the chromium coating's gets a little higher when heavy loads are applied. Clearly, the coefficient of friction for Ni-Co-*X* alloy is lower than that of chromium coating. The values for chromium coating and the alloy coating were about 0.18 and 0.12 respectively.

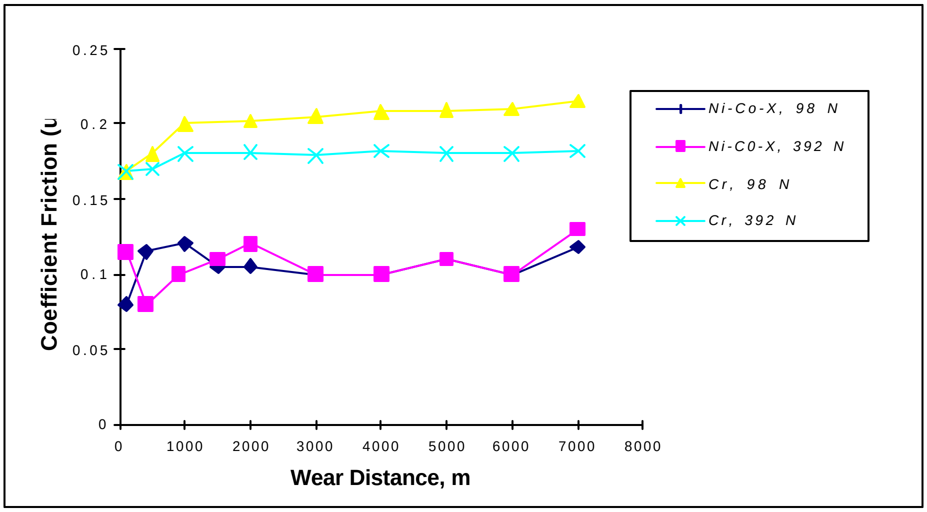
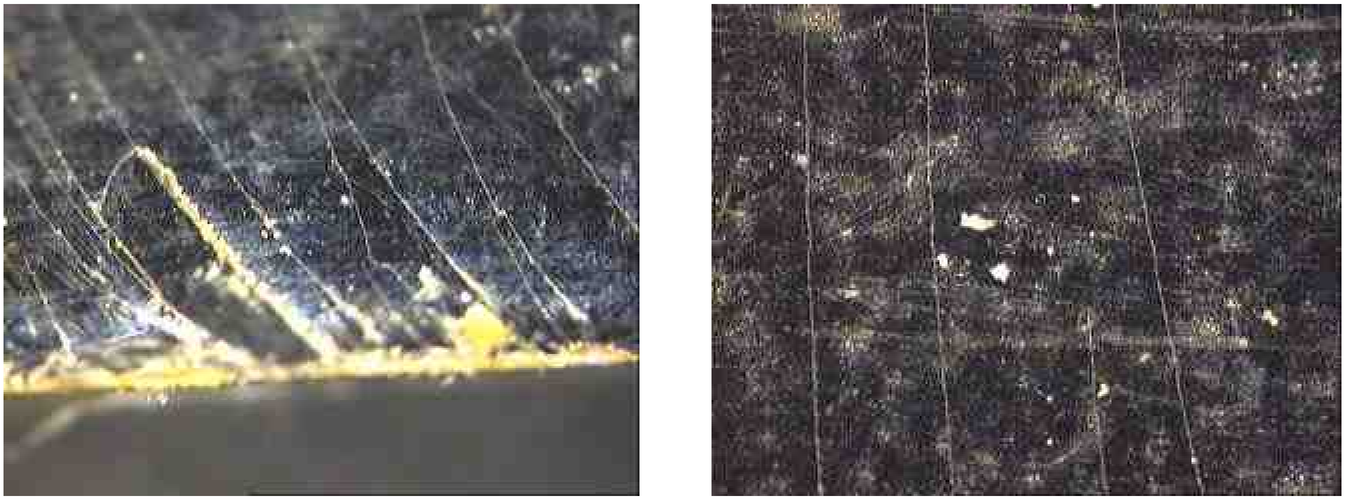


Fig. 2 – Friction coefficient of chromium coating and Ni-Co-X alloy against wear distance under the loads of 98 and 392N

After wear testing, examination of sectional samples showed that a deformed layer was present at the worn surface area for all samples. But the deformed areas in the alloy coating samples were smaller than in the chromium coating samples *Fig. 3(a, b).*

Surface and sub-surface cracks were observed in the transverse and the longitudinal sections of the specimens. Cracks could be found both in the deformed and the highly deformed areas, and along the boundaries among them. *Fig. 4* shows the sub-surface cracks in the chromium coating and alloy coating samples after wear testing under 392 N. Sub-surface cracks in the worn chromium coating are easily found. Under the applied load of 392 N, sub-surface cracks were found up to around 40 ìm deep from the surface in the chromium. But subsurface cracks in the alloy coating samples were shallower and cracks as deep as the one shown in *Fig.* **4(b)** (about 10 ìm in depth) were rare.



(a)

(b)

Fig. 3 – Sections of the chromium (a) and Ni-Co-X alloy (b) after wear testing on the 392 N, showing the deformed areas

In *Fig. 4(a)*, it shows that cracks are at a similar depth level and are capable of joining among one another.

(a)

(b)

Fig. 4 – Sections of the chromium (a) and the Ni-Co-X alloy (b) after wear testing under 392 N, showing sub-surface cracks.

We discovered the surface of the counterpart steel wheels with a layer of the testing material shortly after starting the wear test. This means that materials have been transferred from the testing specimen to the counterpart wheel. This was confirmed by the weight grain of the steel wheels and by EDAX analysis of their surface. After wear test, all the counterpart steel wheels showed a positive weight gain of a few milligrams, as shown in *Fig. 5*. From this Figure, we conclude that, for the same applied load, a larger amount of the chromium coating than the alloy coating was transferred. We also noticed that the amount of materials transferred to the steel wheels increased with the applied load.

The worn surface of the alloy coating and chromium coating are not smooth. The average roughness (Ra) under the applied load of 98, 157 and 392 N are respectively 0.15, 0.17 and 0.19ìm for the alloy coating and 0.20, 0.25 and 0.55 ìm for chromium coating. The interesting phenomenon is that the surface roughness is reduced after wear under the lower applied load (98 N). Same results have happened in industry testing.

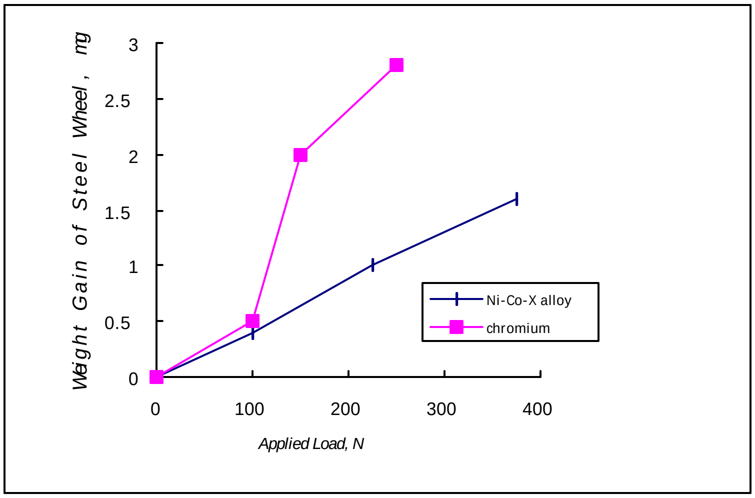


Fig. 5 – Weight gain of counterpart steel wheel after wear test against chromium coating and Ni-Co-X alloy under different loads

4. Discussion

The above results showed that the mechanisms involved in the dry rolling-sliding wear of chromium and alloy coating against steel include both adhesive and delamination wear. Wear debris forms in two ways: Direct formation from the test specimen by delamination wear through the formation extension and linking up of sub-surface cracks and indirect formation. The latter involves the transfer of the material from the test sample to the counterpart wheel by adhesion. Transferred material work-hardens and detaches from the counterpart wheel.

When v = 31m/min(200rpm, Ö50mm), L = 392N, flash temperature $T_f = 1400 - 1500$ °C. At this time, the material becomes softer and its strength become lower, the coefficient of friction and wear rate increases. *Table 1* shows the variation of hardness of both the alloy coating and chromium coating at different temperatures, after 200°C the alloy coating is obviously better than the chromium coating, and at 600°C, the alloy coating can still maintain a considerably satisfactory hardness, while the chromium coating decreased drastically.

Table I

Temp. Coating	Room Temp.	100°C	200°C	300°C	400°C	500°C	600°C
Chromium	950	920	900	770	600	420	350
Ni-Co-*X*	910	910	1120	900	780	710	630

Archad believed that for pure metal adhesive wear rate ω had the following relationship with hardness:

$$\boldsymbol{w} = \frac{kw}{3H} \tag{1}$$

where ω is adhesive wear rate; k is coefficient of wear, w is loads and H is hardness of material.

This is, with the increase of loads, the friction heat increases, and the material becomes softer, resulting in the decrease of hardness and increase of adhesive wear rate. This is why the adhesive wear rate of alloy coating is much better than that of chromium coating samples.

In delamination wear, the effect of friction coefficient on crack nucleation and crack propagation has been discussed in Ref.(4.5). Their work has shown that the depth of void nucleation increases with both normal load and friction coefficient and that the characteristic crack propagation depth and propagation rate also increase with increasing coefficient of friction. Therefore, higher friction coefficient will lead to higher wear loss of the chromium coating.

5. Conclusion

From the above results and discussions, we conclude that this Ni-Co-*X* alloy coating has the following characteristic on the dry rolling-sliding wear behavior against bearing steel (52100) in comparison with chromium coating.

a. Ni-Co-X alloy coating has very good resistance to delamination wear. It has low friction coefficient and excellent microstructure are why it is.
b. Under non-lubrication wear, friction heat softens chromium coating. The reason that chromium's wear rate are greater than that of the alloy coating is that chromium coating adhesive wear have seriously taken place.

Fig. 6 – Transmission electron micrograph of the Ni-Co-X alloy as plated.

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Overview of U.S. HCAT Technology Insertion Program On Qualification of Thermal Spray Coatings As Replacement for Hard Chromium Plating on Aircraft Components

Bruce D. Sartwell, Naval Research Laboratory, Washington, DC

The U.S. Hard Chromium Alternatives Team (HCAT) is currently executing projects to qualify HVOF thermal spray coatings (principally WC/Co) as a technologically superior, cost-effective alternative to electrolytic hard chromium (EHC) plating that is extensively used in manufacturing and repair of aircraft components. There are five projects, each relating to specific types of components: Landing Gear, Propeller Hubs, Hydraulic Actuators, Helicopter Dynamic Components, and Gas Turbine Engine Components. For the latter, several types of plasma-sprayed coatings are also being investigated. Using recommentations from aircraft/component manufacturers and military engineers, Joint Test Protocols (JTP) have been established that delineate all of the materials and component testing required to qualify HVOF coatings. Standards and specifications for deposition, grinding and stripping of the thermal spray coatings are also being developed. This presentation will provide a summary of each of the JTPs and the results obtained to date for testing/evaluation of the coatings, plus the status of actual technology insertion at U.S. military aircraft repair depots. In general, thermal spray coatings have demonstrated superior fatigue, corrosion and wear properties to the EHC coatings, with a few exceptions that will be described.

Paper not available for publication.

For more information, contact:
Bruce D. Sartwell
Naval Research Lab
Code 6170
Washington, DC 20375
Phone: 202-767-0722

Improving Aluminum Ion Vapor Deposition

Lisa Cato, Concurrent Technologies Corporation, Edgefield, SC, USA
Melissa Klingenberg, Concurrent Technologies Corporation, Johnstown, PA, USA

Many Department of Defense (DoD) repair facilities use IVD aluminum to replace cadmium electrodeposits. Chromate conversion coatings, which contain carcinogenic hexavalent chromium, are applied to the IVD coating to impart the necessary corrosion protection and lubricity. Elimination of the chromate conversion coating is desirable. *CTC* has incorporated a pulsed, high voltage power supply into conventional IVD equipment for the purpose of improving coating structure. This may allow a less corrosion resistant, non-chromate pretreatment to be applied, while maintaining or improving the overall corrosion resistance of the coating system. This paper will discuss a National Defense Center for Environmental Excellence (NDCEE) project that is investigating the use of such equipment, the test results to date, and the plan for validating its use and subsequent implementation into DoD facilities.

For more information, contact:
Lisa Cato
Concurrent Technologies Corporation (*CTC*)
100 *CTC* Drive
Edgefield, SC 29824
Phone (803) 637-2516
FAX (803) 637-2510

Introduction

Ion vapor deposition (IVD) of aluminum is a suitable cadmium replacement for many applications, but it does not provide the lubricity of cadmium, nor does it always provide sufficient corrosion protection due to coating porosity. To densify the aluminum coating and improve its adhesion to the substrate material, glass bead peening is often used. Subsequently, a chromate conversion coating is applied to impart greater corrosion resistance, lubricity, and provide a surface amenable to painting.

Conventional chromate conversion coatings use hexavalent chromium, a class one carcinogen. To ensure that mists containing hexavalent chromium are not released into the environment or pose a significant health risk to workers, regulations have been imposed by the Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA). The cost associated with maintaining compliance with these regulations is escalating. Many alternative non-chromate pretreatments have been investigated by private industry and the military, but with limited success.

An improved IVD aluminum process was demonstrated by ISM Technologies, a division of Cutting Edge Products, Inc., in conjunction with the former McDonnell Douglas Aerospace (now part of the Boeing Company). The coating, when combined with conventional chromating processes, showed significant improvement in corrosion resistance over conventional chromated IVD deposits. To implement the improved IVD aluminum process, existing IVD aluminum chambers are retrofitted with a pulsed high voltage power supply. The pulsed high voltage bias is applied to parts during deposition. The negative bias attracts any ionized coating material as well as gaseous ions from the surrounding plasma. Because the bias is a greater negative voltage than that used in conventional IVD processes, the ions experience a greater attraction to the parts and are accelerated at greater velocities. In theory, more momentum is transferred to the depositing coating, resulting in the collapsing of coating voids, which leads to a denser aluminum coating. The improved IVD process combined with a non-chromate conversion coating has the potential to achieve the same product quality as conventional IVD with a chromate conversion coating.

Project Overview

The scope of this project is to demonstrate the pulsed high voltage IVD system, and justify it as a cost effective, environmentally benign process that can eliminate glass bead peening and/or chromate conversion coatings on IVD aluminum. The new process must meet or exceed existing performance and operational requirements. Information obtained in the execution of this project is directly transferable to DoD repair depots using IVD aluminum coatings. It is anticipated that successful completion of this project will enable depots to

- Reduce the use of hexavalent chromium, leading to reductions in environmental, health, and safety costs
- Reduce labor costs, as associated with glass bead peening
- Reduce the generation of solid waste and its associated disposal costs
- Meet the corrosion requirements of the military
- Maintain or improve the component life cycle.

This project is being completed in four activities. The first activity of the project involved the identification of candidate components that are currently treated using conventional IVD. Environmental, health, and safety (EHS) costs and baseline process operations and costs for these components were captured. Specification and testing requirements based on military specifications MIL-DTL-83488, MIL-C-5541 and MIL-C-81706 were identified as well as additional tests necessary for *CTC* to establish a technical performance baseline. These tests include adhesion, corrosion, metallography, and thickness.

The second activity of the project involved identification of alternatives. Because there are many IVD aluminum systems used throughout DoD repair depots, improved IVD aluminum was identified as an alternative coating system through which large capital investments for new systems could be avoided while reducing environmental impact and production costs. To complement the improvements in corrosion protection, use of a non-chromate pretreatment is desired to obtain environmental improvements. Based on previous studies conducted at *CTC* as well as input from the Stakeholders, non-chromate pretreatments were selected for use in this project. Only those non-chromate pretreatments having shown some success will be tested on the improved IVD aluminum coating. *CTC* also performed a preliminary assessment of the production, quality, environmental, health, safety, and economic factors associated with implementing the non-chromate pretreatment alternatives identified. This information will be used for justifying the use of successful alternatives.

The third activity of the project involves demonstrations of the (1) improved IVD aluminum process and (2) the technology(ies) selected for the non-chromate pretreatments. Demonstration activities have been designed to confirm that the technology(ies) selected can meet depots' repair needs and requirements. Several sets of samples are being produced using conventional IVD aluminum and the improved IVD aluminum, with some panels being glass bead peened. Subsequently, these panels will undergo either a chromate or non-chromate pretreatment. The treatment matrix has been designed as follows:

Conventional IVD aluminum, glass bead peened, chromated
Conventional IVD aluminum, unpeened, chromated
Conventional IVD aluminum, glass bead peened, unchromated
Conventional IVD aluminum, unpeened, unchromated
Conventional IVD aluminum, glass bead peened, non-chromate
Conventional IVD aluminum, unpeened, non-chromate
Improved IVD aluminum, glass bead peened, chromated
Improved IVD aluminum, unpeened, chromated
Improved IVD aluminum, glass bead peened, unchromated
Improved IVD aluminum, unpeened, unchromated
Improved IVD aluminum, glass bead peened, non-chromate
Improved IVD aluminum, unpeened, non-chromate.

The conventional coatings will serve as baseline panels against which all other treatments will be compared.

Standard salt fog tests are being used to evaluate corrosion resistance, and a standard bend test is being used for measuring adhesion. Thickness, coating density, defects, and microstructure are being evaluated using a Scanning Electron Microscopy (SEM). The primary criterion for success is that the improved IVD coating combined with a non-chromate pretreatment must provide equal or greater performance than the chromated conventional IVD coating.

The fourth activity involves technology justification. Tools, such as cost-benefit analysis*, return on investment calculations, estimates of the potential reduction in the use and emission of hazardous materials, and estimates of product quality improvements will be used to obtain necessary cost justification data. This activity will be completed upon successful completion of the technical activities and will be captured in a Justification Report.

*Environmental Cost Analysis Methodology (ECAM^{SM}), Concurrent Technologies Corporation, Johnstown, PA.

Upon completing the four activities, *CTC* expects to continue its efforts through follow-on work, which may include component testing and/or additional testing such as fatigue, hydrogen embrittlement, torque tension, or other specialty testing.

Work Completed

Requirements Analysis Task

CTC personnel performed site surveys at Anniston Army Depot (ANAD), Jacksonville Naval Aviation Depot (NADEP JAX), and Oklahoma City Air Logistics Center (OC-ALC). The surveys were conducted to identify the parts being treated using IVD, the current IVD processing methods, including post-treatments (i.e., glass bead peening and chromate conversion coating), and the associated costs for treating the parts. It was determined that most parts at these facilities are constructed of 4340 steel and are engine parts. Specifically, the parts belong to the M48, M60, M80, F-15, F-18, B-52H, C141 and C18 weapon systems. The treatments applied to the parts typically follow Type I or Type II, Class 3 (0.001" thickness) IVD coating application specifications. Type I treatment involves IVD aluminum coating only, and Type II treatment involves a subsequent glass bead peening and chromate conversion coating. The costs obtained during the site survey will be used in the economic justification activity of this task. All information obtained during the site surveys was compiled into a Requirements Report.

Identify Alternatives

CTC procured a pulsed, high voltage power supply from ISM Technologies, Inc., a division of Cutting Edge Products. ISM fabricated and, working with *CTC* personnel, installed the power supply into the IVD system located in the NDCEE Demonstration Factory in Johnstown, PA. To accommodate the new ancillary equipment, software upgrades were performed to ensure that the system functioned properly with the new, as well as the old, IVD process. ISM provided *CTC* with training on the pulsed, high voltage power supply and the associated control system.

Concurrent with equipment procurement, *CTC* identified and evaluated non-chromate conversion coatings for use with the improved IVD system. Non-chromate pretreatment evaluation was based on past projects conducted by *CTC* and the DOD stakeholders. Once candidate treatments were selected, pretreatment vendors were contacted to obtain information related to their respective processes. Vendor-supplied data were organized into an Alternatives Report that provided a technical description of the process, material properties that can be obtained using the alternative, and advantages and limitations associated with each process. Three proprietary alternative conversion coatings** were selected for this project, in addition to a trivalent chromium pretreatment selected by Navy stakeholders.

Technology Demonstration

The test panels being used for this project are fabricated from 4340 steel to ensure that the coating/substrate interface is representative of that expected for components treated at the DOD facilities. Demonstration activities were designed according to a formal Demonstration Plan. This demonstration plan delineated (1) the activities necessary in demonstrating the conventional improved IVD process and each of the selected non-chromate conversion coating alternatives, (2) the activities necessary for developing the baseline, and (3) testing methods and procedures. Test matrices were created to ensure sufficient data was collected to qualify or disqualify the alternatives.

** Alodine 2000, Henkel Surface Technologies, Madison Heights MI
Rainseal^{TM}, Natural Coating Systems, LLC, Martinsville, Indiana
Sanchem's Full Process, Sanchem Inc., Chicago, IL

Although *CTC* has not completed the deposition trials for completion of the test matrix, *CTC* has performed many depositions in an effort to select processing parameters that provide the greatest improvements in coating structure, and, hence, corrosion resistance. The pulse frequency and voltage applied to the parts was varied during these trials. Coatings were deposited to a target coating thickness of 0.3 mils, and no glass bead peening or chromate or non-chromate pretreatments were applied.

Depositions were performed using 2.0, 5.0, 7.5, and 10.0 kV with pulse frequencies ranging from 1.6 to 15.0 kHz, using many combinations of voltage, frequency, and operating pressure. Operating pressures ranged from 1 to 8 mTorr.

Some technical obstacles were encountered and addressed during preliminary trials. Firstly, it was determined that a 15.0 kHz pulse frequency causes the amplitude of the control voltage to be reduced to a point where it can no longer switch the tube, causing uncontrolled pulsing. There are no plans to modify the electronics to provide for a reliable pulsing at 15 kHz. Because the equipment is very reliable up to 10 kHz and the preliminary coating structure and corrosion tests indicate higher pulse rates are not necessary, no further trials will be performed under these conditions. It also should be noted that researchers found that conventional, stainless steel, support bolts used on the parts rack cannot be used during the pulsed, high voltage process. Researchers found that the breakdown voltage of the insulators surrounding the bolts was exceeded at the higher voltages used during processing. Nylon support bolts provided a sufficient insulation path to ensure against short-circuiting during processing.

Samples produced during deposition trials were subjected to corrosion testing per ASTM B 117, where a 5% NaCl salt fog was used. Testing was conducted for 168 hours on the panels, and a standard IVD specimen was used as a baseline. Evaluations were conducted periodically throughout testing to determine the intervals during which white and red corrosion products appeared. Six specimens, representing 5 different processing conditions, performed better than the current IVD process, with varying degrees of improvement. However, in many instances another specimen from the same run performed worse than the conventional IVD process, indicating that the location where the panel is placed in the IVD chamber may have some influence on the coating structure and/or thickness. SEM analysis of the coating topography was performed, with significant differences being noted between conventional IVD coatings and all coatings produced using the pulsed, high voltage method (See Figures 1 and 2). Fracture analysis of the coatings is planned, and is expected to permit further discrimination between the coating trials performed. X-ray diffraction (XRD) was performed on a specimen from each trial. Although detailed analysis of the spectra has not been performed yet, it was noted that some of the coatings deposited by the pulsed, high voltage method displayed slightly broader peaks than conventional IVD, indicating increased disorder and/or smaller grain size. In addition, the different combinations of voltage and frequency produced differences in preferred orientation.

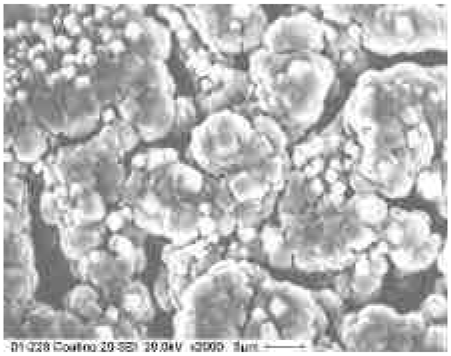


Figure 1. Conventional IVD Coating

Figure 2. Pulsed, High Voltage IVD Coating

Coating thickness was assessed using magnetic means. All of the coatings that demonstrated improved corrosion protection were thinner than the standard IVD coating, as measured using magnetic means. Because all specimens were produced using the same relative deposition rate and duration, it is assumed that the higher voltages and pulse frequencies lead to increased sputter removal of the coating, as is expected. Scanning electron microscopy (SEM) evaluation of the thickness of cross-sections will be used to confirm or disprove this theory and enable researchers to account for sputter removal in the process.

The preliminary proof-of-concept trials provided data that seems to support the original research that showed that the process has the ability to improve the corrosion protection of IVD coatings. Process optimization and subsequent testing will provide the technical justification to proceed or discontinue pursuit of this improved IVD aluminum process. It is anticipated that all demonstration activities will be completed by the time this paper is presented and the results will be compiled in a Demonstration Report.

Summary

Identification of the processing requirements were crucial in establishing a baseline, against which the improved IVD process and non-chromate conversion coating alternatives could be compared. Test results shown previously indicated that the life of the component could be improved, in terms of corrosion resistance, from nearly two-fold to more than three-fold, using the improved IVD process with conventional chromating processes. It is hypothesized that this improvement also can be gained through the use of non-chromate conversion coatings as top coatings. A decreased use of hexavalent chromium also will result in substantial reductions in EHS costs.

Alternative Coatings for Wear and Corrosion:
The Electrospark Deposition Process

Roger N. Johnson, Pacific Northwest National Laboratory, Richland, WA, USA

Nearly all of more than 120 commercially available coating materials and process combinations evaluated for severe service in nuclear reactor applications failed one or more of the acceptance criteria. A micro-welding process, termed Electrospark Deposition (ESD), was developed. It replaced the detonation-gun/HVOF coatings that had been used with an ESD coating that provided orders of magnitude increase in wear and damage resistance, a five-fold improvement in corrosion performance, lower friction, and more than a 50 percent saving in cost, using the same coating material. The process was in production for nuclear components for 10 years without a single coating failure or coating reject. ESD is a consumable electrode, micro-welding process that uses electrical pulses that are typically three orders of magnitude shorter than in other pulse welding processes. The process generates no hazardous wastes, fumes or effluents, and requires no vacuum systems, chambers, chemicals or spray booths. Substrates require no special surface preparation and nearly any metal, alloy or cermet can be applied to metal surfaces. The ESD coatings have been found to be among the most damage-resistant coatings known and are particularly suitable for use in the severe environments involving high stresses, high temperatures, thermal cycling, irradiation, wear, corrosion, and erosion. The process is not limited to coatings. Repairs are routinely made to damaged surfaces by restoring dimensions using original (or better) substrate materials. Examples of applications are described.

For more information, contact:
Roger N. Johnson
Senior Staff Scientist
Pacific Northwest National Laboratory
P.O. Box 999, K3-59
Richland, WA 99352
Phone: 509-375-6906
e-mail: roger.johnson@pnl.gov

Introduction

Chrome electroplating is one of the most widely used surface treatment processes in industry, but represents one of the most significant contributions to hazardous, carcinogenic waste generation and pollution control costs. Alternative technologies are being developed and qualified that will reduce or eliminate the dependence on this process while providing equal or superior performance in wear and corrosion protection. The High Velocity Oxygen Fuel (HVOF) process is one alternative technology that is gradually replacing chrome electroplating in some applications[1-4]. Other alternatives are required for applications where HVOF coatings cannot be applied because of geometry constraints or because of service conditions exceeding the damage resistance of the HVOF coating. Cost-effective, pollution-free coating alternatives are needed to achieve environmental goals without sacrificing performance of key components.

Numerous coating technologies have been developed for material protection including HVOF and other thermal spray processes; electrochemical, such as the chrome electroplating; various vacuum processes, such as magnetron sputtering or other physical vapor deposition (PVD) processes; and chemical vapor deposition (CVD). Each has its advantages and limitations and appropriate applications. In recent years, a novel coating technology has been developed that produces some of the most robust, damage-resistant coatings known. In contrast to most of the above-mentioned coatings, which may produce chemical or mechanical bonds with a substrate, the Electrospark Deposition (ESD) process creates a true metallurgical bond, yet does so while maintaining the substrate at or near ambient temperatures. This prevents thermal distortions or metallurgical changes in critical heat-treated metal substrates.

Background

Electrospark Deposition is a consumable electrode, micro-welding process that uses electrical pulses that are typically three orders of magnitude shorter than in other pulse welding processes. Pulse durations of a few microseconds combined with pulse frequencies in the 0.1 to 2-kilohertz range thus allow substrate heat dissipation over ~99% of the duty cycle while heating only ~1%. The result is cooling rates that may approach 10^5 to 10^6 C/sec, depending on material, and the generation of nano-structures in the deposited material that may be amorphous for some alloys. This structure can produce unique corrosion and tribological benefits. Although a true weld (fused surface) is produced to create a metallurgically bonded coating, the total heat input is so low that the bulk substrate material remains at or near ambient temperatures. (Parts may be hand-held while coating.) This eliminates thermal distortions and metallurgical changes in sensitive substrates, and allows parts to be coated in the final heat-treated or thermo-mechanical condition without subsequent treatment.

The process generates no hazardous wastes, fumes or effluents, and requires no vacuum systems, chambers, chemicals or spray booths. Substrates require no special surface preparation and nearly any metal, alloy or cermet can be applied to metal surfaces.

Modern versions of ESD had their start in the U.S. Department of Energy's nuclear program. A metallurgical coating was needed for severe service with stringent requirements of friction, corrosion, wear, thermal cycling, and irradiation performance[5]. Nearly all of more than 120 commercially available coating materials and process combinations failed one or more of the acceptance criteria[6]. We ultimately tried an early version of a process we later termed electrospark deposition, and found promising results. However, the process lacked adequate reproducibility, was frustratingly slow in its application, and unacceptable in achievable surface finishes or adequacy of coverage, particularly for corrosion barrier applications. After several years of development, we succeeded in achieving the required improvement in the process, equipment and deposition rate, and in the quality and coverage of the coating. The process replaced the detonation-gun/HVOF coatings that had been used with an ESD coating that provided orders of magnitude increase in wear and damage resistance, a five fold improvement in corrosion performance, lower friction, and more than 50 percent saving in cost, using the same material. Much of this was attributed to the metallurgical bond achieved and to the nano-structure inherent in most of these coatings. Figure 1 shows a comparison of the damage resistance of the HVOF type coating and of the ESD coating that replaced it. A more detailed history and description of the process is available in prior literature[7, 8].

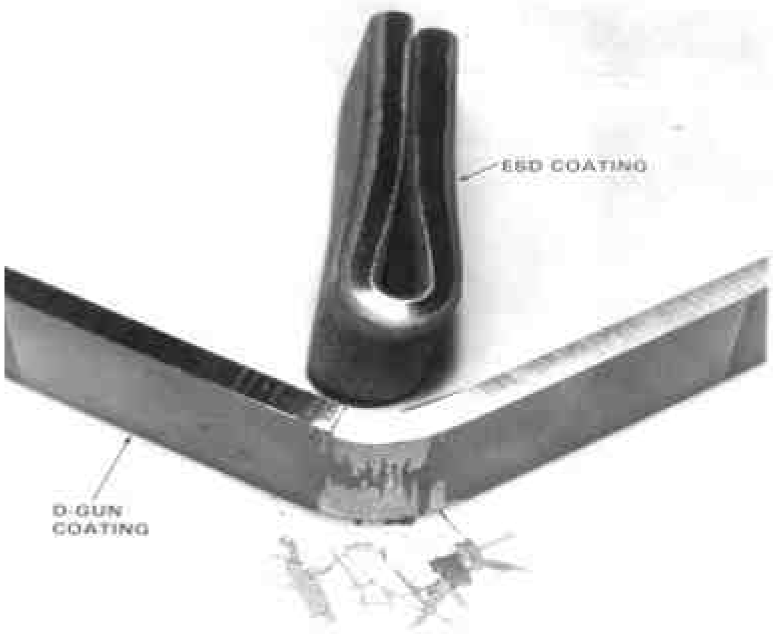


Fig. 1 – Bend tests on detonation-gun/HVOF and ESD coatings of chromium carbide on stainless steel

Process Attributes

The ESD process differs from other welding processes, not only by the exceptionally short duration of the pulse, but also by the contact of the electrode with the substrate. In most welding processes, control of the gap between the electrode and the substrate is a critical parameter. In ESD, the electrode contacts the substrate, and the contact force is the parameter that must be controlled. Direct contact would cause the electrode to weld itself to the substrate if a rapid relative motion were not maintained between the two surfaces. We accomplish this by using rotating, oscillating, or vibrating motion of the electrode, with our best results usually obtained by a rotation of the electrode at several hundred RPM. Figure 2 shows an automated ESD applicator in operation.

The key to the achievement of a commercially viable ESD process was the development of an understanding of the process parameters affecting the deposit and the control of those parameters. The process is basically simple, but as in most new technologies, complex in the details that are important to its success. ESD has the normal parameters that affect most weld processes, but adds a number of parameters that are not immediately apparent. Among the parameters are: electrical (voltage, capacitance, amperes, pulse rate, inductance, pulse duration), environment (cover gas composition, flow rate and geometry, temperature), electrode (composition, density, geometry, rotation speed, traverse speed, orientation, contact force), and substrate (material, surface finish, cleanliness, temperature, geometry).

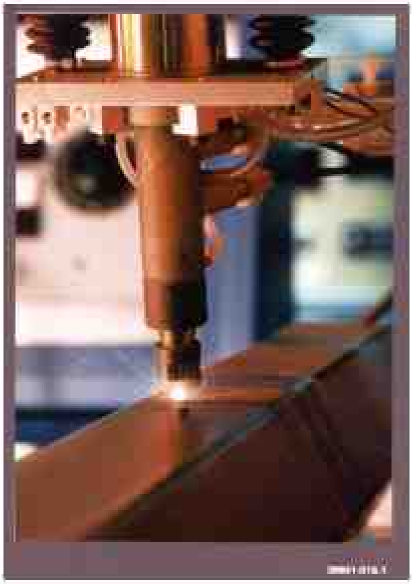


Fig. 2 – Automated ESD applicator with rotating electrode.

The process is very versatile in the number of materials that can be deposited on metal substrates. The primary restriction is that both electrode and substrate must be electrically conductive. An additional requirement is that both materials be capable of being melted in the electric arc without going directly to a gas phase or decomposing. Attempts at depositing bismuth telluride or chromium silicide, for example, were unsuccessful. Presumably the material vaporized or decomposed in the arc without significant transfer of any molten material. Similarly, graphite, which does not have a molten phase at atmospheric pressures, does not transfer from an electrode in any significant quantities. Graphite electrodes have been used, however, to thinly carburize some strong carbide formers such as titanium or zirconium. Table 1 lists some of the materials that have been successfully deposited on metal surfaces using ESD. Table 2 lists the substrates that have been coated by ESD.

Table 1.

ESD Coatings Applied to Date

For Wear Resistance	**For Corrosion Resistance**	**For Build-up or Special Surface Modification**
Hard Carbides[(a)] (of W, Cr, Ti, Ta, Hf, Mo, Zr, V, Nb)	Stainless steels Hastelloys[(b)], Inconels[(b)], Monels[(b)]	Ni-base and Co-base super alloys,
Hardfacing Alloys (Stellites[(b)], Tribaloys[(b)], Colmonoys[(b)], etc.)	Fe, Ni, & Ti Aluminides	Refractory Alloys (W, Ta, Mo, Nb, Re, Hf)
Cr, Ti, Zr& Ta Borides	FeCrAlY, NiCrAlY, CoCrAlY	Noble metals (Au, Pt, Ag, Pd, Ir)
Intermetallics and Cermets	Al and Al Bronze Alloys	Other Alloys (Fe, Ni, Cr, Co, Al, Cu, Ti, V, Sn, Er, Zr, Zn)

[(a)] With metal binders, usually 5-15% Ni or Co

[(b)] Trademarks: Hastelloy – Haynes International, Kokomo, IN
Inconel & Monel – International Nickel Co, Huntington, WV
Stellite & Tribaloy – Deloro-Stellite Co., Goshen, IN
Colmonoy – Wall Colmonoy Corp., Detroit, MI

Table 2

Substrate Alloys Coated by ESD

High and Low Alloy Steels	**Nickel and Cobalt Alloys**	**Refractory Metals (W, Re, Ta, Mo, Nb,)**
Stainless Steels	Titanium Alloys	Chromium
Tool Steels	Aluminum Alloys	Uranium
Zirconium Alloys	Copper Alloys	Erbium

Geometry of the substrate or part to be coated usually does not limit ESD deposits as it can in thermal spray processes. Any surface that can be touched by the electrode, including inside valve bodies, inside diameters and blind holes, can be coated. For example, ESD was used coat the inside diameter of a 9 mm (0.3 in) stainless steel tube, 3.35 m (11 ft) long with an iron aluminide. In another instance, a disk-shaped electrode, as shown in Figure 3, was used to coat another non-line-of-sight geometry. Stress corrosion cracking in the roots of the "Christmas tree" of a steam turbine component was eliminated by an ESD application of a nickel-chrome-molybdenum corrosion-resistant alloy.

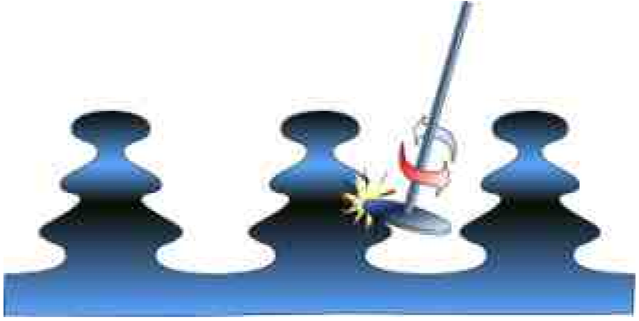


Fig. 3 – Spinning disk electrode used to ESD coat a non-line-of-sight surface on a steam turbine component.

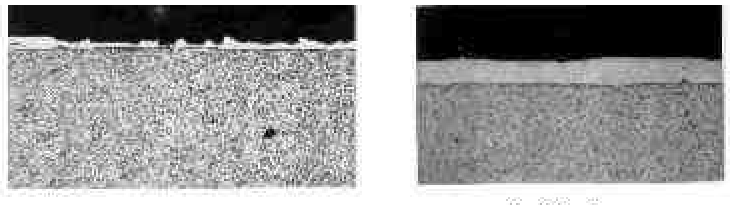
Deposition rates have been increased by over an order of magnitude, to one to 20 cm^2/min for a 25 μm coating. Although the deposition rate is still relatively slow compared to other welding processes and to HVOF, this is mitigated by the minimal time spent in surface preparation, by use of automated coating techniques, by use of multiple applicators, or by the ability to coats parts in-place or in the field. Although further improvements in deposition rate may be possible, there is an inherent limit. At some point, with increasing spark energy and increasing spark frequency, for example, the rapid solidification of the deposit would no longer occur, heat affected zones would become significant, and substrate temperatures would increase to levels that allow metallurgical changes or thermal stress buildup. In other words, the process would become indistinguishable from other arc welding processes.

ESD may still be the lowest cost option for many coating requirements, in spite of its low deposition rate. Ideal applications include those that a) cover or repair small areas, especially those on large or high value parts, or b) involve geometries that cannot be coated by thermal spray or HVOF, or c) require a low heat input to maintain a prior thermo-mechanical condition or to eliminate distortion, or d) require service conditions that exceed the limits of other processes (i.e. high contact stresses, high deformation of coated parts, high temperatures, radiation, thermal cycling, etc.).

Coating thicknesses achievable by ESD depend strongly on the materials involved, and can range from ~25 μm (~1 mil) for some intermetallics and hard, brittle materials, to 5 mm (0.2 in) or more for some more ductile materials. For most applications, thicknesses of less than 100 μm (4 mils) are most desirable and practical. We usually recommend that thicknesses be kept to the minimum that will meet the service requirements. For example, in wear tests of Tribaloy 800 coatings rubbing against each other, a 25 μm thick coating outwore a 100 µm thick coating by six times. The difference was attributed to higher stresses and fracturing in the thicker, brittle material. More recently, ESD has been used to repair high value parts by rebuilding damaged or out-of-tolerance surfaces, as will be discussed later. The original (or a better) material may be used to build up damaged areas by several mm.

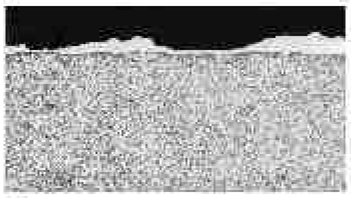
Recent Advances in the ESD Process

A skilled operator can recognize and control parameters to near optimum conditions when the process is fully visible (the normal case). However, when the surface being coated is not visible to the operator, control is more difficult. Pacific Northwest National Laboratory (PNNL), through support from the U.S. Strategic Environmental Research and Development Program, has developed sensors and systems for the automated control of the process in non-line-of-sight applications. This system focuses on control of the contact force between the electrode and the substrate, which is one of the primary parameters of interest. Developments are in progress to not only enable control in automated coating, but also in manual depositions on non-line-of-sight surfaces. Figure 4 shows an example of the effect of contact force on the deposit characteristics. Figure 5 shows the effect of contact force on the weight gain of equal area coupons coated with Stellite 6 under otherwise identical conditions.



a) 15 g force

b) 100 g force



c) 350 g force

Fig. 4 – Effect of electrode contact force on ESD deposit characteristics, Stellite 6 on 4340 steel. a) 15 g force, b) 100 g force, c) 350 g force

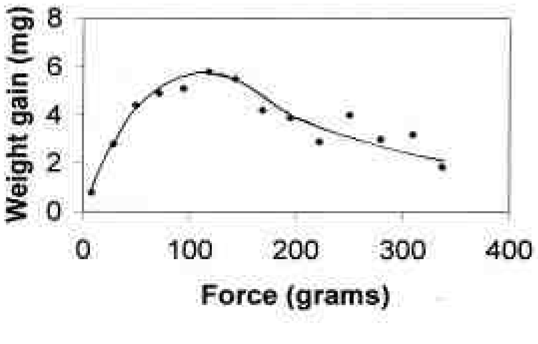


Fig. 5 - Effect of electrode contact force on weight gain of equal area steel coupons during ESD coating with Stellite 6.

Limitations of the ESD Process

Some surfaces are inherently difficult to coat. Because the electrode must contact the surface, any surface geometry that does not allow full contact with the electrode may be coated only on adjacent areas where contact is possible. Figure 6 shows an example of a geometry that is difficult to coat. Internal corners should have a radius proportional to the size of the electrode to assure coverage. Similarly, coating threads on bolts, for example, should not be attempted. Surface waviness with a period less than the electrode diameter may lead to a coating that only builds up on the peaks. Some deposition parameters can result in an initial coverage that leaves some areas uncoated. Since the arc goes to the nearest surface, only the high points will continue to build up with subsequent passes or layers. Figure 7 shows an example of some of the surface textures possible. The rougher surfaces can be desirable where applications require a gripping action, as on some metal handling tools. Generally, the thicker the coating and the higher the deposition rate, the greater will be the as-deposited surface roughness. The minimum as-deposited surface roughness is about 2.5 µm (100 µin) AA.

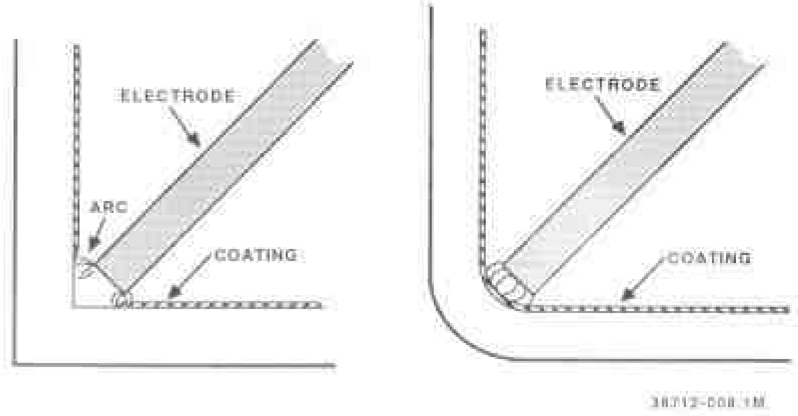


Fig. 6 – Limitation on coating inside corners unless corners are rounded

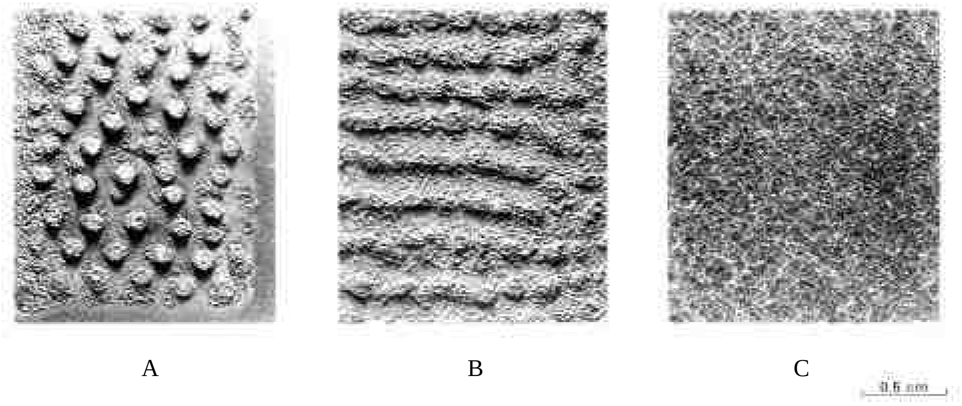

A B C

Fig. 7 – Surface textures possible with ESD

The rapid solidification that occurs in the deposit and the volume change that sometimes results from going from the liquid to the solid state can cause some materials to exhibit stress relief cracking. This often can be reduced or eliminated by pre-heating the substrate, as is common with other welding procedures. However, pre-heating may be undesirable, especially when one of the principal reasons for the use of ESD is its low heat input. During the development of ESD chromium carbide coatings, for example, pre-heat of the substrate was not an option because of the requirement for maintaining 20 percent cold work in the substrate. Extensive parameter development succeeded in eliminating the stress relief cracking in the coating, but testing revealed that the resulting crack-free coating no longer exhibited the wear, friction, and corrosion performance required for the service conditions. An optimum crack pattern, as shown in Figure 8, is now specified for chromium carbide used in nuclear applications. (This is the same structure that survived the bend test shown in Fig. 1.)

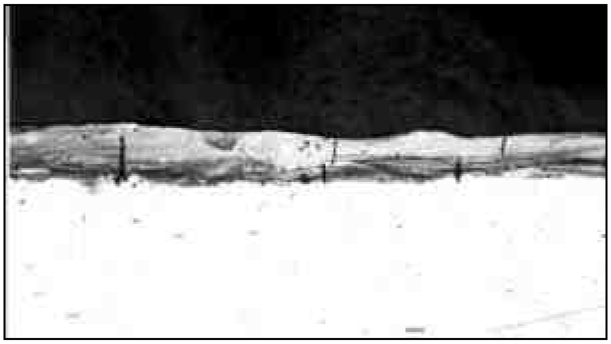


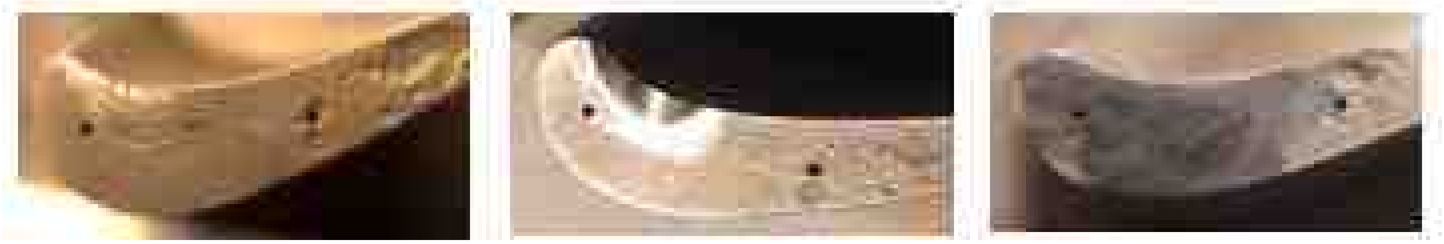
Fig. 8 – ESD Chromium Carbide showing optimum stress-relief crack pattern.

The stress-relief cracking is most frequently observed in the hard carbide deposits (Cr carbide, W carbide, etc.). The wear performance of these materials is still outstanding, as seen in numerous applications (described later). The tough damage resistance of the ESD coatings, including the carbide coatings, has been used to advantage in the final forging of coated parts to achieve geometries that would be difficult to coat otherwise, such as grooves in tools and gun barrels. The forging action not only produces the shape required, without damaging the ESD coating, but also can improve the surface finish of the as-deposited coating. Any coating that exhibits stress-relief cracking, however, may not be a good candidate for protection of surfaces from corrosion, or for use on components subject to fatigue, unless a coating of another appropriate material is applied as a first layer.

Applications

In addition to the nuclear applications previously mentioned, ESD is being increasingly used for coating and repair of high value gas and steam turbine components. Because of its low heat input and freedom from distortion, ESD is used to repair casting defects and mis-machined parts that otherwise would be scrap, often saving thousands of dollars per part. Figure 9 shows a repair of thermal-fatigue cracks in a single-crystal turbine blade accomplished by ESD. Other turbine applications include a) pre-placement of platinum on selected areas of turbine blades for subsequent platinum aluminide diffusion coatings, b) hardsurfacing of blade tips used in ablative seals, c) repair of diffusion coatings, d) pre-placement of braze alloys on difficult-to-wet turbine materials for precision assembly of complex components and e) corrosion and erosion protection of turbine blades in severe environments, such as the corrosive gasses typical of geothermal power plants, and particle erosion from ingestion of sand in military turbines.

Metal working tools frequently are used under severe stresses and temperatures that can challenge the strength and integrity of any coating. The ESD coatings have successfully proven themselves in such applications as cutting tools, dies, drills, shears, forging tools, etc. Improvement in tool life is rarely less than 100%, and frequently approaches an order of magnitude or more. Economic benefits are not just in increased

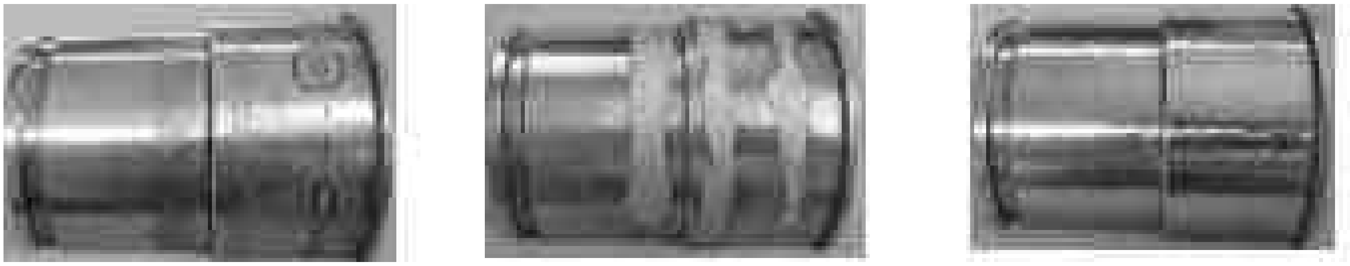


a) b) c)

Fig. 9 – Repair of single-crystal turbine blade by ESD, showing a) as-received blade with thermal fatigue cracks, b) cracks removed by grinding, c) restored by ESD using original material as filler and finished. (Photos courtesy Advanced Surfaces & Processes, Inc.)

tool life, however, but also in production rate increases through higher feeds and speeds for machining tools and drills. Special coatings are in development for end mills to increase speed of metal removal on difficult-to-machine titanium alloys and nickel-base superalloys. Tool steel dies used in the hot extrusion of titanium alloys were ESD coated with a mixture of refractory metal carbides and molybdenum. The normal life of the dies was increased from 300 extrusions to an average of 980 extrusions for the coated dies.

Seawater corrosion is a constant concern in naval components. Figure 10 shows an ESD repair performed on a Cu-Ni alloy bearing on a submarine steering control damaged by pitting corrosion in seawater. The U.S. Navy is qualifying the ESD process for use on shipboard for similar repairs on shafts and bearings in-place, often eliminating the need for expensive disassembly and dry-dock repairs. The small size and portability of the ESD equipment makes such options practical.



a) b) c)

Fig. 10 – Cu-Ni bearing repaired by ESD, a) as-received, b) after filling all pits with the parent metal, c) after finishing to original condition. (Photos courtesy Advanced Surfaces & Processes, Inc.)

Other applications where ESD is replacing hard chrome plate and other processes are:

a) Timber and paper industry – chipper knives, pulp processing doctor blades, plug augers, shredder knives, log debarkers, folder blades, sickle bar guards, and pulp and cement conveyer augers, severe service chain-saw teeth.
b) Automotive industry – titanium carbide coatings on titanium valves for racing engines, metal working and cutting tools,
c) Medical industry – orthopedic drills, orthotic leg and ankle brace components, dental tools, needle holders, hemostats,
d) Nuclear industry – core components, valve guides, steam generator tube supports, electromagnetic pumps, transducers, component positioning hardware, control rods, burnable neutron absorber coatings,
e) Agricultural industry – subsurface hop cutter blades, various harvesting tools and cutters.

Summary

No single process or material, by itself, is likely to replace hard chrome plate. However, the increasing cost of environmental compliance for chromium plating provides a challenge to produce and qualify alternate processes and materials that will provide comparable protection of critical surfaces, and to do so economically. The Electrospark Deposition process offers environmental and performance advantages that make it a candidate for replacement of hard chrome plate in a number of applications. Environmental advantages include no hazardous wastes, fumes, or effluents, no special chambers or sound booths, and minimal surface preparation of substrates. ESD coatings are some of the most robust and damage resistant available, surviving service conditions of high contact stresses, wear, corrosion, deformation, irradiation and thermal cycling that destroy most other coatings. The low heat input and rapid solidification of the deposit result in the nano-structures that contribute to the performance. Complex geometries and non-line-of-sight surfaces can now be coated. Some applications will be limited by the inherently low deposition rates and the limited thicknesses achievable with some materials.

Acknowledgments

This work was supported by the U.S. Government's Strategic Environmental Research and Development Program. We also acknowledge information kindly provided on some of the ESD commercial applications by Advanced Surfaces and Processes, Inc., of Cornelius, OR.

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SESSION E

Water & Rinsewater Workshop

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Getting Health & Safety Right: Economics & Creativity
Philip A. Platcow, C.I.H., SECOR International, Inc., Chestnut Hill, MA
Paper not available

Pre-OSHA Inspection Planning Guidelines
Robert F. Lee, CEF, REA, Rogers Corporation, Rogers, CT

Non-mainstream Regulations
Robert F. Lee, CEF, REA, Rogers Corporation, Rogers, CT

Enhancement of the U.S. EPA's Metal Finishing Facility Risk Screening Tool (MFFRST)
William M. Barrett Jr., Ph.D., P.E. & Paul Harten, Ph.D., National Risk Management Research Laboratory, Cincinnati, OH; Matt Lorber, U.S. EPA, National Center for Environmental Assessment, Washington, DC; & Charles Peck & Steve Schwartz, P.E., Q.E.P., Versar, Inc., Springfield, VA
Paper not available

How to read - and read into - a MSDS

Michael F. Burnson, CEF

A Material Safety Data Sheet (MSDS) can be your most useful tool in maintaining a healthy and safe working environment for your employees. Unfortunately, there are many times in which an MSDS can be a frustrating and confusing document, thereby defeating its primary purpose.

- One MSDS warned that its product should only be handled with rubber gloves and other personal protective equipment (PPE), as the product was made with potassium hydroxide. The product was waterless hand cleaner.
- One MSDS for sodium dichromate refers to it as an oxidizer while another classifies it as a toxic.
- Zinc dust from one manufacturer is labeled dangerous when wet, while another has no hazard warning.

How can these seemingly obvious contradictions arise? The answers lie in various causes: sometimes a lack of chemical knowledge, sometimes confusing regulatory definitions and regulations, other times over-reliance on software. So how are you to know when these details are correct and separate the useful from the useless? Very simply, a diligent approach by your safety officer is the only way. The following information is offered as a starting point in enhancing your diligence.

An MSDS prepared along the requirements of OSHA's standards is a complex and comprehensive document. To most people, it contains vastly more information than would normally be considered useful. In part, this is due to its objective of providing information to a wide variety of users. The same document must provide information to your safety officer, waste treatment operator, shipping/receiving department, inventory controller, plant personnel, first aid personnel, local fire department, and more. That's why most of them are so long, many now more than ten pages.

Regardless of how familiar you may be with your products, it is very important to take the time necessary to understand the MSDSs for every product in your shop. For most people, there are just two or three sections of major importance – but these sections differ among different personnel.

HAZARDOUS INGREDIENTS – Probably the most widely used section, this provides basic information about what a product contains; physical characteristics such as color and specific gravity may be included here or listed separately. For commodity chemicals, this may be obvious, but many things can be hidden in proprietary products. In general, if a hazardous chemical constitutes 1% of a product, it must be listed on the MSDS; if the chemical is carcinogenic, the threshold is 0.1%.

Exposure data may also be included in this section or delegated to a separate one. Look for such data as exposure limits: PEL – permissible exposure limit; TLV – threshold limit value; IDLH – immediate danger to life or health. These can be expressed either as milligrams per cubic meter or parts per million. Toxicity data reflects hazards determined by animal tests and are typically expressed as LD_{50} – lethal dose to 50% of the animals tested. Other expressions include LC_{50} (lethal concentration for gases) and LD_{Lo} as well as observed data.

FIRST AID – Insofar as there may be a chemical hazard in a product, this section may be the most important on the whole MSDS. Skin exposure and inhalation are common in production areas, so personnel should know how to respond. Pay special attention to unusual threats, such as skin absorption of certain toxins (cyanides, fluorides, organics) or delayed effects of exposure. In the shop, first aid materials are a necessary complement to first aid information and techniques.

PERSONAL PROTECTIVE EQUIPMENT – Closely tied to first aid is PPE: it is, in effect, the best guide to precluding the need for first aid. Unfortunately, most processing lines work with several chemicals, and PPE will vary among these chemicals. In this case, select the PPE for the most significant hazard. This may or may not be the most likely hazard.

Next to PPE in prevention of risk is exposure control equipment. This includes information about exhaust, fume scrubbers, and maintenance guidelines. Again, working with hazardous chemicals means providing condition appropriate for the greatest hazard.

FIRE FIGHTING and SPILL CLEAN-UP – Worker exposure isn’t the only emergency situation that you might face. Loss of product or solution may be serious, sometimes requiring outside emergency personnel to assist in control and clean-up; very large spills may even require notification of the EPA (larger than the reportable quantity). A fire will not necessarily be caused by any of the hazardous chemicals; however, they can aggravate a fire or otherwise place fire fighters at risk.

There’s a certain trick in addressing hazardous situations properly. Your MSDS files and information are stored inside your plant or offices – which will be evacuated in the case of a serious emergency. No one is going back into a burning building to look up what’s on the MSDSs! In general, these are things that someone from your company must learn prior to any accidents. Time lost in searching for response information is time lost for addressing the problem.

STORAGE – Many chemicals’ most serious hazards develop when combined with other chemicals: chromium trioxide is most hazardous when it can react with flammable materials, and the greatest hazard from cyanide compounds is being mixed with acids. They are examples of chemicals that must be segregated during storage (and usage). Of course, all chemicals should be stored in a “cool, dry location”, but more details should be available in the MSDS. To be safest, look for information about incompatible materials, conditions to avoid, and similar information.

REGULATORY INFORMATION – This includes such things as shipping (Dept. of Transportation) classification, and EPA and OSHA regulations. Some companies include foreign regulations as well.

So why all the confusion with so many MSDSs? There are three primary sources of this problem: First, there are software programs that generate MSDSs based upon raw materials that the product contains. These programs look up the basic information on each component, but cannot account for combinations. In the example of the waterless hand cleaner, potassium hydroxide is used to saponify the fatty acid component, though an excess of the fatty acid is incorporated into the product. The pH of the final product is close to neutral: there is no potassium hydroxide remaining, only a combination of fatty acid and soap. Inadequate software is perhaps the most common source of this problem, though human error contributes its share to this problem. After all, many MSDS authors miss this same point.

A second source of difficulty is inconsistent interpretations of the myriad EPA and OSHA regulations. Considering that experts cannot agree on many of them, it's easy to understand how this can happen. For example, sodium dichromate is usually considered an oxidizer by manufacturers and distributors. However, some tests indicate that it does not meet the defined criteria of the DOT as an oxidizer, so it may be classified instead as a toxic. Similarly, testing by one company on their zinc dust may indicate that it does not meet the criteria for classification as dangerous when wet nor spontaneously combustible. The problem for you in your shop is that the hazards still exist, but are not so readily obvious to your personnel. The most common reminder of hazard information is product packaging itself; these products don't display any hazard information, and employees tend to think of them as safer than they are.

The opposite happens as well. Many MSDS authors overstate the hazards of their products. Rather than risk a lawsuit from a victim of an industrial accident, product hazards are exaggerated so as to err on the side of safety.

The third common source of confusion is that companies deliberately do not include proper descriptions of hazards on their MSDSs. It happens often that a company either wants to hide a proprietary formula that a competitor might figure out easily, or the author is simply negligent. I have read MSDSs for steel electrocleaners that do not list caustic soda, its primary ingredient, as a hazardous component. Honest mistake? Not very likely. Secret ingredient? Secret as a car with four wheels! Avoiding higher packaging and transportation costs? Well, just maybe…

In all of these cases the problem is to know when an MSDS is correct, when it is exaggerated, or when it is incomplete. There's no way to tell. Each MSDS has to be read and evaluated on its own merits. And you must be diligent as well. Ask questions of suppliers and demand accountability and technical support. If they can't provide it, you and your employees are the ones at risk. Ultimately, it is your responsibility to provide a safe working environment. You and your people deserve cooperation from your suppliers in achieving this goal.

Getting Health & Safety Right: Economics & Creativity

Philip A. Platcow, C.I.H., SECOR International, Inc., Chestnut Hill, MA

Getting health and safety (HS) right in industry today takes business sense, scientific know-how and some creativity. The average back injury costs about $40,000. If a manufactured product unit has a $10 profit, a company must manufacture 4,000 units to pay for that one accident. If the unit requires 15 min to process, then 1,000 hr are utilized creating product to pay for that one accident. If a good lifting program is part of the HS program, then perhaps the injury can be avoided and the 1,000 hr are utilized to create $40,000 of profit. The average cost of an emergency shower is about $500. If there is no significant risk of chemical splash, then 50 product units and about 12.5 hr of manufacturing time are wasted by installing the shower. While HS programs are a vital part of responsible manufacturing and protecting human resources, they should be viewed with a reasonable amount of business sense to ensure value. Creativity is also important. Management and labor issues are often central in HS. Topics such as profit, staffing, qualitative assessment, employee participation, regulatory compliance, and return on investment should be considered for HS programs—just as they are in the design of a product.

Paper not available for publication.

For more Information, contact:
Philip A. Platcow, C.I.H.
Secor International
75 Payson Rd.
Chestnut Hill, MA 02467
Phone: 617-232-7355
FAX: 617-232-7657

PRE-OSHA INSPECTION PLANNING GUIDELINES

Robert F. Lee, CEF REA
Rogers Corporation
One Technology Drive
P.O. Box 188
Rogers, CT 06263-0188

INTRODUCTION

Many facilities have already experienced one or more OSHA site inspections and have first-hand knowledge of what this involves. Other facilities have not, or have had the experience a number of years ago, and thus current management and employees are not familiar with what to expect. Most metal finishing operations can expect at least one visit from an OSHA inspector. For some, this can be a traumatic experience and for others it is viewed as an opportunity to confirm compliance status.

The intent of this paper is not to present a comprehensive outline of how to establish a compliant safety program, but to review the establishment of a protocol to deal with unannounced OSHA inspections before they happen. Having a clear written plan on how to handle those inspections and trained and knowledge employees to participate in these inspections can go a long way in preventing misunderstandings, future problems, and needless stress. It can also preserve your legal rights under the law.

INSPECTIONS

Unless you have requested a voluntary inspection, virtually all OSHA inspections are unannounced. Having an understanding of the nature of the inspection to be conducted at its onset will allow some control by the site management regarding the scope of that inspection. There are a variety of different types of inspections that can occur and each has certain limitations that can be utilized if certain steps are taken at the beginning.

1. Formal Written Complaints

A written complaint to OSHA, usually by an employee, will more often than not trigger an OSHA inspection relatively soon after it is received. The resulting inspection can be limited to the specific area(s) of the written complaint, provided the nature of the inspection is determined beforehand in an opening meeting. (This is probably the most common type of inspection.)

2. Informal Complaints

Generally, these are in the form of a telephone call, e-mail or fax. These may trigger an OSHA follow-up several weeks or months after receipt; follow-up may be an inspection, letter or phone call to the employer to explain the operation(s) involving the complaint. In any case, inspection or comment can be limited to the specific complaint issue(s). (These are less common and more often than not result in a telephone request for information.)

3. Site Specific Targeting

OSHA in 2001, based on 1998 data, conducted inspections of 100% of facilities that reported greater than 14 loss workday incidents above their industry's average levels. Facilities with 8-13 workday losses above industry average ran a better than 60% inspection rate in 2001. It is expected OSHA will continue these inspections in 2002 based on 1999 submitted data. These inspections are difficult to limit in scope due to the normal variability of incident causes.

4. **Targeted Industry/Chemical Inspections**

   Periodically, OSHA will pick an industry (such as a lead battery, rubber compounding or resin manufacturing facility) or a specific chemical (such as cyanide, benzene or toluene diisocyanate) user for broad scope facility inspections. These are open to the entire facility and generally cannot be limited (occurrences are variable).

5. **Serious Injury or Death**

   OSHA will usually follow-up a serious injury or death report within twenty-four to seventy-two hours with an inspector. In these cases, the entire facility is subject to inspection. (These are case dependent occurrences.)

6. **Catastrophic**

   In the event a major explosion, fire or other accident involving significant injuries, multiple deaths or beyond the property line serious impact, OSHA will respond almost immediately. The entire facility is subject to inspection without limitation. (This too is case dependent regarding occurrence.)

Under the United States constitution and rule of law, individuals and companies are protected from unreasonable search and seizure and you have the right to refuse entry to the facility by an OSHA inspector. However, that action should be taken only where very special circumstances exist and only where legal counsel has recommended such action. Denying access to OSHA inspectors will probably result in their obtaining a court ordered search warrant and then coming back to perform an in-depth inspection of the entire facility to try to find what you were trying to hide. In most cases, it is best to deal with inspections without the involvement of legal counsel; however, it is highly recommended that each facility have in place a written and functional regulatory inspection protocol, that has been reviewed by legal counsel, before the inspector arrives.

PRE-INSPECTION PLAN

The first step is to prepare a written plan outlining a general procedures to be followed, designating duties of various individuals, detailing immediate and longer term follow-up actions and informing employees of the inspection and its findings. Employees need to be informed that no inspector is to be allowed onto the property or into the facility without first going to the front office or receptionist and signing in. If an inspector shows up on the property or in the facility without signing in, employees should be instructed to politely escort the individual(s), by taking them outside the facility, to the front door.

The pre-inspection plan generally should consist of six sections: (1) reception, (2) opening meeting, (3) inspection, (4) closing meeting, (5) inspection follow-up, and (6) response.

1. The ***Receptionist*** must be instructed on how to deal with inspectors. The Receptionist should have the inspector(s) sign in, with date and time of arrival. Then, the Receptionist should inform either, or both, the plant manager and person responsible for safety issues at the site that the inspectors have arrived.

Either the plant manager or the safety person should quickly go out to the Reception area and identify themselves and request from the inspector's verification of their identity. If, for some reason, the inspectors do not show proper identification, entry into the plant should be denied until such time as their identity is confirmed. When identity is established, the inspector(s) should be directed to a meeting room where the Opening Meeting can be conducted before the actual inspection occurs.

2. At the ***Opening Meeting***, the plant manager needs to ask specifically what is the nature of the inspection. The inspector(s) will cite the reason for the inspection and the authority under which it is being conducted; this will inform the plant manager just what operation(s) and department(s) will be involved. The plant manager will then delegate the following responsibilities:

   a. Who will escort inspector(s) during inspection. (Under no circumstances is/are inspector(s) to be allowed to wander around the plant unescorted).

   b. Who will take notes during inspection; it is not recommended to tape record inspection. However, someone should be taking down notes of inspector's commentary during the inspec-tion process.

   c. If samples or photos are to be taken by inspectors, who will duplicate the same for the facility?

   d. Who will be the one person charged with answering inspector questions pertaining to various operations; can be more than one person in total, but should not be more than one person per operation/process.

   e. Who will be responsible for document control? Any requests for copies of documentation by inspector(s) will be recorded and then one person will be charged with collating, checking, copying, recording what was copied and arranging for transfer to inspector(s) at the closing meeting.

   f. With operations involving union workers, a union officer is to be included with inspection team.

Plant manager will then define ground rules under which the inspection will operate (except in cases involving accidental death or severe injury, employers have the right to establish certain inspection ground rules):

a. What department(s) or area(s) will be included on inspection; this will be limited only to specific inspector cited areas.

b. What normal business hours are and when identified production area(s) will be available for inspection.

c. What safety equipment inspector(s) will wear and what safety procedures they will follow during inspection; these must be the same, or equivalent to, those used by employees.

d. If the inspector(s) wish to speak to a specific employee, the plant manager will specify when, where and if on company time inspector may meet privately with employee.

e. State that all questions will be truthfully and frankly answered subject to available knowledge and that those questions not readily answerable will be addressed, in writing, as soon as information is available.

f. State that all specifically requested files will be available for inspector review; make sure that only documents requested are made available. If hard copies are requested, inspector will specify which records/files they want and the designated site person for document control will prepare the list, make copies and have inspector sign for their receipt.

g. If restrictions exist pertaining to photographs taken in the plant, these must be spelled out; these restrictions must be the same that apply to all other visitors. Generally, inspectors have the legal right to photograph any citable situation; however, they can be limited to the citable offending area.

Plant manager will then request a closing meeting be held following the inspection.

3. With everything defined in the Opening Meeting, the walk around ***Inspection*** should be a breeze. Nevertheless, some general tips are in order:

   - Be courteous and businesslike.

   - Don't hesitate to ask inspector(s) what they would suggest if an area comes up that seems to bother them. If a particular situation seems to be non-compliant, probe to get at what is the specific issue of concern.

   - Be tactful and remember to answer truthfully questions asked and don't hesitate to say "I don't know, but I will get the answer to your question for you" if you don't know the answer. Don't try to "wing it" if you are not sure of the answer, go to a source that can get the right answer. Never volunteer speculations.

4. The **C*losing Meeting*** should be held immediately following the conclusion of the inspection and should include the original cast that was present during the Opening Meeting. At this meeting, the plant manager asks for a verbal summary of the inspection's findings. At each point raised, try and get inspector(s) to comment on what they would suggest to resolve that situation. If some issues are readily correctable and not contested, plant manager should make a commitment that these issues will be resolved even before the final inspection report will be issued. This "good faith" commitment will be helpful to the company when the inspector(s) write up their official report. All samples and photos taken need to be recorded.

5. ***Following the departure of the inspector(s),*** the plant manager needs to get everyone involved in the inspection to conduct a "debriefing" and record all the

information gathered and observed. This information, along with the minutes of the Opening and Closing Meetings, should be preserved in a separate file; this should be done the same day as the Closing Meeting. The next day, plant personnel need to review the debriefing report and assign priorities to problems likely to be cited; it is important to remember that response time on corrective action is an important measure of the degree of cooperation displayed and can be beneficial in reducing penalties.

6. ***Response*** times to any citation received are critical. Generally, any exception to a citation must be made within 15 calendar days of it's receipt; failure to exercise this right within this period, means you have abdicated your right to appeal, even if the agency is dead wrong. Usually, companies have the right to request a meeting with the agency, before the expiration of the 15 day appeal period, and it is recommended that every company request this meeting. This gives the company an opportunity to review the citation(s) with the agency, understand the regulatory requirement, and to review the progress the company has already achieved in correcting deficiencies noted during the inspection (if applicable); often, extensions to deadlines for completing corrective actions can be negotiated, but if not, then you still have time to appeal.

COMMENTARY

Companies that implement a plan on dealing with OSHA inspections beforehand generally have fewer confrontational issues and end up with lower assessed penalties. This approach is presented as one way to implement such a plan, but should not be viewed as the only one available. Companies should utilize the expertise of either in-house staff or outside consultants to assist them in formulating a plan that is right for them. Also, getting employees directly involved with safety will result in both a safer plant environment and fewer citations.

NON-MAIN STREAM REGULATIONS

By

Robert F. Lee, CEF, REA

INTRODUCTION

Almost everyone is aware of the air, water, waste, and safety regulations that affect their plating and finishing operations; however, there are a number of lesser-known regulations that may have significant impact as well. This paper discusses several of these non-main stream regulations and their requirements; the author has selected the regulations that are reviewed, but cautions the reader these are not the only ones that exist or that may affect your operations.

This paper briefly reviews the following regulations:

1. EPA's Toxic Substances Control Act (TSCA) and Its Import/Export Rules
2. Drug Enforcement Agency's (DEA) Chemical Tracking and Reporting Requirements
3. International Chemical Weapons Treaty Act Notification Requirements
4. Nuclear Regulatory Commission Rules for Managing and Disposing of Beta and Gamma Thickness Gauges

NON-MAIN STREAM REGULATIONS

Toxic Substances Control Act (TSCA) § 12(b), 15 U.S.C. § 2611(b)

TSCA § 12(b) states that EPA notification is required if a person exports or intends to export to a foreign country a chemical substance or mixture. 15 U.S.C. § 2611(b) states that if a chemical substance or mixture is exported as part of or contained in an article, notice is not required unless specified by a rule.

Most platers and finishers, if involved with exporting, would be shipping articles, not chemicals per se and thus not subject to this regulation. However, if you supplied plating and/or finishing chemicals to customers, or if you ship these to one or more of your own facilities, in a foreign country, these regulations apply. Before proceeding, lets examine the definition of what constitutes an article and a mixture under these regulations.

TSCA: "…A manufactured item: (1) which is formed to a specific shape or design during manufacture, (2) which has end use function(s) dependent in whole or in part upon its shape or design during end use, and (3) which has either no change of chemical composition during its end use or only those changes in composition which have no commercial purpose separate from that of the article and that may occur as described in – 710.4 (d) (5); except that fluids and particles are not considered articles regardless of shape or design."

TSCA: "…Any combination of two or more chemical substances if the combination does not occur in nature and is not, in whole or in part, the result of a chemical reaction is a mixture."

These definitions, in the regulations, have a number of caveats applied which, for simplicity, were not included above; refer to the specific regulatory text for more details.

If you export a chemical, then TSCA § 12(b) may require some form of reporting to the EPA. There are a host of reporting and notifications covered, but for the purpose of this paper I will focus on two: *TSCA § 4 and TSCA § 6.*

The EPA has prepared a listing of chemicals that require reporting under TSCA § 12(b) called the “CORR” List; this list includes over 1,000 chemicals. Under these regulations, there are no threshold values to trigger coverage; if the chemical is present, then it must be reported regardless of concentration.

Section 4 lists chemicals subject to special EPA Test Rules and exports of these require a one-time only per country notice of shipment to the EPA. Additionally, Section 4 Reports must include the following information:

- Name of Exporter
- Date Shipped
- Chemical Name
- Chemical Abstract Services Number (CAS#)
- Name of Country Exported To

Section 6 lists chemicals for which special rules have been proposed or promulgated and exports of these require annual per country notice of shipment to the EPA. Exactly the same information required under Section 4 is required under Section 6 to be submitted. However, Section 6 notices must be postmarked within seven days after accepting a definite contractual obligation to export and no later than the date of export.

All records of export notifications must be kept for five years.

Commentary

Now that I have “made your day” with this information, if it applies to your operations, I need to give you some more information that may increase your anxiety further. In March 1999, the EPA issued a memorandum titled: *Issuance of Revised Enforcement Response Policy for TSCA – 8, 12, and 13.* Penalties for violating provisions of these regulations, dependent upon EPA classification could be up to $6,600/ day/ chemical/ shipment/ country. There is no longer a first time amnesty allowed.

If you are planning to export a chemical, you need to review this regulation carefully. If you have historically exported chemicals covered under this regulation, but did not file required notifications, then I strongly urge you to contact your legal counsel in this regard as soon as possible.

DEA Controlled Substance Act, Title 21, Chapter 13, 21 U.S.C.S Section 802

This is often overlooked (by both regulators and users). Act has been on the books since 1970 with a number of more recent amendments having been implemented since then. For the most part, this requirement is invisible to most chemical end users as the manufacturer or distributor has the burden of reporting and tracking. This can impact on metal finishers where a firm may have foreign operations and where regulated chemicals are delivered to an U.S. Based Facility and then shipped from there to the foreign facility or vice versa.

Under this Act, are two different lists of chemicals that require reporting and tracking: List I chemicals, consumed in the actual manufacture of a controlled substance and List II chemicals, necessary to process a controlled substance.

List I Includes:

- Anthranilic Acid, its esters and salts.
- Bezl Cyamide
- Ephedrine, its salts, optical isomers and salts of optical isomers.
- Ergotamine and its salts.
- N-acetylanthranilic acid, its esters and salts.
- Nor psuedo ephedrine, its esters and salts.
- Phenylactic acid, its esters and salts.

- Phenylpropanolamine, its salts, optical isomers and slats of optical isomers.
- Piperidine and its salts.
- Psuedoephedrine, its salts. optical isomers and salts of optical isomers.
- 3,4-methylenedioxyphenyl-2-propane
- Methylamine
- Ethylamine
- Propionic Anhydride
- Insosafrole
- Safrole
- Piperonal
- N-methylephdrine
- N-methylpsudeoephdrine
- Hydriotic Acid
- Benzaldehyde
- Nitroethane

List II Includes:

- Acetic Anhydride
- Acetone
- Benzyl Chloride
- Ethyl Ether
- Potassium Permanganale
- 2-butanone
- Toluene

It is not likely metal finishers would be dealing with List I Chemicals, but List II Chemicals are often used significantly by metal finishers.

Major requirement is the need to register with the DEA, as an importer or exporter of these chemicals and to keep records on shipment quantities and chemical usage. Any significant determinations of chemical loss or diversion are to be reported to the DEA. For chemicals on List I, records of usage shall be kept for four years; for chemicals on List II, they must be kept two years.

The Attorney General may suspend or revoke a registration after showing cause, in which case, List I Chemicals can be either placed under seal with no disposition possible, until the case is legally resolved, or they may seized. Additionally, both civil and criminal charges can be filed for failure to comply.

Chemical Weapons Convention (CWC) Implementation Act of 1998, 15CFR Parts 710 – 722 and Amendments

This law is administered by the Commerce Department's Bureau of Export Administration and first became a reporting burden for U.S. Companies in the spring of 2000. This regulation is the result of the U.S. Senate Ratification of the International Chemical Weapons Convention in 1997. Under these rules, companies are mandated to file initial declarations and annual summaries for facilities that produce, process, or consume certain chemicals in amounts above specified thresholds.

The regulation required companies to file initial declarations by June 2000; most of the major chemical producers and weapons manufacturers have completed this requirement. However, many medium to small facilities have not and some are not even aware this requirement exists. Some 25,000+ chemicals are included on the listings of reportable chemicals and activities. This mass of chemicals is broken into four different categories: (a) Schedule 1 - Substance historically used in weapons production, (b) Schedule 2 – Chemicals that can be use for weapons production but that also have certain legitimate commercial uses, (c) Schedule 3 – Chemicals with significant legitimate uses that could be use in weapons production, and (d) Unscheduled discrete organic chemicals, [substances containing carbon].

See Appendix I for chemical listings.

Reporting of Schedule 1 Chemicals is required if more than 100 grams (aggregate) of the listed chemical was made, processed, or consumed in the prior calendar year. Chemicals in this schedule are not likely to be used in metal finishing. Reporting of Schedule 2 Chemicals gets a little more complex; here the following table indicates quantity levels. Again, it is unlikely any of these are used in metal finishing operations.

Summary of Schedule 2 Quantity Thresholds		
Schedule 2 Chemical	Quantity Threshold for Declaration or Report on Production, Processing, Consumption, Exports or Imports	Quantity Thresholds for Declaration or Report on Exports to or Imports from a Foreign Destination
2A(3)	> 1Kg	>10 grams
2(A)(1) and (2)	> 100 Kg	> 1 Kg
2B	> 1 metric ton	> 10 Kg

Schedule 3 Chemical Reporting is required if more than 30 metric tons have been manufactured, processed, consumed, imported, or exported in the past calendar year. Some of these chemicals have legitimate use in metal finishing operations.

Summary of Schedule 3 Quantity Thresholds	Quantity
Quantity threshold for declaring or reporting production exports or imports.	> 30 metric tons
Quantity threshold for reporting exports to or imports from a foreign destination.	> 0.3 metric tons

Schedule 4 Chemical Reporting is required if more than 200 tons have been manufactured, processed, consumed, imported or exported in the past calendar year. This grouping does not have a specific listing of chemicals, instead the user is left to determine if his operations required reporting by using the CWC's definition of Unscheduled Discrete Organic Chemical (UDOC): "Any chemical (1) belonging to the class of chemical compounds consisting of all compounds of carbon except for its oxides, sulfides, and metal carbonates identifiable by name, by structural formula,…, and CAS#,…."

There are many more aspects to this than I have touched on here; generally, this would apply, if at all, with the larger metal finishers or to chemical suppliers to this industry. Nevertheless, if you are using any of these chemicals, it would be prudent to check to verify your supplier is in compliance to this requirement.

Nuclear Regulatory Commission (NRC) Standard for Portable Radioactive Testing Equipment, 10 CFR 20, 30, 31, and 32.

Many in the metal finishing industry use Beta and Gamma Scopes to measure thickness. All of these are regulated under NRC authority, although most states have been approved to oversee these requirements in their jurisdictions. This paper will briefly review some of the requirements that users must comply with.

1. If the radioactive source is above threshold levels, then you as a user, must be licensed by either the NRC or authorized state agency.

2. Each device, if licensed, must have a Radiation Symbol Warning Label affixed to it in plain view. Label must include device model #, serial #, the isotope, and quantity present and the words *"Caution – Radioactive Material"*.

3. Licensed devices must be leak tested by a swipe test every six months, and on/off and indicator mechanisms must also be tested every six months. (Devices with less than 100 microcuries of beta or gamma or 10 microcuies of alpha material do not require testing.). All testing must be done by

licensed technician. Test records must be kept for three years.

4. The licensee must appoint a Radiation Safety Officer who is responsible to implement these requirements in the work place.

5. It is required to post a copy of Form 3 with NRC information on employee rights and hot line numbers.

6. Transfer and/or disposal of the device shall be only to another properly licensed company or authorized waste hauler. NRC must be notified if a licensed piece of equipment is to be disposed of; immediate notification to NRC is required if licensed material is lost or stolen.

7. Devices held in storage in original packages do not require testing; however when put back in to service or transferred, they must be tested for leakage. A licensee may not hold devices that aren't in use for longer than two years.

8. Worker exposure monitoring, if required by license, is applicable to NRC Limits not OSHA; NRC requires monitoring to begin at 500 MREMS or 10% of the Occupational Limits, whereas OSHA requires monitoring at 5 Rems or 25% of the Occupational Limit.

At the time of the writing of this paper, the NRC Website was shutdown, as a precaution against terrorism, and thus, I was unable to list additional references for this section.

SUMMARY

These four examples of "Non-Mainstream" Regulations show clearly that metal finishers, especially the small to medium sized operators need to stay alert to these other legal requirements. The best way to keep up with these is to work with your trade associations, state and local business groups or Chamber of Commerce and the AESF.

REFERENCES

TSCA

- Toxic Substance Control Act, 15 U.S.C. Sections 2601 et seq.
- EPA Export Regulations, 40 C.F.R. Part 707, Subpart D.
- *"The Enforcement Response Policy for Reporting and Record Keeping Rules and Requirements for TSCA Section 8, 12, and 13,"* - EPA Office of Regulatory Enforcement (March 31, 1999).

DEA

- Controlled Substances Act - Title 21, Chapter 13, 21 U.S.C.S. Section 802
- Public Law 103 – 200 - Domestic Chemical Diversion Control Act of 1993

NRC

- Nuclear Regulatory Commission Standards - 10 C.F.R. 20, 30, 30, 31, and 32.

APPENDIX I

SCHEDULE 1

	Toxic Chemicals	**CAS Registry Number**
1.	O-Alkyl ($\leq C_{10}$, Incl. Cycloalkyl) Alkyl (Me, Et, n-Pr or I-Pr)-Phosphonofluoridates	
	e.g. Sarin: O-Isopropyl Methylphosphonofluoridate	107-44-8
	Soman: O-Pinacolyl Methylphosphonofluoridate	96-64-0
2.	O-Alkyl ($\leq C_{10}$, Incl. Cycloalkyl) N,N-Dialkyl (Me, Et, n-Pr or i-Pr) Phosphoramidocyanidates	
	e.g. Tabun: O-Ethyl N,N-Dimethyl Phosphoramido-cyanidate	77-81-6
3.	O-Alkyl (H or $\leq C_{10}$, Incl. Cycloalkyl) S-2-Dialkyl (Me, Et, n-Pr or i-Pr)-Aminoethyl Alkyl (Me, Et, n-Pr or i-Pr) Phosphonothiolates and Corresponding Alkylated or Protonated Salts	
	e.g. VX: O-Ethyl S-2-Diisopropylaminoethyl Methylphosphonothiolate	50782-69-9
4.	Sulfur Mustards:	
	2-Chloroethylchloro-methylsulfide	2625-76-5
	Mustard Gas: Bis(2-Chloroethyl)Sulfide	505-60-2
	Bis(2-Chloroethylthio)Methane	63869-13-6
	Sesquimustard: 1,2-Bis(2-Chloroethylthio)Ethane	3563-36-8
	1,3-Bis(2-Chloroethylthio)-N-Propane	63905-10-2
	1,4-Bis(2-Chloroethylthio)-N-Butane	142868-93-7
	1,5-Bis(2-Chlorethylthio)-N-Pentane	142868-94-8
	Bis(2-Chloroethylthiomethyl) Ether	63918-90-1
	O-Mustard: Bis(2-Chloroethylthioethyl) Ether	63918-89-8
5.	Lewisites:	
	Lewisite 1: 2-Chlorovinyldichloroarsine	541-25-3
	Lewisite 2: Bis(2-Chlrovinyl)Chloroarsine	40334-69-8
	Lewisite 3: Tris(2-Chlorovinyl)Arsine	40334-70-1
6.	Nitrogen Mustards:	
	HN1: Bis(2-Chloroethyl) Ethylamine	538-07-8
	HN2: Bis(2-Chloroethyl) Methylamine	51-75-2
	HN3; Tris(2-Chloroethyl)Amine	555-77-1
7.	Saxitoxin	35523-89-8
8.	Ricin	9009-86-3
	Precursors	
9.	Alkyl (Me, Et, n-Pr or i-Pr) Phosphonyldifluorides	
	e.g. DF: Methyphosphonyl-difluoride	676-99-3
10.	O-Alkyl (H or $\leq C_{10}$, Incl. Cycloalkyl) O-2-Dialkyl (Me, Et, n-Pr-i-Pr)-Aminoethyl Alkyl (Me, Et, N-Pr or i-Pr) Phosphonitesand Corresponding Alkylated or Protonated Salts	
	e.g. QL: O-Ethyl O-2-Diisopropylaminoethyl Methylphosphonite	57856-11-8
11.	Chlorosarin: O-Isopropyl Methylphosphonochloridate	1445-76-7
12.	Chlorosoman: O-Pinacolyl Methylphosphonochloridate	7040-57-5

SCHEDULE 2

	Toxic Chemicals	CAS Registry Number
1.	Amiton: O,O-Diethyl S-[2-(Diethylamino)Ethyl]Phosphorothiolate and corresponding alkylated or protonated salts	78-53-5
2.	PFIB: 1,1,3,3,3-Pentafluoro-2-(Trifluoromethyl)-1-Propene	382-21-8
3.	BZ: 3-Quinuclidinyl Benzilate	6581-06-2
	Precursors	
4.	Chemicals, except for those listed in Schedule 1, containing a phosphorus atom to which is bonded one methyl, ethyl, or propyl (normal or iso) group but not further carbon atoms.	
	e.g. Methylphosphonyl Dichloride	676-97-1
	Dimethyl Methylphos-phonate	756-79-6
	<u>Exemption:</u> Fonofos: O-Ethyl S-Phenyl Ethylphos-phonothiolothionate	944-22-9
5.	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) Phosphoramidic Dihalides	
6.	Dialkyl (Me, Et, n-Pr or i-Pr) N,N,Dialkyl(Me, Et, n-Pr or i-Pr)-Phosphoramidates	
7.	Arsenic Trichloride	7784-34-1
8.	2,2-Diphenyl-2-Hydroxyacetic Ac	1619-34-7
9.	Quincuclidine-3-ol	1619-34-7
10.	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) Aminoethyl-2-Chlorides and Corresponding Protonated Salts	
11.	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) Aminoethane-2-ols and Corresponding Protonated Salts	
	<u>Exemptions:</u> N,N-Dimethylamino-ethanol and Corresponding Protonated Salts	108-01-0
	N,N-Diethylaminoethanol and Corresponding Protonated Salts	100-37-8
12.	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) Aminoethane-2-Thiols and Corresponding Protonated Salts	
13.	Thiodiglycol: Bis(2-Hydroxyethyl)Sulfide)	111-48-8
14.	Pinacolyl Alcohol: 3,3-Dimethylbutane-2-ol	464-07-3

SCHEDULE 3

	Toxic Chemicals	CAS Registry Number
1.	Phosgene: Carbonyl Dichloride	75-44-5
2.	Cyanogen Chloride	506-77-4
3.	Hydrogen Cyanide	74-90-8
4.	Chloropicrin: Trichloronitromethane	76-06-2
	Precursors:	
5.	Phosphorus Oxychloride	10025-87-3
6.	Phosphorus Trichloride	7719-12-2
7.	Phosphorus Pentachloride	10026-13-8
8.	Trimethyl Phosphite	121-45-9
9.	Triethyl Phosphite	122-52-1
10.	Dimethyl Phosphite	868-85-9
11.	Diethyl Phosphite	762-04-9
12.	Sulfur Monochloride	10025-67-9
13.	Sulfur Dichloride	10545-99-0
14.	Thionyl Chloride	7719-09-7
15.	Ethyldiethanolamine	139-87-7
16.	Methyldiethanolamine	105-59-9
17.	Triethanolamine	102-71-6

Enhancement of the U.S. EPA's Metal Finishing Facility Risk Screening Tool (MFFRST)

William M. Barrett Jr., Ph.D., P.E. & Paul Harten, Ph.D.,
National Risk Management Research Laboratory, Cincinnati, OH;
Matt Lorber, U.S. EPA, National Center for Environmental Assessment, Washington, DC;
& Charles Peck & Steve Schwartz, P.E., Q.E.P.' Versar, Inc., Springfield, VA

Recently, the U.S. EPA completed the development of the first version of MFFRST and made this product available to the general public. MFFRST calculates the air emissions from a plating line and determines the risk to facility employees and the surrounding neighborhood from the air emissions. The next step in the development of MFFRST is to include solid and liquid wastes in the analysis. In order to accurately estimate the risks associated with these waste streams, the quantity of waste generated and the mass of hazardous substances they contain must be known. The second version of MFFRST will utilize process synthesis and integration techniques to simulate the metal finishing process. Process synthesis and integration devolve the process into simple structures that can then be combined to create a model of the plating line. The quantity and composition of waste streams can then be calculated. The model can then be used to analyze the effect of process modifications on waste generation. The ultimate goal of the program is to enable the user to evaluate the process to analyze any of a number of factors, including quantity and composition of wastes generated, cost/benefit analysis of waste reduction processes, and/or life cycle analysis of the metal finishing process.

Paper not available for publication.

For more information, contact:
Dr. William M. Barrett, P.E.
National Risk Management Research Laboratory
U.S. EPA
26 W. Martin Luther King Dr.
MS 445
Cincinnati, OH 45236
Phone: 513-569-7270

AESF
WEEK

SESSION G

Alternative Processes & Technologies II

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Previous Session

Papers included:

Ion Beam & Plasma-based Alternatives to Chrome Plating of Gas Turbine Engine (GTE) Parts
Lisa Cato & Melissa Klingenberg, Concurrent Technologies Corp. (CTC), Greenville, SC & Johnstown, PA, respectively

Non-line-of-sight (NLOS) Hard Chromium Alternatives Status Report
T. Naguy, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH & M. Klingenberg, M. Neidbalson, M. Pavlik & D. Schario, Concurrent Technologies Corp. (CTC), Johnstown, PA
Paper not available

Environmentally Acceptable Technologies for the Replacement of Cadmium Coatings for Defense Applications
Dr. Michael Kane, Naval Air Systems Command, Patuxent River, MD
Paper not available

Trivalent Chromium Pretreatments for Defense Applications
Craig Matsdorf, Naval Air Systems Command, Patuxent River, MD
Paper not available

Ion Beam and Plasma Based Alternatives to Chrome Plating of Gas Turbine Engine Parts

Lisa Cato, Concurrent Technologies Corporation, Edgefield, SC, USA
Melissa Klingenberg, Concurrent Technologies Corporation, Johnstown, PA, USA

The Propulsion Environmental Working Group (PEWG) has supported several projects focusing on electrolytic hard chrome (EHC) plating replacement to refurbish worn or corroded parts. One project has targeted improving the engineering properties of original equipment manufacturer (OEM) components for enhanced service life such that refurbishment with chromium would not be required until later in the component life cycle. This paper will discuss the results of this task, which was conducted through the National Defense Center for Environmental Excellence (NDCEE), in which seven deposition/surface modification techniques were investigated that had shown the potential to provide the required improvements. All techniques were applied to IN718 and 4340 steel and tested for wear and corrosion performance, hardness, adhesion, and overall visual quality. The results of the laboratory screening tests will be presented, as well as future plans for this project.

For more information, contact:
Melissa Klingenberg
Concurrent Technologies Corporation (*CTC*)
100 *CTC* Drive
Johnstown, PA 15904
Phone (814) 269-6415
FAX (814) 269-6847

Introduction

Virtually every military gas turbine engine (GTE) system in service utilizes electrolytic hard chromium (EHC) plating in engine overhaul operations. The Navy, Army, and Air Force repair facilities use EHC in GTE maintenance operations to restore the dimensions of worn or corroded parts and to provide a wear and corrosion resistant surface. This process involves the use and release of hexavalent chromium, a known human carcinogen. During plating, acid mists, which contain hexavalent chromium, are released to the atmosphere. These mists pose a health risk to nearby workers. Therefore, the Occupational Safety and Health Administration (OSHA) has imposed a permissible exposure limit (PEL) on hexavalent chromium at 0.1 mg/m^3 and is considering reducing that PEL to 0.0005 mg/m^3. Chromium compounds are also targeted by the United States Environmental Protection Agency (EPA). The EPA is trying to implement a health standard in which guidelines on training and reporting will be required. Complying with these regulations has become more difficult, and the trend is expected to continue, thereby increasing the total operational costs of EHC plating.

In addition to environmental concerns with EHC, issues related to long-term maintainability and reliability of DoD systems must be considered. Reductions in funding for national defense has necessitated continued operation of aging propulsion systems in aircraft, ships, and certain military vehicles. Although EHC has been an accepted practice for GTE repair for many years, chromium is not necessarily the best material/process in terms of cost and mission effectiveness. The civil aircraft industry and the DoD have initiated a number of efforts to qualify thermal spray coatings, such as tungsten carbide, in aircraft and engine manufacture and rework. However, thermal spray processes are limited to line-of-sight applications (simple geometries) and can input a significant amount of heat into small components. It is estimated that these processes cannot accommodate 25-30 percent of the engine parts currently being refurbished. In addition, processes that are capable of providing surfaces that will perform better than conventional hard chromium are needed. Ideally, a repair process/material combination that only needs to be applied once during the life of the repaired part, complies with green engine initiative guidelines, and is environmentally friendly will be selected. Such a process also may be implemented at the original equipment manufacturer (OEM) level for initial improvements in service life, leading to reduced labor costs in the repair facilities.

The Propulsion Environmental Working Group (PEWG) and the National Defense Center for Environmental Excellence (NDCEE) operated by Concurrent Technologies Corporation (*CTC)* have collaborated on a project to identify, demonstrate, validate, optimize, and justify alternatives to hard chromium plating. The selected alternative must meet all military requirements. This paper discusses the current status of the project and results obtained to date.

Project Overview

The scope of this project is to demonstrate ion beam and plasma-based deposition and surface modification techniques, and justify them as environmentally benign processes that can reduce or eliminate EHC operations. The new process must meet or exceed performance and operational requirements of current processes. Information obtained in the execution of this project is transferable to DoD repair depots and OEMs. Successful completion of this project is expected to

- Reduce the use of hexavalent chromium, leading to reductions in environmental, health, and safety costs
- Reduce the operational costs and labor requirements as a result of eliminating hazardous materials and the associated compliance procedures/processes
- Reduce operator exposure to hexavalent chromium
- Reduce waste generation.

Phase I of this project is being completed in four tasks. The first task involved identifying classes of GTE components that are currently being EHC plated. Testing requirements, based on Federal Specification QQ-C-320B, were identified as well as other tests necessary to establish a technical performance baseline. These tests include adhesion, hardness, thickness, wear, corrosion, profilometry, and metallography. The NDCEE project team and representatives of the PEWG concurred that each test must be performed and the results compared to traditional EHC to determine whether the alternate process is capable of providing a surface of equal or better quality than the EHC coating.

Investigation of alternatives, the second task, began after identifying the requirements. Alternatives focused on dry processing methods, including physical vapor deposition, ion beam and laser technologies, and ion implantation. Performance criteria of the alternatives were evaluated during the selection process. PEWG preferences were solicited and incorporated into the identification of alternatives, where appropriate. Based on the findings, PEWG and the NDCEE project team members selected the most promising of the technologies. These technologies were further investigated in demonstration and validation activities.

The third task of the project involved demonstration of the alternative processes. Panels were treated using the selected technologies. Ion beam assisted deposition (IBAD) coatings were deposited using the ion beam system located in the NDCEE Demonstration Factory. Subcontractors performed the required services for the remaining alternatives, and some performed the work at no cost to this project. EHC coatings also were obtained and used as the baseline panels against which all other treatments will be compared.

Demonstration activities were designed according to a formal Demonstration Plan. This demonstration plan delineated: (1) the activities necessary to demonstrate each of the selected alternatives, and (2) the test methods and procedures used to evaluate the coatings and surface modifications. Test matrices were included to ensure sufficient data was collected to qualify or disqualify the alternatives.

The fourth task, which is occurring simultaneously with demonstration and testing, involves technology justification. The NDCEE project team members are using available EHC plating data to establish an economical and environmental baseline. The baseline information will include the following:

- Environmental, health, and safety (EHS) costs
- Labor costs associated with chromium rework operations
- Waste generation/disposal costs.

Tools, such as environmentally-based costing*, return on investment calculations, estimates of the potential reduction in the use and emission of hazardous materials, and estimates of product quality improvements will be used to obtain necessary cost justification data. This information will be captured in the Justification Report.

Upon completing the four tasks, the NDCEE project team expects to continue its efforts through follow-on work, which may include engine and rig testing and/or additional panel testing such as fatigue, fretting wear, carbon seal wear, or other specialty tests.

Work Completed

Requirements Analysis Task

To acquire all of the pertinent requirements, many discussions were held with members of the PEWG. Additionally, some requirements information was obtained from the Joint Test Protocol (JTP) entitled

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*Environmental Cost Analysis Methodology (ECAM^{SM}), Concurrent Technologies Corporation, Johnstown, PA.

"Validation of Advanced Thermal Spray Coatings as a Replacement for Hard Chrome Plating on Gas Turbine Engines." The information gathered through discussions with PEWG members and the JTP was assembled into a Requirements Report. This report contains information concerning the classes of parts in a GTE, the materials of fabrication, and the required performance characteristics for EHC plating.

Candidate GTE parts have been categorized into five families of components as follows:

- Shafts
- Hubs
- Gears
- Bearing housings
- Accessory gearbox components.

Although a variety of materials are used in the fabrication of GTEs, the most prevalent substrate materials are Inconel 718 (IN718) and 4340 steel. As a result, these materials were used to fabricate the test panels to be used for screening tests. Subsequent treatment and testing of the materials will determine the applicability of the technologies for components fabricated from these materials.

Identify Alternatives

Vendors were contacted to obtain information related to their respective processes. Vendor-supplied data for each of the alternative processes were organized into a Potential Alternatives Report (PAR) that provided a technical description of the process, material properties that can be obtained using the alternative, and advantages and limitations associated with each process. Where possible, performance comparisons to EHC plating were made. Eleven alternative processes were analyzed and seven were selected for demonstration. Based on the analysis results, the following technologies were selected for investigation.

- Ion beam assisted deposition (IBAD)
- Plasma Immersion Ion Processing (PIIP)
- Ion implantation
- Cathodic arc deposition
- Plasma assisted chemical vapor deposition (PACVD)
- Sputtering
- Surface modifications using lasers*

Technology Demonstration

After submission of the PAR and selection of the alternatives, the NDCEE project team contacted industrial vendors or research facilities, where appropriate, that perform the processes of interest to determine the specific, suitable treatment for obtaining the desired performance characteristics. The coatings included niobium nitride, chromium nitride, chromium oxycarbide, varieties of diamond-like carbon, and various metal-bearing carbon coatings. The implant species used for 4340 steel included chromium, titanium/nickel, and titanium. Tantalum, phosphorous, titanium/nickel, and aluminum were implanted into IN718. Sample surfaces were profiled before and after treatment to ascertain whether any treatment had a significant effect on surface roughness. Metallographic cross-sections were analyzed using scanning electron microscopy (SEM) to determine actual coating thickness. Adhesion, corrosion, nanohardness, and wear tests then were performed to evaluate the performance of the coatings. The following sections describe the details of testing.

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*Laser Induced Surface Improvements (LISI^{SM}), Surface Treatment Technologies, Tullahoma, TN.

Profilometry

Surface roughness was measured before and after each coating/implant to provide an understanding of the surface created by the coating/implantation process. The profilometer was operated in accordance with the procedures listed in ANSI B 46.1, The American National Standard for Surface Texture. The measurements taken before each coating/implant were made on randomly selected panels. The average surface roughness was 8.7 rms for the IN718 panels and 8.6 rms for the 4340 steel panels. Measurements made on the undisturbed surfaces were performed at the NDCEE facilities in Johnstown, Pennsylvania. Profilometry also was used to measure the depth of the wear scars. However, measurements of the wear scars were performed using Army Research Laboratory (ARL) facilities.

Metallography

Coating thickness, fracture surface analyses, and coating composition was measured on all coated panels. To measure coating thickness, each coated panel was cross-sectioned and mounted to view and analyze the coating thickness using a scanning electron microscope (SEM). The analyses were performed in accordance with standard test method ASTM B 748, Standard Test Method for Measurement of Thickness of Metallic Coatings by Measurement of Cross Section with a Scanning Electron Microscope. The test was performed on various size panels at the NDCEE facilities in Johnstown, Pennsylvania.

Adhesion

The adhesion of the coating to the substrate was evaluated using a CSEM Micro Scratch Tester (MST). Scratch testing is considered a comparison test; i.e., the critical loads required for delamination depend not only on the mechanical strength of the coating/substrate, but also on the parameters of the test itself and the coating/substrate system. Adhesion of thin films deposited using ion beam and plasma-based methods depends on substrate cleaning prior to deposition, in-situ sputter cleaning, deposition conditions (presence of water vapor in the chamber), the stress of the coating, and the composition of the coating. Substrate hardness, coating thickness, and surface roughness also can have a large influence on the adhesion test [1]. Because the coatings tested varied greatly in thickness and hardness, the adhesion results are not being reported herein. The test was used only to provide a relative comparison of coatings and to provide data to assist in the interpretation of wear results.

Corrosion

A corrosion analysis was performed on all panels in accordance with ASTM B117, Standard Practice for Operating Salt Spray (Fog) Apparatus. The corrosion tests were performed on three 4” x 6” panels per coating/implant at the NDCEE facilities in Johnstown, Pennsylvania. Unscribed, coated panels were placed in the corrosion chamber at a 15° angle from the vertical. The panels were subjected to a corrosive environment created by a heated chamber and an atomized 5% sodium chloride solution was introduced into the sealed chamber. The corrosion rating was based on the percent of visible red rust using guidelines set forth in ASTM D1654. Table 1 shows the basis for the ratings used.

Table 1.
Corrosion Rating

Area Failed (%)	Rating Number
No Failure	10
0 to 1	9
2 to 3	8
4 to 6	7
7 to 10	6
11 to 20	5
21 to 30	4
31 to 40	3
41 to 55	2
56 to 75	1
Over 75	0

Nanohardness

The hardness of a film is affected by microstructure, composition (degree of covalent bonding), and intrinsic film stress. Although the wear properties of a material are not completely dependent upon the hardness of the material, the hardness can have a large influence on the wear properties, depending on the type of material against which it is worn. Nanohardness testing was performed on one 1”x1” panel per coating/implant at the NDCEE facilities in Johnstown, Pennsylvania to provide some insight into the wear properties of the films. Nine hardness measurements were performed on the top surface of each coating/implanted layer rather than the cross-section of the coating (as is often performed with thick coatings) due to the thin layer being measured. For very thin coatings (e.g., less 700 nm) and implanted layers, simple load-displacement tests at a fixed load of 1 mN were performed. For all other coatings, “continuous stiffness to constant depth” tests were performed. For these tests, the indentation depth ranged from 2000 nm for the very thick laser-deposited coating and the EHC baseline to 100 nm for coatings ranging in thickness from 1000 to 5000 nm. The different tests and displacement depths were used to reduce substrate influence in the hardness measurements.

Wear

Sliding wear tests were performed on one 2” x 2” panel per coating/implant at ARL in Aberdeen, Maryland, by NDCEE and ARL personnel to assess the adhesive wear resistance of the treatments. The analysis was performed in accordance with ASTM G99, Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus. Selected panels were retested to ensure repeatability.

Table 2.
Wear Test Pin Material, Loading, and Time

Level	Time (min)	Load (g)	
		Al_2O_3	440 C
1	60	100	-
	30	-	100
2	30	150	125
3	15	300	175

Because the transfer of materials in adhesive wear depends on the nature of the materials in contact, the treatments were tested against spherical, ceramic and metallic pins of ½" in diameter. Others have noted that the transfer of material when similar metals are in sliding contact is 50 to 100 times greater than that of dissimilar metals [2]. Testing polymeric, ceramic, and metallic coatings against different materials was expected to show the differences in the type and severity of wear that may be detected for different combinations in service. Testing conducted with each pin was performed using three different loads, such that the combination of different loads and different materials produced different hertzian contact stresses in the coatings or surface modified layers. Table 2 identifies each test level, the corresponding load, pin material, and duration of testing. The criteria used to determine if the coating or surface modification should proceed to Level 2 testing was based on whether a measurable wear scar and/or debris were visible after testing. The criteria used in determining which coating or surface modification proceeded to Level 3 testing was based on 1) its performance on both the IN718 and 4340 steel panels at Level 2 testing and 2) the area of use in the engine, i.e. hot or cold part. In essence, materials that degrade at high temperatures, e.g., diamond-like carbon and metal-bearing carbon coatings, may have been tested on IN718, although it is not likely that these coatings would be used in the hot part of the engine. Therefore, these coatings may not be applied to IN718, if selected, unless a component is fabricated from IN718 and used in cooler areas of the engine.

Discussion of Results

Since a repair process/material combination that only needs to be applied once during the life of the repaired part was desired, PEWG and the NDCEE project team determined that hardness and wear performance would be the two primary performance criteria when selecting the alternatives. Therefore, vendors were asked to provide the best coating/implant and technology for super hard and super wear resistance for IN718 and 4340 steel. Tables 3 and 4 provide a summary of the hardness and wear data as well as, profilometry, thickness, and corrosion measurements performed on coatings and surface modifications applied to 4340 steel and IN718 substrates, respectively.

From the profilometry results it is clear that the coatings do not have a large impact on surface roughness. The range in surface roughness for unfinished coupons (i.e., those other than laser-treated or EHC-coated coupons), is likely due to replication of the underlying substrate material. However, it should be noted that the IN718 panels tend to be smoother than the coated 4340 panels. This is attributed to the surface finish of the substrate material prior to treatment. It was not expected that any ion beam treatment or PVD coating would provide any leveling of the surface. However, it was not known whether some PVD treatments might contribute to rougher surfaces due to the inclusion of macroparticles emanating from the deposition process. It is clear from the results that any inclusions that may exist do not have a profound effect on the ultimate surface finish. However, it should be noted that the laser-treated coating and the EHC-coated coating all required post-grinding operations. The laser-treated surface forms overlapping stripes that must be subsequently ground to achieve the desired surface finish. The post-ground surfaces of both the laser-treated panels and the EHC-coated panels were somewhat smoother than the other samples. Such smoothness could contribute to increased or decreased wear resistance (e.g., smoother surfaces can lead to increased adhesion between the metallic pin and the coating surface or can lead to decreased abrasive wear action due to reduced likelihood of removal of high asperities).

Coating thickness varied widely for all of the treatments tested, as is displayed in Tables 3 and 4. The coating thickness should be considered when evaluating adhesion and wear results; however, all hardness measurements accounted for coating thickness. The providers of the coatings were permitted to select the coating thickness that they thought would provide the greatest wear resistance. As a result, the thickness measurements are only to be used to understand the wear and corrosion results.

As expected, no thin coating or implant provided a significant level of corrosion protection to the 4340 steel substrates. Coating porosity in thin films typically leads to a reduced level of corrosion protection. The use of implanted species, likewise, does not provide adequate protection. Chromium coatings are not very corrosion resistant, but still provide significantly more protection than thin films or implanted surfaces in severely corrosive environments. It is interesting that the thick, laser-treated surface provided no improved corrosion protection over the thin films. Because IN718 is inherently corrosion-resistant, all of the thin films performed well. However, the presence of the EHC-coating caused black corrosion products to form on the surface of the exposed specimen. Several other samples treated with thin films displayed similar corrosion products, although in reduced frequency, leading to ratings less than 10.

Table 3.
Test Results on 4340

	Technology	Coating/ Implants	Hardness (HV_{100})	Volume of Worn Material (E-06cm^3)						Corrosion Rating	Profilometry - after processing (rms)	Thickness (μm)
				Al_2O_3			440C					
				Level 1	Level 2	Level 3	Level 1	Level 2	Level 3			
Coatings	EHC	Cr (+6)	1208	29.57	32.35	0.17	0.02	debris	38.08	5	1.53*	124 ± 2.0
	Cathodic Arc	CrN - Vendor B	2081	none	none	▨	debris	▨	▨	0	10.50	1.4 ± 0.1
		CrN - Vendor A	341	none	none	▨	debris	▨	▨	0	8.14	3.0 ± 0.1
	IBAD	CrN	1337	none	none	none	none	none	none	0	10.04	2.5 ± 0.1
		NbN	1567	none	none	▨	none	none	▨	0	8.54	1.5 ± 0.1
	Sputtering	Metal Bearing Carbon 1	967	none	none	▨	none	none	▨	0	11.02	2.3 ± 0.1
		Metal Bearing Carbon 2	1151	none	none	▨	none	none	▨	0	11.54	2.5 ± 0.1
		CrN	1134	none	1.29	▨	none	none	▨	0	9.45	2.0 ± 0.1
		Cr+W-C:H	775	none	none	0.52	none	none	none	0	9.32	2.6 ± 0.1
		CrN/NbN (super lattice)	2383	1.64	▨	▨	debris	▨	▨	0	11.81	3.8 ± 0.1
	PIIP	DLC	1147	none	none	0.99	none	none	none	1	9.92	5.0 ± 0.1
		CrC_XO_Y	622	none	4.45	▨	none	debris	▨	0	9.32	0.2 ± 0.1
	PACVD	DLC	1666	none	none	none	none	none	none	0	8.80	0.5 ± 0.1
	LISI	Cr/Cr Diboride	637	0.31	▨	▨	none	debris	▨	0	2.10*	162 ± 2.0
Implants	Ion Implantation	Cr - Vendor C	1003	2.95	▨	▨	1.25	▨	▨	0	9.71	NA
		Cr - Vendor D	1060	1.69	▨	▨	debris	▨	▨	0	9.32	NA
		Ti	961	1.18	▨	none	none	none	none	0	6.83	NA
		Ti/Ni	187	13.31	▨	▨	none	3.75	▨	0	8.92	NA

*After grinding and/or polishing

Table 4.
Test Results on IN718 - Coatings

	Technology	Coating	Hardness (HV_{100})	Volume of Worn Material (E-06cm^3)						Corrosion Rating	Profilometry -after processing (rms)	Thickness (µm)
				Al_2O_3			440C					
				Level 1	Level 2	Level 3	Level 1	Level 2	Level 3			
Coatings	EHC	Cr (+6)	1269	1.79	none	none	debris	none	0.23	7.7	2.58*	150 ± 4.0
	Cathodic Arc	CrN - Vendor B	2533	none	debris	▨	none	▨	▨	9.7	7.09	2.4 ± 0.1
		CrN - Vendor A	1693	0.21	▨	▨	none	▨	▨	10	7.09	2.5 ± 0.1
	IBAD	CrN	1506	none	none	none	none	debris	debris	10	5.98	2.4 ± 0.1
		NbN	1477	none	debris	debris	none	none	debris	9.7	4.46	1.5 ± 0.1
	Sputtering	Metal Bearing Carbon 1	1032	none	debris	▨	none	0.74	▨	9.5	4.07	2.7 ± 0.1
		Metal Bearing Carbon 2	1038	none	none	▨	none	0.48	▨	10	6.82	2.6 ± 0.1
		CrN	1150	none	none	none	debris	▨	debris	10	4.86	2.2 ± 0.2
		Cr+W-C:H	561	none	none	▨	none	none	▨	9.7	5.51	2.6 ± 0.1
		CrN/NbN (super lattice)	NA	none	4.03	▨	none	▨	▨	NA	6.04	3.6 ± 0.1
	PIIP	DLC	1112	NA	debris	none	NA	none	none	NA	NA	5.2 ± 1.0
		CrC_XO_Y	392	11.31	▨	▨	10.96	▨	▨	10	3.68	Not found
	PACVD	DLC	1927	NA	none	▨	NA	none	▨	10	NA	0.7 ± 0.1
	LISI	Cr/Cr Diboride	476	12.87	▨	▨	4.61	▨	▨	10	3.41*	NA
Implants	Ion Implantation	Al	573	0.27	▨	▨	8.06	▨	▨	10	5.51	NA
		P	793	0.82	▨	▨	5.83	▨	▨	10	5.38	NA
		Cr	539	6.6	▨	▨	9.15	▨	▨	10	4.33	NA
		Ta	747	7.41	▨	▨	6.53	▨	▨	10	3.94	NA
		Ti/Ni	774	7.22	▨	▨	10.74	▨	▨	9.7	4.20	NA

*after grinding and/or polishing

In terms of coating hardness, the metal-bearing carbon coatings, CrO_xC_y, one variety of DLC, one variety of CrN, the laser-treatment, and some of the implanted materials displayed hardness values lower than that of EHC. It should be noted that the implanted specimens and extremely thin coatings (CrO_xC_y) were measured using a different mode to reduce the influence of the substrate on the hardness results, but the test is still difficult to perform. These specimens might produce different hardness values if performed using another mode of operation. Nevertheless, the mode was selected after consultation with an expert in hardness testing. Other coatings, often of the same variety (e.g., CrN and DLC produced by other means), displayed hardness values significantly higher than EHC. The differences in hardness within the same coating variety may be attributed to differences in coating stoichiometry, stress, and/or composition.

In terms of wear resistance, the information presented in Tables 3 and 4 must be clarified. Some coatings shown in Table 3 indicate that no wear or debris was measured, yet the sample was not subjected to Level 3 testing. Due to the large matrix of testing that was performed, the team determined that the coatings on 4340 substrates would not be further tested if the coating displayed adhesive wear on IN718 substrates or displayed notable wear scars when mated against aluminum oxide pins. As a result, some coatings (i.e., metal-bearing carbon coatings, the sputtered CrN, the cathodic arc CrN coatings produced by vendors A and B, and the NbN coatings) were not tested at the highest loads. The Cr+W-C:H and metal-bearing carbon (2) coatings on IN718 was not tested at Level 3 because the coatings are known to degrade at temperatures experienced in hot sections of the engine where IN718 is used.

From the tables, it can be seen that the coatings of the highest hardness did not display the greatest wear resistance against either material (e.g., aluminum oxide or stainless steel). Many have noted that stress often contributes greatly to elevated hardness readings, particularly in thin films. Although film stress was not measured in this project, it is thought that some films displaying high hardness, were, likewise, highly stressed. Upon subjecting the films to higher contact stress, a loss in cohesion or adhesion was experienced. Other specimens displayed severe adhesive welding of the 440C pin to the coating and/or removal of the coating and redeposition elsewhere in the scar area. In both instances, the adhesive wear is indicated in the table as having debris accumulated in the wear scar area. The coatings that displayed the greatest potential for use in the hot areas of the engine included CrN coatings produced by IBAD and sputtering. CrN produced by IBAD, a Ti implant, and DLC produced by PACVD showed the most promise for use in cooler sections of the engine (i.e., on 4340 substrates). DLC produced by PIIP and the metal bearing carbon coatings also are being recommended for consideration in follow-on projects.

Summary

Identification of families of components and processing requirements were crucial in establishing a baseline against which the alternative technologies could be compared. The technologies being examined in this project are technologies that are capable of offering next generation coatings. These next generation coatings and surface modifications are being sought to reduce the use of chromium through life extension at the OEM level. It also is believed that slight wear of the next generation coating, that affecting a shallow layer of only a few micrometers deep, may be repaired at the depot level using that same coating. Throughout testing, it was found that most of the coatings and surface modifications performed better than EHC in terms of wear resistance. Although this was a primary criterion of the project, the team will have to review methods by which greater corrosion protection may be imparted to steel substrates. In follow-on projects, the team also will focus on situational wear tests that better approximate the service conditions experienced.

References

[1] J. Valli, “A Review of Adhesion Test Methods for Thin Hard Coatings”, J. Vac. Sci. Technol., Vol. A 4, No. 6, November/December, American Institute of Physics, 1986.

[2] Finkin, E.F., “Adhesive wear: A general review of the state of experimental knowledge and theory”, publication of Allegheny Ludlum Industries, Inc.

Non-line-of-sight (NLOS) Hard Chromium Alternatives Status Report

T. Naguy, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH
& M. Klingenberg, M. Neidbalson, M. Pavlik & D. Schario,
Concurrent Technologies Corp. (CTC), Johnstown, PA

For the past four years, CTC has been working with the U.S. Air Force Research Laboratory (AFRL) through the National Defense Center for Environmental Excellence (NDCEE) to evaluate electrochemical alternatives to hexavalent chromium electroplating for non-line-of-sight (NLOS) applications. In previous papers, the selection methods wre described and the selected alternatives were identified. Specifically, a variety of nickel-based alloys and composite coatings were selected for testing. Since the last paper, initial screening tests have been conducted and the originally selected alternatives have been analyzed for applicability, per Air Force needs and requirements. Secondary testing, which includes corrosion and wear resistance analysis, is currently underway for those alternatives that proved most viable during initial screening. This paper provides a status of the demonstration activities being performed, initial screening test results, and any conclusions that may be made.

Paper not available for publication.

For more information, contact:
T. Naguy
Air Force Research Laboratory
Wright-Patterson Air Force Base
2941 P Street, Suite 1
Wright-Patterson AFB, OH 45433
Phone: 937-255-2465

Environmentally Acceptable Technologies For the Replacement of Cadmium Coatings for Defense Applications

Dr. Michael Kane, Naval Air Systems Command, Patuxent River, MD

Cadmium coatings are used extensively in military and aerospace applications. Many of these coatings are applied to high-strength steel parts used in "critical" applications. Pollution prevention mandates require that cadmium coatings be replaced with environmentally acceptable alternatives. These alternatives need to meet functional performance requirements and be affordable, considering both deposition costs and total ownership costs. Application-specific functional performance requirements will be established and leading alternative technologies will be evaluated. Cost-based analysis of alterative technologies will also be conducted. The best overall alternative technologies will be transitioned. Because of the scope and breadth of applications in which cadmium coatings are currently used, it is likely that several alternative technologies will need to be transitioned in order to replace cadmium coatings.

Paper not available for publication.

For more information, contact:
Dr. Michael Kane
Naval Air Systems Command
48066 Shaw Rd.
Code 4341, Bldg. 2188, Unit 5
Patuxent River, MD 20670

Trivalent Chromium Pretreatments for Defense Applications

Craig Matsdorf, Naval Air Systems Command, Patuxent River, MD

Aluminum pretreatments from aqueous compositions based on trivalent chromium are currently being demonstrated in the field on a variety of defense platforms, including the Navy's F/A-18C/D Hornet, S-3 Viking, and CH-46 Sea Knight, as well as the Marines' Advanced Amphibious Assault Vehicle (AAAV). The trivalent chromium pretreatment (TCP) shows excellent all-around performance from a technical and process point of view and is the best available candidate for a "drop-in" replacement for chromate conversion coatings on a variety of substrates and coating systems. Field test data to date and processing details will be discussed, as well as life cycle impact of implementing TCP.

Paper not available for publication.

For more information, contact:
Craig Matsdorf
Naval Air Systems Command
48066 Shaw Rd.
Code 4341, Bldg. 2188, Unit 5
Patuxent River, MD 20670

AESF
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SESSION H

Wastewater Treatment & Recycling

This is a Q&A/panel discussion session.
No papers available for publication.

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Optimizing Fume Scrubber Efficiency by the Application of Water-soluble Dispersants
Mark E. Andrus, TASKEM, Inc., Brooklyn Heights, OH

Utilization of Polymerized Aluminum Coagulant Technology to Reduce Aquatic Toxicity of the Wastewater from an Integrated Metal Drawing, Tempering & Electroplating Facility
Frederick M. Lehmann & Mark E. Andrus, TASKEM, Inc., Brooklyn Heights, OH

A Non-toxic Alternative to Metal Precipitation
Roy Norcross, Degussa Corporation, Allendale NJ & Ruediger Peldszus, Degussa AG, Hanau-Wolfgang, Germany

Managing Cyanide Effluents: Field Evaluation of Reverse Osmosis for Recycling Copper Cyanide Rinses
N. Rajagopalan, J.M. Pickowitz, C.J. Jahp, J.L Talbott & T. Chow
Paper not available

Optimizing Fume Scrubber Efficiency by the Application of Water Soluble Dispersants

Mark E. Andrus
Water Treatment Division
TASKEM, Inc.
Brooklyn Hts., OH

A manufacturing facility, utilized scrubbers to neutralize and exhaust acidic fumes from metal casting and pickling process applications was experiencing poor removal efficiency and severe scaling upon internal piping and media. A chemical dispersant was added to the scrubber process water to condition dissolved solids and retard carbonate and sulfate deposition. Scrubber efficiencies were increased and waterside deposition of piping, probes, and distribution media was eliminated. By the application of this water-soluble dispersant, maintenance activities were reduced and scrubber efficiency remained within EPA compliance guidelines.

For more information, contact:
Mark Andrus
TASKEM, Inc.
4639 Van Epps Road
Brooklyn Heights, OH 44131

Phone: 216/351-1500
Fax: 216/351-5677
E-Mail: waterdoc@taskem.com

Background

A manufacturing facility, involved in the casting of bimetal alloys upon a continuous strip steel base, requires a hydrochloric acid pickle to remove oxidation of the steel base before casting. The hydrochloric acid pickle tank is ventilated to assure containment of acid vapors and fumes away from worker exposure.

The ventilation system is exhausted to a roof cross-flow fume scrubber system. The scrubber system incorporates a packing distribution deck which utilizes water droplets to "scrub and neutralize" the acidic fumes. (1) pH control assures efficient acid neutralization with the use of sodium hydroxide (2). (*See figure 1*)

Scrubber Operating Specifications

The cross-flow fume scrubber operates at a pH range of 6 to 10 standard units. 95% efficiency of acid removal is obtained at this pH level of operation. This 95% efficiency is required to meet compliance with USEPA (United States Environmental Protection Agency) regulatory guidelines.

The pH is monitored and controlled via an analyzer/controller; this controller activates a caustic feed pump.

The water scrubbing media is gravity flow returned from the packing to a collection sump. From the collection sump, a circulation pump routes the water back up to the packing media. The make-up water volume is controlled at an average of 2 GPM (gallons per minute.)

A blow-down conductivity controller adjusts the total dissolved solids (TDS) of the water to a specific level. Water TDS is a critical factor in the absorption of acidic gas fumes. As a general guideline, the scrubber water TDS should not exceed 15,000 mg/l, or 22,500 mmhos of conductivity.

The characteristics of the make-up water are an important factor that affect the ability of the recycle water to remain soluble without creating hardness deposition by-products of calcium and magnesium salts (3). In this case, the make-up water hardness contained 120 ppm of calcium hardness and 40 ppm of magnesium hardness, (160 ppm of total hardness).

A water make-up meter/controller sends a 4-20mA (milliamp) signal to a chemical feed pump, which activates a chemical dispersant. The chemical dispersant is utilized to inhibit hardness deposition by-products. In this specific case, calcium carbonate salt build-up was excessive at the desired recirculation rate conductivity of 15,000 TDS. (*See figure 2*)

Scrubber Operation Without The Dispersant Additive

As a typical operation, most fume scrubbers are installed without a chemical additive (dispersant.) Make-up water quality, i.e. the level of alkalinity and hardness in the make-up water, as well as the required pH level to meet the required acid scrubbing efficiency, will vary from application to application, and in fact, will vary in different regions of the country (4).

In many locales, water alkalinity/hardness induced deposition is a constant battle, reducing scrubber equipment removal efficiencies. In addition to poor operating efficiency, hardness induced deposition will foul the packing media, internal piping, pump seals and gaskets, conductivity probes, and pH probes.

In this specific case, deposition of calcium carbonate would seize ball valves on the circulation lines, and the recirculation pump would "lock-up" about once per quarter (every three months). Annually, the scrubber would have to be removed from service and drained. Maintenance workers, usually two men, would remove and dispose of all media using a five-gallon bucket to manually remove the media (plastic ½ moon circular shells.) All "broken-off" scale solids would then have to be removed from the sump basin of the scrubber.

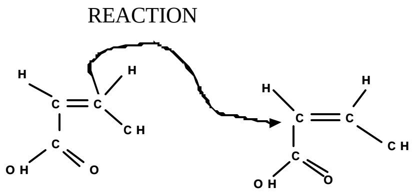
On a monthly basis, an acid cleaning was required to dissolve calcium carbonate from the conductivity and pH probes.

In summary, the scrubber became a maintenance burden and an on-going air discharge compliance concern. (*See figure 3*)

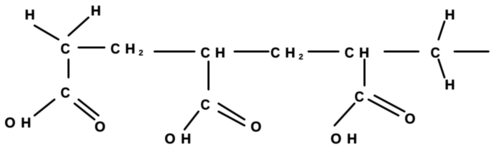
Scrubber Operating With Dispersant Program Implemented

Polyacrylate based dispersants have been widely used by the water treatment industry to inhibit hardness deposition (5). An acrylic base is reacted to form a polyacrylate chain a specific molecular weight.

Base Acrylic Acid Reaction



Polyacrylate Formation

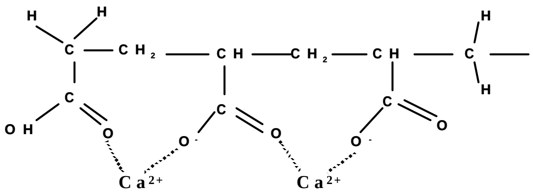


Polyacrylates react with calcium ions to inhibit calcium carbonate formation. A tight bond is created between the polyacrylate molecules and the calcium ion.

This polyacrylate-calcium bond is stronger than the affinity of calcium ions to precipitate, as calcium carbonate, at alkaline pH levels of 9 to 10 standard units.

In the scrubber recirculation water, provided the calcium ion and the polyacrylate molecule concentration are at the proper ratio, calcium carbonate formation is negligible.

Polyacrylate-Calcium Reaction



A polyacrylate dispersant treatment program was implemented on the scrubber system in November of 1999. Water analysis testing indicated a calcium hardness of 2000 ppm in the scrubber recirculation water. A dosage of 300 ppm, as dispersant, was determined to meet the calcium hardness demand in this system. As the make-up water flow was two gallons per minute (2880 gallons per day,) a total daily dispersant dosage of 0.8 gallons (or 3000 milliliters) was set for administration by the chemical feed pump. (*See figure #4*)

Operating Results: A One-Year Evaluation

The dispersant application demonstrated improvement within 30 days after implementation. After 30 days, the pH and conductivity probes no longer required extensive cleaning of calcium scale formation. Scrubber efficiency maintained 95%+ as compliance was routine versus the previous erratic operation.

Chemical demand for the dispersant was minimal, at a dosage of 0.8 gallons per day. The 55-gallon dispersant drum was located below the penthouse level of the roof scrubber, and pumped up to the roof via a liquid metering pump.

Each dispersant drum lasts for 68 factory operation days. The cost associated with utilizing a dispersant was justified, based upon reduced maintenance and on-going compliance.

After one full year of operation the full benefit of the dispersant application was noted, as follows:

- No visible scale was observed upon the plastic distribution media.
- Internal water piping ball valves were working free from occlusion by scale formation.
- The recirculation pump rebuilds were reduced to annual maintenance versus the previous quarterly re-builds of the ceramic seals. This maintenance alone saved $2,400 in pump seal costs.
- The Scrubber manual clean-out, a previous annual requirement, utilizing two men, was eliminated.
- Media replacement was no longer required. No deposition was observed upon the internal media or distribution piping of the scrubber unit.

Summary

The use of polyacrylate dispersants to assist fume scrubbers is not common for most facilities in the metal casting and finishing markets.

Dispersant chemistries are available to improve fume scrubber efficiency, reduce or eliminate hardness deposition, minimize routine maintenance, and reduce a facilities overall cost of meeting air compliance concerns.

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3. *The Nalco Water Handbook*, 2nd edition, Kemmer, Frank N., Ed., McGraw-Hill, New York, N.Y., pp. 4.1-4.7; 1988

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5. *Betz Handbook of Industrial Water Conditioning*, 7th edition, pp. 179–181, Betz Laboratories, Trevose, PA.; 1976

FIGURE #1

SCHEMATIC OF A CROSS-FLOW FUME SCRUBBER

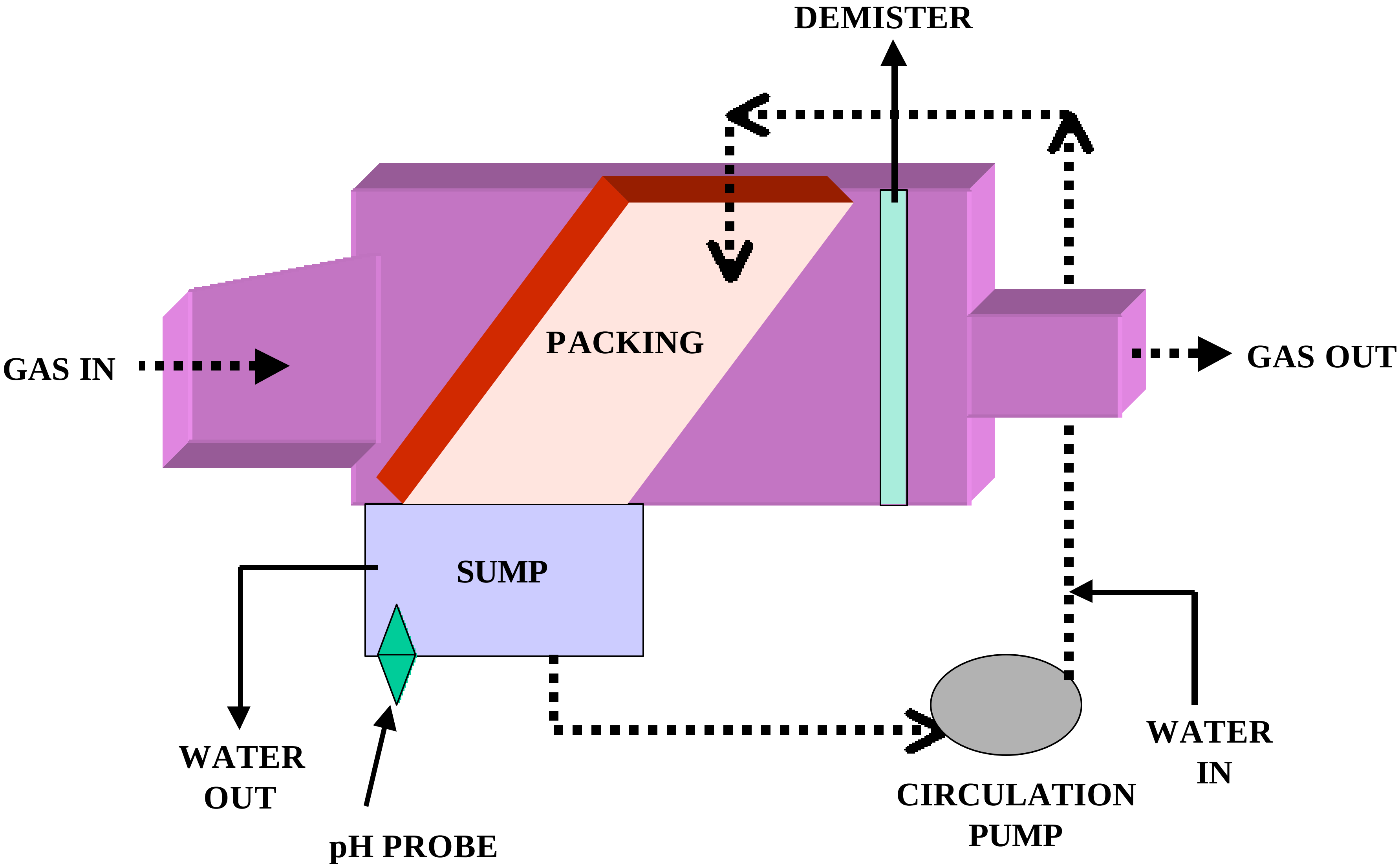


FIGURE #2

CROSS-FLOW FUME SCRUBBER WITH CHEMICAL TREATMENT DISPERSANT

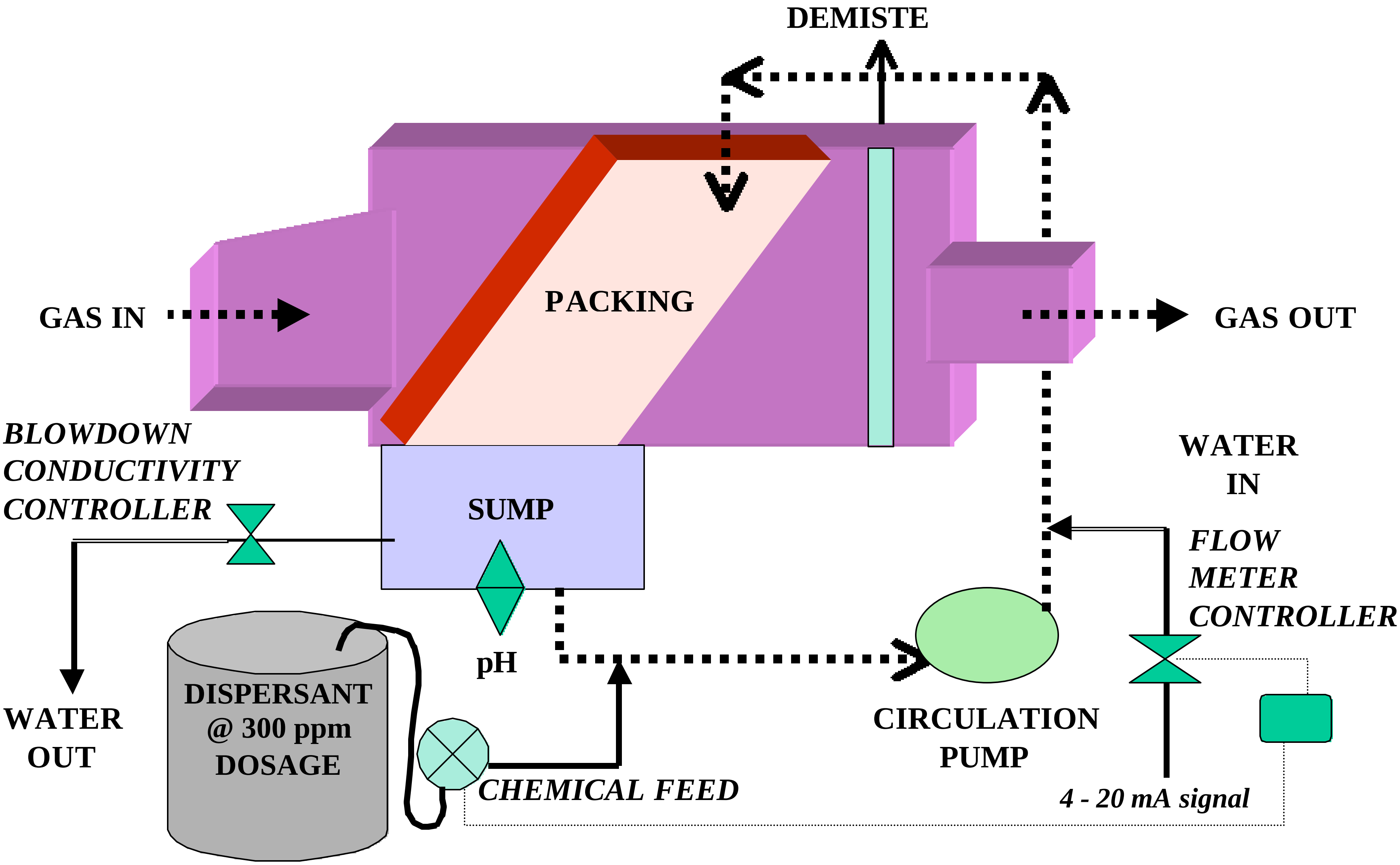
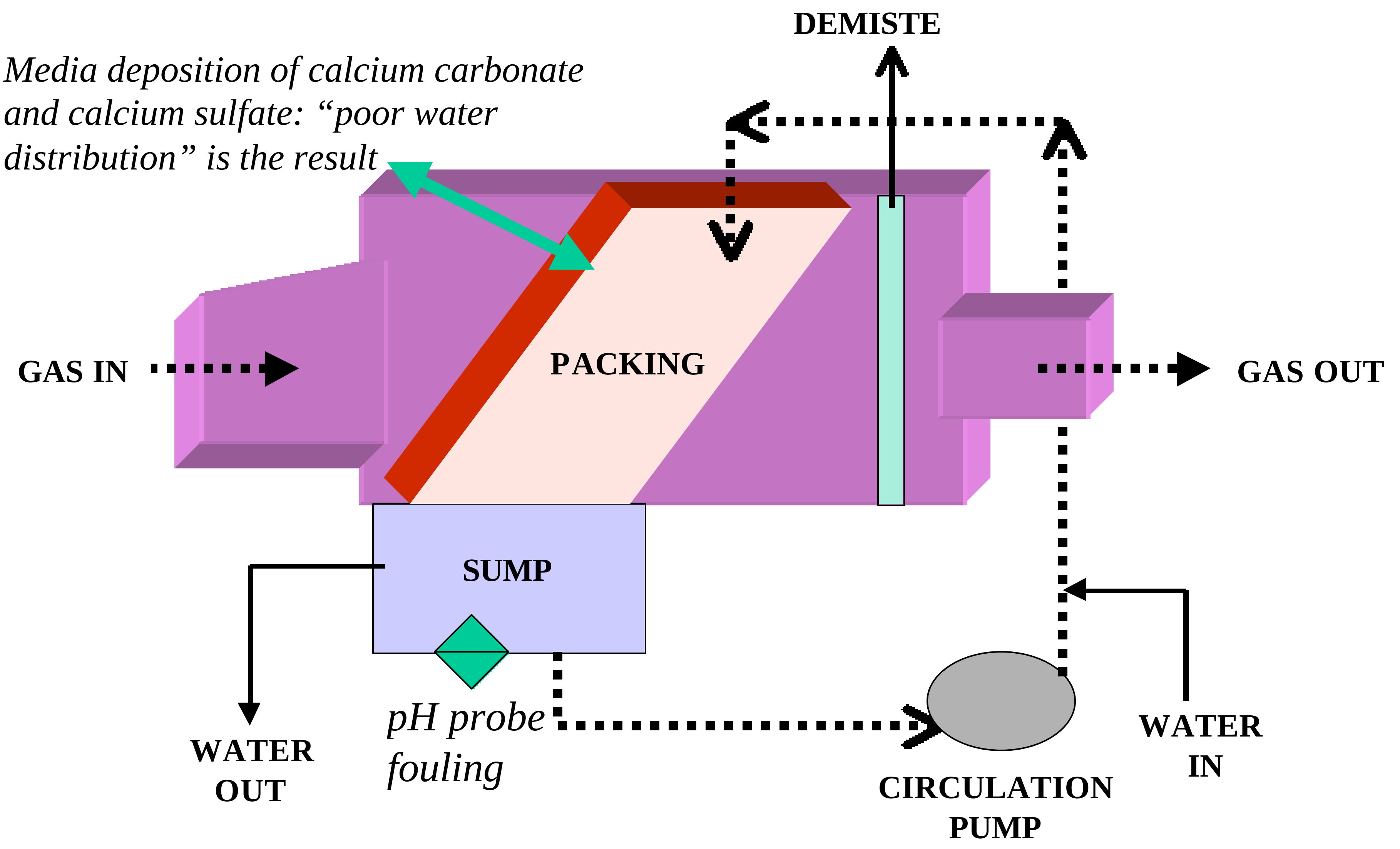


FIGURE #3

CROSS-FLOW FUME SCRUBBER: SCALE/FOULING LOCATIONS



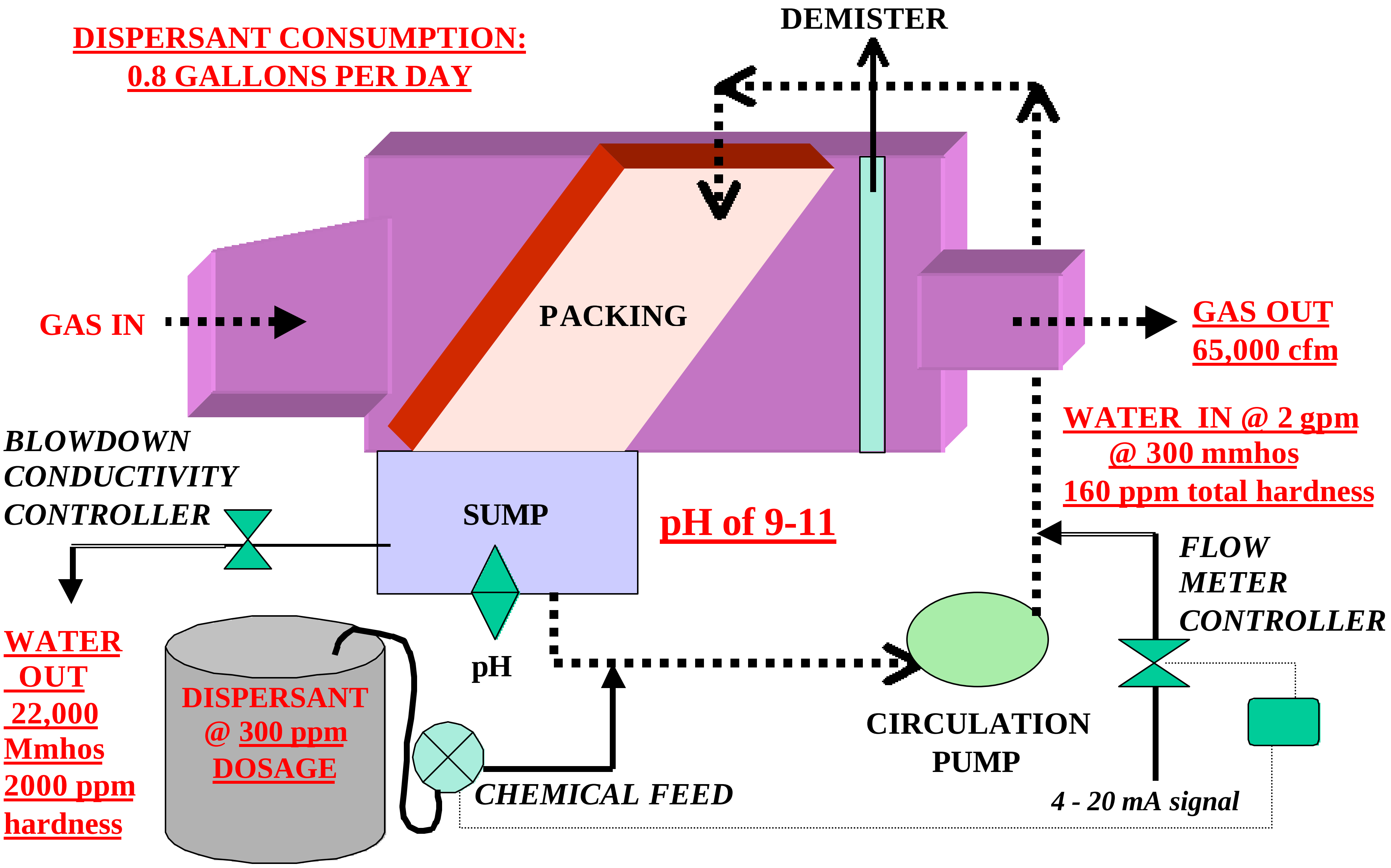
Media deposition of calcium carbonate and calcium sulfate: "poor water distribution" is the result

pH probe fouling

Pump seals and check valves "scale"

FIGURE #4

CROSS-FLOW FUME SCRUBBER WITH CHEMICAL TREATMENT DISPERSANT - OPERATING SPECIFICATIONS



Utilization of Polymerized Aluminum Coagulant Technology to Reduce Toxicity of the Wastewater from an Integrated Metal Drawing, Tempering & Electroplating Facility

Frederick M. Lehmann and Mark E. Andrus
Water Treatment Division
TASKEM, Inc.
Brooklyn Hts., OH

An integrated manufacturing facility, involved in the drawing, tempering, and electroplating of metal parts was required to meet strict metal and aquatic toxicity limits for wastewater discharged directly to an open waterway. Traditional methods of metal removal, suspended solids and oil and grease absorption, utilizing lime and anionic polymer, were not meeting aquatic toxicity requirements for both Fathead Minnows (*Pimephales promelas*) and Daphnia (*Daphnia pulex*). A treatment program that utilized a proprietary polymerized aluminum derivative, caustic and anionic polymer was developed for this facility. Through implementation of this aluminum-based technology, all metal, suspended solids and aquatic toxicity requirements were achieved.

For more information, contact:

Fritz Lehmann
TASKEM, Inc.
4639 Van Epps Road
Brooklyn Heights, OH 44131

Phone: 216/351-1500
Fax: 216/351-5677
E-Mail: waterdoc@taskem.com

Background

A manufacturing facility located on the East Coast was required to meet strict toxicity standards for effluent discharge. Like many manufacturing locations in the Upper Eastern United States, the older infrastructure of the local communities was designed for manufacturing facilities to directly discharge wastewater (after primary treatment) into open waterways, most commonly to rivers and their tributaries. These manufacturing facilities have had to "evolve and update" their waste treatment systems to meet more stringent discharge limits.

The evolution of wastewater requirements leads to today's direct discharge limitations including indigenous organism aquatic toxicity survival requirements upon a facilities discharge. In this specific case, 100% survival of both juvenile, less than 14 day-old, Fathead Minnows (*Pimphales promelus*) and for Daphnia (*Daphnia Pulex*) was required.

Manufacturing Operations and the Impact Upon Waste Treatment

This manufacturing facility is an integrated manufacturer of metal tubing. The process operations include metal drawing, heat-treating, tempering, and electroplating.

In the metal cleaning, drawing, tempering, and heat-treating operations, oils and lubes are applied to the metal parts. The use of nitrites, borax, and sterates (fatty acid organic derivatives) are commonly used in these metal process steps. Both soluble and insoluble oils are generated from these primary metal treatment operations.

The electroplating process' produces a variety of wastewater contaminants, including; pretreatment acid-etch and alkaline cleaners (surfactants, wetting agents, and chelating compounds) and metal electroplating bath & rinse process waste (hexavalent chromium, copper, and nickel) wastewater.

In the case of heavy metals, aquatic toxicity based upon the specific ion concentration, is well known and has been regulated from the on-set of government discharge permitting. The influence of soluble organic contamination, from all of the above listed operations, is much more difficult to characterize with regards to effluent toxicity. Many organics are oxidized or reduced when co-mingled and processed through the various treatment steps. The "mixed" wastewater from the bleed-in of alkaline and acidic waste creates both "fractioned insoluble organics" which can be manually separated from treatment holding tanks, as well as "emulsified and complexed organics" that influence many wastewater characteristics including:

(1) metal hydroxide inhibition and altering cation species solubility,

(2) changing the surface tension of the wastewater, and

(3) influencing the zeta potential, or the net charge differential, of the combined waste sources.

Identified Wastewater Treatment Operations

The wastewater treatment system was engineered to handle flow rates of up to 100,000 gallons per day. Modifications have been made over the years to optimize oil separation, chrome reduction, and the segregation, batch treatment, and bleed-in of concentrated alkaline and acid cleaners.

Here is a summary of the treatment steps:

- *Metal hydroxide precipitation* via the use of lime for both pH adjustment (to a level of 9.5 to 10 standard units) providing solids conditioning/neutralization was the basis of treatment.

- *Segregated waste streams of hexavalent chromium* (reduced to a trivalent species via sodium meta-bisulfite), *alkaline cleaner batches* (pH adjusted with acid), and *spent acid batches* (pH adjusted with alkali) were all engineered to "bleed-in" to an acid/alkaline retention tank.

- *The waste sources from metal forming, drawing, tempering, and heat-treating were "oil skimmed"* and routed to the acid/alkaline retention tank.

- *Upon pH adjustment, anionic polymer induced flocculation and solids' settling was preformed in two lamella style clarifiers*.

- *A sand filter* was used for solids carryover "polishing."

- Before discharge to the open waterway (river) *a final pH adjustment holding tank was used to lower the pH to approximately 8 – 8.5 standard units* with sulfuric acid.

Wastewater treated by the above process provided "marginal" success in meeting the toxicity requirements of 100% survival for Fathead Minnows and Daphnia, for a 48-hour acute toxicity test, on 100% plant effluent.

Upon analysis of the wastewater, the following was postulated as 'likely sources' of wastewater toxicity:

- Elevated sulfates
- Soluble iron, zinc, nickel, and chrome
- Pin-floc 'break-through' of metal hydroxides past the sand filter

Untreated wastewater composites had the following parameter range variance:

Figure 1.

Parameter	**Untreated Neutralization Tank**
pH:	4 .8 - 5.6 S. U.
Conductivity	2600 - 2850 mmhos
TDS	1742 - 1900
"P" alkalinity	0 ppm
"M" alkalinity	30 - 40 ppm
Magnesium hardness	11 - 12 ppm
Calcium hardness	287 - 321 ppm
Total Hardness	298 - 333 ppm
Sulfate	1500 - 1550 ppm
Chloride	140 - 180 ppm
Iron	135 - 227 ppm
Zinc	38 - 64 ppm
Nickel	151 - 183 ppm
Total chromium	76 - 114 ppm

Based upon the weekly composites and daily grab sample analysis of the existing treatment effluent, it became obvious that the existing treatment program was not going to provide compliance with the toxicity requirements of the permit.

Proposed Treatment Program: Development and Implementation

A treatment program that could lower total dissolved solids (TDS), provide low metal concentrations, and provide a means of reducing organic contamination was the objective.

Jar-testing was performed with various coagulant aids that have some known affinity for organic absorption and enhanced metal precipitation. In addition, if the coagulant aid(s) could utilize caustic versus lime for pH adjustment, a drop in TDS would be observed.

A proprietary reacted polymerized aluminum/magnesium inorganic coagulant was selected based upon metal removal and improved water clarity. The water clarity was correlated to soluble organic [emulsified oil] removal from the treated wastewater.

A "hybrid" treatment program provided the best water quality, as follows:

1. A 200-ppm dosage of the reacted polymerized aluminum/magnesium coagulant-added to the neutralization tank.

2. Utilizing a 15% lime - 85% caustic mixture for pH adjustment to a level of 9.5 standard units.

3. Adding a 1.5-ppm anionic emulsion polymer dosage for solids flocculation at the clarifier floc-mixing tanks.

4. A final pH adjustment to 7.0 standard units, in the post sand filtration holding tank, with hydrochloric acid

The supernatant from this treatment process was very clear with a turbidity of (1-3 NTU's) and absorbed the majority of organic surfactant/wetting agents (as was evident by the lack of foaming and surface tension on the air-water interface of the treated samples.)

This treatment process would also provide for improved solids capture, as the solids composition was dense and resistant to shearing, versus the previous 'all-lime' based treatment scheme.

The treatment of wastewater composites and grab samples provided the following treated wastewater quality:

Figure 2.

Parameter	**Proposed Treatment Supernatant**
pH:	7.0 - 7.2 S. U.
Conductivity	2410 - 2490 mmhos
TDS	1600 - 1668
"P" alkalinity	0 ppm
"M" alkalinity	25 - 30 ppm
Magnesium hardness	10 - 11 ppm
Calcium hardness	460 - 580 ppm
Total Hardness	470 - 590 ppm
Sulfate	1150 - 1310 ppm
Chloride	160 - 200 ppm
Iron	0.01 - 0.03 ppm
Zinc	0.01 - 0.02 ppm
Nickel	0.03 - 0.06 ppm
Total chromium	0.02 - 0.03 ppm

The treated wastewater metallic(s) concentration can be considered 'relatively non-toxic.' Unlike metallics, the toxicity derived from organic components cannot be gauged by any other means other then actual aquatic toxicity tests.

Wastewater was collected on-site as two weekly composites. The proposed treatment was preformed in the laboratory, reflecting actual flow/equipment design specifications. *Accuracy in treatment was gauged to match the retention time, mixing, and dosage parameters of the treatment plant.*

Upon completion of this process, the supernatant was evaluated for acute toxicity of Fathead Minnows (*Pimphales promelus*). The following toxicity data was derived for a 96-hour acute test on both weekly composites:

Figure 3.

Mortality of Fathead Minnows
(*Pimphales promelus*)
12 fish per test/2.5 gallons per container - aerated

Exposure	control	composite 1	composite 2
1 hour	0	0	0
8 hour	0	0	0
24 hour	0	0	0
48 hour	1 (8.3%)	0	0
72 hour	0	0	0
96 hour	0	0	0
TOTAL	**1 (8.3%)**	**0**	**0**

Secondary Testing & Confirmation: On-site Testing

As the laboratory tests provided a 100% survival rate to 96 hours of acute toxicity, the program was ready for confirmation on-site using real-time wastewater conditions.

The facility collected (1) weekly composite and (1) grab sample. These samples were treated on-site with the reacted polymerized aluminum/magnesium coagulant and a 15% lime - 85% caustic mixture.

The supernatant from each test was collected and delivered to a certified laboratory for permit required testing: [a 48-hour acute toxicity for juvenile (less than 14-day old) Fathead Minnow (*Promelus Pimphales*) and for Daphnia (*Daphnia pulex*).]

As a means of comparison, actual on-site, current plant discharge wastewater was also submitted for analysis, for both a composite and grab sample event.

The results confirmed the success of the ***proposed treatment program***, as both Fathead Minnow (*Promelus Pimphales*) and Daphnia (*Daphnia pulex*) *survived at 100% (no morality) for the 48-hour permitted specification time interval.*

The ***actual plant wastewater***, with the existing lime program, *failed after 24-hours with both Fathead Minnow and Daphnia experiencing 100% mortality.*

Conclusions and Final Comments

The comparative tests of the reacted polymerized aluminum/magnesium coagulant versus the existing all-lime treatment program confirmed that applying this innovative coagulant technology significantly reduces toxicity.

Metal removal and organic absorption are two benefits of applying this proprietary aluminum/magnesium technology. In addition, a reduction is sludge volume can be gained versus the traditional lime-based treatment program.

At the time this paper was submitted for publication, the facility is in the process of re-engineering the entire wastewater treatment program. A reverse osmosis (RO) system is planned for meeting both effluent compliance and water recovery parameters.

This reacted polymerized aluminum/magnesium coagulant is specified for use as a base “pre-treatment” before the polishing RO system, to gain the benefits of organic absorption, solids conditioning, metal removal, sludge minimization, and toxicity reduction.

A Non-toxic Alternative to Metal Precipitation

Roy Norcross, Degussa Corporation, Allendale , NJ
Ruediger Peldszus, Degussa AG, Hanau-Wolfgang, Germany

Faced with the proposed MP&M standards, many finishers may have to consider new technologies to treat various waste streams in order to meet lower soluble metal limits in effluent. Chemical treatment beyond the standard hydroxide precipitation steps using metal precipitants may provide a viable option. Many of the precipitating agents on the market have been used effectively for many years, however, the toxicity and handling of these compounds must be considered when choosing the best precipitant for metals removal. Some recent, well-publicized spills show the potential hazards associated with some of these commonly used compounds. TMT (trimercapto-s-triazine, trisodium salt) is a non-toxic metal precipitant that effectively precipitates most metals, even metal complexes, in acidic or alkaline solutions. It is presently being used in many industries, including waste incineration, photochemical, mining, chemical synthesis, and metal finishing. This paper will discuss the characteristics of TMT and TMT metal precipitates, the relative benefits over other metal precipitants, as well as the best applications of this product.

For more information, contact:
Roy Norcross
Degussa Corporation
4 Pearl Court
Allendale, New Jersey 07401
Tel: (201)818-3715
Fax: (201)327-7424
E-mail: roy.norcross@degussa.com

The removal of heavy metals from effluents before discharge to the environment has long been a requirement for virtually all industries, and for good reason. Many of these metals, such as mercury, lead, cadmium, copper, nickel, zinc and silver, found in metal processing effluents are toxic and pose a potential threat to the environment. Most of these metals, especially the more common nickel, copper and zinc, can be efficiently removed by the traditional addition of alkali followed by the removal of the resulting insoluble metal hydroxide salts. However, the presence of complexing agents may require the use of other metal removal processes to achieve the desired soluble metal limits. Also, the reduction of the permissible heavy metal concentration in the effluent may force the use of precipitating agents to produce more stable precipitates.

By producing more stable and less soluble precipitates, the use of sulfide based precipitating agents can keep the insoluble heavy metal salts from redissolving, even in the presence of chelating compounds, thereby meeting the low limits required for discharge. This can be done in addition to a hydroxide precipitating stage or separately. The relative stability of TMT metal precipitates over hydroxides is shown in Figure 1. The solubility products for many sulfur based precipitating agents are in the same range.

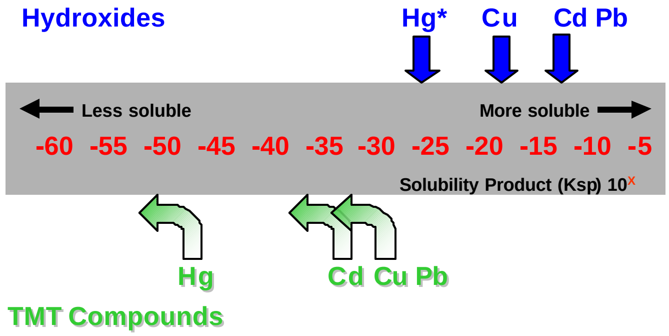


Figure 1. -Solubility Product, Ksp (Ksp = [Cations]^A *x [Anions]*^{B} *where A,B are the stoichiometric factors for the anion, cations, respectively) for hydroxide and TMT metal salts. *Hg does not form a hydroxide*

Other processes can be used such as ion exchange, electrolysis and the use of strong oxidizers to treat complexing agents. However, these processes may not be economically feasible for many effluents, and may require substantial capital investment.

Commonly used sulfide based precipitating agents include:

- Sodium sulfide, Na_2S
- Dithiocarbamates, DTC
- Trithiocarbonates, Na_2CS_3
- Trimercaptotriazine, TMT

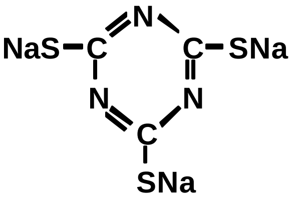
When choosing a precipitation agent, there are a number of factors that one must consider:

1. Effective and economical removal of metals
2. Stability of the precipitate produced
3. Toxicity of the precipitating agent

TMT works economically and efficiently over a broad pH range, producing an easily removed and stable precipitate. Because TMT is not toxic, it does not require treatment before discharge to the environment.

TMT: Product Description

Trimercapto-s-triazine trisodium salt, or TMT, is available as a 15% solution or a 55% salt. The structure is shown below:



Pertinent product data:

CAS #	17766-26-6
Molecular weight.	143.22 g/mol
Odor	Virtually none
TMT 15 pH	approx. 12.5
TMT 15 density	1.12 g/mL

The sulfur groups are the active sites that bond to the metal ions. For divalent metal ions, a 3:2 molar ratio of the metal(M) to TMT is required:

Equation 1: $3M^{2+} + 2TMT^{3-} \rightarrow M_3TMT_2$

For monovalent ions, a 3:1 molar ratio of the metal(M) to TMT is required:

Equation 2: $3M^{+} + TMT^{3-} \rightarrow M_3TMT$

Most transition metals form an insoluble TMT – metal complex. However, some trivalent metals, as shown in Table 1, do not.

Table 1. Application of TMT	
Metals that do precipitate	Metals that do not precipitate
Cadmium (Cd) Copper (Cu) Lead (Pb) Mercury (Hg) Nickel (Ni) Silver (Ag) Tin (Sn) Zinc (Zn)	Aluminum (Al) Chromium (Cr) Iron (Fe)

Figure 2 shows the addition rates of TMT for the various metals that form insoluble TMT complexes. The different addition rates are a function of the molecular weights of the metals, and are given in terms of liters of TMT 15 per kilogram of metal.

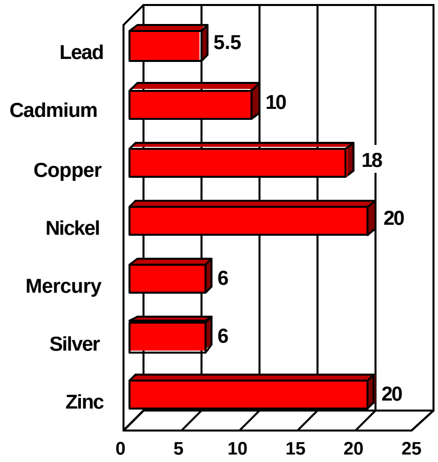


Figure. 2 –TMT addition requirements for various metals in terms of liters of TMT 15 per kilogram of heavy metal. For gallons TMT 15 per pound of heavy metal, multiply the number from the chart by 0.120.

TMT-metal sludges exhibit excellent chemical and thermal stability and may be acceptable for non-hazardous landfills[1]. Table 2 shows the TCLP, Toxic Characteristic Leaching Procedure, test results on sludge samples containing mercury, lead and cadmium. In all cases the TCLP limits are met.

Table 2. TCLP Results on Various TMT-Metal Sludges[2]

Metal	Content in Sludge Initially (ppm)	Content in TCLP Extract (ppm)	TCLP Limit (ppm)
Hg	17.29 27.69	0.004 0.003	0.2
Pb	13.43 24.24	0.22 0.22	5.0
Cd	11.51 11.57	0.21 0.13	1.0

TMT –metal sludges are typically coarse and easily flocculated with non-ionic or anionic polyacrylamides. The addition of iron or aluminum salts may be necessary for solutions containing only small amounts of heavy metals.

Other benefits include:

- Ease of use as liquid or solid
- Ability to precipitate metals in a wide pH range
- Handling ease: non-toxic, virtually no odor
- Excess product does not require detoxification

TMT Applications

For over 20 years, TMT has been used effectively in a variety of industries where the product benefits can be realized.

Combustion plants

Several hundred garbage incineration facilities and coal fired power generation plants presently use TMT primarily for the precipitation of ionic mercury and cadmium in the scrubber solutions. TMT is considered to be state-of-the-art for these applications. Hazardous waste treatment is another area where TMT is used.

Photographic industry

TMT is used to remove silver from photographic waste streams producing silver sludges that can be subsequently recycled. Batch processing can be done for the silver removal process.

Chemical synthesis

The removal of catalysts from chemical processes is another area where TMT is used. Due to the non-toxic nature of the product, pharmaceutical companies use TMT for removal of copper and palladium[3].

Electroplating/ metal finishing

A variety of applications for TMT can be found in the “metal working” industry which includes printed circuit board producers and electroplaters.

Generally, the treatment of these galvanic waste streams require the following steps:

1. Pretreatment stages to treat cyanide or reduce chromium with oxidation processes, for example, using hydrogen peroxide.

2. Precipitation of the uncomplexed metals as hydroxides using lime or caustic.
3. Precipitation of the complexed metals with precipitation agents, such as TMT.

The flow diagram[5] shown in Figure 3 provides a more detailed process using TMT.

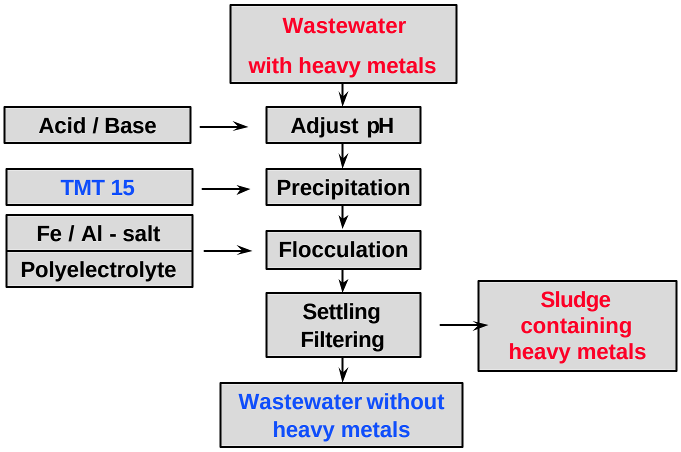


Figure 3. –General flow diagram for treating galvanic effluents containing metals.

Other steps may be required to accommodate a hydroxide recycling stage, or for metals bound with strong complexing agents like EDTA.

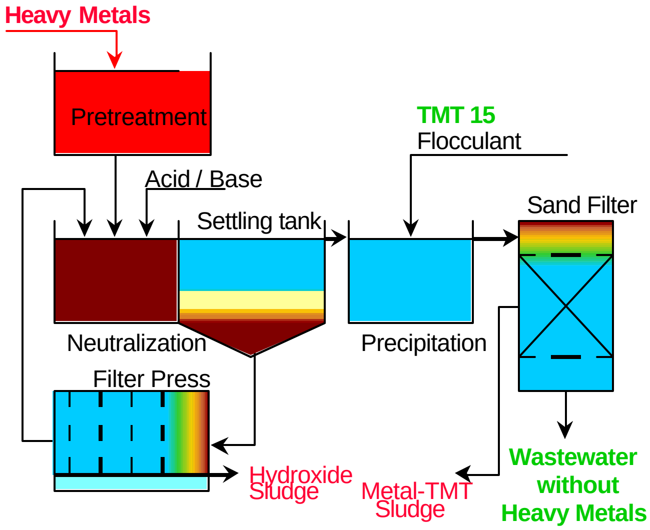


Figure 4 .-Schematic diagram of waste treatment for galvanic effluents containing heavy metals.

In Figure 4, the bulk of the metals are precipitated as hydroxides, while the remaining complexed metals contained in the settling tank overflow are treated with TMT in a polishing step. This allows for the recycling of the hydroxide salts after filtration with, in this case, a filter press. The metal TMT sludge can be sent to a landfill. By precipitating the uncomplexed metals with relatively cheap reagents such as lime or caustic, the more expensive sulfur based precipitating agents, in this case TMT, can be used only where needed, thereby optimizing the treatment costs.

Case Study #1

Problem: An electroplating shop creates a process rinse water effluent containing 24 ppm copper at a pH of 2. It was determined that some of the copper was complexed.

Solution: Using a process design similar to that represented in Figure 4, a two stage process was implemented to meet their copper treatment targets.

Treatment procedure:

- Stage 1
  1. Lime was added to adjust pH from 2 to 9 using 1.0 kg $Ca(OH)_2$ per $10m^3$ (8.3 lb/10,000 gal) of effluent.
  2. Agitated for 30 minutes in reaction tank.
  3. Hydroxide sludge removed with filter press.
- Stage 2
  1. To filtrate from stage 1, 0.61 L TMT 15 per 10 m^3 (0.61 gal/10,000 gal) was added to treat the remaining 3.4 ppm copper (see Figure 2).
  2. 0.1 kg $FeCl_3$ was added per $10m^3$ (0.83 lb/10,000 gal) as a coagulent for the relatively small amount of metals present.
  3. Non-ionic flocculent was added at a rate of 20 L as a 0.05% solution per $10m^3$ (20 gal/10,000 gal).
  4. Metal TMT precipitate was removed via settling and filtration.

Result: The residual copper concentration in the effluent was 0.03 ppm, well below targeted levels.

Case Study #2

Problem: A wire drawing plant needs to treat draw emulsion effluent containing 274 ppm copper and 168 ppm zinc. Due to the presence of ammonia, precipitation using lime or caustic was not successful.

Solution: A single stage circuit using TMT was implemented to treat the effluent in 1 m^3 batches, similar to that shown in Figure 5. No pH adjustment was necessary since the effluent was already at a pH of 7.3.

Treatment procedure:

1. Based on the reagent requirements described in Figure 2 for copper and zinc, 8.1 L of TMT 15 per m^3 (8.1 gal/1,000 gal) was added.
2. A strong anionic flocculent was added at a rate of 40 L as a 0.05% solution per m^3 (40 gal/1,000 gal).
3. Metal TMT precipitate was removed via settling and filtration.

Result: The residual copper and zinc concentrations were 0.03 and 1.4 ppm, respectively.

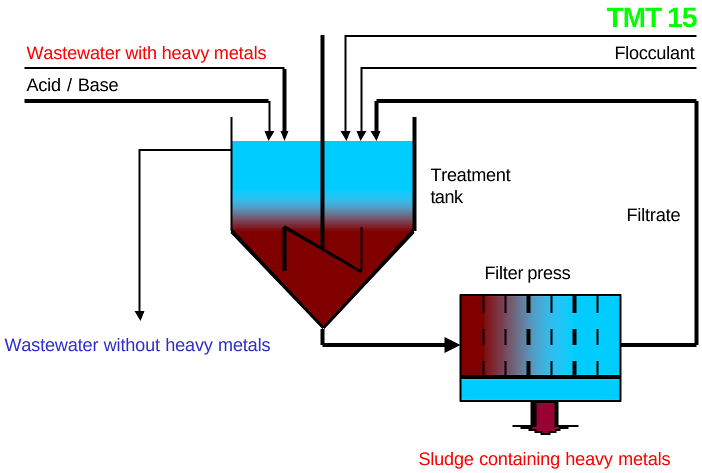


Figure 5. -Batch treatment flowsheet for galvanic effluents containing heavy metals using TMT alone.

Comparison of Sulfur Based Precipitation Agents

When considering which precipitation agent to use, the specific application must be well understood. Table 3 describes some of the relative advantages and disadvantages between these products. Factors such as the pH of the effluent, the metal content, the presence of chelating agents among others, must be taken into account. The all important treatment costs will have to be factored in with handling and disposal costs.

The equipment and the circuit design will also be dependent upon which agent is chosen. For example, if sodium sulfide was chosen, the materials of construction for the reaction tanks, piping, pumps and venting must be able to handle the corrosive nature of the product. For DTC and trithiocarbonates, a residual treatment circuit may be necessary to properly detoxify the effluent. The hazardous nature of some of these products will also dictate the equipment required for the health and safety of the operators.

Table 3. Application of Various Precipitation Agents Advantages and Disadvantages

Precipitating Agent	Advantages	Disadvantages
Sodium Sulfide (Na$_2$S)	-Sludge stability. -Tried and tested -Costs: very low	-Elevated pH only -Floc. Problems -Corrosive -Odor -Difficult handling -Residual treatment probable -Ecology/ toxic properties: poor
Dithiocarbamates (DTC) Trithiocarbonates (NaCS$_3$)	- Proven effective even for strongly chelated metals -DTC frequently used. -Costs: average	-Effective at pH >7 -Odor -Residual treatment likely -Ecology/ toxic properties: poor
Trimercapto-triazine (TMT)	-Ease of handling -Odorless -Sludge stability -Works in wide pH range -No residual treatment required -Ecology/ toxic properties: good -No reaction with ferric flocs	-Strongly chelated metals may require extra stages -Difficulty with Zn and chelated Ni -Costs: above average

Table 4 focuses on the toxicologic and ecological properties of sodium sulfide, trithiocarbonate, dithiocarbamate and TMT. These properties are expressed in terms of acute toxicity and lethal concentration data, as well as the products of decomposition and whether or not they are mutagenic.

Table 4. Toxicological/Ecological Properties of Various Precipitating Agents

	Na_2S	Na_2CS_3	DTC	TMT
Acute Toxicity Rat LD_{50} mg/kg	208	n.a.	3,590	7,878
Lethal Conc. Fish LC mg/L	25 (LC_{50})	55 (LC_{50})	20 (LC_{50})	12,000 *(LC_0)
Products of Decomposition	H_2S	H_2S CS_2	CS_2	none
Mutagenic Yes/No	n.a.	n.a.	Yes	No

*Note: No fish mortality at 12,000 ppm, hence “LC_0”

Sodium sulfide(Na_2S) has a long track record for use as a precipitating agent. It is by far the cheapest of the four, and is still used today. When used on its own, the product produces fine particulates that do not settle easily. Furthmore, sodium sulfide can only be used for solutions with elevated pH levels. If acidified, it releases hydrogen sulfide gas which is extremely toxic. Both the rat and the fish toxicity data reveal why residual sulfide treatment steps may be mandatory. Handling of the product must be done with great care due to the potential release of H_2S and its corrosiveness.

Although sodium trithiocarbonate(Na_2CS_3) is not as frequently used as Na_2S or DTC, it is still an effective precipitating agent with similar application strengths as Na_2S. No acute toxicity or mutagenic property data are available. However, it is very toxic to marine life[6] and could require that any residual Na_2CS_3 be treated before discharge. The decomposition products, hydrogen sulfide and carbon disulfide, are both very hazardous toxins.

For treating strongly complexed metals, DTC is the most effective of the four products. Like sodium sulfide, it is frequently used in the metal finishing industry. However, it is far more expensive. Commonly available as an approximately 40% solution as sodium dimethyl or diethlyldithiocarbamate, it is relatively stable. On the downside, as past environmental exposure would indicate[9 & 10], DTC is the most detrimental to marine life of the four[7]. It is also known to have mutagenic properties[11]. Therefore, worker exposure must be limited. Carbon disulfide, a neurotoxin, is the main product of decomposition. In most cases, detoxification of any residual DTC is required.

TMT works well in effluents in a very wide pH range, and is the only one of the four precipitating agents that works effectively in acidic effluents. It is also the only one that does not produce hazardous products of decomposition. The sludges produced are stable and pass TCLP tests. Due to the product’s lack of toxicity, transport and shipping risks are minimal. Handling and worker exposure problems are virtually eliminated, and residual treatment systems are not necessary. However, disadvantages include extra steps required for strongly chelated metals, difficulties in precipitating zinc and chelated nickel, as well as the higher costs of the product itself.

Summary

The treatment of heavy metal containing waste streams from plating operations is commonly accomplished by hydroxide precipitation. However, the presence of complexing agents and/or a reduction in the permissible discharge limits may force certain facilities to consider additional treatment options, such as sulfur based precipitating agents that produce far more stable precipitates than hydroxides. These chemicals can be used alone or together with hydroxide precipitating steps. When choosing a precipitating agent for a particular process, the performance and costs of the product are the most critical considerations. But the toxicity of some of these products must also be considered since these factors will affect the handling, use and potential treatment of the product as well.

Of the four sulfur based precipitating agents that were discussed in this paper, TMT shows by far the best toxicological and ecological properties. Although the product is more expensive than the others, when one considers other expenses such as those associated with handling and detoxification, TMT may actually be more economical to use. TMT is capable of precipitating heavy metals even in strongly acidic conditions, unlike most precipitating agents, and also produces stable TMT – metal sludges that will pass TCLP test conditions.

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Managing Cyanide Effluents:
Field Evaluation of Reverse Osmosis
For Recycling Copper Cyanide Rinses

N. Rajagopalan, J.M. Pickowitz, C.J. Jahp, J.L Talbott & T. Chow

Membrane-based processes, such as reverse osmosis (RO), offer potential advantages (such as the ability to recover and recycle the cyanide to the process) as compared to methods that focus on chemical transformation of cyanides to less toxic substances. RO has been reported to be particularly suitable for recycling cyanide rinse waters, but very few electroplating facilities have adopted this technology. It is well known that innovation is primarily impeded by the associated uncertainty. The Illinois Waste Management & Research Center has pioneered an approach to accelerate the diffusion of pollution prevention technologies (ADOP^{2}T) through a combination of extensive piloting, customer education, and facilitating peer-to-peer networks, with the major focus on reducing uncertainty at every level of technology integration. This report will focus on a pilot of managing cyanide rinse waters from copper strike through RO. The primary uncertainties addressed deal with (1) fouling productivity of the membrane; (2) effect of feed concentration on flux and rejection; and (3) suitability of the RO concentrate for reuse.

Paper not available for publication.

For more information, contact:
N. Rajagopalan
WRMC
1 East Hazelwood Dr.,
Champaign, IL 61820
Phone: 317-244-8905
FAX: 217-333-8941

AESF WEEK

SESSION K

Pollution Prevention & Control II

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The Impact of Barrel Design on Drag-out Rates
Frank Altmayer, MSF, AESF Fellow; Jeff Zak, P.E., CEF; Kevin Wasag, CEF; & Brian Cavanaugh, Scientific Control Labs, Chicago, IL

Environmentally Benign Manufacturing: Integrated-model-based Process Modification
H.H Lou, Department of Chemical Engineering, Lamar University, Beaumont, TX & Y.L. Huang, Department of Chemical Engineering & Materials Science, Wayne State University, Detroit, MI
Paper not available

Integrating Pollution Prevention, Pollution Control & Energy Efficiency in Surface Finishing through Process Modeling & Engineering Analysis
Kevin Klink, P.E., CH2M Hill, Corvallis, OR; Peter Gallerani, CEF-2, Integrated Technologies, Danville, VT; & Eric Fountain, CEF, CH2M Hill, Corvallis, OR
Paper not available

Treatment & Control of Nickel Electroplating Baths Using Catalyzed Hydrogen Peroxide

By: Peter Forth, Art Vibert, Madeline Busch and Sarah Stevenson
Kuntz Electroplating Inc, 851 Wilson Ave., Kitchener, Ontario, N2C 1J1

Kuntz Electroplating Inc., a large OEM ‘job shop’ located in Kitchener, Ontario, was faced with a unique situation. The configurations of their customers’ products required extensive use of inert auxiliary anodes in order to meet OEM quality standards. The extent of use resulted in a significantly higher amount of organic breakdown products occurring as a result of numerous electrochemical reactions within the electroplating cell and at the auxiliary anode. These organic breakdown products remain within the operating bath and have the potential to alter the structure and physical properties of the deposit. These organics are controlled by regular and frequent activated carbon maintenance which is very costly due to issues such as; downtime requirement, degree of solid and liquid waste generated, loss and replenishment of organic constituents, inefficiencies in established treatment method, employee contact with activated carbon, etc. As a result, Kuntz began investigating alternative methods for control and purification of nickel baths.

Most Watts electrolyte solutions are a mixture of nickel salts and depending on their direct application, a group of specifically formulated organic constituents, used to modify the crystalline electroplated structure. At Kuntz (KEI) the nature of our challenge indicated that focusing on the ‘coumarin’ based semi-bright nickel solution would be the most advantageous. The bath make-up is as follows(Table 1);

Contents		**Optimum Ranges**	**Units**
pH		3.7 to 4.0	
Nickel Sulphate	$NiSO_4.6H_2O$	150 to 450	g/L
Nickel Chloride	$NiCl_2.6H_2O$	37.5 to 150	g/L
Boric Acid	H_3BO_3	37.5 to 60	g/L
Coumarin	$C_9H_6O_2$	0.15 to 0.3	g/L
Organic Surfactants		0.045 to 0.055	g/L

Table 1: Typical semi-bright electrolyte make-up

These particular semi-bright solutions contain organic constituents that are non-sulfur bearing. A view of the organic structure (Figure 1) indicates that coumarin is an aromatic compound, without the presence of sulfur.

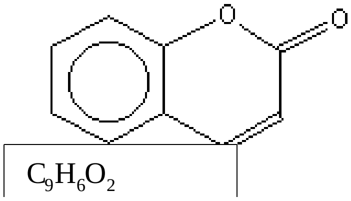

Figure 1. Chemical structure of coumarin.

These semi-bright process tanks as well as most other nickel plating baths contains wetting agents or surfactants, which are normally long straight chained organic compounds. The deposit from a semi-bright plating tank yields a semi-dull high leveling and ductile deposit (Figure 2.). This deposit is an essential component in a multilayer nickel deposit. It is followed by a thin layer of 'high sulfur' bearing nickel, a layer of sulfur containing 'bright' nickel and finally with a thin layer of 'particle' nickel prior to hexchrome plating. This system of nickel layering is the preferred sequence in order to maximize the corrosion resistance of automotive bright products. All nickel plating processes used are proprietary processes.

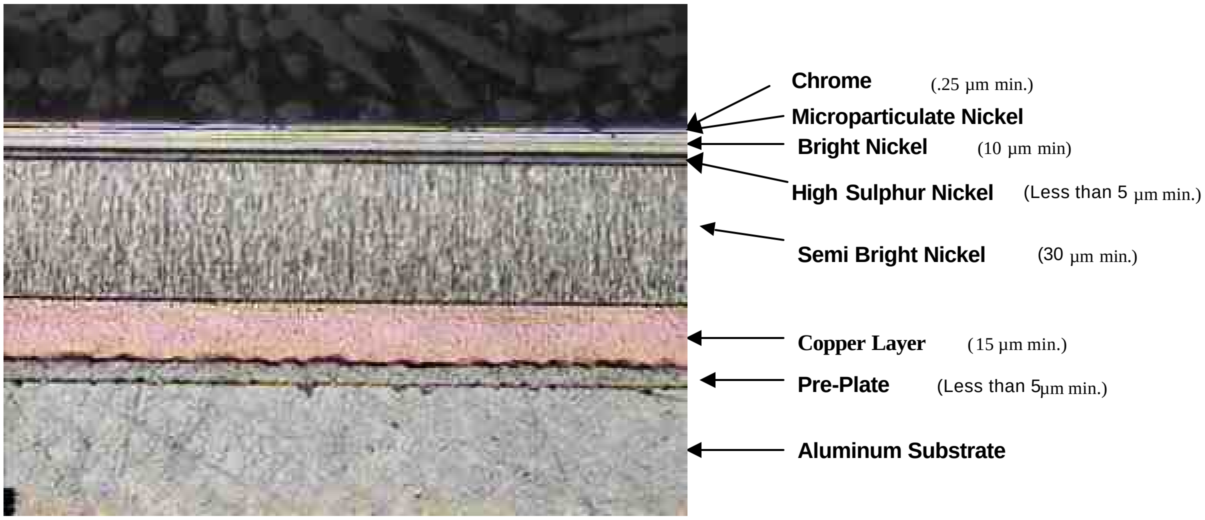

Figure 2: Cross-sectional view of typical multi-layer system

As the semi-bright nickel process is a 'sulfur-free' system, it is essential to maintain a comprehensive testing protocol to ensure that the physical characteristics of the deposit are maintained. Main areas of concern would be ductility, tensile strength and sulfur content. These are normally measured by plating a semi-bright nickel foil and bending it using the measurement ductility = T/2R and by plating a strip on a spiral contractometer. Sulfur levels are measured by burning a semi-bright plated foil in a specially designed furnace. When fluctuations occur in these parameters the regular course of action would be to expose the semi-bright plating solution to a continuous activated carbon pack or undertake a batch treatment in the next scheduled downtime period. Solution treatment using activated carbon alone or in combination with hydrogen peroxide has been the mainstay in the nickel plating industry, for most organic containing solutions including many non-nickel type systems.

The success of the conventional batch hydrogen peroxide/activated carbon treatment system is based on two factors: the oxidative potential of hydrogen peroxide and the adsorptive ability of activated carbon for specific organic compounds. A comparison of the oxidative potentials of other oxidants indicates that other oxidants, such as fluorine, hydroxyl radicals and ozone have high oxidizing potentials(Figure 3). Fluorine, due to its nature, is impractical for use. Ozone, requires the use of a 'generator' unit in order to produce this compound. This is used in a commercial environment in many municipal water purification facilities. Due to the capital cost of such equipment, we did not investigate this as an oxidant. However, hydroxyl radicals are far more economically produced.

Reactive Species	Relative Oxidation Power
Fluorine	2.23
Hydroxyl Radical	2.06
Atomic Oxygen	1.78
Hydrogen Peroxide	1.31
Perhydroxyl Radical	1.25
Permanganate	1.24
Chlorine Dioxide	1.15
Chlorine	1.00
Bromine	0.80
Iodine	0.54

Figure 3: Oxidative potentials, in volts

The use of hydroxyl radical principals for organic compound destruction in aqueous environments is known as "Advanced Oxidation Technologies" or AOT. There are a number of proven methods for generating hydroxyl radicals such as:

- Catalytic ozonation
- Anodic oxidation
- UV Light treatment with Hydrogen Peroxide
- Chemical oxidation
- Titanium dioxide Photocatalysis
- Fenton's Reaction

The principals of AOT have been developed in commercial use over the last 5 – 10 years. Their primary use has been for purification of drinking water; however, documented data indicates success in soil remediation of difficult to treatment organic contaminants. Other developing applications are for the odour control, NOx control from power generating stations and nitric acid stripping solutions, and for producing paint and glass surfaces which stay clean regardless of environment.

Investigating some of the practical methods of generated hydroxyl radicals resulted in the awareness that hydroxyl radicals could be economically generated using chemical oxidation within nickel and copper plating solutions through the use of hydrogen peroxide. Trials of this principal and its subsequent technical investigation indicated that the hydroxyl radical was being generated through a metal catalyzed hybrid Fenton reaction. The reaction is shown below:

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} + Me \Rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^{-} + {}^{\bullet}\mathrm{OH}$$

$$\mathrm{Fe}^{3+} + \mathrm{H_2O_2} + Me \Rightarrow \mathrm{Fe}^{2+} + {}^{\bullet}\mathrm{OOH} + \mathrm{H}^{+}$$

This reaction process not only yielded the oxidant hydroxyl radical but also a second oxidant known as perhydroxyl radical. In combination, under the proper operating conditions, these oxidants are very powerful for the oxidation of most organic compounds. The chemical reactions of the hydroxyl radical in aqueous solutions are of four types:

Addition: ${}^{\bullet}\mathrm{OH} + \mathrm{CnHn} \dashrightarrow {}^{\bullet}\mathrm{(OH)CnHn}$
Where the hydroxyl radical adds to an unsaturated compound.

Hydrogen Abstraction: ${}^{\bullet}\mathrm{OH} + \mathrm{CH_3OH} \dashrightarrow {}^{\bullet}\mathrm{CH_2OH} + \mathrm{H_2O}$
Formulation of organic free radical and water

Electron Transfer: Fe^{2+} converts to Fe^{3+} and metal catalyst ion converts to a higher valence state

Radical Interations: ${}^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \dashrightarrow \mathrm{H_2O_2}$
Hydroxyl radicals and perhydroxyl radicals react with each other to combine or disproportionate

As with most oxidants, the hydroxyl radical is indiscriminate in nature and will ultimately oxidize all organic constituents within the plating solution. The virgin organic brightener and surfactant along with its breakdown products, as a result of electrolysis, will as a result of the interaction of the hydroxyl radical be oxidized through various intermediates and if given enough reaction time will ultimately be converted to carbon dioxide. Our intention was not to proceed to this final stage of carbon dioxide but reduce the organic components to a lower than normal level within the semi-bright process.

Individual organic compounds can be measured within the treatment process using analytical methods however due to oxidation reactions these compounds are difficult to quantify and track. An alternative method to monitoring the process is by measuring the Total Organic

Carbon(TOC). This analytical procedure was used and provides the following results(Figure 4).

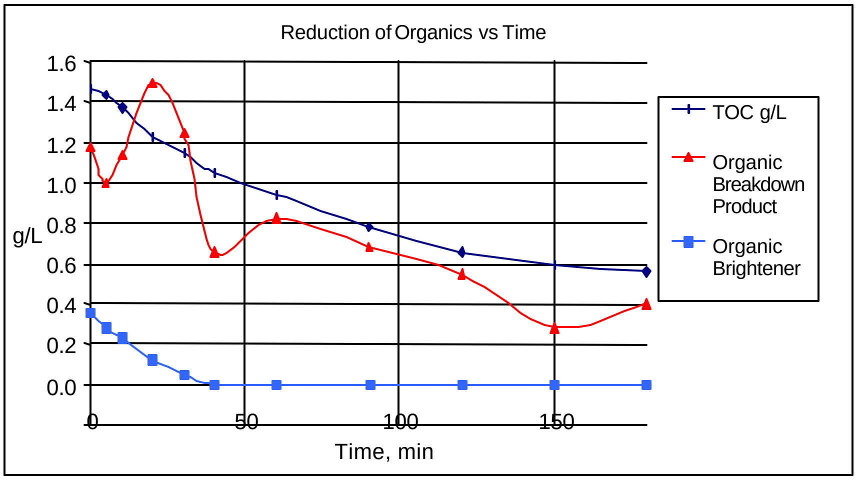

Figure 4. Reduction of organics using catalyzed hydrogen peroxide system.

Multiple trials within the lab environment demonstrated repeatability in results. The next stage in development of the process involved the construction and assessment within a 500 litre 'pilot' unit. A comparison between the conventional treatment method and the catalyzed hydrogen peroxide system is provided (Table 2).

	Conventional H_2O_2 / Carbon Treatment	**Catalyzed Hydrogen Peroxide System**
TOC Reduction	29%	66%
Organic Brightener Reduction	100%	100%
By-product Reduction	21%	38 to 50%

Table 2: Comparison of reduction efficiencies

Initial observations indicated that the catalyzed hydrogen peroxide system(1), removed the virgin organic constituents as well as the conventional hydrogen peroxide/activated carbon system. However, the difference lay in the ability of the catalyzed hydrogen peroxide system to remove substantially more of the unwanted and detrimental organic breakdown products. Based on the TOC levels of semi-bright plating solutions which were about to be treated, due to ductility and internal stress concerns, it was determined that reduction of TOC was economical to TOC levels of 0.3 – 0.5 g/l. Organic constituents concentrations during the treatment period were monitored by conventional testing methods such as UV Spectrophotometer and HPLC. The hydrogen peroxide concentrations were monitored and maintained using a simple wet titration method. Hull Cell testing was used to evaluate completed process solution.

As a result of the efficiency of removal of TOC using the catalyzed hydrogen peroxide system, it was determined that compared to the regular weekly volume of solution requiring hydrogen peroxide/activated carbon treatment, a smaller faction of the original plating bath solution would actually require treatment using this new process. ‘Full’ scale testing commenced to evaluate this observation and also to ensure no detrimental side effects. This trial continued for 12 weeks in a segregated ‘working’ semi-bright nickel plating solution environment. All standard and routine testing was completed in addition to monitoring TOC levels (Figure 5).

The trial yielded very positive results. TOC levels gradually were lowered to level around 1 g/l and maintained at this level. Hull cells were done on the treated SBN solution and the resulting foils tested for ductility, sulphur content and tensile strength. These parameters were within acceptable limits. The results indicated that the catalyzed hydrogen peroxide system continued to be effective in maintaining and controlling all physical deposit characteristics in a plating process which required high amount of inert auxiliary anode use.

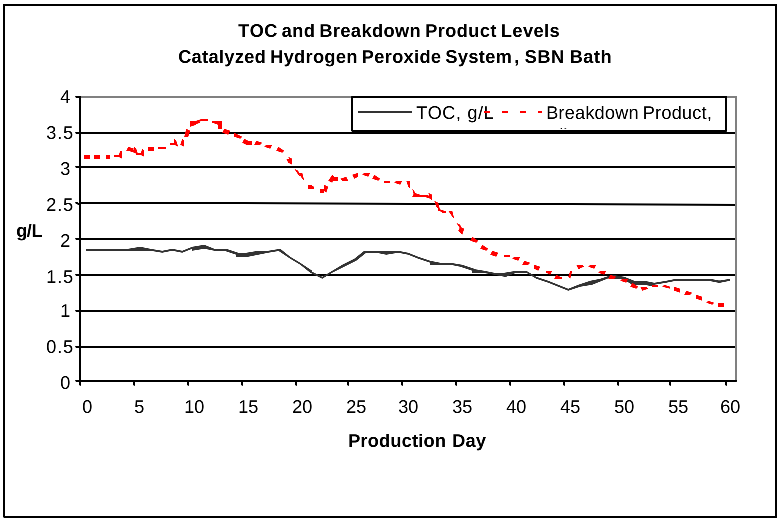

Figure 5; In-process testing results

The advantages documented using the catalyzed hydrogen peroxide system in comparison to the conventional hydrogen peroxide/activated carbon treatment method are as follows:

- ✓ Overall lower TOC values within bath
- ✓ Less replacement chemistries required
- ✓ No solid waste handling required
- ✓ Reduction of nickel plating solution losses due to adsorptive nature of carbon
- ✓ Reduction of human exposure to potentially toxic materials
- ✓ Safe controlled storage and dispensing of hydrogen peroxide
- ✓ Reduction in volume requiring treatment on regular basis
- ✓ Continuous bath treatment possible
- ✓ Significantly shorter treatment time required
- ✓ Easy method for monitoring and controlling treatment process

- ✓ Affective organic control allows for greater flexibility for recycling drag-out rinse waters back to process tanks
- ✓ Lower overall treatment cost

Optimization of the treatment operating parameters, has resulted in the development of a simple controlled equipment setup, Figure 6, which can be automatically controlled so that a minimum of operator interaction is required. Once specific plating bath operating conditions are investigated and understood the catalyzed hydrogen peroxide system reaction process can be monitored using a simple wet titration method.

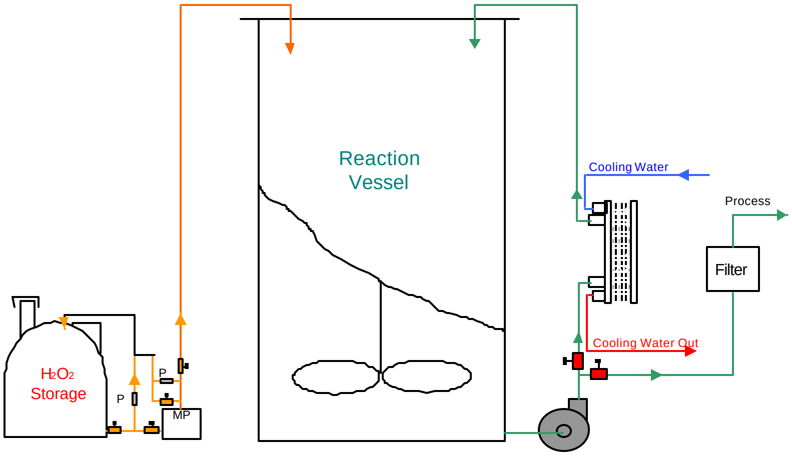

Figure 6; Catalyzed hydrogen peroxide system configuration.

Understanding the chemical reactions occurring within the catalyzed hydrogen peroxide system has led to further investigative work for the treatment of the following plating solutions:

- Non-coumarin based semi-brights
- Bright nickel solutions, including SAS and Pyridine based
- Acid Copper solutions, dye and non-dye based

To date, this work has yielded positive results which would suggest that these and many other organically based electroplating solutions are candidates for controlling their organic breakdown products using this simple and effective catalyzed hydrogen peroxide system.

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Ref. 1 – The catalyzed hydrogen peroxide system is a Kuntz Electroplating Inc patented system, trademarked under the name Oxi-mate.
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The Impact of Barrel Design on Drag-out Rates

By: Frank Altmayer, MSF, AESF Fellow
Jeff Zak, P.E., CEF
Kevin Wasag, CEF
Brian Cavanaugh
Scientific Control Labs., LTD.

New barrels for electroplating have been developed and manufacturers of some of these newer designs have claimed significant improvements in drag-out losses by their new barrels. Since water consumption and waste generation are directly tied to dragout rate from processing solutions, it is clear that there is a need to produce a method of evaluating such barrels, so that the user minimizes pollution.

This study, funded by The Illinois Waste Management Resources Center produced a benchmark test that can be conducted to compare drag-out rates of plating barrels. The study used this test to compare two size ranges of plating barrels, small and large. For small barrels (6" x 12"), testing showed that a reduction in dragout rate, as high as 48%, may be achieved. For large barrels (16" x 36"), testing showed that a reduction as high as 44% may be obtained.

Introduction

Barrel plating pre-dates the past century and is not significantly different today, in that a rotating cylinder with perforations for the purpose of allowing transfer of DC current and processing solution is still used today. However, there have been significant improvement claims in the technology of barrel plating, especially in the area of lowering drag-out rates and improving barrel plating efficiencies.

The American Electroplaters and Surface Finishers Society (AESF, Orlando FL) conducted a research project (AESF Research Project 34) on the Theory of Metal Distribution in Barrel[2], but this study did not cover barrel designs. AESF Research Project 44 studied the optimization of barrel zinc plating solutions[1]. Stein, Teichman and Thompson[4] compared vibratory plating equipment with barrel plating equipment for nickel plating of small parts, and concluded that barrel plating was "more suitable" than vibratory systems for nickel plating of small batches of small sized parts. More recently, LaVine[3] reported on a new barrel design incorporating a staggered cells and meshed walls to improve solution transfer and lower dragout rates. LaVine reported the new design could reduce drag-out rates in nickel plating solutions by 26-49%, when compared to two "traditional" barrel designs. No details of the method of evaluations are given. Tremmel[5] mentions 'tapered slots" as part of a continuous plating system that is designed to replace conventional barrel plating equipment. Additional manufacturers lay claim to reduced drag-out rates[6].

None of the above literature in our background search compared various barrel designs under identical conditions to yield comparative dragout rates and relate results to design parameters and barrel service life. The purpose of this study was to accomplish such a goal.

Barrel electroplating is commonly known to present a higher degree of trouble in recycle-recovery schemes and in wastewater treatment operations due to the high drag-out rates during barrel processing. The high drag-out rates are caused by a combination of high surface area loads and retained liquid on the barrel and superstructure. While little can be done about the part loading/surface area in any given barrel plating operation, there have been revised barrel designs that may result in lower dragout rates.

Complicating the issue of barrel design vs. drag-out reduction is the possibility that a given design may reduce drag-out rate, but will not provide long term service, as some of these designs utilize thin-wall construction, that may fracture over the life of the barrel, reducing productivity and decreasing the acceptability of alternate barrel designs by the industry.

This study intended to determine if significant reductions in drag-out can be achieved by replacing an existing barrel with a newer design.

The study was funded and conducted under the WMRC ADOP2T program which assists industry members in achieving goals in pollution prevention. The study was further sponsored by an individual metal finishing job shop, Northwestern Plating Works, located at 3136 S. Kolin Ave. Chicago IL 60623. Mr. David Jacobs, President allowed us to utilize an actual barrel plating line to conduct our experiments, and provided us with an example of a “traditional” plating barrel that we could use in our study.

Letters of invitation were sent to all barrel manufacturers listed in Metal Finishing Guidebook and Directory. Of eight requests, three barrel manufacturers volunteered to supply us with barrels to include in the study (a fourth also volunteered, but was not included due to miscommunication between the sponsor plating company and the barrel manufacturer). Also, Artistic Plating Company, Milwaukee WI, Mr. John Lindstedt, President; Reinewald Plating Company, Chicago IL, Mr. Ted Reinewald, President ; and The Stutz Company, Mr. Gerry Stutz, added additional barrels for testing.

The intent of our study was not to create a “competition” between barrel manufacturers to see who could lay claim to the lowest dragout rate and therefore we do not identify which company manufactured which barrel.

This study had the following goals:

1. We wished to relate performance in dragout reduction (or lack thereof) to specific design parameters, so that future barrel designs might incorporate the better ideas.
2. We also wanted to provide guidance to metal finishers as to barrel designs that would allow them to reduce dragout rates.
3. Our last goal was to begin the establishment of a “benchmarking” system that could be used to determine if a metal finisher was using barrel plating equipment that was above average in reducing pollution loading.

Barrel Descriptions

A total of eight (8) different plating barrels were evaluated in this study. To keep the comparisons as fair as possible, we separated the barrels into two size groups. Of the eight barrels evaluated, four were small barrels (six inch diameter) and four were large barrels (14 to 16 inch diameters). The following are descriptions of each barrel tested, any unique features in the barrel that may affect dragout, and the estimated cost of the barrel.

1. Small Barrels Evaluated

Barrel Design-1

Description of Barrel:

Barrel one is a 6” x 12” hexagonal plating barrel with replaceable mesh sides. Mesh sides have slots measuring 0.010” x 0.150” with approximately 384 slots per panel and 6 panels per side Slots are tapered slightly and are larger on the outside of the barrel then on the inside. (See Figs. C-1, C-2 and C-3.)

Unique Feature(s):

Vertical Drive Shaft, Replaceable Mesh Side Panels, Variable Speed Drive System

Approximate Cost:	$1,000
	$ 550 (Cylinder, gears only)

Barrel Design-2

Description of Barrel

Barrel is a 6” x 12” round corrugated plating barrel with round holes. Holes are 3/32” in diameter and there are approximately 36 holes per square inch. The corrugated barrel provides more holes for drainage than a standard round barrel with the same dimensions. (See Figs. C-4 and C-5.)

Unique Feature(s)

Corrugated sidewalls, Gear driven on only one side.

Approximate Cost:	$1300
	$ 510 (Cylinder, gears only)

Barrel Design-3

Description of Barrel

Barrel is a 6” x 12” octagonal plating barrel. The sides of the barrel are ribbed on the outside and have holes between the ribs. This barrel has square holes 0.100” x 0.100” with approximately 30 holes per square inch. (See Figs. C-6 and C-7.)

Unique Feature(s)

Ribbed walls increase strength while allowing areas with holes to be made thin. Gear driven on both sides for better distribution of torque. However, the teeth on the gears are a large source of dragout. (See Fig. C-8.)Square holes help break surface tension of solutions to allow better drainage.

Approximate Cost: $1200
$ 600 (Cylinder, gears only)

Barrel Design-4

Description of Barrel

Barrel is a 6" x 12" round plating barrel with a finely woven mesh sides. The sides of the barrel are ribbed and covered in a woven plastic mesh. This barrel is gear driven on one end but the drive mechanism can be placed on either end of the barrel. (See Figs. C-9 and C-10.)

Unique Feature(s)

Woven mesh sides will retain all sizes of parts. The ribbed sides provide added strength. Gear driven on only one side.

Approximate Cost $1200
$ 650 (Cylinder, gears only)

2. Large Barrels Evaluated

Barrel Design-5

Description of Barrel

Barrel is a 16" x 36" hexagonal plating barrel. This barrel has ¼" round holes and has approximately 695 holes per side. The barrel is mounted on a frame and is belt driven. (See Figs. C-11 and C-12.)

Unique Feature(s)

Barrel is belt driven providing less surface area than a gear driven barrel.

Approximate Cost: $2250
$1500 (Cylinder, gears only)

Barrel Design-6

Description of Barrel

Barrel is a 14" x 36" hexagonal, belt driven plating barrel. This barrel has a unique hole design consisting of 3/32" round holes on the outside of the barrel with 0.220" square on the inside of the barrel walls tapered to the round external holes (See Figure C-14). There are approximately 16 holes per square inch. (See Figs. C-13 and C-14.)

Unique Feature(s)

Square to round hole design "funnels" the solution out of the barrel. Belt driven design reduces overall surface area.

Approximate Cost: $2000
$1300 (Cylinder, gears only)

Barrel Design-7

Description of Barrel

Barrel is a portable oblique plater designed to replace 16” x 36” horizontal plating barrels. This barrel has two (2) rotating baskets with 3/16” diameter round holes. There are approximately 10 holes per square inch. The baskets are set at an angle of about 45^o. (See Fig. C-15.)

Unique Feature(s)

Easier to load and unload manually or on an automated basis (no door), different baskets can be used in same frame improving versatility.

Approximate Cost $2,000

Barrel Design-8

Description of Barrel

Barrel eight is a 14” x 36” hexagonal, gear driven plating barrel. This barrel has staggered 0.16” x 1.0” and 0.16” x 0.5” slots. There are approximately 572 slots per side. (See Figs. C-16 and C-17.)

Unique Feature(s)

Utilizes slots instead of holes. Irregular shape of slots prevents liquid from staying in opening.

Approximate Cost: $2400 (Cylinder, gears only)

Testing/Evaluation Procedure:

This section will discuss the methodologies used to determine dragout from the different barrels and barrel toughness.

1. Drag-out evaluation

The following equipment was used and conditions adhered to during the dragout evaluation:

A. Single process tank made of polypropylene
B. Single static rinse tank
C. Manual barrel handling
D. Process solution contained only metal salt (copper sulfate), acid and water (no rinse aid)
E. Measured the increase in metal ion concentration in the rinse tank after each barrel load rinse.
F. Barrels from volunteer manufacturers or metal finishers

Process Solution:

The dragout evaluation was performed using a solution of copper sulfate, sulfuric acid and water. These ingredients were chosen to keep the process solution as simple and free of additional variables (such as wetters) as possible. This also allows an individual metal finisher to duplicate our experiment with his own equipment in order to compare his performance with the equipment tested here. The initial copper concentration in the copper sulfate solution ranged from 117.00 ppm to 846.00 ppm and is relatively unimportant to the results obtained, as long as the concentration of copper can be reliably measured in the rinse. Comparative tests conducted by others should use solutions of similar concentrations to minimize viscosity effects (from concentration differences).

Plating barrels tested were charged with 6 pounds of assorted stainless steel fasteners for the small barrels and 150 pounds of assorted stainless steel fasteners in the large barrels. The fasteners used were an equal mixture by weight of: 3/8" tapered hex washer head screws, 1" flat head Phillips screws and 1" slotted head cap screws. The exact same load of fasteners was used for each barrel evaluation.

A total of three (3) trials were performed on each plating barrel tested. The steps were:

a) The copper sulfate solution was made up containing 117.00 to 846.00 ppm of copper.
b) A second tank used to simulate a dead rinse was filled with tap water.
c) A sample was collected from each tank prior to starting the test.
d) The plating barrel to be tested was loaded with the proper amount of parts and then lowered into the copper sulfate solution.
e) The barrel was rotated in the solution for thirty seconds and then removed from the tank.
f) After being removed from the copper sulfate solution tank, the barrel was rotated 1-½ revolutions, stopped, and then allowed to drain for a total time of thirty seconds above the process tank.
g) The plating barrel was then lowered into the rinse water and rotated for thirty seconds.
h) The plating barrel was then removed from the rinse tank, rotated 1-½ revolutions above the rinse tank, and then allowed to drain for thirty seconds.
i) After mixing the water in the rinse tank manually, a sample of the rinse tank was collected for use in determining the amount of dragout.
j) Steps e through i were then repeated nine more times to conclude the trial.
k) After all ten (10) runs were completed a final sample from the copper sulfate tank was taken to check if the amount of copper in the rinse tank matches the amount of copper removed from the copper sulfate tank.

After all ten runs were completed, the samples (thirteen (13) total) were analyzed for copper concentration using ICP (Inductively Coupled Plasma). The concentrations provided by the analyses were used to calculate the amount of solution dragged out by each respective barrel tested.

Dragout Rates Measured from Various Barrel Types

1. Small Barrels

Barrel Number	Trial Number	Pounds of Parts in Barrel	Dragout* (ml)	Dragout (ml) per Pounds of Parts*
1	1	6	160.3	26.7
	2	6	138.3	23.0
	3	6	142.5	23.7
			147.0	**24.5**
2	1	6	266.4	44.4
	2	6	256.7	42.8
	3	6	289.3	48.2
			270.8	**45.1**
3	1	6	245.7	40.9
	2	6	237.6	39.6
	3	6	240.8	40.1
			241.4	**40.2**
4	1	6	150.1	25.0
	2	6	138.4	23.1
	3	6	138.1	23.0
			142.2	**23.7**

2. Large Barrels

5	1	150	2295	15.3
	2	150	2498	16.7
	3	150	2100	14.0
			2298	**15.3**
6	1	150	2916	19.4
	2	150	2933	19.6
	3	150	3109	20.7
			2986[2]/3881	**19.9/25.9**
7	1	150	1890[1]	12.6
	2	150	1633[1]	10.9
	3	150	1728[1]	11.5
			1750[1]	**11.7**
8	1	150	1394	9.3
	2	150	1337	8.9
	3	150	1125	7.5
			1285[2]/1670	**8.6[2]/11.2**

**Each individual trial result is an average of the ten individual runs conducted in each trial*

[1] *The dragout results for Barrel 7 were based on the first seven runs only. Runs 8, 9, and 10 in* ***all three trials*** *were erratic and significantly higher than the first seven runs. Including Runs 8, 9, and 10, the average dragout for Barrel7 would be 4800 mls.*

2 The dragout results for Barrels 6 and 8 are based upon testing a 14 x 36 barrel, while the others are 16 x 36. Second set of numbers are adjusted by a factor of 1.3 to compensate for size difference.

RESULT SUMMARY

Summary of Drag-out Rates-Small Barrels

Lowest Dragout Rate	142.2 mL, 23.7 mL/lb. of parts
Highest Dragout rate	270.8 mL, 45.1 mL/lb. of parts
Average of 4 Barrels	200.35 mL, 33.4 mL/lb. of parts

Testing showed that a significant reduction in dragout rate can be achieved by replacing older design barrels with newer designs. A reduction as high as 48% may be obtained.

Summary of Drag-out Rates-Large Barrels

Lowest Dragout Rate	1670 mL, 11.18 mL/lb of parts.*
Highest Dragout rate	3881 mL, 25.9 mL/lb. of parts*
Average of 4 Barrels	2079 mL, 13.9 mL/lb. of parts

Testing showed that a significant reduction in dragout rate can be achieved by replacing older design barrels with newer designs. A reduction as high as 44% may be obtained*.

** This barrel was 14" x 36 vs. while the others were 16" x 36" (we were unable to obtain a 16 x 36 slotted barrel, as the manufacturer declined participation in this study). We have adjusted by the difference in area of a **solid** 14 x 36 cylinder vs a **solid** 16 x 36 cylinder (a factor of 1.3) the adjusted dragout rate of this barrel is as shown. The actual results obtained with the smaller barrel are shown in the table.*

Discussion/Economics-Small Barrels

A plater using a plating barrel of similar size to those we evaluated should expect a dragout rate of less than 200 mL (33.4 mL/lb. of parts) when tested as described in this report for above average levels of pollution prevention.

Barrel 1:

This performed very well in the dragout evaluation, dragging out an average of 147 ml per cycle. The low dragout rate may be attributed to several design features:

1) A vertical drive shaft that reduces the size of the gear (and, consequently, the number of teeth on the gear).

2) A very narrow side frame (approximately 7.5 inches compared to 10 inches for the other small barrels we evaluated)

3) Unique gear positioning. We noticed that the more traditional gears tended to trap liquid between gear teeth.

4) This barrel had a gear on only one side as compared to the others (gears on both sides).

All four of these design features reduced the amount of surface area of the barrel that comes in contact with the plating solution, thus reducing the amount of “wetted” area of the barrel and the amount of solution dragged out by the barrel itself.

The low dragout rate of Barrel 1 may also be attributed to the fact that the openings in the barrel are slots. As discovered while evaluating the large barrels, slots seem to be more efficient in draining solution than holes. Some barrel manufacturers claim that round holes tend to generate equal wall pressure and surface tension that causes the liquid to be entrapped within the holes.

Barrel 2:
This barrel produced 270.8 mL (45.1 mL/lb. of parts) of dragout rate, yielding results that were significantly above the average of the four barrels. The higher drag-out rate may be attributed to the fact that this barrel had two, large gears that entrapped a significant amount of liquid (See Figure C-8). Also, the side frames were significantly wider than on Barrel 1 (10” x 10” vs. 7” x 10”). This barrel had an estimated 60 square inches more of surface area contacting the solution than Barrel 1.

Barrel 3:
This barrel produced 241.4 mL (40.2 mL/lb. of parts) of dragout rate, yielding results that were significantly above the average of the four barrels. The higher drag-out rate may be attributed to the fact that this barrel had two, large gears that entrapped a significant amount of liquid (See Figure C-8). Also, the side frames were significantly wider than on Barrel 1 (10” x 10” vs. 7” x 10”). This barrel had an estimated 60 square inches more of surface area contacting the solution than Barrel 1.

Also, Barrel 2 was corrugated. Some think that the corrugated sides allow for an increased number of holes, thus, increasing drainage efficiency. The test data indicate otherwise.

Barrel 4:
This barrel yielded dragout losses similar to Barrel 1, dragging out and average of 142 mL per use. This barrel had the identical frame and gears as Barrels 2 and 3. However, the barrel itself was constructed of a very fine, replaceable, woven mesh. Even with similar areas or wetted surface due to the large frame and the two large gears, this barrel outperformed drilled holes.

Economics-Small Barrels
The sponsor plating company for this project does not use barrels of this size. A metal finisher that uses such small barrels can consider the following options:

Option 1 Replacing Barrels En Masse:

A newer design barrel costs about $1200.00 and saves about 140 mL of processing solution in each process step (soak clean, electroclean, acid dip, electroplate, post plate dip) per run. Assuming 1,000 runs per barrel per year, and 5 processing steps, a total of 185 gallons of processing solution would be saved annually. The value of the processing solution saved, plus labor to make up the solution, cost of chemicals for waste treatment, and cost of disposal of hazardous waste would need to be $3.24/gallon for a two-year payback.

Option 2 Replacing Barrels As They Are "Consumed":
Since there is either no cost difference between the newer slotted barrels and traditional designs, or because mesh wall barrels may actually be lower in cost than traditional units, it appears that instant cost savings can be realized by replacing traditional barrel designs with one of the newer ones (mesh wall or slotted), as the need to replace a barrel arises. The mesh walled barrels should be carefully evaluated for wall life. The mesh walled barrel design we tested was actually 20-30% lower in cost vs. traditional designs and allowed for easy replacement of the mesh.

Discussion/Economics-Large Barrels

Barrel Number 5 (traditional design):
This barrel was in use by the sponsor plating company. The dragout loss per barrel was almost 2300 mL (15.3 mL/lb of parts); which was below the average performance for the four barrels tested.

Barrel Number 6 (the square to round holes):
This barrel was only 14" x 36", yet it yielded the highest level of dragout in this evaluation, dragging out 2986 mL per cycle. If corrected for surface area (factor 1.3) to allow for a more accurate comparison with the 16 x 36 barrels, the dragout rate would be 3881 mL (25.87 mL/lb. of parts). In fairness, the holes in this barrel were too small for the parts that were plated. Larger holes would have been usable and would have resulted in better performance. If anything, the data reported confirm the importance of matching hole size to part size to reduce dragout and improve plating efficiency (a task often ignored by metal finishers).

Barrel 7 (the portable oblique barrel):
Test results for this barrel were based on only the first seven runs of the trial. Runs 8, 9, and 10 in all three trials showed **significantly** more dragout than the Runs 1-7 and the results, for unexplained reasons were highly erratic. We have therefore used the data from only the first 7 runs in each trial. Further investigation into the erratic results towards the end of each run is warranted, especially in light of the modified results being the second best over-all performance in dragout reduction. When the last three runs in each trail are deleted, this equipment yields similar results to the slotted barrel (after the slotted barrel results are adjusted for size differences).

The portable oblique plater yields lower levels of dragout because each basket has a curved wall that acts much like a "funnel" channeling trapped solution to a "low-point" in the curved basket wall where hydraulic pressure tends to build up, forcing more liquid through the holes than if the walls were horizontal as in a conventional barrel.

Barrel-8 (slotted holes barrel):
This was the best performing large barrel in our study, dragging out 1285 mL, 8.6 mL/lb. of parts (1670 mL, 11.2 mL/lb. of parts when adjusted for size difference).

Although the dwell time of each barrels evaluated was 30 seconds, test personnel noticed a significant difference in drain time. Water tended to “gush” out of this barrel in noticeably less time.

Economics-Large Barrels

The sponsor plating company for this project turns over approximately nine barrels per hour or approximately 18,720 barrels per year in a nine (9) station plating tank. Since the slotted barrel drags out approximately 0.6 liters per cycle less than their current barrels (slotted barrel results adjusted to simulate a 16” diameter barrel), the pilot plating company would save approximately 3100 gallons each of soak cleaner, electrocleaner, acid and electroplating solution each year. The metal finisher would have at least two options:

Option 1-Replacing All Barrels At One Time:

Nine replacement slotted barrels would cost an estimated $21,600.00. Nine replacement portable oblique plating systems would cost about $18,000.00. For a two year payback, the total sum value of the processing solutions plus labor costs to produce the solutions, plus waste treatment and disposal of hazardous waste would need to be $3.32/3.48 per gallon (portable oblique system/slotted barrel), which is below the cost/value of most barrel plating solutions used in metal finishing. Based on the dragout evaluation results, the pilot plating company would save approximately 2700 gallons of process solutions per year using the portable oblique system versus the current plating barrel.

Option-2 Replacing Barrels As They Are “Consumed”:

In this option the metal finisher would replace barrels that are damaged beyond repair with one of the new designs. The “cost” basis would then be the difference between the cost of the new design vs. a traditional barrel.

For the slotted barrel, the difference in cost is approximately $900.00. If one of the nine barrels is replaced with the new design, it would save 344 gallons of processing solution per year. The total value of the saved processing solutions would need to be $1.31/gallon for a two year payback on the difference in cost between the two barrel designs.

For the portable oblique barrel, the difference in cost is $500.00 (cost of replacement of cylinder and gear for traditional barrel vs. cost of entire portable oblique barrel system). The total value of the processing solutions would then need to be $0.83 or less for a two year payback.

A metal finisher replacing only a portion of a set of barrels may be faced with varying plating efficiencies between the newer designs (tend to be higher in plating efficiency) and older designs. On manual lines, adjustments may be possible (the plater can remove the more efficient barrel sooner), but on automated lines, it would most probably be best to replace all barrels at one time.

The additional benefit of higher productivity with the new barrel designs was not part of this study and has therefore not been included in our economic analysis.

Conclusions

1. We have developed a procedure for “benchmarking” barrels used in various metal finishing operations. This procedure is relatively easy to conduct and can be conducted by any metal finisher at reasonable effort and cost.

2. We have demonstrated that there is a significant difference in dragout rate produced by different barrel designs, with newer designs reducing dragout rate almost 50%. Our results compare favorably with those reported by one barrel manufacturer[4] who indicated that 26 to 49% reduction in dragout rate can be achieved by changing from a traditional barrel with drilled holes to one with a mesh pattern.

Recommendations

Based on this study we would recommend that any metal finisher utilizing traditional barrels evaluate the economics of changing over to one of the newer designs such as the portable oblique plating system or a newer design horizontal barrel incorporating either a mesh pattern or slots.

The portable oblique barrel is a radical departure from existing barrel plating technology, and may offer advantages in plating efficiency not realizable in traditional horizontal barrel systems. Careful evaluation for suitability is warranted, due to the radical design difference. The favorable cost comparison and significant reduction in dragout rate make this system desirable.

The slotted barrel appeared to us to be highly desirable in manual operations, where workers may not allow the barrel to drain fully. Since the slotted barrel appears to “gush” most of the liquid it will drain in the first few seconds, it would appear that this equipment would allow most of the dragout benefits, even when a worker impatiently moves a barrel to the next station prematurely.

We are aware that our study was limited in scope and that there are numerous other barrel designs that may offer even better results. The benchmarking procedure described in this report can be used to yield comparative data on any of these barrels.

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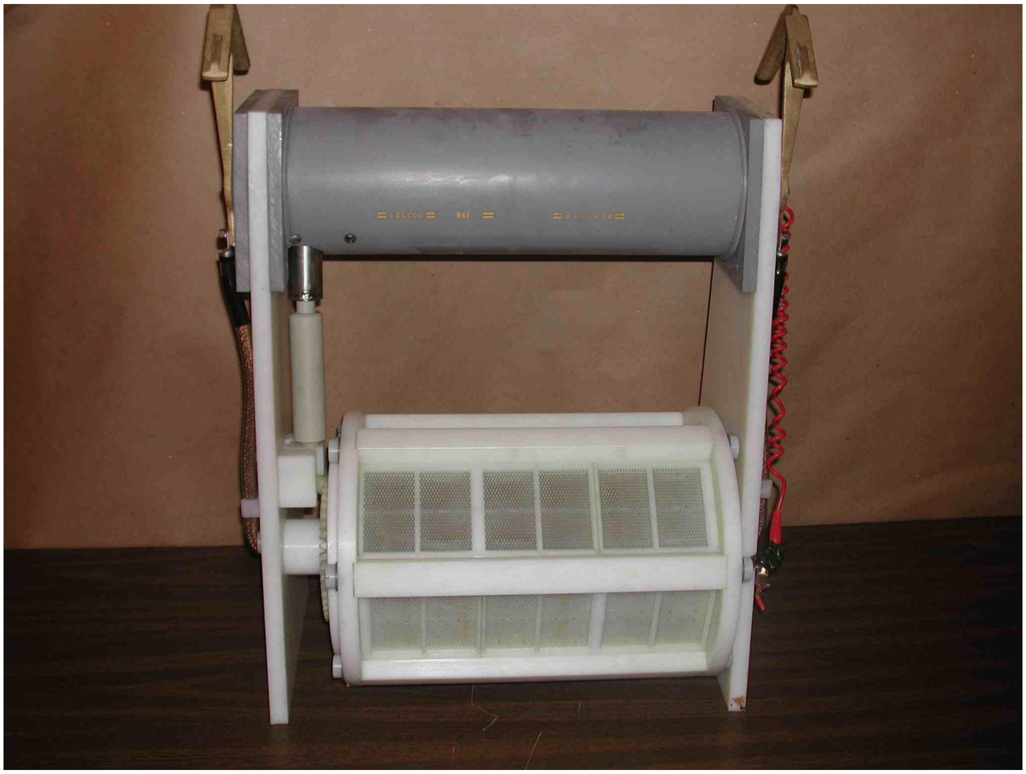


Figure C-1

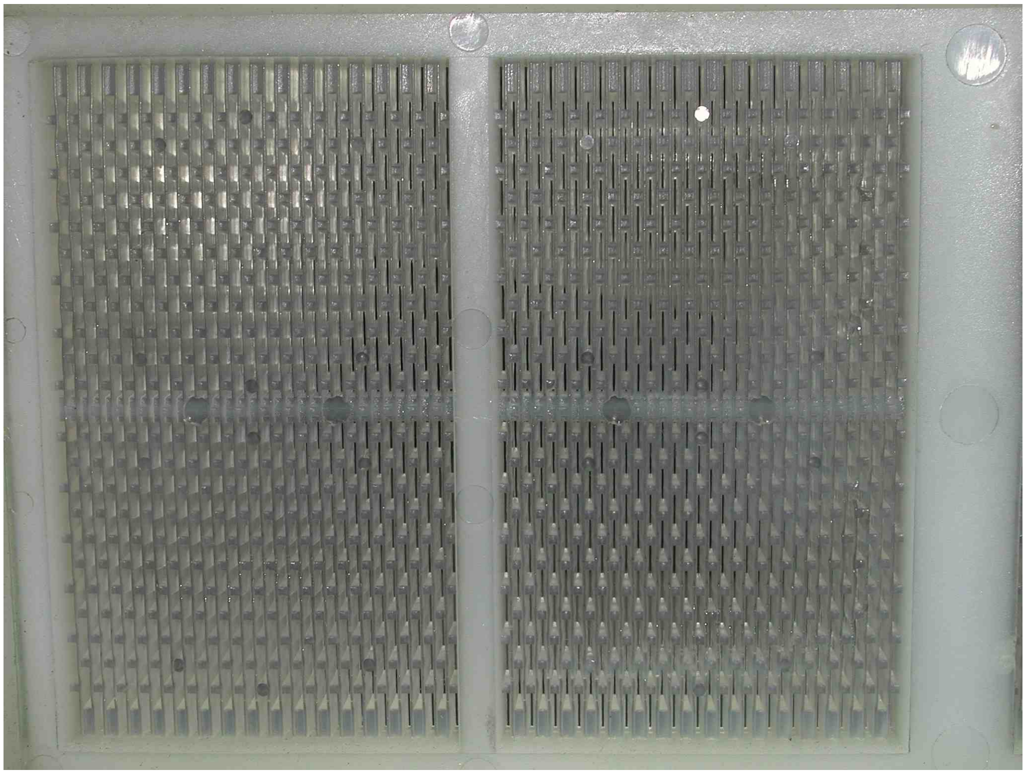


Figure C-2

Figure C-3

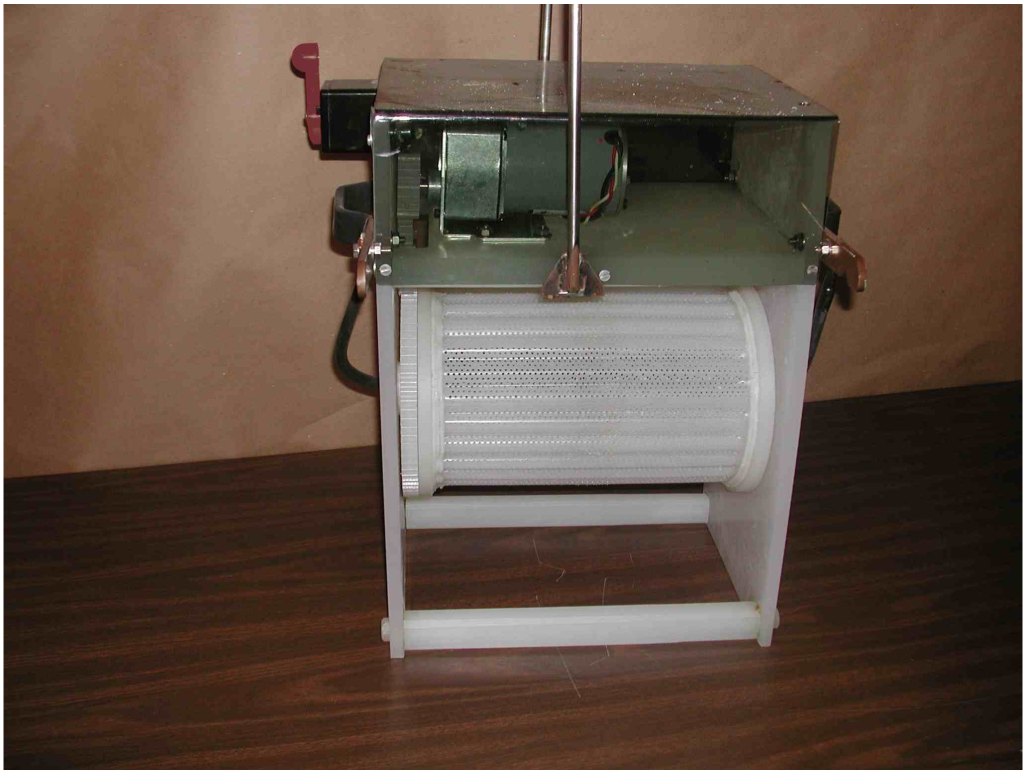
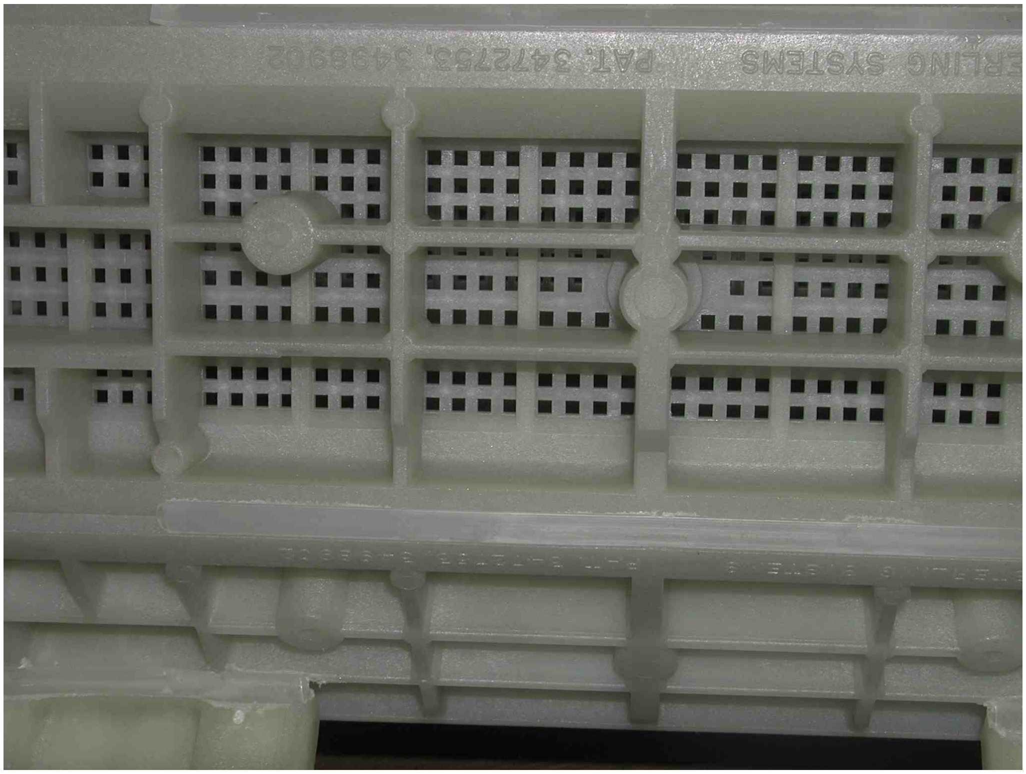


Figure C-4

Figure C-5

Figure C-6



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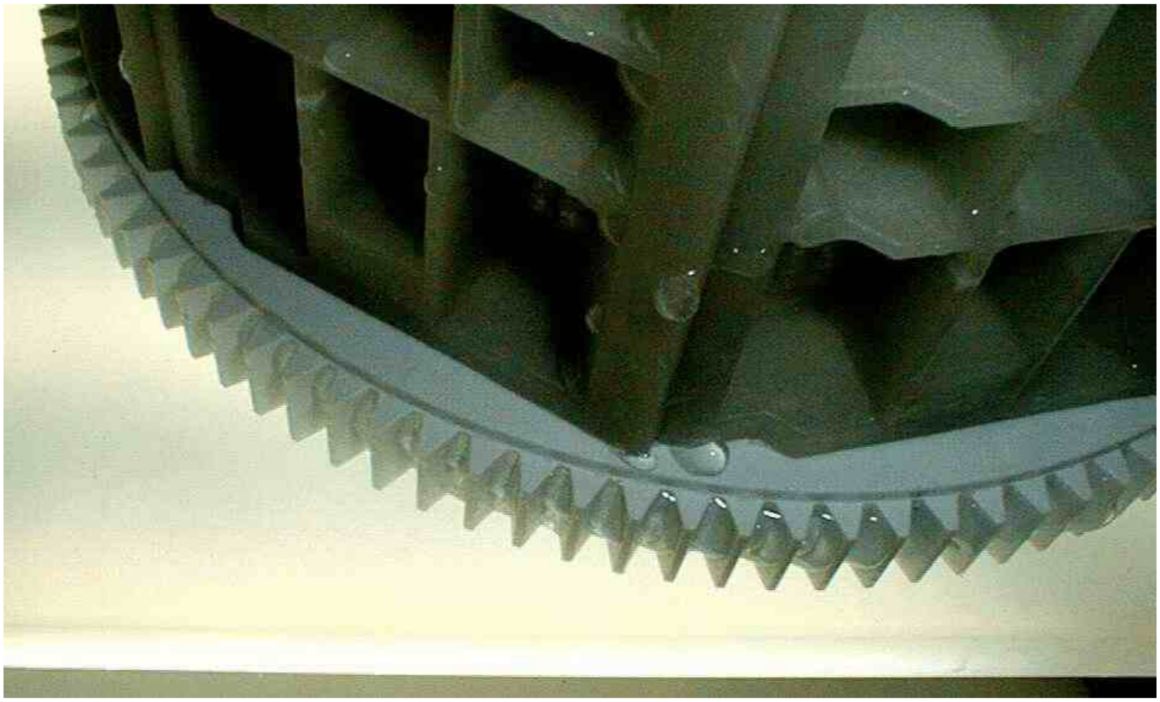


Figure C-8

Figure C-9

Figure C-10

Figure C-11

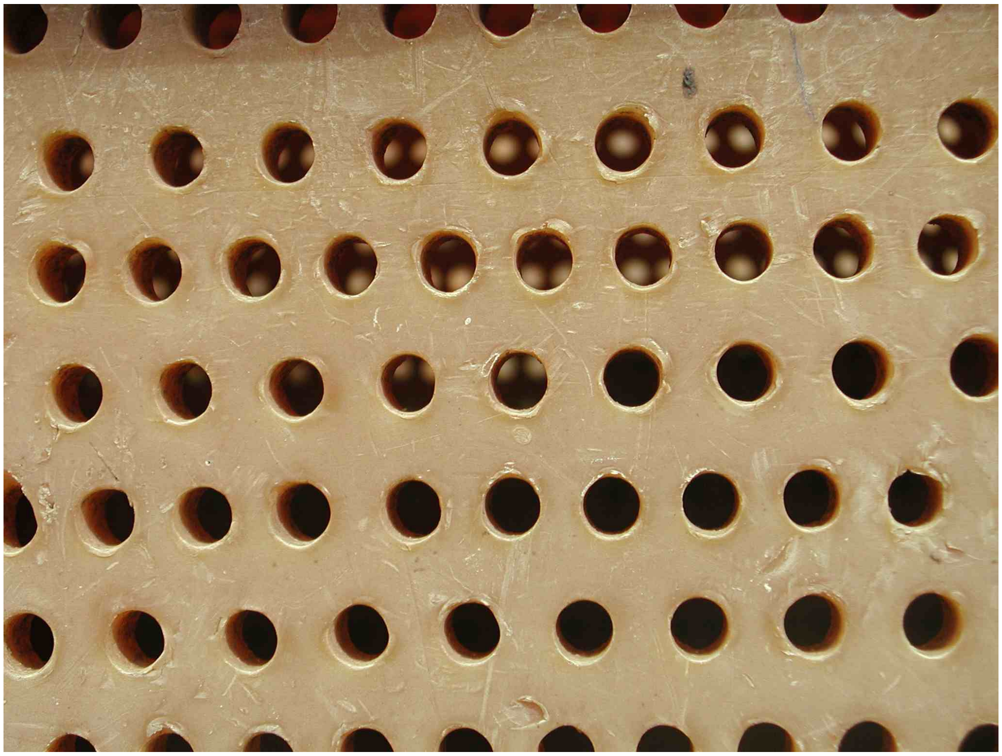
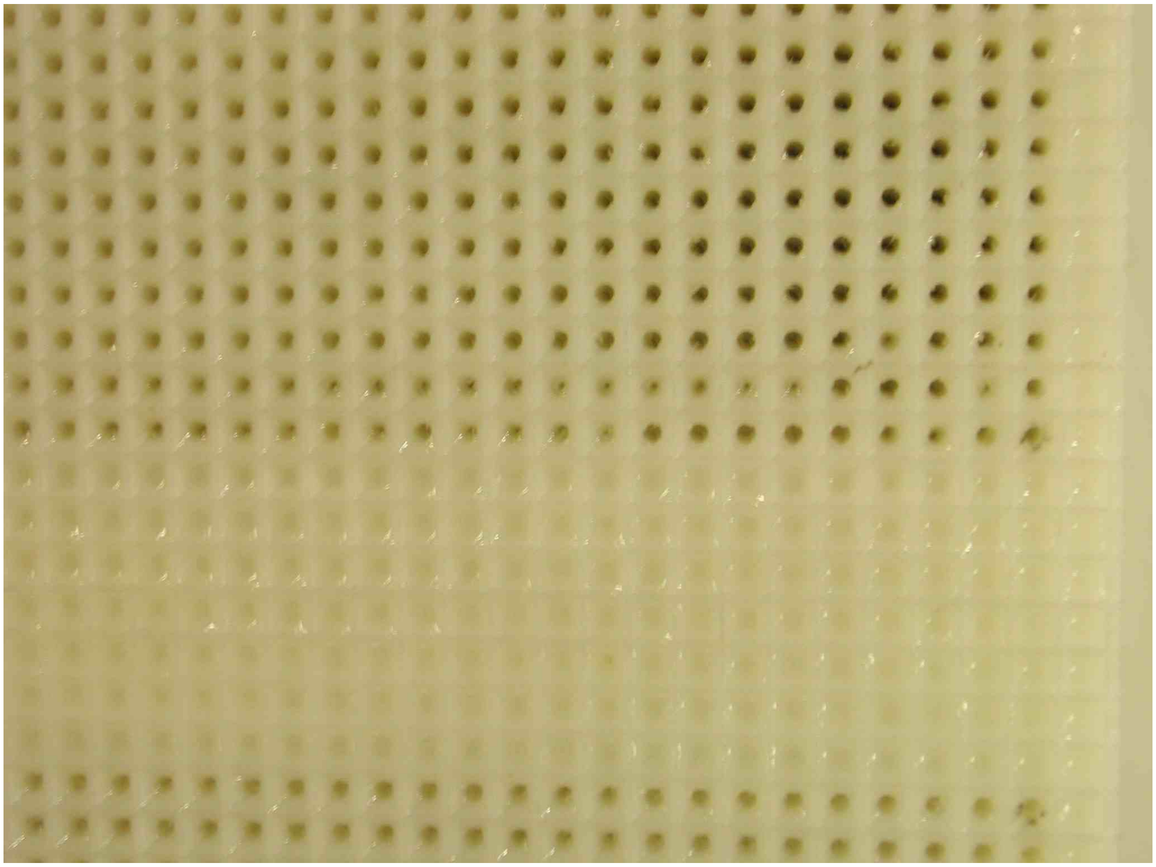


Figure C-12

Figure C-13



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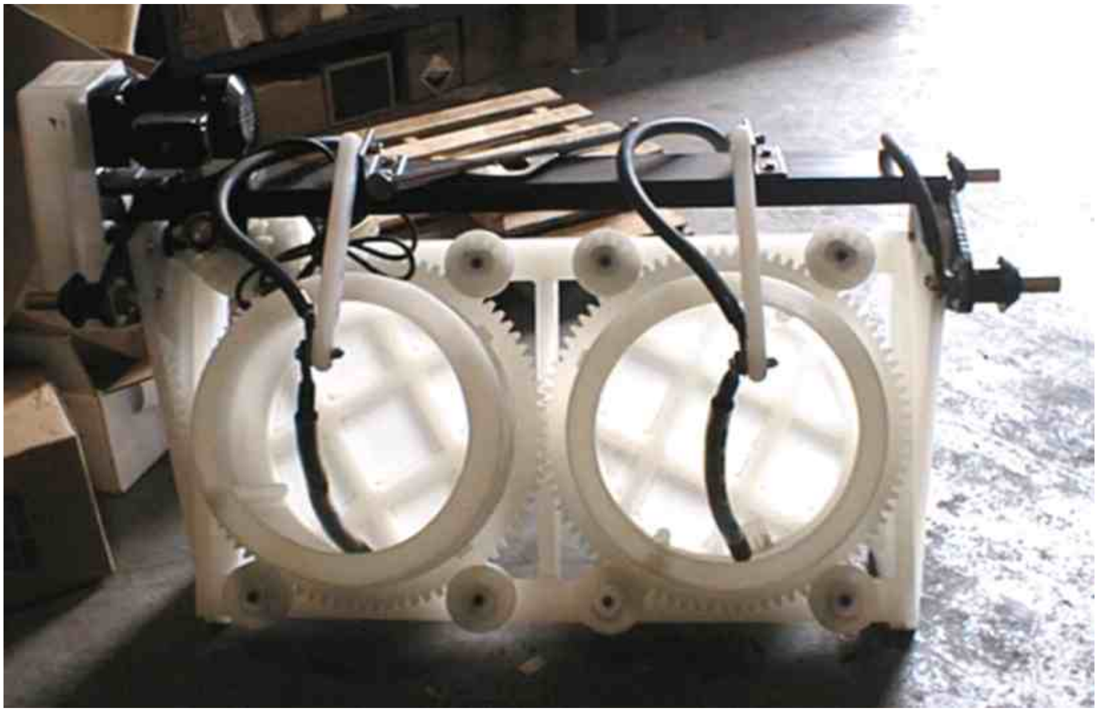

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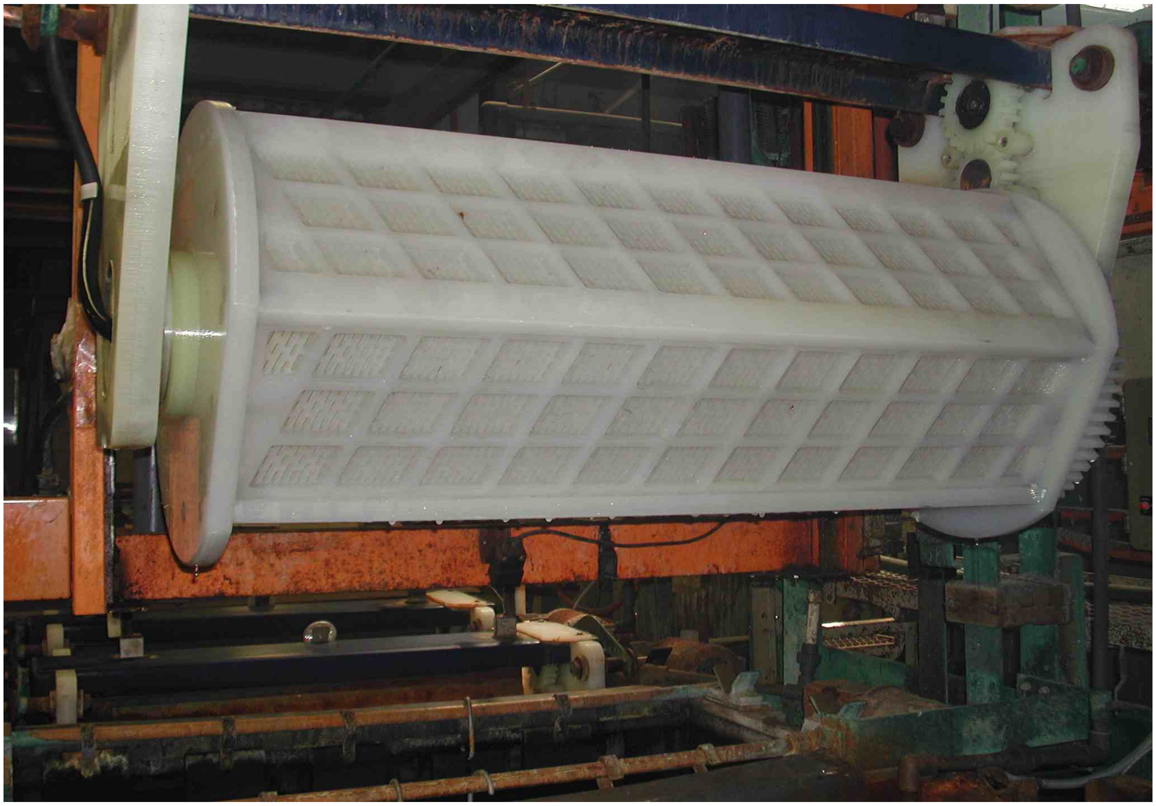

Figure C-16

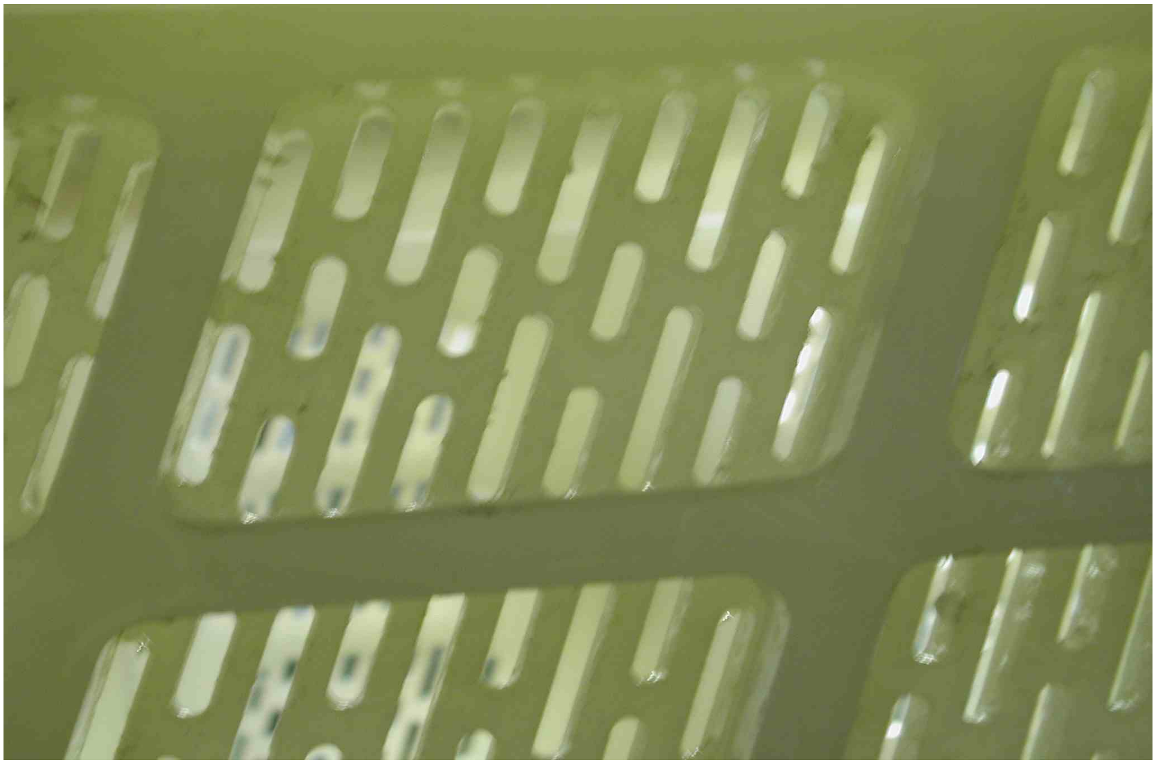

Figure C-17

Environmentally Benign Manufacturing: Integrated-model-based Process Modification

H.H Lou, Department of Chemical Engineering, Lamar University, Beaumont, TX
& Y.L. Huang, Department of Chemical Engineering & Materials Science,
Wayne State University, Detroit, MI

Most effective waste reduction technologies implemented in electroplating plants are essentially for in-plant waste treatment and then material reuse. While the waste that leaves the plant (end-of-plant waste) can be truly reduced, the waste generated from plating lines (end-of-line waste) remains the same. This is certainly a passive approach for source reduction. The minimization of end-of-line waste is always risky, however, because it is very likely to exert a reverse impact on production. Nevertheless, end-of-line waste minimization should be our focus because it focuses on waste sources. In this direction, the fundamental basis of process-focused pollution prevention (P2) is the deep understanding of the design and operation of a plating line. This paper introduces a model-based design methodology that can be used to evaluate the design optimality of multi-stage cleaning and rinsing systems from the environmental and economic points of view. An optimal solution will be derived using sophisticated mixed integer nonlinear programming (MINLP) techniques. The methodology has been successfully used to modify an existing plating line. The resultant process can reduce two rinsing tanks, while cleaning and rinsing quality can be ensured. The chemicals in wastewater and the volumetric flowrate of wastewater in the new design can be reduced by 10 and 15 percent, respectively. This design methodology is general so that it is applicable to any plating line.

Paper not available for publication.

For more information, contact:
Dr. Y.L. Huang
Wayne State University
Department of Chemical Engineering
Detroit, MI 48202
Phone: 313-577-3771

Integrating Pollution Prevention, Pollution Control & Energy Efficiency In Surface Finishing through Process Modeling & Engineering Analysis

Kevin Klink, P.E., CH2M Hill, Corvallis, OR;
Peter Gallerani, CEF-2, Integrated Technologies, Danville, VT;
& Eric Fountain, CEF, CH2M Hill, Corvallis, OR

Surface finishing facilities are complex operations. Changes in a single process can significantly improve or disrupt integrated processes. Facility optimization requires a comprehensive analytical approach because the number of variables (process chemistries, water sources, rinsing, solution maintenance, wastewater treatment and recycling, drag-in and drag-out control, etc.) to be optimized in this kind of integrated facility are overwhelming. Opportunities for the optimization of surface finishing processes and facilities are numerous and synergistic, however, the lack of tools to facilitate complex modeling and analysis of alternatives has hindered integrated planning of pollution prevention, pollution control, energy efficiency and production improvements. Recent aerospace industry projects will highlight a new approach to surface finishing facility optimization planning, utilizing a combination of software modeling and engineering analysis.

Paper not available for publication.

For more information:
Kevin Klink, P.E.
CH2M Hill
2300 NW Walnut Blvd.
Corvalis, OR 97330
Phone: 541-758-0235

SESSION L

Environmental Technology Verification & Technical Assistance

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Previous Session

Papers included:

Performance Verification of an Industrial Wastewater Recycling System
Scott Maurer, Concurrent Technologies Corporation, Largo, FL; Chris Start, MMTC, Plymouth, MI; & Alva Daniels, U.S. EPA, Cincinnati, OH
Paper not available

Metals Removal to Low Levels Using Chemical Precipitants
Angela Kowalski, ONDEO Nalco Company, Naperville, IL

MP&M Compliance Using a Patented Vapor Compression Flash Evaporation System
Bob Torstrick, Vacom LLC, Smyrna, GA

Electrodeposited Nanocrystalline Cobalt-Iron Alloys as an Environmentally Benign Replacement to Hard Chrome Plating
J.L. McCrea, G. Palumbo, M. Marcoccia & U. Erb, Integran Technologies Inc., Toronto, Canada
Paper not available

Performance Verification of an Industrial Wastewater Recycling System

Scott Maurer, Concurrent Technologies Corporation, Largo, FL;
Chris Start, MMTC, Plymouth, MI;
& Alva Daniels, U.S. EPA, Cincinnati, OH

Results will be presented of a performance verification project that was conducted under the U.S. EPA's ETV-MF Program. Testing was performed under actual production conditions at Honeywell's Kansas City Plant (KCP) in Kansas City, MO. Testing evaluated the ability of the RO unit to process post-conventionally-treated industrial wastewater in order to condition the water for reuse within the facility. A waste generation analysis and a cost analysis were also performed.

Paper not available for publication.

For more information, contact:
Scott Maurer
Concurrent Technologies
7990 114th Ave.
Largo, FL 33773
Phone: 727-549-7031
FAX: 727-549-7010

Metals Removal to Low Levels Using Chemical Precipitants

Angela Kowalski, ONDEO Nalco Company, Naperville, IL, USA

For many plating plants, the proposed Metal Products and Machinery (MP&M) reductions in effluent discharge limits for heavy metals would require improvements in existing wastewater treatment programs to ensure compliance. Effective metals removal by precipitation requires rendering soluble metals insoluble followed by good solids/liquid separation of the precipitated metals from the treated water. This presentation will review and compare chemical programs for heavy metals removal. These programs include sulfide precipitation, iron precipitation, small organic metal ion precipitants such as alkyl dithiocarbamates, clay blends and polymeric metal ion precipitants. The polymeric metal ion precipitant program may offer advantages over conventional programs. The polymeric program can effectively remove and flocculate metals and is expected to meet the new MP&M limits, even in the presence of chelants or complexing agents. A reduction in sludge generation may also be realized with the polymeric program and, in many cases, chemical feed can be automated.

For more information, contact:
Angela Kowalski
ONDEO Nalco Company
ONDEO Nalco Center
Naperville, IL 60563
akowalski@ondeo-nalco.com

INTRODUCTION

Increasing environmental concerns about heavy metals discharge have continued to fuel tightening metals discharge limits. The proposed Metal Products and Machinery (MP&M) effluent discharge limits for metals are, in many cases, significantly lower than existing limits.[1] Figure 1 compares the current and proposed regulations. Meeting these low discharge limits will necessitate making changes to existing wastewater treatment systems and plant operations.

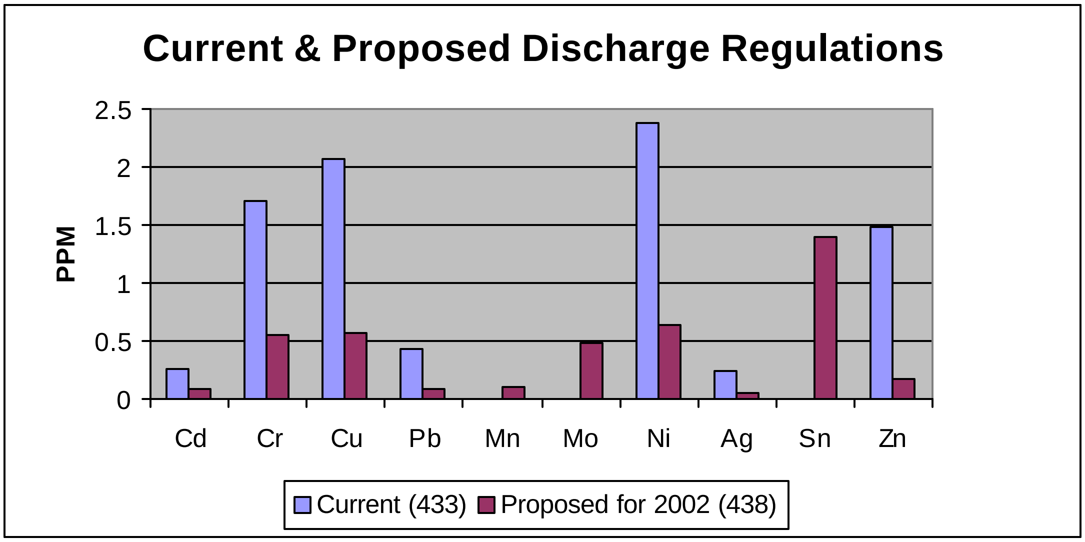

Figure 1. Current and proposed MP&M metal discharge limits.

The most widely used process for the removal of heavy metals from waste streams is chemical precipitation. This method is used by approximately 75 percent of the facilities that treat aqueous metal-bearing wastes. The choice of chemical program depends on the metals being removed, target levels of effluent metals, if metals are chelated or complexed and other components of the waste stream. Other considerations include whether a batch or continuous treatment process is used and sludge handling.

Effective chemical precipitation of metals depends upon one or more of the following variables: 1) maintenance of an alkaline pH through the precipitation reaction and subsequent settling; 2) addition of a sufficient excess of treatment ions to drive the precipitation reaction to completion; 3) addition of an adequate supply of sacrificial ions (such as iron or aluminum) to ensure precipitation and removal of specific target ions; and 4) effective removal of precipitated solids.

OPTIONS FOR CHEMICAL PRECIPITATION OF METALS

Precipitation techniques currently being practiced on aqueous metal wastes include hydroxide (e.g., caustic or lime), ferrous sulfate, sulfide (soluble and insoluble), organic precipitants and polymeric precipitants. Each of these processes will be reviewed.

Hydroxide Precipitation

Precipitation as the metal hydroxide represents one of the least expensive treatments for heavy metals removal. The preferred reagent, from a cost standpoint, is quick lime, CaO or hydrated lime, $Ca(OH)_2$. Other precipitants such as caustic soda, NaOH, and to a lesser extent, magnesium hydroxide $Mg(OH)_2$, are also common. Caustic soda or sodium hydroxide (NaOH) has numerous advantages over lime: homogeneity of feed solution, production of soluble by-products under all pH conditions, rapid formation of hydroxyl ions, and excellent neutralization efficiency. However, caustic soda is always more expensive to use than lime. Magnesium oxide, MgO, or magnesium hydroxide, $Mg(OH)_2$, precipitation systems have shown to be effective in treating metal-bearing waste streams that contain lower concentrations of dissolved metals (~50 mg/L). Since it is insoluble, MgO is a dense solid and the lower sludge volume results from compaction of the metal hydroxides. However, three- to four-fold stoichiometric excess of MgO must be added to reach pH values ranging between 8 and 9, which can cancel out its benefits.

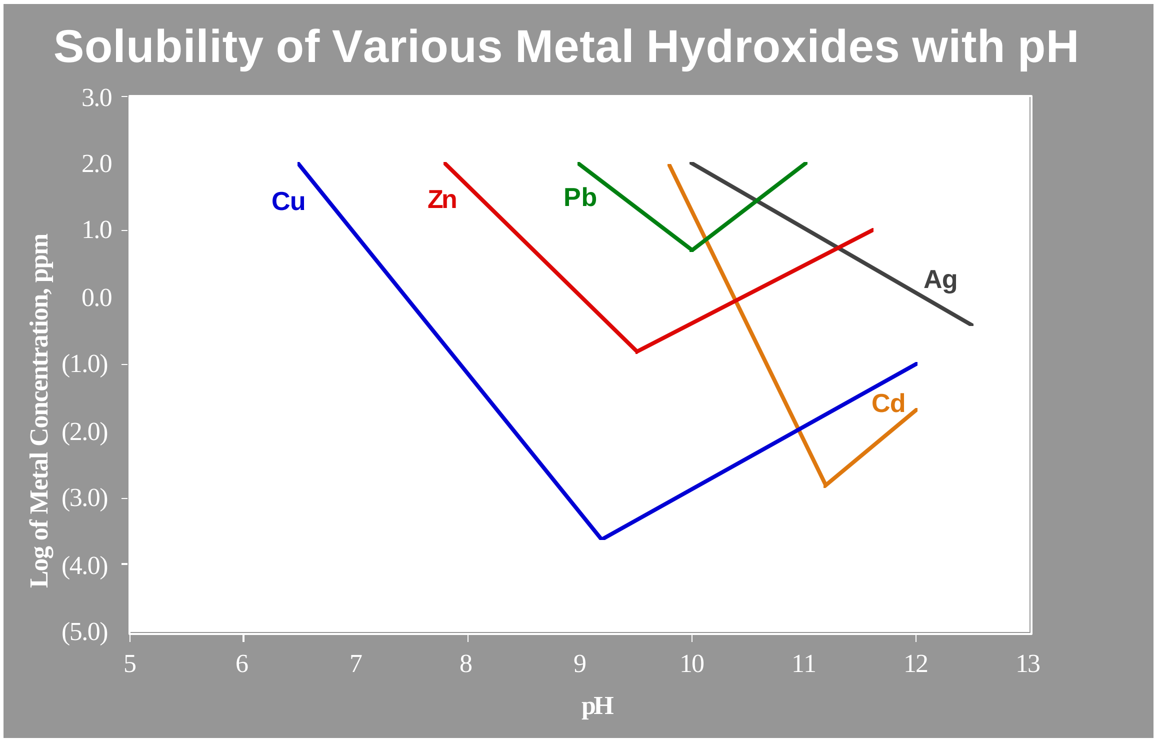

Figure 2. Solubilities for Metal Hydroxides as a function of pH

Hydroxide precipitation can be automatically controlled by pH and has been used effectively in industry. Figure 2 shows optimum pH for some metal hydroxides. When followed by flocculation and filtration, it can remove metals to below 1 ppm, if optimized. However, there are many limitations to this technology, as follows:

1. The hydroxide sludge tends to resolubilize as pH is increased or decreased.
2. The precipitation is ineffective in the presence of chelants or complexing agents.
3. In mixed metals wastes, the optimum pH for each metal varies, and multiple precipitation steps have to be practiced to remove all metals to low levels. This is often impractical.
4. Some metals (such as Pb) are difficult to remove to < 1 ppm by hydroxide precipitation.
5. Metal hydroxides take a relatively long mixing time to form discrete particles; thus, in systems with large flows and short retention times, this method is impractical.
6. Hydroxide sludge is amorphous, voluminous and difficult to dewater, resulting in high sludge haul-off costs.

Free Versus Chelated or Complexed Metals

When metal compounds are dissolved in water, the metallic components exist as positively charged, freely moving ions in the solution. These “free” metal ions react to surround themselves with negative ions or polar molecules present in the solution. The number of such molecules or negative ions that coordinate with the metal ion varies, but for most heavy metals (copper, nickel and iron - the common metals of industry) it is usually 4 or 6. These centers of activity for the metal may be termed reactive sites. In an aqueous solution containing only a simple metal salt, water molecules occupy the reactive sites.

When materials are added that interact more strongly or compete more effectively than water for the reaction site, the water is displaced, and the metal ion acquires a new set of properties. This happens when chelants or complexing agents are present. Many industrial wastewaters contain these materials, such as ammonia. As an example, when hydrated copper ions come into contact with ammonia, the four reactive sites with water are displaced by ammonia. Because the ammonia forms a stronger attachment than does the water, the resultant ammonia-copper complex is stable in solution. The ammonia can only be replaced by adding to the system a material that forms an even more stable complex with copper.

The presence of chelants and complexing agents in wastewater keeps metals dissolved over a broad pH range. In order to treat and remove these dissolved metals, an insoluble metal complex has to be formed, i.e., use of a metal ion precipitant. The following chemical precipitants can be used to remove both non-chelated and chelated metals.

Iron Displacement

Metals removal using iron co-precipitation is very common. The metals-bearing wastewater is mixed with a ferrous salt ($FeSO_4$). At low pH (pH 4), the iron displaces the chelant from the metal of interest, and then the pH is raised (pH 7-9) with alkali to precipitate the metal hydroxide. A polymer flocculant is sometimes added to aid settling. Although ferrous sulfate is relatively inexpensive and can be used to treat chelated or complexed metals, the program has some disadvantages including:

1. Very high sludge volumes because the program requires high doses of ferrous sulfate that generate iron hydroxide.
2. Use of ferrous sulfate contributes sulfates to treated water.
3. Use of a lot of acids/bases.
4. Difficult to achieve the metals discharge limits consistently because there is no automation.

Sulfide Precipitation

Similar to hydroxide precipitation, sulfide precipitation is a process that converts soluble metal ions into insoluble sulfide compounds (MS) through contact between a metal ion (M^{2+}) and a sulfide ion (S^{2-}):

$$M^{2+} + S^{2-} \rightarrow MS$$

Sulfide precipitation offers several advantages:

1. Attainment of a high degree of metal removal due to low solubility of metal sulfides.
2. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
3. Sludge is less subject to leaching than the corresponding hydroxide sludge.
4. Sludge is easier to filter and dewater than hydroxide sludge.

Disadvantages include:

1. Coagulation/flocculation is necessary for good metal removal, but optimization of this process can be difficult.
2. Hydrogen sulfide (H_2S) generation and toxicity to humans is a concern.
3. Excess sulfide is a regulated contaminant in many effluents.

The two main processes for sulfide precipitation are soluble sulfide precipitation (SSP) and insoluble sulfide precipitation (ISP).

In soluble sulfide precipitation (SSP), water-soluble sulfides such as sodium sulfide, Na_2S, or sodium hydrosulfide, NaHS, are used. The major problem with sulfide reagents is potential production of hydrogen sulfide, H_2S, especially when acidic wastewater is being treated. Also, the sulfide ion itself is toxic to aquatic organisms and must be rigidly controlled to minimize excess sulfide in treated water. If the dosage of dissolved sulfide is too high, the precipitation will yield particulate fines that are slow to settle and difficult to filter. The addition of coagulants, such as calcium or aluminum salts and cationic polymer, helps remedy this problem, but coagulant demand changes rapidly, making optimizing of solids-liquids separation difficult to achieve.

The insoluble sulfide process (ISP) mixes a wastewater with a slurry of slightly soluble FeS that dissociates to sulfide and iron ions. The sulfide is released in the presence of other heavy metals having more affinity for the sulfide ion than iron. By maintaining the pH between 8.5 and 9, free iron forms the hydroxide complex and precipitates out of solution. Excess FeS is filtered or settled along with the metal sulfide precipitate, generating a sulfide-free effluent. Like the SSP method, coagulants or flocculants will enhance the removal of metal sulfides. The following reactions occur when FeS is added to a solution containing dissolved metals and metal hydroxides:

$$FeS \rightarrow Fe^{2+} + S^{2-}$$

$$M^{2+} + S^{2-} \rightarrow MS$$

$$M(OH)_2 \rightarrow M^{2+} + 2(OH)^-$$

$$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2$$

Several proprietary systems are currently available that incorporate various aspects of the ISP to achieve metals reduction and removal. One process uses a FeS slurry prepared fresh from $FeSO_4$ and NaHS. The concurrently released Fe will precipitate as its hydroxide. Despite increased metals removal, this method produces more sludge than either the hydroxide or SSP systems. Handling of these chemicals is also a concern.

Small Organic Precipitants

Small molecule organic precipitants such as alkyl dithiocarbamates (DTC) and trithiocarbonates (TTC) are used extensively in metal finishing and electronics industries in the U.S. These precipitants react stoichiometrically with metal ions and show similar characteristics in use. In this discussion, we will use DTC as an example, but keep in mind that TTC shows similar characteristics. Like sodium sulfide, the small molecule organic precipitants can remove metals in the presence of chelants and complexing agents, but safety and handling concerns about using these precipitants are reduced relative to sodium sulfide.

In treating dilute rinse waters containing low concentrations of metals, say below 50 ppm (mg/L), the resulting metal-DTC complexes form colloidal particles in suspension, i.e., particles that will not settle in a reasonable period of time. In some wastewaters, these particles are so small that they appear only as color, carrying metal ions into the effluent. Thus, efficient removal of metal ions from plant effluent necessitates using appropriate coagulation/flocculation techniques for colloidal suspensions.

To destabilize colloidal suspensions, two basic mechanisms have been described as helping to form sufficiently large aggregates to cause settling. The first, referred to as “coagulation,” reduces the net electrostatic repulsion at the particle surface; the product that performs this function is a “coagulant.” The second, known as “flocculation,” is aggregation by chemical bridging between particles; the product for this function is a “flocculant.” Typically, both coagulants and flocculants are used with DTC and TTC.

Small organic molecule precipitation can be difficult to optimize. This is because most wastewaters contain dispersants such as dissolved oils, organics and surfactants. These dispersants inhibit the aggregation of particles, increasing the dosage requirements for coagulants and, sometimes, flocculants. In many of these applications, small organic precipitants are overfed to guarantee compliance. Since these precipitants are negatively charged molecules, product overfeed tends to disperse the precipitated particles. In applications where the initial metals levels are less than 5 ppm, it is more difficult to achieve discharge limits using small organic molecule precipitants, because the low solids make it difficult to form good floc.

To summarize, advantages are:

1. Attainment of a high degree of metal removal due to low solubility of metal-small molecule complex.
2. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
3. Decreased safety and handling concerns relative to sodium sulfide.
4. Sludge is less subject to leaching than the corresponding hydroxide sludge.
5. Sludge is easier to filter and dewater than hydroxide sludge.

Disadvantages are:

1. May be difficult to optimize coagulation/flocculation, solids/liquid separation.
2. May not be effective for low level metal removal due to carryover solids.
3. Automation for small molecule precipitant feed (ORP), but not for coagulant feed.
4. DTC is now regulated in some effluents.

Polymeric Metal Ion Precipitant

A polymeric metal ion precipitant[*] reacts with soluble metals to form insoluble complexes just like the small molecule organic precipitants. However, because the metal binding groups are bound to a polymer backbone, simultaneous metal precipitation and clarification occur. As such, good solids/liquid separation is easier to achieve and usually does not require optimization of a second chemical (coagulant). Another advantage of the metal precipitating groups being attached to the polymer is that the aquatic toxicity is reduced relative to alkyl DTC.

The polymeric precipitant works over a wide pH range, but in most applications works best at near neutral pH (7-9). The pH of treatment is chosen to optimize solids/liquid separation of the polymer-precipitated metals. In cases where a mixture of chelated and free metals are present, there is a trade-off between hydroxide co-precipitation and polymer precipitation. Testing over a pH range is necessary to determine the best treatment pH for the application.

The sludge generated from polymeric precipitant treatment can be hazardous or non-hazardous, depending on the application and the customer's permit. In most applications, there is a 25-90% decrease in sludge volume over conventional technology. This can reduce sludge disposal costs. A lower sludge volume results in a higher metals content of the sludge. If the opportunity for metals recovery from the sludge exists, the higher metals content can make the sludge more valuable. Sludge volume can be further minimized when feed of the polymeric precipitant is automated. The proprietary automation[**] can minimize chemical use and cost and ensure enough chemical is fed as demand fluctuates.

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[*] NALMET®, ONDEO Nalco Company, Naperville, IL

[**] NALMET® Monitor & Controller, ONDEO Nalco Company, Naperville, IL

In some applications, there is a high charge demand from other contaminants, such as detergents or dispersed oils. In these cases, it may be necessary to pre-treat the water to remove charge demand for cost-effective polymeric precipitant treatment.

To summarize, advantages of using a polymeric precipitant are:

1. Use one product instead of two.
2. Consistently effective metals removal due to low solubility of metal polymer complex and good solids/liquid separation.
3. Effective removal in the presence of chelants and complexing agents. (Cyanide must be oxidized prior to treatment.)
4. Decreased toxicity relative to alkyl-DTC.
5. Ease of use - it's automated!
6. Sludge is less subject to leaching than the corresponding hydroxide sludge.
7. Sludge is easier to filter and dewater than hydroxide sludge.

COMPARISON OF HEAVY METAL TREATMENT TECHNOLOGIES

Table 1 gives a quick comparison on available precipitation technologies commonly employed today for soluble metal removal.

Table 1. Comparison of Commercial Metal Precipitant Chemistries

	Polymeric Precipitant	OH	Na_2S	$FeSO_4$	DTC	TTC
Chemical Cost	mod	low	low	low	mod	mod
Sludge Disposal Cost	mod	high	high	high	mod	mod
Treat Chelated Metals?	yes	no	yes	yes	yes	yes
Low Levels?	yes	maybe	maybe	maybe	maybe	maybe
Mixed Metals?	yes	maybe	maybe	maybe	yes	yes
Solid/Liquid Separation	easy	tough	tough	tough	tough	tough
Toxicity of product	mod	non-toxic	human toxic	mod	high	mod
Automation Available?	Proprietary Controller	pH	no	no	ORP	ORP
Ease of use	easy	easy	hard	hard	hard	hard

OH = hydroxide precipitation; DTC = alkyl dithiocarbamate; TTC = trithiocarbonate

CLAY BLENDS FOR METALS REMOVAL

Clays have historically been used for wastewater. They are used as weighting agents and can add bulk to the voluminous metal-hydroxide sludge, making them easier to flocculate and settle. Blended, clay-based products are currently being used for metals removal. These products are different from the metal ion precipitants in that they are intended to pH adjust, coagulate and flocculate wastewater in one step. The products are fed dry or, in some cases, can be slurried. It is thought that metals adsorb onto clay surface. The blended product may contain a metal ion precipitant to remove chelated or complexed metals. These products may be effective for wastewaters with oil or dispersancy because these contaminants can also adsorb onto the clay surface. High doses of these products are used, so the resulting high sludge volumes can create high sludge disposal costs. Also, clay retains water, so sludge may be difficult to dewater.

WHAT CAN BE DONE TO OPTIMIZE THE CURRENT WASTEWATER TREATMENT SYSTEM?

A survey of production and the waste treatment system may reveal practices that can be changed to improve operations in the waste treatment system. It is always optimal to equalize waste streams in metals removal applications. Equalization of wastewaters from all of the processes in the plant going to the waste treatment system ensures a homogeneous wastewater is entering the waste treatment system. This minimizes adjustment of chemical doses and ensures effective removal of metals. Good mixing and long retention times in tanks where the metal ion precipitant is fed also improve metals removal.

Concentrated baths of metals are sometimes “dumped” into the waste treatment system. When these baths contain an excess of the chelant or complexing agent, this practice can have a significant negative impact on the waste treatment system and should be avoided. Excess chelants present in the wastewater sharply increase metals removal chemical required to effectively remove chelated metals because the precipitant must compete with chelant to form the metal-precipitant complex and precipitate the metal. The greater the concentration of chelant, the larger the precipitant dose required. Also, surfactants and dispersants in the baths can have a negative impact on solids/liquid separation, resulting in carryover floc. Efforts should be made to minimize large dumps of chelants to prevent upsets to the waste treatment system and to minimize the dose of precipitant dose required for effective metals removal. If baths containing chelants or complexing agents are dumped periodically, consider segregating the spent baths and slowly “bleeding” them into the waste treatment system.

In the waste treatment system, solids/liquid separation must be optimized to prevent floc carryover. Metals discharge limits are based on total metals (soluble and insoluble) in the effluent wastewater, so any metals-containing floc will increase the total metals in the wastewater. Because upsets to the waste treatment system can occur, barrier filtration, including membrane filtration, should be considered prior to water discharge. Barrier filtration eliminates the possibility of solids carryover.

Even after optimizing solids/liquid separation, some applications may find that target metals levels cannot be met. In these cases, effluent “polishing” should be considered. Effluent “polishing” should also be considered when the wastewater contains a mixture of chelated and non-chelated metals. Non-chelated metals can be removed by hydroxide precipitation and the resulting wastewater can be treated with a metal ion precipitant; precipitated solids are removed by filtration. The polymeric metal ion precipitant is a good choice for polishing applications because metals precipitation and coagulation result from using a single chemistry. This two-stage approach can be more cost effective than using a metal ion precipitant to treat all of the wastewater.

SUMMARY

Metals removal is a two-stage process, rendering soluble metals insoluble, followed by good solids/liquid separation. If chelants or complexing agents are present in the wastewater, hydroxide precipitation cannot be used for metals removal, and a metal ion precipitant must be used. If target metals levels are not being met, a plant survey can identify improvements/practical operational changes to minimize challenges in the waste treatment system and improve metals removal. If these efforts do not produce target effluent metals levels, then one can explore using other metal precipitating chemistries and augment the system with polishing filtration equipment, if necessary.

ACKNOWLEDGEMENTS

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MP&M Compliance Using a Patented Vapor Compression Flash Evaporation System

Bob Torstrick, Vacom LLC, Smyrna, Georgia, USA

A patented vapor compression flash evaporation process can be used to evaporate and then condense clean water from wastewater contaminated with metals and oils. Metals and oils are concentrated to a ratio of 20 to 100:1. In other words, the contaminants are concentrated to 1/20th to 1/100th of the treated volume of wastewater. At the same time, oils can be concentrated for recovery to over 80%. The balance is clean water effluent. Metals in the effluent have proven to be at "non-detect" levels. Effluent can be reused as boiler feed or cooling water makeup, process water or discharged to the local POTW. Currently, four such systems operating at MP&M-designated plants are producing effluents with "non-detect" levels of heavy metals, while at the same time concentrating oils for recovery. Case studies will be presented.

For more information, contact:
Bob Torstrick
Vacom LLC
1880 Cedar Cliff Dr.
Smyrna, GA 30080
770-435-6030
770-435-6528 Fax
E-mail: bob@vacomllc.com

Overview

MP&M compliance requires facilities under this rule to treat their wastewater to achieve heavy metal contaminant levels to generally less than 0.5 ppm. Each metal has its own limit with some as low as 0.03 ppm (lead). Traditionally, wastewater treatment to remove metals involves raising the pH of the wastewater to the point of minimum solubility with some form of hydroxide (NaOH, KOH, etc.) and thereby precipitating metal hydroxides prior to filtration. In some cases sulfide chemistry is also used. When discharge limits were higher (typically by an order of magnitude), hydroxide precipitation was effective. With the discharge limits being lowered to generally less than 0.5 ppm, precipitation treatments will not yield consistent results, even when followed by microfiltration.

That leaves two processes that will achieve the desired results. The first is reverse osmosis and the second is evaporation. Reverse osmosis will remove heavy metals from the wastewater to the desired level, but requires pretreatment steps to remove suspended solids and oils. Additionally, large volumes of concentrated wastewater are generated. Evaporation techniques will also yield the desired level of treatment while generating significantly less concentrated wastewater. Conventional single-stage or 2-stage evaporation processes have high operating costs, as they do not recover heat efficiently. Typical operating costs are in the $0.04-0.07 per feed gallon range.

A patented vapor compression flash evaporation system* (hereinafter called the system) is well suited to ensure MP&M compliance at a low operating cost ranging from $0.0075-0.015 per feed gallon. Additionally, the system does not require chemistry, pretreatment steps or a full-time operator. Labor required is 2-4 hours per week for preventative maintenance.

The system effluent is, in essence, demineralized water having “non-detect” levels of heavy metals. Most of the time the effluent is suitable for reuse as boiler feed makeup, process water or cooling tower makeup. It can also be discharged to the local POTW. The concentrate from the system can be disposed of in several ways depending on the nature of the contaminants present. If oil is present, the wastewater will be concentrated until the oil is in the 60-80% range. It can then be incorporated in a fuels blending program or recovered. If oils are not present, then the concentrate would have to be disposed of in accordance with state and federal regulations.

System process description

The system bases its operation on the combination of mechanical vapor recompression and externally mounted heat exchangers, which are designed with self-cleaning turbulent flows. Active boiling only occurs in a separate disengagement or flash vessel. The result is a system (vapor compression flash evaporation), which can concentrate further than conventional evaporators at lower operating costs. It is also a system that has proven to be competitive with conventional physical/chemical treatment trains and membrane systems without the maintenance and operator attention required for them. An evaporation process, long accepted as a technically sound solution to oils and metals removal from wastewater, has evolved to compete with conventional processes without the problems associated with fluctuating contaminant loadings. The process diagram is depicted on the following page.

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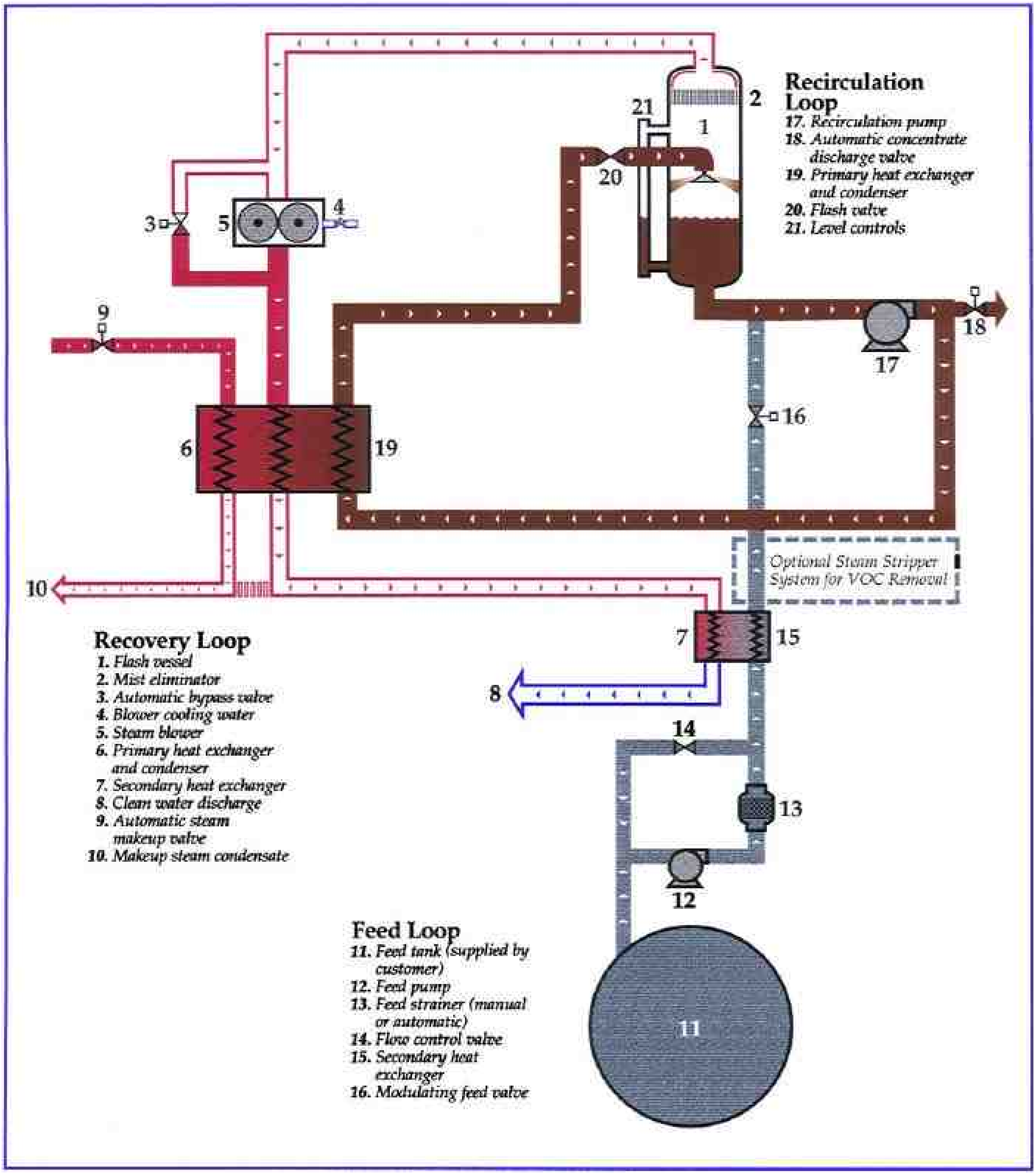
*VCD2000, Vacom LLC, Atlanta, GA



Schematic of vapor compression flash evaporation system.

Wastewater is pumped from a storage tank thru a filtration device. The filtration device can be either a manual basket strainer or an automated filter. From the filtration device, the wastewater enters a secondary heat exchanger (plate and frame or shell and tube) for preheating prior to entering the primary recirculation loop. Within the primary recirculation loop, the temperature is elevated to create separation of steam generated from the liquid. The wastewater is continuously pumped out of a "flash" vessel thru a primary heat exchanger (plate and frame) and back into the vessel across a flash diffuser located above the liquid level in the vessel. Flows and velocities within the primary recirculation loop are designed to create turbulent self-cleaning action within the primary heat exchanger. The system is also designed to eliminate evaporation within the primary heat exchanger and create a steam separation or "flash" zone within the vessel only.

Steam generated from the boiling wastewater is recycled and the heat recovered by evacuating the steam off the flash vessel thru a blower. The blower imparts a pressure and temperature rise to the steam. The steam is blown back into the primary heat exchanger where it transfers all of its latent heat of vaporization and completely condenses. Pressures and temperatures within the flash vessel and primary heat exchanger are automatically controlled.

Steam that is evacuated from the flash vessel passes thru a mist eliminator. Below the mist eliminator is a spool section, which confines the boiling pool and also allows for enough headspace to disengage froth or foam, developed during active boiling, from the liberated steam.

The condensate from the primary heat exchanger is pressurized by the blower and then passes thru a secondary or pre-heat exchanger. The secondary exchanger is used to recover heat from the condensate by preheating the incoming wastewater. Condensate, now effluent, exits the system after the secondary heat exchanger at approximately 95-100 degrees Fahrenheit.

Heat losses of 2-5% are expected. Make-up heat for heat losses and heat required for initial start-up need to be supplied in the form of low pressure (15-25 PSIG) steam. Make-up steam is introduced thru a control valve, which is automated via a temperature controller, and introduced indirectly into the primary exchanger.

The wastewater feed stream excess (the feed pump is sized at 1.25 times the feed rate) is continuously recirculated back to the head of the feed pump. The feed rate to the system is controlled to match the evaporation rate via level controls housed in an external standpipe attached to the flash vessel. The level controls are used to measure the liquid level within the flash vessel, indicate high and low level alarm functions, and automatically shut the system down should an alarm function occur and to control the feed/recirculation modulating valve. As the wastewater evaporates, the liquid level drops. The modulating valve controls the quantity of feed entering the recirculation loop.

Contaminants are continuously recirculated and concentrated within the vapor compression flash evaporation system. These concentrates are periodically purged from the system by actuating a discharge valve located on the primary recirculation loop. The valve is controlled from a timer, within the PLC, set to achieve the ratio of concentration relative to the volume required for the application. As the valve opens, the recirculation pump pumps concentrates from the system. The concentrate valve can also be controlled automatically via on-line concentrate analytical devices depending on the application.

A proprietary stripper system can be provided to remove contaminant compounds (VOC's) that have a boiling point equal to or less than water. That will ensure the ability to meet the oil and grease (O&G) requirement of the MP&M regulation.

The system is designed for unattended operation and controlled with a programmable logic controller (PLC).

Testing

Bench testing is advisable on all applications and mandatory on some applications. In addition to testing on the bench, thermal studies can be conducted to determine heat and mass transfer properties. Bench testing of a representative sample will determine process feasibility, concentration ratio, effluent quality and concentrate physical properties (viscosity, specific gravity, % oil, etc.).

Case Histories

1) Tier I supplier to the automotive industry. Plant manufactures metal parts. Wastewater contains oil, coolant compounds and heavy metals.
   - Flow – 20,000 GPD
   - Influent – 2% oils, coolant compounds and heavy metals
   - Concentration ratio – 40/1
   - Concentrate volume – 500 GPD
   - Effluent – discharged to POTW – below detectable limits on heavy metals
   - Energy operating cost - $0.01/feed gallon
   - Concentrate post treated to yield 90%+ oil and collected by an oil recycler

2) Manufacturer of forklifts. Contaminants are oils, heavy metals, coolant compounds and grinding swarf.
   - Flow – 6,000 GPD
   - Influent – 1-4% oils, coolant compounds, heavy metals and grinding swarf.
   - Concentration ratio – 20/1
   - Concentrate volume – 300 GPD
   - Effluent – discharged to POTW – below detectable limits on heavy metals
   - Energy operating costs - $0.01/feed gallon
   - Concentrate post treated and collected by an oil recycler

Summary

The vapor compression flash evaporation system will enable all MP&M designated plants to meet compliance with effluent heavy metals below detection limits. Plants with oil and heavy metals can possibly go zero discharge with effluent reuse and concentrate recycling. Operating costs are minimal at $0.01 per feed gallon and operator attention is low at 2-4 hours per week.

Electrodeposited Nanocrystalline Cobalt-Iron Alloys As an Environmentally Benign Replacement to Hard Chrome Plating

J.L. McCrea, G. Palumbo, M. Marcoccia & U. Erb,
Integran Technologies Inc., Toronto, Canada

Electrodeposited nanocrystalline cobalt-iron alloy coatings have been investigated as a potential hard chrome replacement system. Via extreme grain refinement (3nm to 100nm average grain size) and Hall-Petch strengthening, hard nanocrystalline coatings can be produced that meet or exceed the hardness and wear performance of current hard chromium plating technologies. The mechanical properties (micro-hardness, wear, etc.) of electrodeposited nanocrystalline cobalt-iron alloys will be discussed, and where possible, correlated with the structure, composition and average grain size of the alloy.

Paper not available for publication.

For more information, contact:
J.L. McCrea
Integran Technologies
1 Meridian Rd.
Toronto, Ontario
M9W 4Z6 Canada
Phone: 416-675-6266