

Session G—Environmental I



International Technical

Conference Proceedings

June 21–24, 1993

SUR/FIN[®] '9²













American Electroplaters and Surface Finishers Society, Inc. 80th Annual Conference—Anaheim

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RECYCLING AND RECOVERY OF CLEANING SOLUTIONS

Thomas J.M. Weaver President/CEO PROSYS Corporation

ABSTRACT:

The proper cleaning of components in the metal finishing industry is the key to quality in the process. Almost every plating operation commences with a cleaning process. In painting operations, cleaning of the components is essential to the proper adhesion of the paint. For years, chlorinated solvents have offered a robust solution to the problem of removing oils and greases from the product. Alkaline cleaners have been used to remove dirt and prepare the surface of the product for plating. The basic cleaning operation has been reliable and relatively inexpensive.

As a result of the Montreal protocol, chlorinated solvents are now being phased out in favor of the protection of the ozone layer. The relative ease of cleaning is now being replaced with complex cleaning operations; complex cleaning operations using soap and water. As a result, usage of alkaline cleaners has increased. Newer aqueous and semi-aqueous cleaners are being introduced as the replacement to solvent cleaning. Complete redesigns of components, cutting oils replacements and manufacturing process changes are now being accomplished in an effort to replace solvents.

Aqueous and alkaline cleaners, both the concentrated solution and the rinse water, pose many handling problems not previously encountered with solvent cleaners. Aqueous cleaners require component rinsing following the clean cycle. Companies are finding that the new cleaning processes actually remove dirt and solid material, which the solvents never touched. The cleaners are relatively expensive. And, the aqueous cleaners cause severe upsets when introduced into many waste treatment operations.

An alternative to the discharge of the cleaners now exists. Most cleaners may be selectively filtered to produce a cleaner which is free of oil, grease, and other contaminants while allowing the wetting agents, additives, dispersant and cleaner components to pass through the membrane. This regeneration of the cleaner maintains a fresh cleaner, increases the operational life of the cleaner, reduces the amount of cleaner used in the operation and ensures continuous quality cleaning of the components.

Definitions:

(1) Microfiltration: Filtration techniques with a membrane whose pore size is greater than .2 microns.

(2) Ultrafiltration: Filtration techniques with a membrane whose pore size is between .001 and .1 microns.

(3) Reverse Osmosis: Filtration techniques with a membrane whose pore size is less than .001 microns.

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(4) Cleaner: A solution which removes dirt, oil, grease, metal and other contaminants from the product piece of work.

(5) Aqueous Cleaner: A solution similar to Item 4 which contains water, surface active agents, wetting agents, dispersants and other components. Typical aqueous cleaners are caustic solutions and organic formulations.

(6) Semi-Aqueous Cleaners: A solution similar to Item 4 which is comprised of organic acids, such as turpines. This type of cleaner will typically operate at full strength in the cleaner bath without dilution.

INTRODUCTION:

There are many different cleaners and cleaning equipment components available which will replace solvent cleaning. Each process and component manufactured requires different types of cleaning to ensure product quality. As such, the change to aqueous cleaning is complex and time consuming. The bottom line is that solvents are OUT, and aqueous cleaners are IN.

The changeover requires coordination between the manufactures of the cleaning equipment, the company process engineers and the cleaning chemical manufacturer. A battery of items must be examined to determine which method of cleaning will produce the most reliable quality. Temperature, strength of the cleaner, contaminants being removed, rinsing procedures, and material compatibility must be addressed prior to the selection of a cleaner method. In fact, the company must determine "How clean is clean?" Finally, the cleaner must be treated for discharge when it is exhausted.

It may be easy to ignore the treatment of a spent cleaner, especially when the company has an operational waste treatment system. However, the very items which enable a cleaner to clean, make the cleaner one of the most difficult components to treat in a wastewater treatment system. Cleaners cause resin beads to fail. Cleaners cause clarifier systems to burp. Cleaners coat sand filters, decreasing the effectiveness of the filtering media. When determining the best cleaner operation for the company, energy and effort must be expended to determine the method in which the spent cleaner will be treated.

As the cleaner loads with contaminants, the reliability of the cleaning process is decreased. Typically, more cleaner is added to the process to extend the operational life of the cleaner. This masks a developing problem in the entire operation. Dirty spent cleaner is dragged from the cleaner tank to the rinse stream. Unrinsed cleaner is dragged to acid baths. Within a matter of a few hours of heavy cleaning, the spent cleaner has contaminated the entire process line.

Conventional waste treatment processes are affected by the cleaners. In a clarification system, gravity is employed to pull the precipitated contaminant from the waste stream. Polymers are added as well as coprecipitating agents to increase the weight of the contaminant and aid in settling. The cleaners are comprised of wetting agents and dispersant. Simply stated, dispersant push solids and contaminants apart so that a component may be rinsed. This action in a clarifier leads to non-compliant discharges. Continual addition of dirty cleaner only makes the problem

CLEANING PROCESS

The cleaning process is simple. Components must be placed in a position so that the maximum amount of cleaner contacts the components and removes the maximum amount of dirt, oil and grease. Depending upon the type of components, there are three effective means to accomplish the cleaning task. Rack mountable components are dipped in a tank, large items are typically sprayed, and small components are loaded into a barrel for the washing operation. Ultrasonics or other means may be used to agitate the cleaner solution to ensure that all the cracks and crevices of the component are properly cleaned. Depending upon the cleaner, the entire operation may be conducted at elevated temperatures.

Following the cleaning operation, the components must be thoroughly rinsed prior to further operations. Rinsing can be as complicated as the cleaning step. If all the cleaner is not removed, the product may spot. Some processes require dry parts. As with plating operations, the rinsing of the product following cleaning uses large amounts of water. In some companies, the wastewater treatment system is operating at maximum capacity. Increased water usage only aggravates compliance issues.

Consider the Cleaning Tank in Figure 1. The process typically starts with a fresh batch of cleaner and water. As the process continues during the course of the day, new cleaner is added to the tank to maintain the strength of the cleaner. Oil, grease, contaminants and other components are removed from the work by the cleaner. Water is added to maintain the level in the cleaning tank. Dragout is comprised of oil, grease, cleaner, water and other items to the rinse stream. Experience



dictates that components are cleaned more reliably and with a higher degree of quality if the cleaner is clean. If fact, the rinsing operation performs better with clean cleaner. As the cleaner continues to operate, the cleaner gets dirty. Floating oils start to appear as the solubility limit of the cleaner is exceeded. Solids buildup in the cleaner tank and settle to the bottom. Clean parts are pulled out of the cleaner tank through a veil of oil. As the cleaner degenerates, the quality of the dragout worsens. The rinse water turns cloudy. In barrel operations, the rinse water may start to look like the cleaner bath.

This operation is not cleaning. This operation is wasting capital

funds, operator time and product, which will be rejected by quality control functions. As stated previously, this operation will result in wastewater treatment operations which cannot provide compliant discharges. However, these problems describe many cleaning operations. Complicating the issue is the treatment of the concentrated cleaners. When the cleaning tanks are spent, the cleaner is dumped to the waste treatment area. The cleaner tanks are thoroughly cleaned and rinsed prior to generating a new cleaner bath. All the wash and rinse water used is sent to the waste treatment area. Depending upon the treatment method, the cleaners are either slowly bled into the treatment process or the cleaners are hauled to a disposal site.

SOLUTION

Microfiltration membranes can selectively remove the contaminants of a cleaner bath while allowing the cleaner components and the water to pass through the membrane. Microfiltration membranes clean the cleaner. As the MF system operates, the contaminants, which have a larger size than the pore size of the MF membrane, are concentrated. The components of the cleaner pass through the membrane and are returned to the cleaner tank with the filtered water.

As shown in Figure 2, Cleaning the Cleaner, the system operation is rather simple. A small slip-stream of cleaner is directed to a Concentration Tank. The cleaner is then pumped through the MF membrane at the required flowrate and pressure. The cross-flow filtration rejects the contaminants, while allowing the permeate to pass through the membrane, where it is returned to the cleaner tank.





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As the contaminants in the concentration tank build in concentration, the ability of the cleaner to hold the oils and solids in solution is exceeded. This results in the cracking of the emulsified oils and the settling of the solids. This separation is further enhanced by decreasing the solubility of the fluid by lowering the temperature. As a result, free oils are removed by an oil removal device and solids are removed by a filter press or bag filter. The net result is that the cleaning tank stays clean, the process quality stays constant and the waste treatment issues are avoided.

Operationally, there are many factors which affect the operation of the cleaner regeneration system. Operating temperature, the size of the cleaner tank, the operational life of the cleaner itself, and the method employed to ensure that the contaminants are removed from the cleaner tank. In addition, cleaner recycle units should not cross-contaminate other types of cleaners. It is important that cleaners stay segregated, as different cleaners are required for different operations.

Figure 3, Recycled Cleaning Tank Mass Balance, illustrates the mass balance of a cleaner tank which is maintained in a clean condition. Many process operations are simplified. The cleaner solution maintains a higher cleaning potential. Rinse water flowrates are not as critical. Downstream tanks are not contaminated with oils and other contaminants. The cleaner operational life is extended.



The recycling of the cleaner bath does not greatly reduce the cleaner addition requirements. The majority of the cleaner is lost due to dragout. When contaminants are removed, the cleaner components which dispersed the solids and emulsified the oils stay with the contaminants. However, the cleaner operates more efficiently when it is clean. When the bath is maintained, cleaner additions are conducted when the alkalinity drops below an acceptable level.

As indicated in Figure 3, salt buildup will occur in the cleaner tank. Consideration should be given to providing RO or DI water when making up fresh cleaner baths or when increasing the operational level of the cleaner tank. When the cleaner is regenerated, salt may prove to be the limiting factor in the operational life of the cleaner. Table 1, Aqueous Cleaner Recycle Results, shows results compiled for companies testing and implementing aqueous cleaner recycle methods using membranes.

		Concentrat	tion(ppm)	
Application	<u>Contaminants</u>	Before	After D	isposition
Metal Finish	* Molly Lube	-2200 O&G -TSS Heavy	-26 O&G -TSS Clear	Reuse
Hardware Mfg	* Stamping oils	-200 O&G -TSS Heavy	-40 O&G -TSS Clear	Reuse
Jet Engines	* Cutting oils	-1600 O&G -TSS 176	-308 O&G -TSS 52	Reuse

When the cleaner tank is maintained in a clean condition, the cleanup of the rinse water may be addressed. In a similar fashion as the cleaner bath, membranes may be utilized to clean the rinse water. Ultrafiltration or Reverse Osmosis offer the pore sizes necessary to selectively remove the cleaner and cleaner additives from the rinsewater itself. As the cleaner is concentrated in the concentration tank, it is possible to return the cleaner to the cleaner bath. DI treatment of the rinse water is possible after the cleaner ingredients are removed.

Turpines and other semi-aqueous cleaners may be addressed by the use of membranes. In this case, the rinse water from the operation is filtered using a microfiltration membrane. This membrane rejects the semi-aqueous cleaner while allowing the water to pass through. The concentrated cleaner bath is typically operated until it is exhausted. Membranes are not selective enough to remove the contaminants of the turpines without removing the actual turpine components.

IMPLEMENTATION

The implementation of the recycling of cleaners is a difficult decision and requires planning. Table 2, Questions To Consider, lists various items which should be addressed prior to the purchasing of any equipment.

The discussion generated by Table 2 highlights many of the concerns when it has been decided to regenerate cleaners. Different cleaners require different systems, as cross contamination of cleaners can adversely affect the process. Multiple cleaners may require multiple systems, however, cost becomes an issue. If the rinse water is not going to be recycled, batch treatment of spent cleaners offers a less expensive alternative to multiple systems. The operating temperature of the process determines which membrane should be used in the process. Ceramic membranes are available, but they are more expensive than polymeric membranes.

Tab	le 2: Questions To Consider
1.	How many cleaner lines are there in the facility?
2.	What are the sizes of the cleaner tanks?
з.	How often are the cleaners dumped?
4.	What is the cost of the chemicals to replenish the cleaner?
5.	What is the method of disposal?
6.	What is the cost of the disposal?
7.	How much labor is required to change the cleaner tank?
8.	How many different types of cleaners are used?
9.	Is it necessary to use different cleaners?
10.	Why are the cleaners dumped?

Sizing of the equipment is important. The flowrate required to maintain the cleaner bath is a function of the dragin, the membrane configuration and the nominal operational life of the cleaner bath without cleaning. If a bath is to be processed on-line, it is important to turnover the bath 3 to 5 times during the nominal operational life of the cleaner. This processing will extend the bath life over 10 fold. If the cleaner is to be processed in the batch mode, the sizing of the system depends solely upon the quantity of the cleaner and the amount of time the system can operate to process the cleaner.

OPERATIONAL RESULTS

Case study 1: An alkaline cleaner of 900 gallons was dumped once every week. The operating temperature of the process was 160°F. The solution was hauled to a disposal site as treatment with a conventional 150 GPM system resulted in non-compliance. A MF system was placed on unit. The solution was maintained for a period of 16 weeks without dumping. The alkaline solution was adjusted periodically to replenish cleaner that was removed from the tank due to dragout or removal with the oil and solids. The company has purchased a unit for the process.

Case Study 2: A company had 12,000 gallons of Soak Cleaner and 10,000 gallons of electrocleaner which was dumped every 4 weeks. The solution was hauled as conventional treatment resulted in non-compliance with regard to COD/BOD. The nine cleaner tanks were in 4 different lines. The company purchased a single MF system for treatment of the solution. When the cleaner gets dirty, the cleaner is pumped to a holding tank where it is allowed to cool. When the solution is cool, the spent cleaner is process through the membrane system and stored in a secondary tank. When required, this tank replenishes spent cleaners. Upon completion of the regeneration, the MF system is flushed with water to avoid crosscontamination. It is estimated that yearly hauling volumes will be reduced to less than 4,000 gallons.

<u>Case Study 3:</u> A company had a 500 gallon cyanide based cleaner tank which was required to remove heavy stains of the product prior to final assembly. The process parts were cleaned with barrels. Dragout from the components was excessive at best. It was assumed that the dragout of the cleaner accounted for the unexplained waste treatment problems. A regeneration system was placed on the cleaner tank. Within one day of operations at .5 GPM, the rinse water tank returned to a clear color. Over a period of six weeks, the waste treatment system operation improved, with no compliance issues. Upon removal of the recycling unit, all the previous waste treatment issues returned. The company has authorized funds to purchase a recycling unit.

CONCLUSION

Although the change from solvent cleaning to aqueous cleaning is difficult, the change will result in cleaner components. In addition, the change is mandated in an effort to protect the ozone layer. Proper planning and testing are required so that the proper cleaning procedure is placed in operation; a procedure which meets the quality and manufacturing needs of the company. Membrane filtration provides the necessary methods to deal with spent cleaners and rinse water. By implementing membranes, cleaner life is extended. The cleaner bath maintains a high cleaning potential. Recovery of the rinse water becomes a reality. And the wastewater treatment issues are simplified. Aqueous cleaner recycle units provide a cost effective means to save chemicals, decrease operator attention and avoid waste treatment incidents. The change in cleaning procedures is worth the investment.

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THE SEARCH FOR CADMIUM PLATING ALTERNATIVES A COOPERATIVE APPROACH

by Steve Schachameyer, Terry Halmstad, and Robert Bauer

Eaton Corporation, Milwaukee, WI

and

John Newman of Master Lock Company, Milwaukee, WI

This paper describes how two companies in disrelated fields of business worked together on a cooperative basis to share information and review results. This approach lead both concerns to ultimately find acceptable substitutes for cadmium plating of their respective products.

ABOUT THE COMPANIES AND THEIR USES FOR CADMIUM PLATING

Eaton Corporation

Eaton Corporation is a large international company with significant core businesses in vehicle components and the electrical controls industry. Within the electrical controls business are both commercial/industrial segments and a military segment; the latter is a supplier of key components such as relays, contactors, starters and switches of all ratings.

Cadmium plating for Eaton Corporation began very early, with the first production baths being the "Udylite" process, then the first proprietary process that was introduced in the 1920's. Cadmium plating was widely used throughout the electrical components part of the business as it was a relatively simple process that could be plated on ferrous and non-ferrous parts. For high current and relatively high voltage applications, cadmium provided a stable electrical contact. The attributes of an engineering coating that cadmium provides are:

- · electrical conductivity
- · thermal conductivity
- · solderability
- · weldability
- material compatibility to retard galvanic corrosion
- · consistent torque requirements
- · anti-galling
- · rivetability
- · minimal white salt corrosion
- · wear resistance
- · cost

When the environmental, health and safety issues surrounding cadmium, and its potential redistribution throughout the environment brought about by the corrosion of cadmium plated articles came to head in 1977 (ref. 1), the company began a program to eliminate

cadmium plating of commercial/industrial product lines. We successfully completed this program by 1980 and made use of a series of existing coatings to substitute for cadmium:

- · ferrous hardware zinc and nickel plating
- · non-ferrous hardware tin plating
- · solderability/weldability tin plating
- · anti-galling tin plating plus wax coating

This process did not extend to parts produced for any military components at this time as we could not perceive any overt movement by the branches of service to rescind QQ-P-416.

Starting in 1992, several significant events occurred to cause Eaton to reconsider extending the process to military applications. First, EEC Directive 91/338/EEC prohibits the use of cadmium plating after January 1, 1993 for a number of applications which include European military applications. Secondly, QQ-P-416, revision F, contained a new section which suggested that a number of environmentally sounder coatings should be considered as substitutes for cadmium. Finally, OSHA issued the new cadmium standard, CFR 1919.1027, which lowers by a factor of 20 the permissible employee exposure level to airborne cadmium compounds.

Master Lock Company

Master Lock Company is a large manufacturer of padlocks, door locks, and other security hardware. The padlock division is the largest padlock manufacturer in the world. The facility has a very large captive metal finishing shop that produces a wide variety of metallic and organic finishes.

European bans and restrictive standards for products that contain cadmium discouraged long-term commitments to existing cadmium finishes, which limited the global marketing of Master Lock's product lines. The new OSHA cadmium regulation effected the operations with numerous restrictions. The cadmium plating operations were very large and deeply integrated into the manufacturing operations.

The research for an alternative to cadmium plating continued for over two years. Several properties of cadmium were utilized for Master Lock's products. These important properties are:

- 1) highly reflective and decorative finish
- 2) galvanically protect the steel products
- 3) less bulky corrosion by-products than most other sacrificial finishes
- 4) lubricity aided in the locking mechanism
- 5) cost

There were certain obstacles to plating an assembled laminated lockbody that made the job of finding an appropriate substitute very difficult. Over the course of this research approximately 20 different finishes were thoroughly evaluated. A few of the finishes that

were found to be of significant interest were zinc, zinc-nickel, nickel-cobalt, nickel-tin, tin-zinc (1% zinc), tin over tin-zinc (30% zinc), tin, and various organic finishes. Each of the finishes noted above, were tested with many types of post-plating operations such as lacquers, urethanes, chromates, teflon, and highly alkaline post finishes. The salt spray comparisons for most the finishes referenced above can be seen in Figure 1. It can be seen from Figure 1 that tin-zinc was identified as an excellent possibility for

cadmium replacement.

THE APPROACH

The companies decided that the most expeditious approach, considering the relatively short time frame to make significant material changes in their respective products, was to work together via a mutual confidentiality agreement. Both companies had been viewing the developments of tin-zinc alloy plating as promoted by the Tin Research Institute as a more universal alternative to replace cadmium plating. Tin-zinc plating was early on identified by Brenner (ref.2) as a versatile coating, but the electrolyte of that period was an energy intensive alkaline cyanide solution which did not merit consideration in today's environmental climate.

In the beginning of the project the vendors of the proprietary processes listed above were asked to prepare the sample parts for evaluation. Eventually this procedure was found to be unsatisfactory because the vendors processed the materials differently than specified. In addition, the vendors rarely revealed all the information needed to completely evaluate the "total process". To overcome these obstacles a dedicated pilot line was constructed at Master Lock and Eaton Corporation. Experimental baths, post finishes, drying techniques, etc were subjected to actual production conditions in the shop. As a result the total process was evaluated and documented for scaling up to large operations.

The testing method used at the beginning of the research for Master Lock was the 5% neutral pH salt spray. This method yielded much different results from the observations in the field tests (ie.natural environment). A new test method ASTM 11.2.2.1, hereafter referred to as the cycling test, was used. The samples were subjected to a cycle of environmental conditions rather than a single environment. This method exposed the samples to 96 hours of 5% neutral pH salt spray, 16 hours of a 100% humidity environment with ultraviolet light exposure, and 16 hours of drying (60 oF) with ultraviolet light exposure. This method yielded results that were comparable to the results that natural exposure delivered to the product.

These test results and experimental procedures led Master Lock to find a process that delivered a higher quality finish than that of cadmium, a tin-zinc alloy. Two tin-zinc alloys were studied under different production conditions. The three tin-zinc processes studied can be seen in Table 1.

Table 1

- 1) tin-zinc alloy deposit with 1% zinc Two Processes Researched
 - A) sulfuric acid electrolyte with anodes made of tin-zinc (25% zinc)
 - B) sulfuric acid electrolyte with anodes made of pure tin
- 2) tin-zinc alloy deposit with 30% zinc
 - A) neutral pH proprietary electrolyte

RESULTS

TABLE 2

EVALUATION OF THE DIFFERENT TIN-ZINC PROCESSES

The two tin-zinc baths that produced the 1% zinc in the deposit each used a different anode system. Each bath supplied zinc to the solution through a different mechanism. In case 1A, the process used a tin-zinc alloy anode (25% zinc) and high tin metal concentrations. The zinc in the solution is provided by the electrolysis of the anodes. In case 1B, the bath used a pure tin anode, and low tin metal concentrations. The bath was then supplemented with zinc sulfate. The difference in the amount of zinc found in the alloys between the two processes were found to vary from 0.008% zinc to 0.661% zinc. The actual alloys deposited can be seen in Table 2. It should be noted that for the purposes of this paper the 1% tin-zinc process is used to name a alloy that can have a variety of different alloy compositions. The performance of the finishes does not seem to vary significantly when the percentage of zinc changed. The reason for this variance was found to depend largely on two factors:

1. The level of proprietary brighteners\complexers found in the bath.

2. The amount of amp-hours the bath has seen.

DATE	VENDOR	%ZINC	
5\21\92	1A	0.661	
5\21\92	1A	0.719	
11\20\92	1A	0.008	
11\20\92	1B	0.243	
1\21\93	1A	0.11	
1\21\93	1B	0.15	-

% ZINC FOUND IN 1% TIN-ZINC ALLOY

The tin-zinc bath that produced the 30% alloy was found to produce a color and luster that was not to Master Lock's standards. However, the salt spray results revealed the finish delivered excellent protection of the steel. It was decided to plate over the finish to give it the appropriate color.

A test was designed to plate pure bright tin as well as the 1% tin-zinc alloy over the 30% tin-zinc finish. There was zinc migration through the pure tin deposit and it discolored the finish, although, the salt spray results were still much better than for cadmium. The 1% tin-zinc alloy plated over the 30% tin-zinc alloy delivered a stable color but the salt spray performance was slightly less than that of the 1% tin-zinc alloy alone. Therefore, the 30% alloy was eliminated from further consideration.

DEPOSITION MECHANISM

There is a very small amount of zinc in the deposit. It was hypothesized that the zinc distorts the cell lattice of the deposit and prevents migration of the base metal. This stabilizes the color and allows the main constituent tin, (Sn), to perform the bulk of the corrosion protection.

Through numerous tests it was determined that the zinc found in the 1% alloy was deposited through a mechanism of inclusion. In other words, the zinc was pulled along with the tin as the process of deposition occurred at the surface of the substrate. As an analogy, the same type of mechanism is employed when an electroless nickel bath needed teflon, or diamond impregnation. The zinc (teflon or diamond) acts like a major impurity in the bath was pulled along with the main constituent and co-deposited.

CORROSION RESISTANCE OF THE TIN ZINC ALLOY

The two vendors, 1A and 1B, were evaluated on several different products at different thicknesses. See Figure 2. There were four thicknesses studied 0.30, 0.55, 0.70, and 0.85 mils. The important fact gained from these tests was that a minimum thickness, 0.55, was needed. The finishes plated at higher thicknesses only slightly improved performance to red rust on the product. There were other factors that contributed to red rust that limits the overall performance. At the minimum thickness of 0.55 mils vendor 1A performed better than 1B. It should be noted that there are significant differences in costs between the two tin-zinc processes for the 1% alloy and that costs must be factored into any final decision.

A determination of the relative corrosion resistance of each coating compared to cadmium plating and zinc plating was made. In addition to using salt spray testing to verify a degree of equivalency by this much abused quality control test (ASTM B-117), A Electrochemical Impedance Spectroscopy (EIS) test was performed, with the results summarized with respect to time and corrosion rate in Figure 3. The significant finding with respect to either of the tin-zinc deposits was that the corrosion resistance, expressed as a corrosion rate of mils/year, versus hours of exposure to a 5% salt solution, was approximately an order of magnitude better than chromated cadmium or zinc plated

articles. There was also a more than discernable level of improved corrosion resistance to be gained from the low zinc (1 percent) tin alloy over the nominal 30% zinc-tin alloy.

PASSIVATION OF THE TIN-ZINC ALLOY

One of the potential concerns one might have for a tin-zinc alloy, particularly the 1 percent alloy, might be the corrosion products of more or less pure tin, which tend to be white salt formations similar to cadmium. Considering the 1 percent coating to be a pure tin coating, it is known that tin can be chromated, forming stable and unstable oxides which are protective in nature. These oxide films are colorless and quite thin, so there is no yellow color developed as a result of "chromating" in a dilute chromic acid/sulfuric acid mixture (some superficial staining may occur). It is well known from experience with acid thin deposits that the coating can be passivated by strongly alkaline solutions, which in comparison to a chromate solution, would be preferable to use from a total environmental point of view.

EIS was once again employed to study the relative degree of passivation of chromated versus alkaline rinsed tin-1% zinc alloy coatings. The results are presented in Figure 4, which shows there is no substantial difference in the degree of passivity achieved, making the alkaline dip an environmentally sound solution and well as a reliable one.

CONCLUSION

The tin-zinc finish on steel also gave the additional benefit of being specifically excluded from the EPA's F-006 listed waste category. If properly segregated from other plating wastes, this would lead to significantly reduced disposal costs.

The cycling tests performed at Master Lock revealed that the alloy with 1% zinc outperformed the alloy at 30% zinc. These results can be seen in Figure 1. It showed that significant red rust developed on the 30% tin-zinc alloy at 288 hours compared to the 1% alloy at 576 hours. The 1% tin-zinc alloy produced a stable brilliant silver metal deposit that met all functional, decorative, and regulatory goals established for the project.

The tin-zinc alloy would be used for different properties and purposes at Master Lock and Eaton Corporation. Through independent research, both companies arrived at the same conclusion that a 1% tin-zinc alloy delivered the best overall performance as a direct cadmium substitute.

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COMPARISON OF CADMIUM ALTERNATIVES FIGURE 1



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MASTER LOCK COMPANY TIN-ZINC FINISHES AT DIFFERENT THICKNESSES FIGURE 2



Figure 4. Comparison of chromated vs. no chromate in 5% NaCl Tin (low zinc) plated on steel



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Figure 3. Corrosion Rate, plated machine screws in 5% NaCl

The use of Vacuum Distillation in the Treatment and Recycling of Plating Solution

by Mario Fabro / Drew Resource Corporation

Foreword

Since the beginning of "environmental consciousness", the metal finishing industry has been a major target for legislators. The basic problem is known: the use of hazardous chemicals and the discharge of large amounts of wastewaters.

Concepts such as pollution prevention, waste minimization and waste treatment are therefore clear to everybody in this industry.

Two directions have been initially followed to achieve the goal of an environmentally-friendly operation:

- use of less hazardous chemicals
- treatment of waste flows to comply with discharge regulations

To these two, a third important concept has been recently added, which has, and will continue to have, a tremendous effect on the general process technology and philosophy:

 reduction and recycle of process baths and rinse water

The traditional treatment and the new approach.

Initially, the major concern was the removal of polluting elements from rinse water and spent chemicals. Technology was aimed at the separation of water from heavy metals, cyanide, chlorides etc. This was achieved through a chemical process, by adding to the waste flow some binding compounds able to conglomerate together the salts until they precipitate.

The process is known as flocculation and the end products are clean water, discharged

by overflow from the process tank, and a metal salt sludge, usually extracted with a pump and then sent to a filterpress and then to final disposal.

This technological process has been used since the first half of this century. Although it has been subject to constant development, this process can not fulfill anymore all the requirements of the modern treatmentrecycling course. Basic drawbacks are:

- a) Uncertainty of the result: the chemical additives need to be dosed with absolute precision and, since the waste flow may change in composition, require constant supervision and adjustments.
- b) High costs in flocculation additives: this is a high operational cost, since these products are quite expensive. Since the selection of the right chemical is of great importance, this process is also timeconsuming.



Fig 1: The traditional and the new approach

- c) Large quantities of sludge produced: besides the salts separated in the process, the flocculant agents themselves become a waste product; thus, greatly increasing in volume the amount of sludge produced.
- Need for specialized supervision: a good knowledge of chemistry is needed to supervise the plant, and this, beside a normal mechanical maintenance, represents a primary cost
- e) "Dirty" treatment: the system frequently creates smells and can create overflows and splashes.
- f) Outdated technology: the concept of adding "pollution to the pollution" by using additives that result in waste sludge is not seen anymore as a practical method. The metals in the sludge are difficult to recover, due to the effect of the flocculation chemicals.

Some of these concerns have been addressed by a relatively new filtration technology: ion exchange. In this system, special resins exchange the chemically charged metallic ions with "harmless" ions such as sodium (Na⁺), hydrogen (H⁺) or hydroxy (OH⁻). The resins can be designed to hold only particular kinds of ions, which makes this system a very effective treatment technology. However, there is a price for it. The main concerns are:

a) Resins need to be regenerated: their filtration effect vanishes once all the ions have been exchanged. This requires regeneration with chemicals (such as sulfuric or hydrochloric acid) able to "strip off" the metallic ions and replace them with the original ones. This will produce a waste flow, called eluate, which, in final analysis, holds all the metal salts separated from the water flow. This can sometimes be plated out, to produce metal, but will still remain a waste flow.

b) Resins have limited filtration capacity: since they need to be regenerated, and the regeneration frequency should be kept as low as possible to avoid extra production of eluate. Resins are effective only on relatively "clean" water, such as the final rinses, and can not be used with drag out or plating solutions.

In more recent times, new technologies have been developed in order to answer these concerns. These system are based on physical treatment processes, rather than chemical. The most important are:

- filtration technologies (ultrafiltration, microfiltration, reverse osmosis and electrodialysis)
- distillation and evaporation.

In this paper we will explore this last process.

Evaporation and distillation

Evaporation is a widely known natural process. Evaporation combined with the condensation of the vapors, creates the distillation process. Evaporation alone does not correctly address all the main concerns, since it performs only a "change of state" of the pollution, from liquid to gaseous.

Distillation, on the other hand, produces two flows that can be recycled:

- a distilled water and
- a more concentrated flow, either in liquid or semi-solid form.



Fig. 2: Relative distillation performance

Distillation can be performed at different pressures. Therefore, we could further divide it into:

- distillation under pressure (thermal compression)
- distillation at atmospheric pressure
- distillation under vacuum.

For the treatment of plating solutions, with the goal of closed loop recycling, vacuum distillation is preferred since the evaporation occurs at low temperature (35°C-95°F) without any chemical breakdown of the solution.

In the cyanide baths, for example, temperatures higher than 70 °C (160 °F) will breakdown cyanide and build-up carbonates. Other negative effects of high temperatures may be also hydrolysis of some compounds.

Vacuum distillation operates at temperatures well below this limit and, in many cases, within the plating temperatures of the baths (average, 30-65 °C = 85-150 °F). Furthermore, under vacuum the relative distillation performance is higher, as indicated in Fig. 2. As an example, at 0.2 bar and 65 °C, it is possible to distill a chromic bath with 350-600 gr/l of CrO_3 (1).

Finally, vacuum distillation represents a valid energy saving method, since by operating at 13.9 PSI the energy required is only 1/6th of that required at atmospheric pressure.

Vacuum distillation systems

There are several different models of vacuum distillers on the market. Basically they differ for the following characteristics:

- a) evaporation heat source and condensation system
- b) vacuum system

In the most common systems, heat can be produced using conventional electric energy or steam. Usually the latter are much larger systems. The units using electric energy have a wider application spectrum, since only very large facilities are capable of producing in-house steam.

The most effective electric heat source is the heat pump, which operates on the basis on the compression and expansion of refrigerant gases. As explained in Fig. 3, initially the gas is compressed from 8 to 22 bar and therefore its temperature rises. This heat is then transferred to the solution (2).

During this phase, the refrigerant gas is partially recondensed. (therefore its temperature drops). It is furtherly cooled to 17 °C (62 °F) in an air heat exchanger (where it totally recondenses in a liquid form). An expansion valve then drops its pressure from 22 to 8 bar. At this moment, the cold liquid is used to recondense water vapors in the distiller. This final phase evaporates the refrigerant that eventually reaches the compressor to begin another cycle.



Fig. 3: Vacuum distiller, standard type

Therefore, with only one main utility (the compressor) both the evaporation heat and condensation cold is supplied.

In the vacuum distiller, the boiling chamber is under negative pressure, to allow low temperature boiling. This vacuum is usually provided by a specific pump that extracts the air from the chamber (Fig. 3).

Another system uses a water recirculation pump and an ejector that, due to the venturi principle, provides the vacuuming action. Furthermore, by using its own distilled water in the vacuum circuit, this system also provides the extraction of the condensed water (Fig. 4). Finally, since all water is recondensed, there is no vapor or gas escape, such as with the vacuum pump system. This is important when treating cyanide or strong acids.

Another applicative difference, is in the way that heat and refrigeration are added to the solution. In the system described in Fig. 3, both the heating coil and the condensation coil are installed inside the boiling chamber. A better system is the one described in Fig. 4, where the heat is supplied by an external heating mantle, avoiding the inconvenience of frequent coil cleaning. Some systems are also provided with scrapers to keep the heating surface clean, increasing its efficiency.

For large units, the heat can be supplied an external by heat exchanger, by continuously recirculating the solution through it. This system allows easy maintenance of the heating elements and also provides automatic discharge of the concentrate (Fig. 5). Other positive developments are the use of special demisters that increase the efficiency of separation between solids and water vapors.

Finally, importance should be given to the selection of the distiller construction material, with particular attention to the parts in contact with the solution (boiling chamber, heat exchangers, pumps etc.).

For non-corrosive flows, such as cyanides, sulphamates and basic solutions, 316 L stainless steel is the best available material. This gives the system a greater value, overall mechanical resistance and longer life compared to cheaper materials such as iron or plastics.

Fig. 4: Vacuum distiller with heating mantle





Fig. 5: Vacuum distiller with heat exchanger

For strong acid solutions containing chlorides, fluorides or other corrosive elements, special steels are required, such as Haynes Hastelloy C[®] or Sandvick Sanicro 28[®].

Chromic acid, finally, is one of the most corrosive elements and the only known chemically resistant material to effectively resist it is titanium.

Basically, the choice of a system should address all these points:

- a) economy of operation (energy required for distillation)
- b) ease of maintenance (particularly for the heating elements)
- c) distillate quality (accomplished by use of demisters etc).
- concentration capacity (specific gravity of the sludge produced)
- e) automatic controls and alarms

The vacuum distiller in surface finishing

Since this treatment technology allows recycling of plating solutions, the vacuum distiller can be applied in two specific applications:

- a) closed loop recycling of drag-out tanks
- b) terminal treatment of waste flows.

Closed loop recycling

The closed loop recycling of the drag-out implies utilization of counter flow rinsing. The system is explained in Fig. 6 and works as an add-on to the plating line.

The counter-flow rinsing system is well known in the industry. By carefully designing the number of tanks and the quantity of water flow required, the dimension of the distiller can be reduced to a minimum.

In this application, the water produced is sent back to the beginning of the counterflow rinse. The concentrate flow, being chemically unaltered, can be recycled to the plating bath.



Fig. 6: Closed loop recycling

Unfortunately, there is no such thing as "100% recycling" since in many cases there is a production of by-products in the plating process, such as carbonates, that are not removed by the distiller and will keep building up in the recycling loop. These products must be separated by appropriate systems (selective ion exchange or carbonates crystallizer are two of the possibilities).

As an example, the drag-out of chromic baths is rich in metallic cations, produced by oxidizing agents in the plating bath Closed loop recycling of such concentrate will then require a pre-separation of such impurities (3).

Another solution, for smaller lines where the equipment investment is not profitable, is to limit the recycling of the concentrate to 80%-90%, sending the excess solution to the final treatment.

The advantages of closed loop recycling are the following:

- a) Plating solutions and water costs savings
- b) Due to constant treatment of the dragout tanks, the final rinse will be much cleaner, allowing in certain cases its direct discharge to the sewer. In cases where ion exchange is used to recycle the flowing wash, these systems will be much more effective and their regeneration frequency will be greatly reduced.
- c) Total recycling of drag-out tanks and rinse water gives additional benefits like getting "off the hook" with the environmental agencies

Obviously, a detailed R.O.I. study has to be undertaken since the investment is quite high and there is need of a unit for each different plating line.

Terminal treatment

In the terminal treatment of the waste flows, the distillation system substitutes the traditional chemical flocculation and precipitation system.

We have already seen the advantages of this system, despite its major cost. Bottom line is that distillation is a much more advanced treatment technology that can accept a wide range of flows (spent solutions, drag-out tanks, rinses and eluates from resin regeneration), as seen in Fig. 7, with minor set-up changes (basically only the concentration ratio must be checked).



Fig. 7: Terminal treatment

Case study: a Swiss manufacturing company with hardening and plating lines.

The management of a Swiss manufacturing company decided to revamp its operation in an effort to more easily achieve both regulatory limits and greater economy of operation. Processes were radically altered in favor of total recycling in a new facility.

The company manufactures a large amount of metallic parts. Its operations include electroplating and hardening. For the hardening operations, a salt bath containing molten $NaNO_3$ and $NaNO_2$ is generally used. For plating, a zinc cyanide process is used. The bath composition is as follows:

-	Sodium cyanide	60 g/l
-	Zinc	30 g/l
	And a set of a	

- Sodium hydroxide 90 g/l

The plating line includes three counterflow rinses, with a total flow rate of 250 l/hr. All the rinsewater coming from the electroplating and from the hardening processes were at that time fully treated by a chemical system and discharged.

The main goal for the company in deciding to build a new plant was the recovery of resources, such as hardening salts, plating chemistry and water. Further, the use of problematic chemistry (such as hydrochloric acid, tri-sodium hypochlorite) had to be reduced or avoided. Therefore, the company introduced a new approach in the ecological treatment of plating and hardening solutions - total recycling.

Recycling in the Hardening Line

Pollution concentration in the rinsewater is relatively low. The rinsewater is collected from the four tanks of the hardening lines. A total flow of about 2000 l /hr is collected in an 8000-I tank. The concentration of hardening salts, concentration in this flow is below 10g/I. The solution, rich in dissolved hardening salts'is then passed through a mechanical filter, in order to remove all large solid particles, then sent to an electrodialysis unit, where the flow is directed through the filter membranes by an electric field.

The unit produces 90-percent salt-free water that is collected and recycled in the hardening line, and a 10-percent concentrate flow, with more than 100 g/l of salts, that is passed to a vacuum distiller for further concentration.

The distiller concentrates the solution by a factor 4 and produces 100 l /hr of distilled water, which is collected for recycling, and 25 l /hr of concentrate with more than 400 g/l of hardening salts. These salts are solidified in a crystallizer and then re-cycled to the hardening bath. Production is about 15 to 20 kg/day of salts (30-45 lb.).

The water collected from the electrodialyses and from the vacuum distiller is returned to the rinse baths without further treatment. Figure 8 shows the treatment flow for the hardening line.



Fig. 8:Recycling in the hardening line

Recycling in the Plating Line

Rinsewater coming from the first rinse tank is first collected in a storage tank. The composition of the flow is 98 to 99 percent water and 1 to 2 percent plating solution. There are about 10 g/l of dissolved salts in the rinsewater.

From the storage tank, the solution is fed to another vacuum distiller, where the water is evaporated and re-condensed. The distiller produces 95-percent salt-free water and 5 percent concentrated solution, with 200-250 g/l of salts. The water is collected in a tank, then recycled to the counter-flow rinse of the plating line. The concentrate, having the same composition as the original plating bath, may then be recycled.

In order to keep the plating bath as pure as possible to extend its life, a small amount of concentrated solution is removed from the recycling loop and for sent off-site disposal. This is necessary to prevent a build-up of the carbonate concentration and is the only exception to total recycling. Figure 9 shows the treatment flow for the plating line.



Fig. 9:Recycling in the plating line

<u>COST ANALYSIS:</u> <u>Salt Recycling in the Hardening Line</u>

•	Total investment, hardening line	\$375,000
·	Investment costs - 12-year depreciation plan - linear interest, K/2 x 10%	\$31,250 \$18,750
•	Total year investment costs	\$50,000
•	Running costs: Savings - recycling of hardening salt (60 tons/yr) - reduction in use of sodium	s \$70,000
	 hypoclorate water consumption saving 	\$61,000 s \$2,000
•	Total savings - less energy consumption	\$133,000 \$16,000
•	Subtotal savings per year	\$117,000
	Balance - subtotal savings - less investment costs	\$117,000 \$50,000
	Total savings per year	\$67 000

Solution Recycling in the Plating Line

- . Total investment, plating line \$275,000
- . Investment costs
 - 12-year depreciation plan \$22,900
 - linear interest, K/2 x 10% \$13,750
- . Total year investment costs \$36,650
- . Running costs: Savings
 - recycling of plating solution + savings in disposal costs \$42,000
- . Balance
 - savings \$42,000
 - less investment costs \$36,560
- Total savings per year \$5,350

Satisfaction of Requirements: Environmental and Economical

The treatment plant has reached its ambitious goal: Treatment of washwaters with a modern system that meets both environmental and economic requirements. Seven important factors have been addressed (4):

- The sewer limits for nitrite and cyanide discharge in wastewater are fully met.
- 2. There is no salt discharge in the wastewater.
- Ninety-eight percent of the hardening salts are recycled.
- Water consumption was reduced by 95 percent.
- 5. More careful handling of valuable resources resulted.
- Use of sodium hypochlorate has ended and handling of other potentially dangerous chemicals has been reduced.
- The old treatment plant is now operated in a more economical and progressive way.

Conclusions

Waste water vacuum distillation is certainly an expensive investment but the applications that this technology has made possible are extremely interesting and advanced. Vacuum distillation, together with membrane technology and ion exchange, represents a newer approach targeted to the future of pollution control: cloosed loop recycling. These new systems reach even greater possibilities when combined. As an example, vacuum distilation can treat regeneration chemicals from ion exchange as well as work as a further concentrator of ultra filtration reject.

The general philosophy at the base of these technologies is no longer an end-ofpipe treatment system disconnected from the production cycle but the realization of a piece of equipment to be integrated in the production cycle, following its requirements for quality, performance and endurance.

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About the author:

Mario Fabro has been working in design and marketing of waste treatment systems in civil and industrial fields since 1981. He holds an engineering degree and has been European sales manager for LED Italia s.r.l. He is currently responsible for the U.S. market with Drew Resource Corp., Berkeley, CA and has recently published some studies in both Plating and Surface Finishing and in Metal Finishing on the use of Vacuum Distillation.

LOD, LOQ, MDL AND PQL: ACRONYMS FOR DETECTION LIMIT METHODOLOGIES; THE DRIVING FORCE OF THE NEXT GENERATION OF REGULATIONS FOR THE SURFACE FINISHING INDUSTRY

JOHN LINDSTEDT ARTISTIC PLATING COMPANY, INC. MILWAUKEE, WISCONSIN 53212

INTRODUCTION

The requirement to improve environmental quality is a force that will shape the national conscience as the decade unfolds. This environmental awareness is creating a generation of regulations that have as their focus the restriction of chemicals at everdecreasing concentrations. The concentrations of pollutants in many cases are being regulated at the limit of detection. This is especially true where the regulations are driven by water qualitybased effluent limitations for toxic organoleptic substances and toxins with bioaccumulation factors over 250.

The Clean Water Act is being reauthorized in 1992 and contains, in its initial draft, provisions which prohibit the discharge of eight chemicals. To have an understanding of the basis of these regulations, which require specific pollutants to be absent or exist at extremely low concentrations, and to be able to work with agencies charged with their enforcement, the metal finishing industry needs to understand the concept, definition, and use of the Limit Of Detection (LOD).

The concept of LOD is a very important and unusual issue in environmental regulation because it moves the work of the analytical laboratory below the level of quantitation and into an imprecise area where an analyte can be detected but the exact amount of that analyte cannot be precisely measured. This provides an opening for many regulatory schemes based on perception vice fact. Analytes measured at detection are generally reported in the parts-per-billion (ppb) or parts-per-trillion (ppt) range in complex matrices. This low level detection in itself presents unique difficulties for the analytical laboratory. In addition, LOD is a confusing concept because there are many definitions of it. Many of these definitions have been misused and intermingled with each other. This has caused unnecessary difficulties in creating environmental statutes, in interpreting that legislation, and in equitably enforcing those laws. Semantics can further complicate matters in that sometimes zero discharge is used in place of LOD terminology, or the terms are used interchangeably.

Three major agencies provide direction and definition in detection limit discourse. They are the American Chemical Society (ACS), the International Union of Pure and Applied Chemistry (IUPAC), and the United States Environmental Protection Agency (EPA). The definitions of Limit of Detection (LOD), Limit of Quantitation (LOQ), Method Detection Limit (MDL), and Practical Quantitation Limit (PQL), their basis, and the intended use of each methodology will be developed and analyzed in this paper.

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IUPAC/ACS METHODOLOGY

As a response to the confusion that existed in academia and the chemical literature regarding numerous and conflicting data on detection limits, the IUPAC adopted a model for these calculations in 1975 (1). The ACS Subcommittee on Environmental Analytical Chemistry reaffirmed this standard in 1980 (2). The IUPAC definition of 1975 states:

The limit of detection expressed as a concentration, c_L , is derived from the smallest signal, x_L , that can be detected with reasonable certainty for a given analytical procedure (1).

However, analysts have been slow to adopt the IUPAC/ACS methodology, and this has necessitated additional symposia and committee reports to reaffirm the preferred method for determining the detection limit (3,4).

The limit of detection is a statistical concept that is intended to reflect the magnitude of unavoidable random fluctuations in measurements at low analyte concentrations. The detection limit of an analytical procedure is a number expressed as the lowest concentration of an analyte that can be distinguished with reasonable statistical confidence from a field blank. The blank is a hypothetical sample containing zero concentrations of the analyte (5).

The entire ACS procedure is based upon blank measurements and the calculation of the standard deviation of those measurements. The blank used most often is reagent grade water or a solvent of interest that is both reproducible and controllable. The detection limit is estimated from the response or signal of an instrument to the blank, but is usually reported in terms of concentration or mass. The conversion of signal output to concentration limits is accomplished with the analytical calibration curve. Most analytical methods require the construction of an analytical calibration curve for the determination of unknowns. The relationship between signal and concentration is provide by the calibration curve shown in Figure 1.



Figure 1. Analytical calibration curve of signal, x, vs. concentration, c.

The analytical calibration relationship can be expressed as (1)

$$x = mc + i$$

where m = slope or analytical sensitively

i = intercept

The functionality between x and c can be obtained by performing a linear regression analysis on the data which generates the calibration curve. The ability to solve accurately for concentration, c, is dependent upon how well the sensitivity and intercept are known. When the calibration curve is obtained in the linear response region of the method and the number of data points used in the construction of the calibration curve is maximized, the values of m and i will be better defined.

The amount of error associated with a measurement of signal, x, can be statistically estimated. If a large number of observations are made and the results are plotted versus the frequency of occurrences, a normal error curve will result. The population mean value of the response, μ , occurs at the center of the gaussian curve which is symmetrical about the mean. The population standard deviation, σ , defines the width of the curve from the mean. The curve is shown in Figure 2 and is given by the formula: (2)

$$y = \frac{1}{\sigma\sqrt{2}\pi} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

For an infinite set of data, the curve is characterized by the mean and standard deviation. For a finite set of data, μ and σ are approximated by the arithmetic mean, \bar{x} and the standard deviation, S. These two parameters are given by the following formulas:

$$\bar{x} = \frac{\sum_{i} x_{i}}{n}$$
(3)

$$S = \frac{\sqrt{\sum_{i} (x_{i} - \bar{x})^{2}}}{n - 1}$$
 (4)

where n = the total number of finite data points





Figure 2. Normal distribution curve for a measured variable, x, with standard deviation, σ , and mean of μ .

Since this curve includes all values of x, the area under the curve can be expressed in terms of probability that a measured value would fall somewhere under the curve. The relationship between area and probability can be measured to estimate the chance that a newly measured x value, x_E , would be a certain number of standard deviation units away from the mean response.

The specifics of the ACS methodology for the calculation of LOD will be useful in further explaining the relationship of the normal distribution of data with calibration curves that the data generates. The ACS LOD is calculated as follows: A statistically significant number of measurements of the blank sample containing a zero concentration of analyte are made. At least 10, and up to 20, replicates are needed for sufficient accuracy in standard deviation calculations (3). The blanks should be treated exactly like samples and should be passed through the entire analytical procedure. Sixteen measurements are generally selected to minimize the rate of change of the error introduced in the calculations. This can be shown graphically in Figure 3 as (6):

NUMBER OF CALCULATIONS

Figure 3. Error vs. replicate calculations in an analytical procedure

- The standard deviation of the 16 blanks, S_b, is calculated using equation 3 and 4. (The units of the standard deviation are units of signal and not concentration).
- 3. Five solutions of varying analyte concentrations in the solvent of the

blank are made. These solutions are run by the methodology of choice, the data collected and the analytical calibration curve of signal, x, vs. concentration, c, is constructed using linear regression.

 The LOD in units of concentration is calculated from the derived slope of the calibration curve and the calculated S_b in units of signal. By definition

$$x_L = \overline{x_b} + kS_b \tag{5}$$

where

- x_{L} = smallest discernible analytical signal
- \bar{x}_{b} = average signal from replicate blank determinations.
- k = a numerical factor chosen in accordance with the desired confidence level

This is shown graphically in Figure 4.



ANALYTE CONCENTRATION -----

Figure 4. Analytical calibration curve with limiting concentration, c_L , determined to be statistically different than mean of blank measurements, \bar{x}_b , by kS_b

4

The concentration, c_L , which corresponds to the smallest discernable analytical signal, x_L , is written as:

$$c_L = \frac{(x_L - \overline{x_b})}{m} \tag{6}$$

Because the mean blank reading, \bar{x}_{b} , is not always 0, the signal must be background corrected $(x_{L} - \bar{x}_{b})$. By substituting Equation 5 into Equation 6.

$$c_L = \frac{kS_b}{m} \tag{7}$$

If k = 3 (3 standard deviations), which allows for a confidence level of 99.86% that the signal developed by the analyte will be very much larger than the average signal calculated from replicate blank determinations, then

$$c_L = \frac{3S_b}{m} = LOD \tag{8}$$

 c_L is a true reflection of the limit of detection when m is well defined and i is essentially zero. Equation 8 is the ACS definition of limit of detection. The selection of three standard deviation units (k=3) is the choice of the society to insure that the smallest discernible analytical signal, x_L , can be measured and is not caused by random fluctuations of the blank signal.

The key features of ACS LOD analysis are:

- 1. Multiple replicate blanks;
- 2. Blank measurement devoid of analyte;

- 3. Blank must be reproducible;
- 4. Non-iterative process;
- 5. Calibration curve required to calculate the slope and thus derive the LOD.

There are other approaches to calculating c₁ values which are similar to the IUPAC/ACS model in that S_k and k factors are involved. However, some authors have recommended other values of k which significantly alters the resultant value of $c_1(7)$. Thus, when other limiting concentrations are reported as the detection limit but the confidence level k is different, obviously confusion results. It is for this reason that the IUPAC and ACS have recommended that x_L be reported in all literature with their k value, x_L (k=3). It would be very helpful to add the next logical step and include the k values when c_{L} values are reported, c_{L} (k=3) (5).

Another source of confusion in the literature compounding the LOD anomalies is the use of multiple standard deviations. The standard deviation of the mean, standard error of the mean, (8) the pooled standard deviation of the mean, S_P , (9,10) or the relative standard deviation, RSD, (9,11) have been used by various authors.

Each of these standard deviation expressions is important and has its place in analytical chemistry. However, the use of these expressions in calculating c_L may result in significant deviations from the IUPAC/ACS model and further complicate the reporting of a consistent LOD.

LIMIT OF QUANTITATION

The LOD is designed to statistically separate the blank measurement signals from the true analyte signals. As such, it is an analytical concept which provides information regarding the detect/no detect decisions. It is not a value which has <u>quantitative analytical significance</u>. Several authors have recognized the need to define a "minimum working concentration" which is an elevated concentration of analyte that provides analytical certainty of quantitation (2,12). The idea behind these higher limits is that the analyte can be determined with a reasonable degree of precision when present at levels significantly above its LOD.

When the analyte concentration increases as the analyte signal increases above its smallest detectable signal, x_L , a minimum criterion representing the ability to quantify the sample can be established reasonably far away from the average signal calculated from replicate analysis of the blank, x_b . This criteria is called the Limit Of Quantitation.

For limit of detection work, LOQ is defined by the ACS as 10 standard deviations away from the x_b (2). Samples that are measured having a signal, x, where $x > 10S_b$ are termed to be in the region of quantitation. Samples having a signal, x, where $10S_b > x > 3S_b$ are termed in the region of detection. Samples having a signal where $x < 3S_b$ are not detectable.

This may be shown graphically as:



FIGURE 5. Relationship of LOD and LOQ to signal strength.

METHOD DETECTION LIMIT

In the real world, the requirement to calculate a detection limit based on a field blank presents an enormous problem. The chemical background in which regulated pollutants exist is most often complex. The matrices which provide the background for practical detection limit work are commonly municipal sewerage, effluent from complex industrial operations, the outfall from domestic sources with its bewildering array of consumer products, and land run-off. To create a blank which duplicates such matrices and could be used with the ACS LOD methodology (devoid of analyte) is a chemical problem of enormous proportions. Therefore, for pragmatic reasons, a detection limit procedure was developed which focuses on an operational definition of detection limit. This procedure, adopted by the United States Environmental Protection Agency (EPA), is the Method Detection Limit (8,13).

The MDL is a procedure whereby the limit of detection is established with the analyte of concern in a complex matrix. The procedure establishes a relationship between detectability and analytical precision, i.e. an indicator of the reproductibility of a determination. This method is very different from ACS methodology, where the chemistry of the blank in a relatively simple or reproducible matrix is used as the basis for detection. The method detection limit refers to samples processed through all the steps comprising an established analytical procedure. The emphasis in the MDL approach is on the operational characteristics of the definition. The MDL is considered meaningful only when

the method is in the detect mode, i.e., the analyte must be present (8).

The EPA defines the Method Detection Limit as

"the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analysis of a sample in a given matrix containing the analyte" (13).

The MDL can be presented as an error distribution. The definition of MDL implies that on an average, 99% of the trials measuring the analyte concentration at the MDL must be significantly different from zero analyte concentration. The assumptions implicit in the methodology are that the error distribution associated with the analytical measurement has a homogeneous variance, is normally distributed, and that the variability as measured by the standard deviation is a function of the concentration being measured. The exact mathematical definition of MDL is

$$MDL = S(t_{n-1}) \tag{9}$$

where

S = standard deviation of <u>all</u> replicate measurements of analyte in the matrix of interest. S is defined as in equation 4.

 $(t_{n-1}) =$ "Students t" distributions for 99% confidence level for n-1 degrees of freedom.

This may be depicted graphically as in Figure 6.



Figure 6. Method Detection Limit, MDL, depicted as an error distribution where $S(t_n)$ is selected for 99% confidence that MDL >0. (13)

The exact methodology for MDL determination is listed in several references. ^(8,13) It is a method which establishes a relationship between detectability and analytical precision based on an iterative process for analyzing the analyte in a given matrix. It is a procedure which was developed for applicability to a broad variety of physical and chemical methods including reagent grade water as the analyte or matrix change. It does require a complete and well defined analytical method. Because the MDL will vary as the analyte or matrix change, it is site specific.

To determine MDL, the analyst must perform at least seven aliquots of sample which may have been spiked from one to five times of an estimated MDL level (knowledge of the analyst and methodology is a key to this parameter). The final calculated MDL of the replicate analysis is then compared to the original estimate to determine its reasonableness. If the result fails, the iteration begins again with a new estimate of MDL.

The specifics of the EPA methodology for the MDL calculation will be useful in explaining the relationship between operational data and the limit of detection. The MDL procedure is summarized as follows:

- 1. Make an estimate of the detection limit. This estimate is dependent on the experience of the analyst. It is based on any of the following estimates:
 - a. 2.5 5.0 times the instrument signal to noise ratio;
 - b. 3 times the standard deviation of replicate analysis of the analyte in reagent grade water;
 - c. that region of the standard calibration curve that exhibits a significant change of sensitivity;
 - d. instrumental limitations.
 - 2. Analyze the sample in the matrix of interest. If the result is less than the estimated level (i.e. no detect), spike the unknown with analyte to bring the level of analyte between 1 and 5 times the estimated detection limit. If the sample result is within 1-5 times the estimated detection limit, proceed to step 3. If the sample is greater than 5 times the estimated detection limit, there are two options:
 - a. obtain a sample with a lower level of analyte;
 - b. the sample may be used if the analyte level is not greater than 10 times the MDL of the analyte in reagent grade water. The variance of the analytical method changes as

- the concentration changes. Therefore, as the concentration moves away from lower levels, the MDL may not truly reflect the variance at lower analyte levels.
- 3. Take a minimum of seven aliquots of the sample and analyze through the entire analytical procedure. If a blank measurement is required by the analytical procedure, obtain a separate blank for each sample aliquot.
- 4. Calculate the standard deviation S, as in equation 4, and variance S² as

$$S^{2} = \frac{\sum_{i}^{n} (x_{i} \ \bar{x})^{2}}{n-1}$$
(10)

- 5. Compute the MDL as with Equation 9.
- 6. If the calculated MDL is within 1 5 times the estimated MDL, the value is the detection limit for that procedure in the matrix of interest. Compute the 95% confidence interval estimates for the MDL. The lower confidence limit equals (.64)(MDL) and the upper confidence limit equals (2.20) (MDL). These confidence limits are derived from percentiles of the chi-square distribution (a non-normal distribution).
- 7. If the calculated MDL is not within 1 -5 times the estimated MDL, use this calculated value as a new estimate of MDL. Spike the analyte into 7 new aliquots at the level of the estimated MDL and proceed with step 3 - step 6. If this second calculated value is within 1-5 times the estimated MDL, the procedure is complete. If not, use the second calculated MDL as the estimate for the next iteration of detection limit. The iterations continue until the calculated MDL falls within 1-5 times the estimated MDL.

8. When the detection limit is calculated, a new aliquot is spiked at 1 -2 times the calculated MDL. This sample is run through the analytical procedure and the percent recovery is calculated. A recovery of greater than 75% is generally accepted as evidence of a useable MDL.

There are limitations to the MDL procedure which must be recognized so that analysts, engineers and regulators can understand the basis of the methodologies they are using in regulations. These limitations are:

- 1. The basic assumption of MDL that precision is indicative of detectability may not always be applicable;
- The procedure does not take into account the effects of poor accuracy (bias). It is possible to be very precise without being accurate;
- Precision is not entirely independent of concentration; the concentrations chosen for an MDL study can make a difference in the MDLs obtained;
- 4. The procedure warns that it may be necessary to determine a lower concentration of analyte that will result in a lower MDL, but provides only limited help in estimating this lower level via the two aliquot process and reestimating the MDL;
- 5. The most significant objection to MDLs is one for which the procedure is not to be blamed. Most laboratories tend to perform MDL determinations with replicates in reagent grade water, thus disregarding the effect of complex matrix components. When the MDL is determined under these conditions, the value obtained is one that can only be considered achievable by the laboratory

under the most favorable circumstances.

It is the detection limit of the "perfect sample" (14). These MDLs are used by individual laboratories to determine the laboratory specific minimum detection capabilities. Laboratories have an obligation to identify that these idealized detection limits are performed on reagent grade water.

The EPA has derived and published MDLs for a number of methods and substances in reagent grade water (15,16,17), but it acknowledges that those values will vary depending on both instrument sensitivity and matrix effects (15,17). As such it states that these published "idealized" MDLs should never be used as a basis for setting regulatory compliance (18). Several authors and members of the regulated community have expressed concern and frustration with the use of MDL values obtained under ideal situations as the basis of regulation and their nonachieveability in real world matrices (19,20,21). It is important to realize that these limits are not to be used as the basis of regulation. Some value greater than those must be selected so as to account for interference incumbent in complex matrices.

An additional and equally important reason for not using these MDLs is the question of false positives. By definition of the MDL, there is a 1% chance that a measurement of an effluent will be greater than the MDL. That is, if 100 measurements are made on blanks which are devoid of analyte, one detect is expected. There is a statistical variability on the 100 measurements in that there may be no detect or two or more. The chance of getting no detects out of 100 observations is $0.99^{100} = 0.36$ or 36%. The complementary probability of getting at least one detect is 100 - 36 = 64%. Thus, there is a 64% probability that the

blank effluent will be declared in violation by the time 100 tests have been made on the effluent (22). The risk of being declared in violation when in fact the effluent is in compliance associated with a set of 100 samples is 64%. As the sample size increases, the discharges risk also increases and approaches 100%. What this means is that eventually even blank effluent will be declared in violation. It is only a matter of time and number of samples collected!

PRACTICAL QUANTITATION LIMIT

The MDL is matrix, laboratory, instrument, and analyst (for certain methodologies) specific (18,23). As such, it does not provide a useful measure of limit of detection which allows qualified laboratories to communicate. The MDL is not a measure of an analyte which has quantitative significance. It is a litmus test of detection, not quantitation. Because of a need to provide a more workable detection limit method between laboratories, the EPA has defined a Practical Quantitation Level (PQL). The EPA defines this term as:

"The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions is the Practical Quantitation Level (PQL). The PQL thus represents the lowest level achievable by good laboratories within specified limits during routine laboratory operating conditions. The PQL is determined through inter-laboratory studies. Differences between MDLs and PQLs are expected since the MDL represents the lowest achievable level under ideal laboratory conditions whereas the PQL represents the lowest achievable level under PRACTICAL and routine laboratory conditions.

If data are unavailable from interlaboratory studies, PQLs are estimated based upon the MDL and an estimate of a higher level which would represent a practical and routinely achievable level with relatively good certainty that the reported value is reliable" (24).

The basis for setting PQLs is:

- 1. Quantitation;
- 2. Precision and accuracy;
- 3. Normal operations of a laboratory;
- 4. The fundamental need in a compliance monitoring program to have a sufficient number of laboratories available to conduct analysis.

The PQL is analogous to the LOQ as defined by the American Chemical Society in that both define the concentration of an analyte above which is the region of quantitation and below which is the region of less certain quantitation. The PQL is a real world number which has analytical significance, whereas the MDL is a measure of the detect/no detect decision under controlled ideal research-type conditions. The difference between PQL and LOQ is that the PQL is an interlaboratory concept while the LOQ is specific to an individual laboratory. The EPA developed the PQL concept to define a measure of concentration that is time and laboratory independent for regulatory purposes. The LOO and MDL, although useful to individual laboratories, do not provide a uniform measurement of concentration that could be used to set standards (18).

PQLs are estimated from the MDL when inter-laboratory data is lacking. The working quantitation limit may therefore be written as (11)

$$PQL = (F)(MDL)$$

where F is a multiplier to represent matrix difficulties. The multiplier applied to the MDL must reflect interferences in the background matrix which will affect interlaboratory bias of the analytical methodology. As the background matrix grows more complex, the factor must grow larger. That is to say, the multiplier is highly matrix dependent (17). Sample factors provided by the USEPA and others are:

MATRIX TYPE	<u>FACTOR, F</u>
Drinking Water (25)	5-10
Ground Water (17)	10
Waste Water to POTW (26)	13
Water Miscible Liquid Waste	(17) 500

OTHER METHODOLOGIES

The ACS and EPA methodologies are not the only methods in use to calculate detection limits. A graphical approach is used which expresses the slope, m, as a confidence interval, $m \pm t_{\alpha}S_{m}$, where S_{m} is the standard deviation of the slope and t_{α} is a t distribution value chosen for the desired confidence level, α and the degrees of freedom, v(5). The insertion of this interval into Equation 7 produces

$$c_L = \frac{kS_b}{m \pm t_{\alpha} S_m}$$
(12)

The effect of this inclusion is to bracket the slope of the analytical calibration curve with error bars which provide a maximum and minimum slope. These will provide detection levels for c_L at reduced sensitivity, c_R , and increased sensitivity. Generally only the larger value of concentration c_R is reported as the limit of detection. This can be shown graphically in Figure 7.



Figure 7. Graphical approach to the limit of detection calculation using the analytical calibration curve of signal, x, and concentration, c. The detection limit at reduced sensitivity, c_R is shown.

In an additional approach, the error in the intercept, i, as well as the slope, m, is considered. This method, the propagation of errors approach, considers the contribution of each term to the total error; a complete discussion of this method can be found in reference 5.

Finally, Instrumental Detection Limits (IDL) are often used in the literature. They are provided by analysts who develop new or modified instrumentation for trace analysis (4). The IDL are most often defined in terms of standard deviation of measurements of the blank usually with the value of k = 2. The blank used is not a field blank containing some matrix, but simply the solvent in which the sample is presented to the instrument. The IDL has value when viewed as a rapid way of comparing instruments which are constantly evolving in their ability to detect

trace amounts of analyte. A caution is needed with the use of IDL. These limits in relation to practical analysis are unrealistically low. These results often cannot be matched in practical application outside of the idealized laboratory setting.

EMERGING EPA METHODOLOGIES

In late 1991, the EPA presented at the American Water Works Association Water Quality Technology Conference revised definitions of detection limits. These definitions which are proposed to replace MDL and PQL were first presented and discussed by Keith (27). PQLs have been criticized for lacking a strong technical basis since they are derived by the application of a multiplication factor to MDL (28). The main critical emphasis centers on:

- 1. The use of the word "limit as a misnomer;
- The use of a 99% confidence level is inappropriate. Higher confidence levels are required;
- 3. The questions of false positives;
- 4. The use of zero as an arbitrary reference point.

The revised definitions for low-level analysis are Method Detection Level (MDL'), Reliable Detection Level (RDL) and Reliable Quantitation Level (RQL). The intent of these definitions is to provide a consistent set of rules that reflect the operations necessary to provide realistic low level analytical results for both regulators and those regulated. These definitions need to be broad to cover a large spectrum of environmental situations. It will also be advantageous to have a set of definitions which would receive broad acceptance within the scientific and regulatory community. The new definitions have been drafted so that they will provide clearer definitions, provide definitions with accompanying recommendations, provide definitions with accompanying usage guidance, and provide clearly interrelated terms.

The proposed revisions to method detection limit will:

- 1. replace "limit" with "level";
- accommodate both zero and background signals of an analyte as a reference point;
- accommodate statistically variable confidence levels that may be used as a basis for estimating the probability of eliminating false positive detections;
- take a representative matrix into consideration when making analytical measurements; and
- 5. provide guidance on use and limitations of certainty in individual measurements.

The MDL' is defined as:

The lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and representative matrix. An intralaboratory MDL' estimate represents the average detection capability of a single laboratory for a specific analyte method and matrix at a given point in time. An interlaboratory MDL' estimate represents the method detection capability for a specific analyte and specific matrix determined in more than one laboratory (28). The RDL is defined as :

For a given MDL', method and representative matrix, a single analysis should consistently detect analytes present at concentrations equal to or greater than the RDL. When sufficient data are available, the RDL is the experimentally determined concentration at which false negative and false positive rates are specified. Otherwise, the RDL is the concentration which is twice that of the Method Detection Level (RDL = 2 xMDL'). The RDL is the recommended lowest level for qualitative decisions based on individual measurements and it provides a much lower statistical probability of false negative determinations than the MDL (28).

The RQL is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. The RQL is the concentration which is two times the Reliable Detection Level (RQL = 2 x RDL). This recognizes that the RDL estimates produced at different times by different operators for different representative matrices will not often exceed the RQL (28).

The EPA has published these draft regulations in the June 1992 edition of the Federal Register. It is important to note that these are draft regulations and as such are subject to change. However, during an ACS sponsored environmental symposium entitled "Regulatory Problems and Solutions with Method Detection Limits" (April 6, 1992), there was overwhelming support for a change from the current method detection limit definition to those identified above.

CONCLUSION

As regulations develop in the present decade, the trend toward ever more stringent numerical standards is clear. Analytical variability, if not adequately understood and appropriately defined, can exacerbate the compliance obligation and regulatory burdens of both the regulator and regulated community. It is important for the metal finishing industry to be knowledgeable in the definition and application of detection limit methodologies since they are becoming increasingly more common in its industrial regulations.

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Increasing Removal Efficiencies of Typical Heavy Metal Precipitate from Electroplating Wastewater, Using Adsorptive Exchange and Co-Precipitation Methodologies

John S. Lindstedt and Wenzhong An, Artistic Plating Company, Inc., 405 W. Cherry Street, Milwaukee, WI, 53212 414/271-8138 FAX 414/271-4972

Increasing the removal efficiencies of specific metal hydroxides shows promise with the addition of select transition metal hydroxides and others. Freshly made precipitants of ferric/ferrous hydroxides, zirconium hydroxide, tin hydroxide and manganese(IV) hydroxide can be used to remove copper and nickel ammonium complexes effectively to lower levels as dictated by traditional precipitation techniques. The removal efficiency is determined primarily by the pH of the system, but the relative amount of co-precipitant also affects the removal efficiency. The removal mechanisms are considered to be inorganic ion exchange, co-precipitation and/or the adsorption of metal cations on the surface of the co-precipitants. Proposed mechanisms for the multiple precipitation reaction will be presented and data provided to substantiate the parameters of system pH and additive concentrates on synthesized and operational wastewater.

CATERPILLAR, PENNSYLVANIA RECOVERS HARD CHROME

Bob Jeanmenne, Caterpillar, Inc. Stephen Perrone, Aqualogic, Inc.

In the summer of 1991, Caterpillar Inc. of York, PA made a to purchase a hard chrome pl commitment new plating automated machine to replace the existing hard chrome operation. The new line would use a high speed proprietary hard chrome plating process. The new chemistry was felt to be superior to the old baths, however, the new process was considerably more expensive to use. Caterpillar contracted with Aqualogic to design and build a chrome recovery system. The system would allow the conversion of the old line to the new chemistry and close the loop at the source. POLLUTION PREVENTION. The system had to be capable of being moved to the new line when it was installed.

The existing plating operation was observed in operation and the baths, drag-out and rinse tanks were sampled. A general plan was developed based upon the analytical data generated in Aqualogic's laboratory. It became apparent that we had to address the drag-out tank, rinses and the automatic washdown of the scrubber hoods. The analytical results indicated that the sources to be recovered contained contaminants of iron, copper, and trivalent chromium. The tests further indicated that hexavalent chrome content, the although exceptionally high by rinse standards was still low by plating standards.

OBJECTIVE:

The objective became clear. We had multiple tasks that needed to be accomplished if we were going to recover the chrome.

1. The three sources had to be collected and equalized.

2. The trivalent chrome, tramp iron and copper had to be removed prior to recovery. 3. The "cleaned" and recovered chrome had to be concentrated before being returned to the chrome plating tank.

4. The water recovered from the evaporator is to be reused.

PROCESS:

The plating process has a drag-in tank, plating and drag-out tanks, and rinse stations. As the parts pass through the plating cycle, chrome is carried to the drag-out tank. In this case we have two drag-out tanks which are counterflowed to each other.

The rinsewater is used as make-up for the drag-out tanks. The dragout is then removed at the rate of 30-60 gallons per hour. The chromebearing waste water is collected in a holding tank and combined with the automatic washdown of the scrubber. The solution is then passed through a dual trained, cation-only ion-exchange system. The resins remove the contaminants and the dilute, "cleaned" chrome is collected and held for transfer on demand to the evaporator.

The ion-exchange module is designed as a dual-train system with an on-line train containing tandem cylinders and a similar backup train which goes on-line when the first system needs regeneration. The system alternates between the two trains for continuous operation on a 24-hour basis.

A vacuum evaporator was selected concentrate the "cleaned" to chrome. The evaporator is made primarily of glass, and its fairly open construction allows ease of cleaning, monitoring, and maintenance. The unit requires steam as its heat source. The evaporator receives approximately 30 1-gallon batches automatically from the cleaned chrome holding vessel.

FLOW DIAGRAM A: CHROME MAKE-UP LC LC DRAG CHROME DRAG DRAG COUNTER WORK COUNTER IN PLATE OUT OUT FLOW FIOW FLOW 1 11 RINSE RINSE CHROME HOLD ION DISTILLATE **EVAPORATOR** EXCHANGE CONCENTRATED CHROME

The chrome is then concentrated to 35-37 oz. per gallon. The concentrated chrome is held in a vessel and an automatic feed system transfers the solution to the plating tanks on demand.

The distillate from the evaporator is returned to the last rinse tank in the plating process and counterflowed through the entire chrome plating process and the auto-scrubber and hood washdown.

The entire system is controlled with a central PLC located on the ion-exchange package. modularized feeds, The level controls and transfers to and from the evaporator all function from this single source. Flow Diagram A illustrates the basic process.

PRODUCTS OF THE PROCESS:

1. Chromic acid solution (35-37 oz. per gallon) which is pumped to four chrome plating tanks on demand.

2. Distilled water which is pumped back to the rinse tank on demand.

3. Sulfuric acid (20%) used in the regeneration process of the ion-exchange system (approximately 50 gallons per month).

BENEFITS OF THE PROJECT:

The old method of chrome treatment required the use of SO2 as the reducing agent. The volume of chrome to be treated was substantial and the S02 was purchased in 1-ton cylinders.

The new system virtually recovers all of the chrome and discharges no wastewater from the process plating line. The recovery system has been in operation since April, 1992 and has achieved dramatic results.

The system returns in excess of 200 gallons per week of concentrated chrome to the plating tanks. This equates to a recovered solution at 36 oz. per gallon (271 g/l). The actual savings in chrome is 450 lbs. of chromic acid each With the current cost of week. HEEF-25 at \$3.44 per pound, the weekly savings amounts to \$1,548 and the annual savings is \$77,000!

The existing system requires 3 gpm of rinsewater discharged to the treatment system. With the new system couterflowing all of the water back through the rinses and tanks, drag-out the water is captured and fed through the evaporator with the distillate being used for make-up. The old methods required more than 1,000,000 gallons of water annually and with the current cost of water placed at \$9.57 per 1,000 gallons, the annual savings is \$10,300

CONCLUSION: The success of the project is further emphasized by the approval of a grant from the Pennsylvania State of after installation and verification of the performance of the system. The grant, which provides partial reimbursement for hazardous waste recycling equipment, awarded Caterpillar a check for \$46,112.22 in July of 1992.

100 % Effluent Recycle in German Zinc Plating Facility

By B.Czeska

Galvatek GmbH, an OUTOKUMPU Technology Company

German restrictions and standards for effluent have continuously become more stringent over the years. Some areas are defined as "Water Protected Zones". In these areas no effluent is allowed from factories. Knipping, a manufacturer of screws for the German automobile industry, have their production facilities in such a zone. A new zinc plating process line has just been completed in the facility. The process sequence includes pretreatment, phosphating, zinc plating, heat treatment, and passivation. The entire line has been completed with zero liquid discharge from the process. All water flows are treated and internally recycled.

This paper will briefly discuss the environmental regulations in Germany. The plating process will be described. Effluent treatment and analysis will be provided for each step of the process sequence. The final results of the project in terms of process line performance and economics will be discussed.

Environmental regulations

German authorities control the limiting values for substances passing into the natural water resources (for metals 0.5 ppm) as well as the waste water treatment technology. For all plating lines they prescribe technically and economically reasonable recovery systems. The rinse must have at least three stages. Water consumption must be minimized.

Plating line

This line produces 20 t/day of zinced screws and 5 t/day of phosphated screws in 3 shifts. The line is completely automatic, all charges can be treated separately (several thousand types of screws !) with complete documentation of the treatment. The barrels are loaded automatically and an individual program can be selected. After treatment the plated screws leave the installation together with the protocol. For the zincing process see Table 1.

Table 1

Process sequence for zinc plating

	step	chemicals	volume
1.	hot degreasing	NaOH	5000 I
2.	pickling	HCI 16%	5000 I
З.	anodic degreasing	NaOH	6000 I
4.	pickling	HCI 3%	30001
5.	zinc plating	Zn, Cl-	45000 I
6.	heat treatment		
7.	activation	see 4.	
8.	zinc plating	see 5.	
9.	activation	HNO3	600 I
10.	passivation	Cr	5001

Step 1. - 5. is done in barrels; step 6. in special containers; step 7. - 8. in barrels; step 9.-10. in baskets.

Heat treatment is necessary to avoid hydrogen brittleness. In a first step the goods are plated to 3 microns (see table 1). After the heat treatment (200 °C; 10 h) they will be plated to 10 - 12 microns. Three different passivation steps can be applied : black, blue and yellow.

The whole plant is separated in 2 floors (Fig1). On the first floor you will find the production unit with the treatment of the screws. The water treatment with all physical and chemical processes (warming, cooling, dosing, filtration...)takes place on the ground floor.



Fig. 1 - The two floors of the building

Process water treatment

Rinse technology

An effective water treatment starts with a good rinsing system. The better the rinsing technology the easier is the water treatment. An effective way for barrel lines is the application of counter flow cascade rinses.

A simple formula ¹⁻² for calculating a cascade rinse is given by :

$$W = V (c_0/c_n)^{1/n}$$
 (1)

$$c_n = (V/W)^n c_0$$
 (2)

W = volume of fresh water V = drag out c_0 = concentration of the bath c_n = concentration of the n-rinse n = number of rinses

This formula is very simplified, but its effectivity is proven in practice. In order to work with a very small volume of rinse water a 6-stage counter flow rinse has been chosen (n = 6).



Fig. 2 - compact rinse at the pickling bath

It is impossible to have 6 rinse tanks in a galvanoplating line. The space is restricted and the rinse period is too long. This problem was solved by developping a so-called "Compact Rinse". The principle is illustrated by the scheme of the pickling bath (Fig. 2). In the galvanoplating line only one rinse tank with round bottom is installed. The rinse water comes from the ground floor by means of compressed air (1.5 bars). The barrel is transported from the pickling bath directly to the rinse tank. Then the water from the first rinse step is fed into this tank. The barrel turns and after the rinse period the water flows back to the first rinse tank. Then the second rinse tank is used and the same procedure starts up to the last rinse tank. The whole system is fed by fresh water and circulates through all six rinse steps as in a counter flow cascade rinse. A highly concentrated water coming from the first rinse step is passed to the water treatment (no reasonable recovery method is known until now). Several other cold bathes, which cannot be recovered, are treated on the same way.

The shortest rinse period for all six steps is about 6 min. The volume of transported water in each rinse step is about 800 I. The average volume of fresh water needed is about 120 I/h.

In the case of a hot bath the same principle is used. Due to the atmospheric evaporation on the bath surface part of the concentrate rinse water can be re-used (Fig. 3).

For the hot degreasing bath a recovery rate of 80% is realized.



Fig. 3 - flow chart on hot degreasing

Recovery of valuable substances

It is useful and economic to recover the plating bath. The content of such a bath is valuable and must be treated with chemicals at high costs when not recovered.

The water from the first rinse is concentrated with a vacuum evaporator (Fig. 4).



Fig. 4 - Recovery with a vacuum evaporator

The concentrate is given back to the bath and the distillate is re-used for rinsing. The loop is completely closed. The recovery rate is about 100% and impurities, such as Fe, organics, organic decomposition compounds, are concentrated, too. The Zn content will increase, as well. On the buffer tank all the procedures for cleaning are involved (Fig. 4). A filter for removing particles as iron and a membrane electrolysis for the zinc are connected with this tank. Dosing pumps for brightener, acid, wetting agent are also mounted onto this tank. The removal of organics can be carried through easily.

The capacity of this evaporator is about 230 l/h. The distillate is of good quality for re-use :

Table 2 Analysis of distillate (Zn bath evaporation)

Conductivity : 30 - 50 μS Zn : 2 mg/l Cl- : 4 mg/l COD : 1000 mg/l

Due to the high content of organics in this bath the COD is relatevely high.



Fig. 5 - Principle of vacuum evaporation

Special features of the vacuum evaporator

The evaporator consists mainly of a closed container in stainless steel or PVDF, divided into evaporating and condensing chambers (see Fig. 5). An integral heat pump (using Freon R22, R134a, Ammonia;" reversed refrigerator principle"), gives heat to the liquid in the evaporator chamber and at the same time cools the vapour in the condensing chamber. The water vapour condenses on the cooling coil and the droplets are trapped in a collecting tank. A water jet pump (venturi principle) creates the necessary vacuum in the evaporator shell and pulls the condensate into a separate distillate collector. The installation operates semi- continuously and automatically. Solution is pulled into the

chamber by opening a valve, and the concentrate is discharged by a pump, controlled by time or density. The distillate runs continuously from the distillate collector.

Table 3

Technical data of the vacuum evaporators

Energy requirement	0.15 kWh per litre
	of distillate
Evaporation capacity	70 - 6000 l/day
Vacuum	-920 to -950 mbar
Boiling temperature	35°C

The low boiling temperature prevents the decomposition of the product. This is especially important when treating cyanide bearing solutions. Two types of vacuum evaporators are used in this project :

One type is conceived to concentrate a product up to a maximum density (sludge or dry product). This type is called "dryer".

The other type concentrates a product up to a defined density (but still liquid and pumpable), as used for the zinc bath.

This type is called "concentrator".

These evaporators are used also for other baths (Ni, Cu, cyanide baths, Cr).

Chemical treatment of non-recoverable products

Rinse water from the pretreatment and the passivation steps cannot be recovered directly. The content is not valuable and the recovery is not economic (actually). This water is treated in the conventional way using neutralisation units (see Fig. 6).





In order to avoid extreme use of chemicals, the Cr - reduction as well as the cyanide oxidation are done by electrolysis. As final control step, small quantities of sodium bisulfite for chromium reduction and sodium hypochloride for cyanide oxidation are dosed. The chromium sludge is separated from the neutralisation sludge, because of the high costs for chromium waste disposal. In fact sludge containing only traces from chromium can be re-used in pyrometallurgical or hydrometallurgical processes. It is evident, that the reuse of sludge is less expensive than waste disposal.

Closed loop

The neutralized water (about 1000l/h) contains about 10 g/l of salts (90% sodium chloride). Normally this water is filtered, passing through a final control system and then is fed into the sewer.

In our case this water must be re-used. A thermal recompression evaporator concentrates this liquid up to about 300 g/l (Fig. 7).





evaporator is shown in Fig. 8.

This concentrate is dryed in a vacuum evaporator (type "dryer"). The dry waste salt is deposited in salt domes. The distillate shows a conductivity of 50 μ S (COD : 200 mg/l) and can be re-used completely as rinse water. The water loop is closed and the line runs totally free of waste water. The principle of the thermal recompression



Fig. 8 - Thermal recompression evaporator

The boiling temperature is about 50°C. The energy consumption is about 20 kWh/1000 I of distillate. This value is very low and it is due to the fact that the steam itself is used to warm up the product.

Economic view

The whole plant worked for 5 months in 3 shifts. The economical data we have are only rough estimations.

The investment costs for a waste water free factory are higher than for a conventional one. This higher price is due to the additional costs for evaporators and the compact rinses mainly. On the other side are the savings for a big ion exchanger unit which is not needed (because of the high quality of the compact rinses) and a smaller neutralisation plant. The comparison between savings and costs results in a higher price which is about 10 to 15%.

A very important economic factor of such a plant are the costs for waste disposal. Table 4 shows the amount of solid wastes compared with a conventional line.

Table 4

Waste disposal (tons/year)

solid waste	conventional	waste water free
salts	0	20
phosphate sludge	4	1.5
Hydroxide sludge	130	24
others (filtrates, charcoal etc.	2	5

In a conventional line no salts will appear. In a closed loop system good cleaning of baths is absolutely necessary. During recovery also impurities are recovered. That is why more wastes from cleaning will occur (in a conventional line impurities disappear through the drag out).

The reduction of hydroxide sludge is enormous. It amounts to only about 20% of the sludge produced in a conventional line. Furthermore the costs for the purchase of chemicals are reduced, as well. The average costs for 1 ton of hydroxide sludge are about 1000 DM in Germany at present. The savings by a sludge reduction of 100 tons a year are enormous.

The rest of 24 tons/year is mainly produced in the pickling bath and in the passivation steps. Here work is still left to be done : For these products a recovery system must be found.

The current costs for a waste water free factory are smaller as shown on Table 5.

Table 5 Current costs (in millions DM)

	conventional	waste water free
personal	0.6	0.4
chemicals	0.6	0.3
energy	0.2	0.4
maintenance	0.2	0.2
waste disposal	0.4	0.1
	2.0	1.4

Only the energy required for a waste water free process is more expensive, due to the thermal processes. Maintenance costs is identical, but their nature is different. In a conventional line most work must be done for waste water treatment. In a waste water free process maintenance is little more than cleaning and controlling. The staff in a waste water free line are reduced, but they must have better qualifications.

Conclusions

The complete process is illustrated in Fig 9. Galvano plating can be done free of waste water. The key technologies are an efficient rinse system combined with recovery units (vacuum evaporator). The investment costs for such a line are slightly higher, the current costs are smaller than for a conventional line. The Galvano plating line free of waste water is at present not yet a must, but is available when needed (e.g. in "water protected zones"). In the future environmental legislation will enforce further restrictions. A limiting value for neutral salts is already being discussed. In order to avoid future problems it is better to adapt installations today to the needs of tomorrow. The neutralisation unit for such a plant will become smaller and smaller, and finally disappear. The concentrates will be transported to specialized factories and be recovered there. In the plating shop you will find nothing but "concentrators".



Fig. 9 - Black box diagram waste water free galvanoplating line

References

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